M13 BACTERIOPHAGE-ENABLED ASSEMBLY OF NANOCOMPOSITES:
SYNTHESIS AND APPLICATION IN ENERGY CONVERSION DEVICES

by

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Abstract

Lack of energy supply and non-uniform distribution of traditional energy sources, such as coal, oil, and natural gas, have brought up tremendous social issues. To solve these issues, highly efficient energy conversion devices including solar cells, water splitting cells, and lithium-ion batteries are required. In this thesis, by utilizing the biological scaffolds of M13 bacteriophage, nanocomposites with novel nanostructures and various functional nanomaterials have been synthesized, assembled, and fabricated into devices. Using excellent properties from each functional material in the nanocomposites, performance of the energy conversion devices has been improved. Specifically, in dye-sensitized solar cells, the electron collection efficiency is improved by the complex of the viruses and single-walled carbon nanotubes. The light harvesting efficiency is also improved by localized surface plasmon-enhanced photo-absorption of dye-molecules, with and without adding viruses into the titania photoanodes of dye-sensitized solar cells. In addition, virus-graphene complex is utilized to enhance the performance of lithium-ion batteries, by increasing the electron conductivity throughout the cathode active materials. Moreover, two types of virus-templated perovskite ternary metal oxide materials (strontium titanate and bismuth ferrite) are synthesized and demonstrated for photocatalytic and photovoltaic properties.

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Chapter 1. Introduction

1.1. Energy consumption, energy sources, and energy devices

1.1.1. Importance of renewable energy

In 2008, total worldwide energy consumption was 474 exajoules (1 exa = $10^{18}$), with 80 to 90 percent derived from the combustion of fossil fuels\(^1\). The estimates of remaining non-renewable worldwide energy resources vary, with the remaining fossil fuels totaling an estimated 0.4 YJ (1 YJ = $10^{24}$ J). However, not all of these fossil fuels can be accessed as easily as today. In fact, only a very small amount of these fossil fuels can be utilized cost-effectively. Based on the rate of usage of energy in 2005, the conventional oil will run out in 40 years, and coal in 154 years.

Furthermore, running out of fossil fuels might not be the greatest challenge we are facing. Burning fossil fuels since the beginning of the industrial revolution has substantially increased the levels of carbon dioxide in the atmosphere. Carbon dioxide concentrations in the atmosphere have gone up by approximately 35 percent since the 1900s, rising from 280 parts per million by volume to 387 parts per million in 2009\(^2,3\). Due to the strong IR absorption of CO\(_2\) molecules, increasing concentration of CO\(_2\) in atmosphere results in global surface temperature increasing of $0.74\pm0.18^\circ$C between the start and the end of the 20\(^{th}\) century, and probably, climate model projections summarized a further 1.1 to 6.4\(^\circ\)C during the 21\(^{st}\) century\(^4\). As a result, extreme weather conditions, regional climate change, sea level rise, and all types of effects and impacts will be upon us.
In order to solve these issues, fossil fuels need to be replaced by renewable energy. Thus, technologies of utilizing renewable energy must be developed.

### 1.1.2. Energy sources and energy devices

According to the energy consumption rate of 2008, the average power we are using is $1.5 \times 10^{13}$ W. Among all the renewable energy we can utilize, the only type which is possible to provide us enough energy is solar energy. There are $89 \text{ PW} \ (1 \text{ PW} = 10^{15} \text{ W})$ of solar power falling on the planet’s surface, and only 0.02% of the 89 PW will be enough for us. However, there exist difficulties in utilizing solar energy. First of all, the solar energy is dilute, in terms of the energy intensity per area, especially at high latitude. For instance, if 0.1% area of the earth is covered by the expensive solar panels, which is huge, at least 20% efficiency of solar cells need to be developed and manufactured in large quantities. Second, the solar energy is not constant at different time, and methods for storing the energy collected in the sunny daytime are required. Additionally, transporting the energy in the form of chemical energy from solar power rich area to solar power poor area is also demanded. All of these requirements urge us to develop different types of energy conversion devices to convert energy between, solar, electric, and chemical energy.

### 1.2. Nanocomposites assembled by biological scaffolds

#### 1.2.1. Nanocomposites in energy conversion devices

In energy conversion devices, materials with different functional properties are needed for different parts and functions of the devices. For instance, to absorb light, the
absorbents need to have high extinction coefficient and broad absorbing range; as active electrodes, the materials need to have high electron/hole mobility and sometimes transparent to let light pass through. However, very often it is difficult to find the materials with all the desired properties. For instance, we need some materials to be excellent in more than one physical properties (e.g. proper band gap in visible to near infrared range and high electron/hole mobility of semiconductors), and at most time these material properties are not independent, which makes it very challenging to find or design the desired materials. To solve this issue, assembling different functional materials into nanocomposites with novel nanostructure and proper composition will be crucial.

1.2.2. M13 bacteriophage

We have mentioned that nanocomposites can improve the performance of energy conversion devices by combining materials with different functions together, and letting them form a uniform complex system. In most of the methods demonstrated in this thesis, genetically modified M13 virus plays an important role.
Figure 1.1. Molecular surface of a partial segment of M13 bacteriophage. Only pVIII peptides are shown, minor coating peptides present at the end of viruses.

M13 is a filamentous bacteriophage, about 880 nm in length and 6.5 nm in diameter, composed of circular single stranded DNA (ssDNA) which is 6407 nucleotides long encapsulated in approximately 2700 copies of the major coat protein pVIII, and capped with 5 copies of four different minor coat proteins (pIX, pVII, pVI, and pIII) on the ends. Figure 1.1 shows about 100 copies of pVIII peptides, without minor coating peptides, which should be at the end of the virus. Many research groups including our group have been performing genetic modification to pVIII, pIII, and pIX peptides, by means of both mutants at specific DNA sites and selection from a phage library, which is a large set of phages (millions to billions) having random sequence of amino acids on one of the major or minor coating peptide. After achieving a virus that specific binds to the material of interest, this material can be either attached or directly nucleated on the surface of the virus. Research on virus-templated different materials including compound semiconductors, magnetic materials, metals, metal oxides, and others have been demonstrated. In general, the process of biomineralization happens at a relatively mild
condition and is more environmentally friendly. Products of biomineralization often show unique properties different from other methods with respect to particle size, morphology, phase structure, crystallinity, and catalytic properties. Additionally, using M13 viruses with multiple modified genes/peptides or single peptide modified into different motifs can assemble different functional materials in a programmable way.

1.3. Solar cells

Solar cells are devices that convert energy of sunlight directly into electricity by photovoltaic effect. Currently, the best efficiency researchers have been achieved from multi-junction solar cells was about 43%, which is sufficient to utilize for energy production. However, considering the cost of the highly pure materials and the complexity of the fabrication process, it is impossible to have enough money and time to manufacture them for worldwide civilian use. Comparing with bulk solar cells (with relatively thick photo-absorbing films), the manufacturing/material cost has been substantially reduced in thin film solar cells like thin film silicon cells, CIGS (copper indium gallium selenide), and DSSCs (dye-sensitized solar cells). Particularly, for DSSCs the environment-friendly processing, low cost of materials, and easy fabrication have drawn great attention to both communities of research and industry.

1.4. Dye-sensitized solar cells

1.4.1. Principles of dye-sensitized solar cells

DSSC was first invented by Gräztel’s group in 1991\textsuperscript{10}. This cell is extremely promising due to low-cost materials and simple apparatus to manufacture. It is much less expensive
than conventional solid-state cell designs. It can be assembled onto flexible substrates, which are also mechanically robust. Compared to silicon solar cells, the semiconductor, \textit{i.e.} titania at most time, in the dye-sensitized solar cells is used solely for charge transport; the photoelectrons are generated by the photosensitive dye-molecules. The charge separation occurs at the interfaces between the dye, semiconductor, and electrolyte. In order to capture most of the incoming light, a 3-dimensional scaffold is utilized to hold large numbers of the dye molecules. In the existing designs, this scaffold is also provided by the semiconductor nanomaterial.

When shining light through transparent conductive electrode (FTO, fluorine doped tin oxide in this case), electrons of sensitizers, \textit{e.g.} a ruthenium complex, are excited from the HOMO (highest occupied molecular orbital) level to the LUMO (lowest unoccupied molecular orbital) level. Then the electrons inject from dye-molecules to the conduction band of the TiO$_2$ nanoparticles and transport via particle/particle contacts to the FTO and are collected. On the other side of the photoelectrochemical reaction, iodide and triiodide species in the electrolyte operate in a redox reaction to regenerate the excited sensitizers, and the electrolyte itself gets regenerated at the surface of Pt counter electrode after ionic diffusion. The ruthenium complex N719 (also named red dye) is the common dye used for standard DSSCs fabrication$^{11}$.

1.4.2. Developments of dye-sensitized solar cells

Currently, research on DSSCs has been focusing on improving the efficiency via developing new photoanode nanostructures, dye molecules, and electrolytes, improving lifetime by modifying dye molecule structures, and using solid or quasi-solid electrolyte,
and making DSSCs on flexible substrate. Till today, the best efficiency of DSSCs has been achieved by Graztel, 12%, with a novel porphyrin-type sensitizer.
Chapter 2. Virus-templated self-assembled single-walled carbon nanotubes for highly efficient electron collection in photovoltaic devices

2.1. Abstract

The performance of photovoltaic devices could be improved by using rationally-designed nanocomposites with high electron mobility to efficiently collect photo-generated electrons. Single-walled carbon nanotubes (SWNT) exhibit very high electron mobility, but the incorporation of such nanotubes into nanocomposites to create efficient photovoltaic devices is challenging. Here we report the synthesis of SWNT-TiO$_2$ nanocrystal core-shell nanocomposites using a genetically engineered M13 virus as a template. By using the nanocomposites as photoanodes in dye-sensitized solar cells (DSSCs), we demonstrate that even small fractions of nanotubes improve the power conversion efficiency by increasing the electron collection efficiency. We also show that both the electronic type and degree of bundling of the nanotubes in the SWNT/TiO$_2$ complex are critical factors in device performance. With our approach, we achieve a power conversion efficiency in the dye-sensitized solar cells of 10.6%.

2.2. Introduction

Preserving non-renewable energy and lowering carbon dioxide emission requires efficient and inexpensive approaches to utilize solar energy. Nanoporous solar cells are promising due to lower cost and potentially higher efficiency than silicon solar cells, enabled by high internal quantum efficiency$^{12}$, large surface-to-volume ratio$^{10}$, and tunable absorption range$^{13}$. However, in some cases fast recombination and slow carrier diffusion in nanoporous photovoltaic devices result in low power conversion efficiency$^{14}$. 
Various methods have been investigated to increase the power conversion efficiency of nanoporous solar cells by improving the incident photon-to-current conversion efficiency (IPCE). While increasing light absorption and charge separation efficiency have been studied widely\textsuperscript{11,13,15-18}, improving photoelectron collection efficiency has been reported only in a few papers\textsuperscript{19}. Most of them are devoted to developing materials with higher electron mobility and/or nanostructures with facilitated electron paths, such as vertical nanotube/nanowire arrays\textsuperscript{20,21}. Increasing electron diffusion length by changing materials or nanostructures, however, alters other important material and device properties such as charge separation and recombination, and surface area of thin films. Thus far, a method capable of increasing electron diffusion length while keeping other essential device physics parameters unaffected is absent.

Making nanocomposites from combinations of materials, each with its unique functional advantage, is another approach to improve electron collection. Single-walled carbon nanotubes (SWNTs) have been regarded for a long time as a promising component for nanocomposite photoanodes in photovoltaic devices\textsuperscript{22,23} because of their excellent electron mobility and one-dimensional shape\textsuperscript{24}. However, no report has shown pronounced improvement in power conversion efficiency of SWNT-incorporated solar cells due to several factors. First, as-produced SWNTs are an ensemble of metallic and semiconducting SWNTs. While semiconducting SWNTs can provide efficient electron diffusion paths without recombination, metallic components provide short-circuit paths, negating any possible improvements. Moreover, the strong tendency for SWNTs to form bundles\textsuperscript{25} creates contact between SWNTs, transferring electrons from semiconducting SWNTs to metallic ones\textsuperscript{26}. Chemical modifications\textsuperscript{27} and surfactants\textsuperscript{22,23} have been used
to prevent SWNT bundling, but these methods either deteriorate the electronic properties\textsuperscript{28} of SWNTs or make the heterogeneous nucleation of nanocrystals on SWNTs difficult. Therefore, it is desirable to develop methods to incorporate SWNTs in photovoltaic devices effectively.

M13 virus is a filamentous bacteriophage which can be genetically engineered to express peptides selected for materials\textsuperscript{7,29,30}. Here we present a general and programmable method to integrate SWNTs into photovoltaic devices for highly efficient electron collection using M13 viruses as biological templates. Importantly, this method does not significantly affect electron transfer between semiconducting nanocrystals and SWNTs nor change the pristine properties of SWNTs. SWNTs are bound along the genetically engineered M13 viruses and dispersed. In our virus/SWNT complex scheme, part of the SWNT surface is exposed to water, enabling a direct contact between biomineralized inorganic nanocrystals and SWNTs. Moreover, nanocrystals templated on viruses aid the complete encapsulation of SWNTs, which is challenging to realize with surfactant-dispersed SWNTs. With SWNT/TiO\textsubscript{2} complexes synthesized using our method, we successfully incorporate SWNTs into photoanodes of dye-sensitized solar cells (DSSCs), and demonstrate that semiconducting SWNTs increase power conversion efficiency of photovoltaic devices through increased electron diffusion length, thus higher electron collection efficiency. With the combination of debundled SWNTs and compact SWNT/TiO\textsubscript{2} nanocomposites, only enabled by the virus, we also explicitly show that semiconducting and metallic SWNTs affect device performance in opposite ways. Furthermore, through controlling the microstructure of virus/SWNT complexes, we show that bundling of SWNTs indeed affects photovoltaic device performance.
2.3. Results and discussion

Synthesis of Nanocomposites: Complexation and Biomineralization

To synthesize SWNT/TiO$_2$ nanocomposites, virus/SWNT complexes are made, and then TiO$_2$ nanocrystals are biomineralized on the complexes. Figure 2.1a illustrates the synthesis of virus-templated SWNT/TiO$_2$ nanocomposites. To bind and disperse SWNTs non-covalently along the viruses wrapped by pVIII major coat proteins, a pVIII library was constructed and viruses with binding affinity toward SWNTs were identified through a bio-panning method (Experimental). In the pVIII library construction, the gene for pVIII, g8, is engineered to express foreign peptide inserts, and therefore all 2,700 copies of pVIII coat proteins express the peptide inserts, enabling cooperative and multivalent interaction between the surface of viruses and SWNTs. Among several identified clones, a specific virus with the pVIII insert sequence of DSPHTELP was selected for SWNT binding for two reasons. First, it has an aromatic residue, histidine (H), which is expected to interact with SWNTs through $\pi-\pi$ stacking at all pH ranges. Second, the pK$_a$ of the side chain of histidine is around 6, and therefore histidine in the selected sequence allows us to neutralize the virus surface without disrupting the virus stability. Sodium cholate-dispersed SWNTs are initially negatively charged due to the cholate ions non-covalently adsorbed on the SWNTs, and viruses are also negatively charged at pH of D.I. water, 6. Therefore, the overall interaction between viruses and SWNTs during the surfactant exchange is determined by competition between binding affinity and electrostatic repulsion. To minimize the initial electrostatic repulsion between viruses and SWNTs, thus facilitating the binding, the pH of the dialyzing solution was set to the pI of the virus,
5.3 (Figure 2.7). After the complexation was completed, the pH was increased to 10, at which point the zeta potential of the virus becomes around -35 mV. This increased negative surface charge of the virus is advantageous for both colloidal stability\textsuperscript{34} of the complexes and nucleation of TiO\textsubscript{2} on the complex template. Using histidine as a pH-switch, the repulsion between viruses and SWNTs is reduced, while the repulsion between cholate-SWNTs still exists in the early stage of the complexation, minimizing possible bundling of SWNTs. By utilizing the pH-switch, SWNTs are expected to be better dispersed. The virus/SWNT complexes made with this pH-switch retained 82% of the integrated photoluminescence (PL) intensity (935 nm~1,250 nm) of the starting SWNT solution (Figure 2.9), increasing by 2.8 times compared to those made at constant pH 10 (Figure 2.8). Since metallic SWNTs in the small bundles of SWNTs quench PL\textsuperscript{26}, higher PL intensity implies better dispersion of SWNTs. Therefore, the selected virus allows efficient binding and dispersion of SWNTs through pH-dependent control. The binding between SWNTs and viruses was confirmed using a magnetic separation method (Figure 2.2a, Experimental). To visualize the bound SWNT along the major coat proteins of the virus, high-resolution transmission electron microscopy (HRTEM) was used (Figure 2.2b,c). Because part of the SWNT surface is exposed to water, biomineralized nanocrystals on viruses make a direct contact with SWNTs.

After SWNTs are bound by viruses, biomineralization of TiO\textsubscript{2} on the virus/SWNT template was optimized to achieve heterogeneous nucleation of TiO\textsubscript{2} and maintain the structural integrity of the virus/SWNT complexes during the synthesis. To suppress fast hydrolysis of titanium alkoxides at room temperature\textsuperscript{35}, TiO\textsubscript{2} was biomineralized at lowered temperature (-20°C) and in 75% ethanol solution (typical SWNT-to-TiO\textsubscript{2} weight
ratio is 1:100). In Figure 2.2d, the wire-like structure in the TEM micrograph confirms the templated growth of TiO$_2$ on the virus. Raman spectrum of the photoanode after the device fabrication (see next section) shows radial breathing mode (RBM) peaks and the G peak from SWNTs$^{36}$, implying the presence of SWNT/TiO$_2$ complexes (Figure 2.2e). Compared to other methods for making TiO$_2$/CNT complexes$^{22,23,27,37}$, this virus-enabled self-assembly method has several advantages. First, SWNTs are bound and stabilized by viruses through non-covalent binding, and therefore no chemical modifications are required, preserving high electron mobility of SWNTs. Second, the partially exposed surface of SWNT in the virus/SWNT complex enables direct contact between SWNTs and TiO$_2$, facilitating electron transfer at the interface. Lastly, an excess of virus is not required to disperse SWNTs. Surfactants need to be at a higher concentration than critical micelle concentration, typically ten to a hundred times more than the viruses used for stabilizing SWNTs. These free surfactants make heterogeneous nucleation of TiO$_2$ on the surface of SWNTs difficult.

**Effect of Electronic Type of SWNTs on Photovoltaic Device Performance**

To investigate the effect of SWNTs on electron collection in photovoltaic devices, we chose DSSCs as a model application due to their potential as practical devices and their well-understood device physics$^{10,15,38}$. For easy comparison, DSSCs with only TiO$_2$ nanoparticles as photoanodes were fabricated with the same method that other groups reported, and used as a control (Methods). The SWNT/TiO$_2$ nanocomposites were mixed with TiO$_2$ nanoparticles (SWNT concentration in TiO$_2$ matrix varies from 0 to 0.2 wt%) and fabricated for DSSCs using the same method, except that the devices were annealed.
in an Ar atmosphere (instead of air) to protect SWNTs and at elevated temperature (600°C instead of 500°C) to remove viruses and polymers. Devices with only TiO$_2$ nanoparticles annealed at two different conditions showed similar power conversion efficiencies, confirming the different annealing conditions used here did not affect the power conversion efficiency (Figure 2.14). Device structures and photoelectrochemical processes in SWNT-incorporated DSSCs are described in Figure 2.1b. TiO$_2$ nanoparticles accept electrons from photo-excited dyes, and these electrons are transferred to the conduction band of SWNTs after diffusion among TiO$_2$ nanoparticles. Then, SWNTs transport the electrons quickly to the current collector (fluorine-doped tin oxide, FTO) to prevent back-electron transfer and recombination. In Figure 2.3a, I-V curves of DSSCs with different electronic types of SWNTs incorporated into photoanodes are shown. When pure semiconducting SWNTs (99% semiconducting components) are used, the short-circuit current (I$_{SC}$) increases by 27%, while pure metallic SWNTs (99% metallic components) decreases I$_{SC}$ by 20% compared to TiO$_2$-only DSSCs. All fill factors are approximately 0.7, and all open-circuit voltages are around 780 mV. Electron diffusion lengths of photoanodes are calculated from electrochemical impedance spectroscopy$^{38}$ and shown in Figure 2.3b (Experimental). Electron diffusion length increases by incorporating semiconducting SWNTs, but decreases when metallic SWNTs are incorporated. These changed electron diffusion lengths result in different electron collection efficiencies of the devices, and account for the different power conversion efficiencies (Experimental). Therefore, semiconducting or metallic SWNTs affect the device power efficiency differently by increasing or decreasing electron diffusion length, thus electron collection efficiency. These opposing
effects can be understood from the different electronic band structures of semiconducting and metallic SWNTs (Figure 2.1c,d). Semiconducting SWNTs have a non-continuous band structure with a diameter-dependent bandgap\textsuperscript{24}. The electrons in the SWNT conduction band, transferred from the TiO\textsubscript{2} conduction band, can transport quickly to FTO without recombination or back reaction. In contrast, metallic SWNTs have a continuous band structure, and therefore electrons transferred from TiO\textsubscript{2} can stay at continuous energy levels near the Fermi level, accelerating recombination of electrons to dye or back reaction to tri-iodide in the electrolyte.

The importance of the virus/SWNT template for synthesizing compact SWNT/TiO\textsubscript{2} complexes and effectively incorporating them into DSSCs is demonstrated by following control experiments (Figure 2.13). DSSCs with virus/TiO\textsubscript{2} complexes but without SWNTs show similar performance to the devices with only TiO\textsubscript{2} nanoparticles. This indicates that the viruses do not participate in the photoelectrochemical processes (The template mass is only about 10\% of the total TiO\textsubscript{2}), and one-dimensional morphology of the virus/TiO\textsubscript{2} complexes does not affect device performance significantly. Instead, viruses bind SWNTs, prevent SWNTs from bundling, and act as templates for synthesizing SWNT/TiO\textsubscript{2} core-shell nanocomposites. Another control experiment using cholate-stabilized SWNTs shows lower device efficiency. Free surfactants in solution favor homogeneous nucleation as opposed to heterogeneous nucleation for the encapsulation of SWNTs in TiO\textsubscript{2} when using virus-stabilized SWNTs. Homogeneous nucleation of TiO\textsubscript{2} results in SWNTs with exposed surfaces (SWNT bundles appear after synthesis), increasing electron recombination and back reaction in DSSCs. Additionally, more surfactants than viruses are required to stabilize SWNTs, resulting in more
impurities. Decreased efficiencies induced by bundling and impurities are also observed in the control experiment where as-produced SWNTs without surfactants were used.

To optimize the electron collection, SWNT concentration dependence of power conversion efficiency was studied. Various concentrations from 0 to 0.2 wt% of SWNTs with different compositions of semiconducting and metallic components were incorporated into photoanodes. DSSCs incorporated with pure semiconducting SWNTs show continuous increases of efficiency, followed by saturation (from 8.3% for devices with only TiO$_2$ nanoparticles to 10.3% for devices with 0.2 wt% SWNTs), as shown in Figure 2.3c. The increase of the power efficiency is mainly due to the increased photocurrent. One possible explanation for the saturation could be that the concentration of SWNTs in the TiO$_2$ matrix is sufficient for electrons to transfer quickly to SWNTs (Approximate calculation shows that electrons can transfer to SWNTs after several hops between TiO$_2$ nanoparticles with 0.1 wt% SWNTs.). When SWNTs with more metallic components are incorporated, however, the concentration dependence of the device efficiencies varies from having an optimized value with CoMoCAT SWNTs (about 10% metallic components) to a monotonic decrease with Hipco SWNTs (about 33% metallic components) and pure metallic SWNTs (about 99% metallic components). Although there have been reports on using other carbon-based nanomaterials for photovoltaic devices, for example, multi-walled carbon nanotubes$^{39}$, mixed semiconducting and metallic SWNTs$^{22,23}$, and graphene$^{40-42}$, there has been no report explicitly showing the opposing effects of metallic and semiconducting SWNTs on photovoltaic device performance. The differences between results in this report and those from others could be attributed to the following explanations. First, the efficiencies of our devices with only
TiO$_2$ nanoparticles are relatively high (Figure 2.3a), implying that the recombination and back reaction are not severe. Therefore, these devices are more sensitive to additional metallic components. Second, well-dispersed SWNTs and compact SWNT/TiO$_2$ nanocomposites allow us to systematically investigate the effect of semiconducting and metallic components separately. Third, annealing condition of 600°C and Ar atmosphere ensures better contact between SWNTs and TiO$_2$ and prevents SWNT loss in device fabrication.

Since SWNTs also absorb visible light, the possible effect of optical loss from SWNTs on device performance was investigated. The spectral response of IPCE for DSSCs with and without SWNTs, and SWNTs of different electronic types and concentrations were measured (Figure 2.15). For metallic SWNTs, the maximal absorption wavelength in the visible region is around 700 nm, which does not overlap with the absorption peaks of N719 dye (Figure 2.16). Therefore, the optical loss from metallic SWNTs does not affect the spectral shape of IPCE. For semiconducting SWNTs, although the maximal absorption wavelength in the visible region is around 500 nm, overlapping with the absorption peak of N719 dye, IPCE does not show significant change around 500 nm. This indicates that optical loss from semiconducting SWNTs is not severe and does not affect the spectral shape of IPCE (Experimental). Therefore, the different device performances we observed do not result from optical loss of SWNTs.

**Effect of the Degree of Bundling on Photovoltaic Device Performance**

The observed effects of semiconducting SWNTs and metallic SWNTs on the device performance motivated further tuning of the degree of bundling of SWNTs with the virus.
To investigate the effect of bundling of SWNTs on device performance, virus/SWNT complexes with virus-to-SWNT ratios of 1:2.5, 1:5, and 1:10 were made. Since the PL is more sensitive to bundle formation\textsuperscript{26} than the absorption, PL spectra of complexes are used to analyze degree of bundling of SWNTs. Because all the starting SWNT solutions used for complexation are from the same batch and at the same concentration, the change of PL intensity is directly related to the degree of bundling of SWNTs. The integrated PL intensity (930 nm~1,250 nm) of the 1:10 sample is 5 times smaller than the 1:2.5 sample, whereas the 1:5 sample is only 1.67 times smaller (Figure 2.9). The lowest PL intensity of the 1:10 sample implies a more bundled state than the 1:2.5 and 1:5 samples. The severer bundling of SWNTs in the 1:10 sample was further confirmed by PL excitation (PLE) map. In the PLE map of the 1:10 sample, the relative PL intensity of (7,5)-chirality is higher than both (8,3)- and (6,5)-chiralities, which is the opposite in the PLE maps of the 1:2.5 and 1:5 samples (Figure 2.4a,b,c). In bundled SWNTs, in addition to the quenching of PL, excitons in ‘donor’ SWNTs with larger bandgap, can transfer to ‘acceptor’ SWNTs with smaller bandgap, and radiatively recombine to produce photons of lower energy\textsuperscript{43,44}. Therefore, the reverse of relative PL intensity of (7,5)-SWNTs in 1:10 sample can be explained as exciton energy transfer from donor (8,3)- and (6,5)-SWNT to acceptor (7,5)-SWNT. The PLE mapping results show similar tendency of degree of bundling to PL spectra.

Complexes with different virus-to-SWNT ratios were fabricated into DSSCs. The devices with the most bundled SWNTs (1:10) have the lowest power conversion efficiency, 9.1%, while devices with less bundled SWNTs (1:2.5 and 1:5) show higher values, 9.9% and 10% (Figure 2.4d). Therefore, the degree of bundling of SWNTs also plays an important role
in photovoltaic device performance. Moreover, the 1:2.5 ratio gives a two times higher density of virus/SWNT complexes in TiO$_2$ matrix than the 1:5 ratio for the same concentration of SWNT. Thus, tuning the degree of bundling of SWNTs can reduce the amount of incorporated SWNTs further. By optimizing the effect of electronic properties of SWNTs and the microstructure of the template, we achieved a non-trivial improvement of power efficiency of DSSCs from 8.3% to 10.6% by incorporating only 0.1 wt% SWNTs (Figure 2.5). This 10.6% power conversion efficiency of DSSCs is the best result for any SWNT-incorporated photovoltaic devices.

2.4. Conclusion

We developed a general and programmable method to template compact core-shell SWNT/nanocrystals nanocomposites using a genetically engineered virus. Using this method, SWNTs are stabilized without surfactants and surface modifications, and their electronic properties are preserved. With the developed biological template approach, we demonstrate that well-dispersed semiconducting SWNTs can improve the power conversion efficiency of DSSCs to 10.6%. We also explicitly show that metallic and semiconducting SWNTs affect the device performance in the opposite way, and aggregation states of SWNTs affect the device performance, guiding further studies in incorporating SWNTs in photovoltaic devices.

Because SWNTs have good thermal conductivity in addition to high electron mobility, this approach might improve the stability of large DSSC modules. Moreover, biological engineering of multiple genes of the virus can extend this approach to creation of more complex structures. Though the route to DSSC improvement lies in the development of
dyes with absorption extending into the infrared and better redox couples for higher voltages\textsuperscript{46}, we believe that our approach will enable the utilization of SWNTs in many practical photovoltaic devices that require efficient electron diffusion and reduced electron recombination, for instance, quantum dot solar cells\textsuperscript{47}, organic solar cells, and photoelectrochemical cells.

2.5. Figures
Figure 2.1. A schematic diagram for the virus-enabled SWNT/TiO$_2$ DSSCs.  

a, Process of virus/SWNT compelexation, and biomineralization of TiO$_2$ on the surface of virus/SWNT complex. b, The scheme of DSSCs incorporated with SWNT/TiO$_2$ complex.  

Energy diagrams of DSSCs incorporated with semiconducting SWNTs (c) and metallic
SWNTs (d): Dye absorbs photons and generates electron-hole pairs, and then instant charge separation occurs at the dye/TiO₂ interface preventing back-electron transfer and charge recombination. Semiconducting SWNTs improve electron collection to FTO electrodes, whereas incorporation of metallic SWNTs results in recombination and back reaction.
Figure 2.2. Characterization of virus/SWNT complex and biomineralization of TiO$_2$ on virus/SWNT complex. a, Magnetic separation of virus/SWNT complexes i, SWNT
binding viruses of which pIII are enzymatically biotinylized were complexed with SWNTs (left), combined with streptavidin-coated magnetic beads (right), and (ii) incubated. (iii), Incubated solution is pulled out using magnet placed external to the tube of the solution. (iv), The supernatant is compared with the starting virus/SWNT solution, confirming binding of SWNT to the virus. (b,c), HRTEM micrographs of virus-SWNT complexes. SWNTs are pointed by an arrow. Virus is indicated by dashed lines. Part of the virus was intentionally burned off during imaging in order to clearly identify the bound SWNTs. (d), TEM micrograph of TiO\textsubscript{2} biomineralized on virus/SWNT complex. (e), Raman spectrum of the photoanode incorporated with SWNT/TiO\textsubscript{2} complex after being annealed in Ar at 600°C. In addition to peaks of SWNTs, peaks of anatase TiO\textsubscript{2}\textsuperscript{35} are also shown.
Figure 2.3. Device performance and characterization. a, I-V curves and b, Calculated electron diffusion lengths from three DSSCs: with only TiO₂ nanoparticles, with 0.2 wt% pure semiconducting SWNTs, and with 0.2 wt% pure metallic SWNTs. $L$ is the film thickness and $L_n$ is the electron diffusion length. c, Dependence of the power conversion
efficiency and short-circuit current of DSSCs on the electronic type and the concentration of SWNTs incorporated in TiO₂ matrix. Virus-to-SWNT ratio of 1:5 was used for all devices.

Figure 2.4. The effect of bundling of SWNTs in virus/SWNT complexes on device performance. PLE maps of virus/SWNT complexes with virus-to-SWNT ratios of 1:2.5 (a), 1:5 (b) and 1:10 (c). CoMoCAT SWNTs are used for the complexation. Known SWNT chiralities are assigned in the map. d, Dependence of power conversion efficiency
and short circuit current on the degree of bundling of SWNTs, controlled by virus-to-SWNT ratio. CoMoCAT SWNTs are used with the concentration of 0.1 wt% in DSSCs.

Figure 2.5. Device performance of the best DSSC in this study. Current density and Power efficiency versus voltage curves of the DSSC with 0.1 wt% SWNTs of 99% semiconducting component incorporated ((6,5)-chirality-enriched SWNT (Methods)). The highest power conversion efficiency is 10.6%. The virus-to-SWNT ratio is 1:2.5.

Figure 2.6. A scheme of an M13 virus and its cloning vector for genetic engineering.
Figure 2.7. Zeta potential of the SWNT-binding virus (DSPHTELP).

Figure 2.8. The effect of pH-switch on complexation. The integrated PL intensity (935 nm ~ 1,250 nm) for the complexes, made with pH-switch method, increases by 2.8 times, implying better dispersion of SWNTs. For with pH-switch samples, the pH of the dialyzing solution was set as 5.3 (pI of the virus), and then increased to 10 after the complexation. In contrast, for the without pH-switch complexes, the pH of the dialyzing solution was kept as 10 during and after the complexation. The virus-to-SWNT ratio is 1:1 for both complexes, and CoMoCAT SWNTs were used for the complexation.
Figure 2.9. PL spectra of virus-SWNT complex solutions with various virus-to-SWNT ratios. The integrated PL intensity (935 nm ~ 1,250 nm) of the 1:1 complex is 82% of the starting SWNTs in 2wt% SC aqueous solution. This high quantum yield of the virus-SWNT complexes suggests that the developed virus-SWNT complexation method is an efficient way of dispersing SWNTs in aqueous solution. CoMoCAT SWNTs were used for the complexation.

Figure 2.10. Magnetic separation of SWNTs in 2wt% SC aqueous solution.
Figure 2.11. XRD of photoanodes with SWNT/TiO$_2$ complex annealed in Ar at 600°C. Only anatase phase of TiO$_2$ presents after annealing.

Figure 2.12. Raman spectrum of photoanode with SWNT/TiO$_2$ complex annealed in air at 600°C. There is no radial breathing mode peak and G peak of SWNT in Raman spectrum if annealing the photoanode in air at high temperature, implying the decomposition of SWNT at this condition.
Figure 2.13. Device performance of control DSSCs. Device performance of DSSCs with only TiO$_2$ nanoparticles (black line), TiO$_2$ nanoparticles and virus/TiO$_2$ complex without SWNT (red line), TiO$_2$ nanoparticles with surfactant-stabilized SWNT (blue line), and TiO$_2$ nanoparticles with as-produced SWNT powders (cyan line).

Figure 2.14. Effect of annealing condition on device performance of DSSCs. I-V curves from DSSCs with only TiO$_2$ nanoparticles as photoanodes annealed at 600°C in Ar (blue line) and at 500°C in air (red line) are shown.
Figure 2.15. **IPCE measured for various DSSCs.** DSSCs with only TiO$_2$ nanoparticles and with different SWNTs of various concentrations are compared.

Figure 2.16. **Comparison of absorption spectra from SWNTs and N719 dye in the visible region.** The concentrations of measured solutions are not scaled with the final concentration used in the DSSCs to show the spectral difference more effectively. The concentration of semiconducting and metallic SWNTs aqueous solution is 10 μg/mL, and the concentration of N719 dye in the solution of acetonitrile/tert-butyl alcohol (volume ratio 1:1) is 5×10$^{-5}$ M.
Figure 2.17. Equivalent circuit impedance model of DSSCs. $R_s$: Ohmic series resistance of the cell. $R_{CO}$ and $C_{CO}$: Contact resistance and capacitance at the interface between the conducting substrate and the TiO$_2$ photoanode film. $R_{SU}$ and $C_{SU}$: Charge transfer resistance and double layer capacitance at the substrate/electrolyte interface. $R_{Pt}$ and $C_{Pt}$: Charge transfer resistance and double layer capacitance at the counter electrode-electrolyte interface. $Z_{TiO2}$: transmission line impedance of the TiO$_2$ photoanode film consisting of the elements $r_T$ (resistivity of electron transport in the photoanode film), $r_{REC}$ (charge recombination resistance at the TiO$_2$/dye/electrolyte interface), and $c_\mu$ (chemical capacitance of the photoanode film). $Z_{Electrolyte}$: mass transport impedance at the counter electrode.
Experimental data are presented by symbols, and fitted results using the equivalent circuit in Figure 2.17 are shown as solid lines. The bias applied to all the devices during measurement is 600 mV. For DSSC incorporated with 0.2 wt% pure semiconducting SWNT, $R_{REC}=1007 \ \Omega$, $R_T=15.3 \ \Omega$, thus $L_0/L=8.1$; for DSSC with only TiO$_2$ nanoparticles, $R_{REC}=710 \ \Omega$, $R_T=207 \ \Omega$, thus $L_0/L=1.8$; for DSSC with 0.2 wt% pure metallic SWNT, $R_{REC}=347 \ \Omega$, $R_T=1190 \ \Omega$, thus $L_0/L=0.54$.

2.6 Experimental

PVIII phage-display library construction

M13SK, a vector derived from a commercially available M13KE vector (New England Biolabs. Inc.), was used for pVIII library construction$^{31}$. Library oligonucleotide (purchased from IDT (idtdna.com)) was designed to fuse randomized 8-mer peptide sequence onto pVIII with digestion enzyme recognition sites for BamH I and Pst I, 3’ AC GAC AGA AAG CGA CGT CNM NNM NNM NNM NNM NNM NNC CTA
GGA ACA TCA TC-5’ where N can be one of A, T, C, and G, whereas M can be either A or C. The designed primer sequence for extension was 5’- G ATG CTG TCT TTC GCT GCA G-3’. The primer and random oligonucleotides were annealed and extended to make complementary sequence of the random sequence. The extended DNA duplexes were double digested with BamHI and PstI and purified using polyacrylamide gel electrophoresis. M13SK vector was double-digested using PstI and BamHI and dephosphorylated using Antarctic phosphatase. Dephosphorylated vector was ligated with double cut-DNA duplex at 16°C overnight, purified, and concentrated. (All enzymes were purchased from New England Biolabs. Inc.) 1 μl of concentrated ligated vector was electrotransformed into XL-1 blue, electro-competent cells at 1.8 kV/cm, and total 10 transformations were used for library construction. Transformed cells were incubated for 45 min and fractions of several transformants were plated on IPTG-XGal/TET agar to determine the diversity of the pVIII library while the rest were amplified. The final diversity of the pVIII library was 2×10^6 plaque-forming units (PFU). The relatively lower diversity of pVIII library compared to pIII one (commercially available pIII library has a diversity of ~10^9) is due to the more stringent requirement for virus assembly process with pVIII.

**PVIII phage-display library screening: a bio-panning**

For the bio-panning experiment, SWNTs were prepared in a form of thin films on glass substrates to maximize the direct contact of the virus to SWNT and a constructed pVIII phage-display library was used. 10 μl of the library solution, 10^{10} viruses of 2 ×10^6 different pVIII sequences, was diluted with 250 μl of Tris-buffered saline (TBS, 100 mM...
Tris-HCl, 150 mM NaCl, pH 7.5) with different concentration of Tween-20 (TBS-T, Tween-20 concentration of 0.1-0.5 v/v%), and then was applied to SWNT-films and incubated for an hour with gentle rocking. The SWNT-film was rinsed with 1 ml of TBS-T ten times to wash off unbound phage. Bound phages were eluted by 100 μl of 0.2 M Glycine-HCl, pH 2.2 and/or mid-log E.coli culture to harvest strongly bound virus not eluted by acid solution. The eluted phages were amplified and the same procedures were repeated for further rounds with increasing detergent concentration. After each round of panning, the numbers of eluted and amplified phage, counted as PFU, were measured using agar plates containing X-gal/isopropyl-β-D-1-thiogalactopyranoside (IPTG)/tetracycline. The input number of phage for each round was kept the same. Moreover, plaques from each round were amplified and DNA-sequenced. DNA sequencing was done in the Biopolymers laboratory at MIT.

**Zeta potential measurement**

The concentration of virus (phage) solution used was $10^{12}$/ml in water with 10 mM NaCl. The stock solution of virus (~ $10^{14}$/ml) was initially dissolved in 10 mM Tris, 15 mM NaCl before diluting in 10 mM NaCl in ddH$_2$O. The solution amount used to generate curve was 30 ml. The ionic concentration of the solution was as set to 10 mM NaCl for all samples to minimize the fluctuation of ionic strength during pH adjustment. The pH was then adjusted using 0.1 M NaOH until the pH was around 10. Zeta potential were then measured at an accumulation time of 10 with 5 measurements per sample at 20 V using DelsaNano (Beckman Coulter). Electrophoretic mobility was calculated using the
Smoluchowski approximation (used for particles larger than 0.2 μm in 1 mM or greater salt solution). pH was then adjusted with 0.1 M HCl.

**Genetic engineering for M13-BAP**

Biotin accepting peptide (BAP, or Avi-Tag), GLNDIFEAQKIEWHE, identified through phage-display technique, was engineered onto pIII of SWNT-binding virus. Oligonucleotides, 5[Phos]’ GTA CCT TTC TAT TCT CAC TCT GGC CTG AAC GAC ATC TTC GAG GCT CAG AAA ATC GAA TGG CAC GAG TC 3’ and 5[Phos]’ GGC CGA CTC GTG CCA TTC GAT TTT CTG AGC CTC GAA GAT GTC GTT CAG GCC AGA GTG AGA ATA GAA AG 3’, were purchased from IDT (idtdna.com) and annealed to form a DNA duplex. The cloning vector was extracted from SWNT binding virus using standard miniprep kit (QIAGEN). The extracted vector was digested with Eag I and Acc65 I enzymes dephosphorylated, and agarose-gel purified. Purified vector and DNA duplex were ligated using T4 DNA ligase at 16°C overnight, and electrotransformed to electrocompetent XL-1 blue cells. Transformed cells were incubated for 1 hr, plated, and incubated at 37°C overnight. Blue plaques were amplified and DNA sequenced to confirm the insertion of oligonucleotides for BAP on pIII.

**Preparation of starting SWNTs**

1) HiPco and CoMoCAT solutions

Raw HiPco or CoMoCAT nanotubes were purchased from Unidym (R-SWNT, batch# R0513) and Sigma-Aldrich (product# 704148), respectively. Both HiPco and CoMoCAT SWNTs were first mixed with D.I. water with 2wt% sodium cholate (SC). For HiPco
SWNTs, the mixture was homogenized for 1 hour and cup-horn sonicated for 10 min at 90% amplitude, while CoMoCAT SWNTs were probe-tip sonicated for 2 hours at 40% amplitude. The resulting solutions were centrifuged at 22°C and 30,000 rpm for 4 hours to obtain individually dispersed SWNTs.

2) 99% metallic SWNTs (IsoNanotubes-M<sup>TM</sup>) and 99% semiconducting SWNTs (IsoNanotubes-S<sup>TM</sup>) were purchased from NanoIntegris in a solution form. The as-received SWNT solutions were dialyzed against 2wt% SC aqueous solution before complexation with the virus.

3) (6,5)-enriched SWNTs

Separation of (6,5)-enriched SWNTs, based on density difference, was performed using a modified density gradient procedure from the literature<sup>44,48</sup>. CoMoCAT SWNTs in 2wt% SC aqueous solution was first mixed with 2 wt% sodium dodecyl sulfate (SDS) solution to a final ratio of SDS:SC = 1:4. A density gradient was made using a non-ionic medium, iodixanol (OptiPrep, 60 w/v% iodixanol, Sigma-Aldrich). The concentration of initial gradient was adjusted to be 15, 20, 25, 30 w/v% with a volume of 6 ml, and was positioned on top of 60 w/v% stop layer solution with a volume of 3 ml. All iodixanol layers contained 2 wt% surfactant in a ratio of SDS:SC = 1:4. Four ml of 1:4 SDS:SC SWNT solution was added on the top of the gradient, and was centrifuged at 22°C and 32,000 rpm for 12 hours. The resulting gradient was fractionated at every 250 μl after centrifugation using a fraction recovery system (Beckman Coulter), and characterized by UV-vis-nIR absorption spectroscopy and fluorescence. Fractions enriched in the (6,5) nanotube species were collected and dialyzed against 2wt% SC aqueous solution.
Complexation of virus/SWNT

Various starting SWNTs were either prepared according to the previously reported methods or purchased from NanoIntegris (Experimental). Calculated amount of SWNT-binding virus solution was mixed with the calculated volume of SWNTs dispersed by 2 wt% sodium cholate (SC) in water. The mixed solution was dialyzed against water (10 mM NaCl, pH =5.3) for two days with frequent solution changes. After two days of dialysis, the pH of the dialyzing solution was increased to 10. A dialysis membrane, MWCO of 12,000-14,000 (SpectraLabs.com) was used for all dialysis procedure.

Calculation of the virus-to-SWNT ratio

The concentration of the virus was calculated using the empirical equation, \( (A_{269nm@1mm} - A_{320nm@1mm}) \times 6 \times 10^{17}/\text{# of base pair of the viral DNA (7234)} = \text{# of viral particles/ml}. \)

The concentration of CoMoCAT was calculated using the equation, \( A_{990nm@1cm} \times 13 = \mu g/ml \). For Hipco, an empirical equation, \( A_{632@1cm} \times 27.8 = \mu g/ml \), was used. For 99% metallic and 99% semiconducting SWNTs, the starting concentration was 10 \( \mu g/ml \) (NanoIntegris). For the calculation of the number of SWNT per \( \mu g \) of SWNT, we used 1 \( \mu g \) of SWNT = \( 1.06 \times 10^{12} \) assuming 0.8 nm in diameter and 500 nm in length. Since different SWNT solutions have different mean length, the actual number of SWNTs can be different for various SWNTs. The mean lengths of the used SWNTs are similar to or longer than 500 nm but still shorter than 1 \( \mu m \), and therefore the calculated number of SWNT could be overestimated but not more than by a factor of two. Accordingly, the actual virus-to-SWNT ratio of 1:5 could be less than that but not higher than 1:2.5. Based
on our data, since the device performance of the SWNT-DSSCs was not sensitive in the virus-to-SWNT ratios from 1:2.5 to 1:5, the effect of electronic type of SWNTs on device performance is still valid. For the study of the effect of the bundling, since the same SWNTs were used for the complexation, the discussion is also valid.

**Magnetic separation method**

For the magnetic separation method, the M13-BAP was biotinylated (Figure 2.6). Biotinylated SWNT-binding viruses were complexed with SWNTs and incubated with streptavidin-coated magnetic beads. After incubation, the magnetic beads were pulled out of the solution, and the remaining solution was compared with the initial virus-SWNT solution (Figure 2a). The remaining solution was clear whereas nonspecific binding of SWNT onto the streptavidin-coated magnetic beads in a control sample was negligible (Figure 2.10), implying the successful binding of SWNT on the virus.

**Photoluminescence (PL) measurement**

PL from SWNTs was measured with a home-built near-infrared (NIR) PL microscope. An inverted microscope was coupled to a Princeton Instruments OMA V 1D InGaAs array detector through a PI Acton SP2500 spectrometer. As excitation sources, a 785 nm-laser and a Xe lamp coupled to a monochromator were used for PL spectra and PLE mapping, respectively.

**High-resolution transmission electron microscopy (HRTEM)**
For HRTEM, JEOL 2010F TEM was used. For TEM analysis, virus-SWNT solutions were dropped onto Cu Quanti-foil holy grid (TedPella), washed with ddH₂O several times, and dried.

**Biominalization of TiO₂ on the surface of virus/SWNT: synthesis and characterization**

Once negative charges have been induced on the surface of virus/SWNT complex, the TiO₂ biomineralization was completed using an alkoxide precursor. In a typical experiment, 50 μL of titanium n-butoxide (sigma Aldrich) was dissolved in 30 mL ethanol and the solution was stirred at -20°C. 10 mL of aqueous solution of each different virus/SWNT complex, which was pre-cooled at 4°C, was poured into the ethanol solution under vigorously stirring (about 700 rpm). The final solution typically consists of 25% of water and 75% of ethanol. The SWNT/TiO₂ weight ratio is about 1/100 for virus-to-SWNT 1:5 sample, and the template/TiO₂ ratio was fixed when virus-to-SWNT ratio was changed to 1:2.5 or 1:10. After one hour of stirring, the precipitates were centrifuged at 3000 rpm, washed with ethanol two times and water two times, and then dried in vacuum oven at room temperature overnight. The yield of biomineralized TiO₂ was higher than 90%. The templated nanowire morphology was observed using TEM under 200 kV (JEOL 200CX TEM and JEOL 2010F TEM).

**Characterization of photoanodes: Raman spectroscopy and X-ray diffraction (XRD)**

Raman spectra of the final photoanode thin films were measured using a 785 nm-laser for excitation (Kaiser Optical Co.) to confirm the existence of SWNTs after the device
annealing procedure. XRD of the photoanode thin films was measured using Cu Kα radiation and a Rigaku RU300 powder diffractometer. The thickness of the devices was measured using profilometer (Tencor P-10 Surface Profilometer).

Fabrication of DSSCs

Synthesis of 20 nm-particle-sized TiO₂ colloids and preparation of doctor-blading paste were performed using a procedure from literature¹⁵. The fabrication of the photoanodes of DSSCs was followed. The FTO glass (TEC15 2.2 mm thickness, 15 Ω/□, Pilkington, USA) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. After treatment in an air plasma system for 1 min, the FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 80°C for 30 min and washed with water and ethanol. A layer of paste was coated on the FTO glass plates by doctor blading, left for 3 min to reduce the surface irregularity of the paste, and then dried for 5 min at 120°C. Then the film was annealed at 500°C for 10 min. This doctor blading procedure with paste (coating, storing, drying, and annealing) was repeated to get an appropriate thickness about 13 mm for the photoanodes. The TiO₂ film was treated with 40 mM TiCl₄ solution at 80°C for 30 min again, rinsed with water and ethanol, and then sintered at 500°C for 30 min. After cooling to 80°C, the TiO₂ electrode was immersed into a 0.5 mM N719 dye (Solaronix) in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1), and kept at room temperature for 24 hours. The photoanodes incorporated with virus/SWNT complex were fabricated with modifications as following. Various amounts of SWNT/TiO₂ complexes (obtained by grinding thoroughly with a mortar and a pestle after biomineralization) were mixed with TiO₂ paste, stirred, and
sonicated repeatedly. Ethanol and water were removed by rotary-evaporator. The photoanodes were annealed at 600°C in Ar gas to protect SWNTs from burning. The counter electrode was 100-nm-thick platinum, sputtered on ITO substrate (Delta Technologies). The electrolyte was a solution of 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich), 0.03 M I₂ (Sigma Aldrich), 0.10 M guanidinium thiocyanate (Sigma Aldrich) and 0.5 M 4-tert-butyl pyridine (Sigma Aldrich) in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). The dye-adsorbed TiO₂ or SWNT/TiO₂ photoanodes and Pt counter electrodes were assembled into a sandwich type cell and sealed with a hot-melt surlyn of 25 mm in thickness (Solaronix). The size of the TiO₂ electrodes used was 0.16 cm² (4 mm×4 mm). The aperture of the Surlyn frame was larger than that of the TiO₂ area by 2 mm. Copper tape was adhered on the edge of the FTO outside of the cell. The position of the tape was 1 mm away from the edge of the Surlyn gasket and 4 mm away from the edge of the TiO₂ layer. Light reflection losses were eliminated using a self-adhesive fluorinated polymer film (Arktop, Asahi Glass) that also served as a 380 nm UV cut-off filter. Masks made of black plastic tape were attached on the Arktop filter.

**Characterization of DSSCs**

Photovoltaic measurements were performed using an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to 100 mW/cm² by using a reference Si photodiode with a powermeter (1835-C, Newport) and a reference Si solar cell in order to reduce the mismatch between the simulated light and AM 1.5. I-V curves were obtained by applying an external bias to the cell and measuring the generated
photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively.

Electrochemical impedance spectra of DSSCs were measured using a Solartron 1260 frequency response analyzer. The obtained impedance spectra were fitted with the Z-view software (v3.2b, Scribner Associates Inc.). The spectra were measured at various forward bias voltages (from -0.85 to -0.45 V) in the frequency range of 0.1 Hz~1 MHz with oscillation potential amplitudes of 10 mV at room temperature. The photoanode was connected to the working electrode. The Pt electrode was connected to the auxiliary electrode and the reference electrode. The impedance measurements were carried out in dark conditions. The transmission line model was used for fitting the electrochemical impedance data (Experimental).

**Electrochemical impedance spectroscopy (EIS)**

Electrochemical impedance spectra measurements of DSSCs were performed with a Solartron 1260 frequency response analyzer. The spectra were measured at various forward bias voltages (from -0.85 to -0.45 V) in the frequency range of 0.1 Hz~1 MHz with oscillation potential amplitudes of 10 mV at room temperature. The photoanode was connected to the working electrode. The Pt electrode was connected to the auxiliary electrode and the reference electrode. The impedance measurements were carried out in dark conditions.

**Calculation of electron diffusion length from electrochemical impedance spectra**
The electron diffusion length, $L_n$, can be calculated from $L_n = L (R_{REC}/R_T)^{1/2}$, where $L$ is the film thickness, $R_{REC}$ is electron recombination resistance, and $R_T$ is electron transport resistance. $R_{REC}$ and $R_T$ were obtained by fitting the measured electrochemical impedance spectra to the equivalent circuit (known as transmission line model, shown in Figure 2.17) with the Z-view software (v3.2b, Scribner Associates Inc). The transmission line component ($Z_{TiO2}$ in Figure 2.17) in an equivalent circuit is often used to represent the interface resistance and capacitance for a porous structure, which is the case for the photoanodes of DSSCs. During fitting the electrochemical impedance spectra to the transmission line model, the resistance and capacitance at the substrate/TiO$_2$ interface, and the substrate/electrolyte interface were assumed negligible due to good contact between substrate and TiO$_2$ and blocking layer of TiO$_2$, achieved by TiCl$_4$ treatment to the substrate. In Figure 2.18, electrochemical impedance spectra from each of three types of DSSCs, measured at 600 mV, are shown in symbols. The fitted results are shown as solid lines. For more detailed information about fitting electrochemical impedance spectra to the transmission line model and extracting electron diffusion length from fitted electrochemical impedance spectra, refer references 38,50-53.

**Calculation of electron collection efficiency from electron diffusion length**

The electron collection efficiency is$^{38}$:

$$
\eta_{COL} = \frac{-L \alpha \cosh \left( \frac{d}{L} \right) + \sinh \left( \frac{d}{L} \right) + L \alpha e^{-a d}}{(1 - e^{-a d}) \cdot [1 - L^2 \alpha^2] \cosh \left( \frac{d}{L} \right)},
$$
where $d$ is the thickness of the TiO$_2$ film, $L$ is the electron diffusion length, and $\alpha$ is the extinction coefficient of dye sensitized TiO$_2$ film. (The notation is different from that we used in the manuscript: we used $L$ for the thickness of the TiO$_2$ film and $L_n$ for the electron diffusion length.) For the calculation, we assume $\alpha d$ equals to 1, indicating 90% of the incident light is absorbed. For semiconducting SWNTs-incorporated DSSCs, $L/d=8, \eta_{COL}=1$; for DSSCs with only-TiO$_2$-nanoparticles, $L/d=2, \eta_{COL}=0.93$; for metallic SWNTs-incorporated DSSCs, $L/d=0.5, \eta_{COL}=0.54$ (all $L/d$ values were taken at a bias value of 600 mV, as shown in Figure 2.3b). Since the electron generation efficiency and charge separation efficiency are similar for the devices without and with different electronic types of SWNTs, the electron collection efficiency (decided by electron diffusion length) should fit to the difference of the power conversion efficiency. In fact, the calculated ratio of electron collection efficiency for semiconducting SWNTs incorporated DSSCs, DSSCs with only TiO$_2$ nanoparticles, and metallic SWNTs incorporated DSSCs is 1:0.93:0.54, and the measured power conversion efficiency ratio is 1:0.79:0.63. Therefore, the order of magnitude differences in extrapolated diffusion length account for the difference in power conversion efficiency.

**Spectral response of incident photon-to-current conversion efficiency (IPCE)**

IPCE spectra were measured with a commercial IPCE measurement system (Model QEX7, PV Measurements, Inc.). Under full computer control, light from a xenon arc lamp was focused through a grating monochromator, equipped with two 1200 g/mm diffraction gratings, onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum (from 350 nm to 750 nm) to generate the
spectral response of IPCE with a spectral resolution of 10 nm. The incident photon flux was determined using a calibrated silicon photodiode (calibrated by PV Measurements, Inc.). Measurements were performed in a short-circuit condition, while the cell was under background illumination from a bias light of 50 mW/cm². Bias illumination was from the same direction as the monochromatic light, which was from the FTO side. The monochromatic beam was chopped using a computer-controlled shutter at a frequency of 4 Hz, and averaging of up to 40 shutter cycles was employed.

**Calculation of optical loss from SWNTs in the devices**

The estimated optical loss from SWNTs in the devices is small as calculated below. We assume that N719 dye absorbs 90% of incident light (the transmission is 10%) in absence of SWNTs, therefore the absorbance of N719 dye is 1 (Absorbance=-log(Transmission)). We also assume that SWNTs absorb 10% of the incident light (the transmission is 90%) in absence of N719, and the absorbance of SWNTs is 0.046. If we put N719 dye and SWNTs together in the devices, the overall absorbance is 1.046, and 91% (1-10^{-Abs}=1-10^{-1.046}=0.91) of incident light is absorbed by N719 dye and SWNTs together. The light absorbed by them separately is 87% for N719 dye (91%×Abs(N719)/Abs(overall)=91%×1/(1+0.046)) and 4% for SWNTs (91%×Abs(SWNTs)/Abs(overall)=91%×0.046/(1+0.046)). Thus, the actual optical losses from SWNTs are about 3% of incident light (90%-87%=3%) at the maximal absorption wavelength of SWNTs. (If N719 dye absorbs 99% of incident light in absence of SWNTs, the calculated result of optical losses from SWNTs is 2%.) When integrated throughout the entire visible wavelength range, the effects of optical losses from SWNTs should be
much less. (The assumption we made on the transmission and the absorbance of SWNTs is valid for 0.1 wt% SWNTs: the mass/volume concentration for 0.1 wt% SWNTs in TiO$_2$ is about 200 $\mu$g/cm$^3$, considering that the density of TiO$_2$ is about 4 g/cm$^3$ and the porosity of TiO$_2$ film is estimated as 0.5. If we approximate the optical length for SWNTs in TiO$_2$ is 50 $\mu$m (considering the scattering effect of nanoporous TiO$_2$), the absorbance of SWNTs is $0.05 \mu g^{-1} cm^{-2} \times 200 \mu g^{-1} cm^{-3} \times 50 \mu m = 0.05$.)

*This project was in collaboration with Dr. Hyunjung Yi. The genetic engineering of M13 virus and the magnetic separation of M13 virus/SWNT complex were performed by Dr. Yi.
Chapter 3. Highly efficient plasmon-enhanced dye-sensitized solar cells through metal@oxide core-shell nanostructure

3.1. Abstract

We have investigated the effects of localized surface plasmon (LSP) on the performance of dye-sensitized solar cells (DSSCs). The LSP from Ag nanoparticles (NPs) increases the absorption of the dye molecules, allowing us to decrease the thickness of photoanodes, which improves electron collection and device performance. The plasmon-enhanced DSSCs became feasible through incorporating core-shell Ag@TiO$_2$ NPs into conventional TiO$_2$ photoanodes. The thin shell keeps the photo-electrons from recombining on the surface of metal NPs with dye and electrolyte and improves the stability of metal NPs. With 0.6 wt% Ag@TiO$_2$ NPs, the power conversion efficiency of DSSCs with thin photoanodes (1.5 $\mu$m) increases from 3.1% to 4.4%. Moreover, a small amount of Ag@TiO$_2$ NPs (0.1 wt%) improves efficiency from 7.8% to 9.0% while decreasing photoanode thickness by 25% for improved electron collection. In addition, plasmon-enhanced DSSCs require 62% less materials to maintain the same efficiency as conventional DSSCs.

3.2. Introduction

Dye-sensitized solar cells (DSSCs), consisting of a meso-porous TiO$_2$ film covered by a monolayer of charge-transfer dye molecules, have attracted great attention for high power conversion efficiency (PCE) up to 11% and the low cost of materials and fabrication processes$^{10,11,15,54,55}$ To improve the PCE of DSSCs, conventional approaches include
enhancing absorption of incident light\textsuperscript{11,15} and improving collection of photo-generated carriers.\textsuperscript{20,21} By changing the thickness or morphology (e.g., vertically aligned ZnO\textsuperscript{6} or TiO\textsubscript{2}\textsuperscript{7} nanowire arrays) of the photoanode, the light absorption and carrier collection, however, is often affected in opposite ways. Effort has also been devoted to developing new dyes\textsuperscript{55-57} and using semiconductor quantum dots.\textsuperscript{12} Nevertheless, employing new dyes or quantum dots could change the adsorption of the sensitizers on TiO\textsubscript{2}, as well as their energy band positions relative to the conduction band of TiO\textsubscript{2} and the redox potential of electrolyte, affecting charge separation. Therefore, improving light harvest or carrier collection without affecting other factors has been considered a more effective approach to improve device performance.\textsuperscript{58} Localized surface plasmon (LSP) has potential for improving performance of DSSCs for the unique capability to improve the light absorption of dye with minimal impact on other material properties.

Generally, there are three types of plasmonic light-trapping geometries,\textsuperscript{59} including far-field scattering, near-field LSP and surface plasmon polaritons at the metal/semiconductor interface. Surface plasmon arising from metal nanoparticles (NPs) has been applied to increase the optical absorption and/or photocurrent in a wide range of solar cell configurations, e.g., silicon solar cells,\textsuperscript{60-63} organic solar cells,\textsuperscript{64-66} organic bulk heterojunction solar cells,\textsuperscript{67} CdSe/Si heterostructures\textsuperscript{68} and DSSCs.\textsuperscript{69-76} However, most of the previous work on plasmon-enhanced DSSCs only reported improved dye absorption or photocurrent, while the improved device performance was not observed.\textsuperscript{69-72} In addition, the earlier plasmonic geometries contained metal NPs in direct contact with the dye and the electrolyte,\textsuperscript{69-71,73,74} resulting in recombination and back reaction of photo-generated carriers and corrosion of metal NPs by electrolyte. Recently core-shell
Au@SiO₂ NPs have been applied to achieve enhanced PCE by preventing the recombination and back reaction.76 However, by using an insulating shell, part of the photo-generated carriers from the most absorption-enhanced dye molecules located on the surfaces of SiO₂ would be lost due to the difficulty in the injection to SiO₂.

Here we report an approach towards plasmon-enhanced DSSC by incorporating Ag@TiO₂ nanostructures into the TiO₂ photoanode. Our approach is demonstrated with following advantages. First, a shell covering metal NPs is utilized for avoiding recombination and back reaction, protecting metal NPs during device fabrication, as well as preventing metal NPs from corrosion by electrolyte. Second, we choose TiO₂ rather than insulating components as the shell material because the carriers can be easily transferred to surrounding TiO₂ nanoparticles which are in contact with the shell. Third, in order to maximize the effect of LSP, we use a small Ag core and a very thin shell of TiO₂ (2 nm). By utilizing Ag@TiO₂ core-shell nanostructures, we demonstrate that the optical absorption of dye molecules in solution and thin film is enhanced by the strong localized electric field generated by LSP. By incorporating Ag@TiO₂ NPs, the PCE of DSSCs with very thin photoanodes (1.5 μm) is increased from 3.1% to 4.4%. Moreover, a small amount of Ag@TiO₂ NPs (0.1 wt%) improved efficiency from 7.8% to 9.0% while decreasing the photoanode thickness by 25% for improved electron collection. In addition, 62% less materials is required for plasmon-enhanced DSSCs to maintain the same efficiency as conventional DSSCs (6.5%).

3.3. Results and discussion
The structure and mechanism for the conventional and plasmon-enhanced DSSCs is shown in Figure 3.1a-d. In the conventional DSSCs, the dyes absorb incident light and generate electrons in excited states, which inject into the TiO₂ NPs. The oxidized dye molecules are regenerated by electrons transferred from iodide. The regenerative cycle is completed by reducing triiodide to iodide at the Pt cathode. The electrons in TiO₂ diffuse to the current collector (fluorine-doped tin oxide, FTO). In the plasmon-enhanced DSSCs, the LSP arising from Ag@TiO₂ NPs increases dye absorption, allowing us to decrease the thickness of photoanode. By decreasing the thickness of photoanode, less materials is required, and the recombination as well as back reaction of photo-carriers is reduced, which improves the electron collection efficiency and thus the device performance. The core-shell nanostructure is crucial for plasmon-enhanced DSSC as shown in Figure 3.1e,f, since the oxide shell reduces the recombination and back reaction of electrons on the surface of metal NPs by providing an energy barrier between metal and dye/electrolyte. The oxide layer also protects metal NPs from etching by the electrolyte.

Geometric design and synthesis of core-shell nanostructure of Ag@TiO₂.

The induced electric field of the surface plasmon of a metal NP strongly depends on the radial distance, \( r \), from the NP\(^{77,78}\)

\[
E_{\text{out}}(r) = E_0, \hat{z} - \left( \frac{\varepsilon_{\text{in}} - \varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + 2\varepsilon_{\text{out}}} \right) a^3 E_0 \left[ \frac{\hat{z}}{r^2} - \frac{3z}{r^5} r \right],
\]

(Equation 1)

where \( E_0 \), and \( E_{\text{out}} \) are the electric field of incident light and the electric field outside the metal NP; \( \varepsilon_{\text{in}} \) and \( \varepsilon_{\text{out}} \) are the dielectric constant of the metal NP and that of the external
environment; $a$ is the radius of the spherical metal NP. The surface plasmon induced electric field decreases quickly with increasing distance from the NP. Therefore, a thinner shell corresponds to a stronger electric field induced by LSP on or close to the surface of the core-shell NP, thus more absorption enhancement of the dye molecules surrounding the core-shell NP (experimental evidence can be found in Figure 3.7 and Figure 3.8). In addition, LSP plays a dominant role only when the NP size is much smaller than the wavelength of incident light, since larger metal NPs scatter light more. Therefore, we utilize the core-shell nanostructure with a small metal core and a thin oxide shell, i.e. Ag@TiO$_2$ nanostructure, to maximize the effects of LSP on optical absorption of dye molecules and the performance of DSSCs. We synthesized Ag@TiO$_2$ NPs using a two-step chemical reaction, forming Ag NPs at 120°C and forming TiO$_2$ shells at room temperature (see methods). Figure 3.2a shows the transmission electron microscope (TEM) image of Ag@TiO$_2$ NPs and Figure 3.2b,c show the high-resolution TEM (HRTEM) images of an individual Ag@TiO$_2$ NP with the lattice fringes of Ag crystalline structure and an amorphous TiO$_2$ shell about 2 nm thick. The formation of Ag@TiO$_2$ nanostructure was also confirmed by optical absorption spectroscopy (Figure 3.2d). The absorption peak from the surface plasmon resonance shifts from 403 nm to longer wavelength of 421 nm, due to the higher dielectric constant surrounding the Ag NPs of amorphous TiO$_2$ than that of polyvinylpyrrolidone (PVP).

To investigate the stability of Ag@TiO$_2$ NPs during device fabrication, we examined the structure of the core-shell NPs before and after the annealing process through x-ray diffraction (XRD). Figure 3.3 shows XRD patterns of Ag@TiO$_2$ NPs as-synthesized and annealed at 500°C. For the core-shell NPs as-synthesized at room temperature, the
diffraction patterns from (111), (200), (220) and (311) planes of cubic structured Ag NPs were clearly seen, while a broad peak at 22.4° was ascribed to the x-ray scattering from the amorphous structured TiO₂ shells. After annealing, the broad amorphous peak disappeared; while the diffraction patterns from (101), (200), (105) and (211) planes of anatase structured TiO₂ shells were observed. The crystallinity of the Ag NPs was also improved by annealing, observed by both XRD and HRTEM. It is considered that the shell layer protects the Ag cores from reacting with the environment or aggregating to form larger particles during the annealing process. In addition, the shell layer is also considered to protect the Ag cores from corrosion by the electrolyte during solar cell operation.

**Effect of LSP on the optical absorption of dye molecule.**

The effect of LSP from metal NPs on the absorption of ruthenium dye is investigated in both solution and thin film. At first, we studied the LSP effect on dye absorption in the solution of dye and Ag or Ag@TiO₂ NPs. The LSP effect in solution simulates the effect in plasmon-enhanced DSSC, and the concentrations of NPs and dyes can be precisely controlled. As shown in Figure 3.4a-c, the absorption of dye increases with the presence of Ag NPs in solution, and the absorption peak position shifts from 530 nm to shorter wavelength of 510 nm (Figure 3.4a). The maximum relative enhancement of dye absorption occurs at 450 nm (Figure 3.4c), close to the LSP resonance peak of Ag NPs around 403 nm instead of the dye absorption peak at 535 nm, suggesting that the increase of dye absorption mainly arises from LSP of Ag NPs. Figure 3.4d-f show that the dye absorption in solution can also be enhanced by incorporating Ag@TiO₂ NPs. Moreover,
this enhancement of dye absorption increases with time after mixing dye and core-shell NPs (Figure 3.4d), which could be the effect of the dye molecules adsorbing on the surface of TiO₂ shell. While increasing the time after mixing, the number of dye molecules adsorbed on the Ag@TiO₂ NPs increases, reducing the average distance between dye molecules and Ag cores, thus further enhancing the dye absorption. This time-dependent (dye-to-NP distance-dependent) behavior of absorption enhancement agrees with our intention of utilizing a thin shell to maximize the LSP effect. In addition, the adsorption of dye on Ag@TiO₂ in solution is similar to that in the thin films where the dye molecules are adsorbed on or near the surface of Ag@TiO₂ NPs. In order to study the LSP effect on the absorption of dye molecules in meso-porous TiO₂ thin films, 1 μm thick films were prepared by spin-coating TiO₂ NPs and TiO₂ NPs blended with Ag@TiO₂ NPs (Ag:TiO₂=0.2 wt%) and annealed at 500°C (See methods). Compared to the dyed TiO₂ film, there is an increase of absorption for the film incorporated with Ag@TiO₂ NPs (Figure 3.4g), and the enhancement is similar to that in the solution (Figure 3.4i). It also agrees with the previously reported observations on plasmon-enhanced dye absorption.⁶⁹,⁷⁰,⁷²,⁷⁶ The increase of absorption of dye molecules could be attributed to the interaction of dye molecular dipole and enhanced electric field surrounding the NPs, together with the increase of light scattering also induced by the LSP which increased the optical path.

**Effect of LSP on the performance of DSSC.**

To investigate the effect of LSP on device performance, we compared the performance of plasmon-enhanced DSSCs and standard DSSCs with only TiO₂ NPs as photoanodes. The
TiO₂-only DSSCs were fabricated using the conventional method, while the Ag@TiO₂ NPs (0.02 to 1.2 wt%) were incorporated into TiO₂ paste to fabricate the plasmon-enhanced DSSCs (See methods). Figure 3.5a shows the photocurrent density-voltage characteristics ($J-V$ curves) of the most efficient plasmon-enhanced DSSC and TiO₂-only DSSC with the same photoanode thickness of 1.5 μm. The TiO₂-only DSSC showed a PCE ($\eta$) of 3.1%; whereas, the plasmon-enhanced DSSC with Ag@TiO₂ NPs exhibited a PCE of 4.4% (increased by 42%). Compared with the TiO₂-only DSSC, the fill factor ($FF$) and open-circuit voltage ($V_{OC}$) of the plasmon-enhanced DSSC were close; while the short-circuit current density ($J_{sc}$) significantly increased by 37%, from 6.07 mA/cm² to 8.31 mA/cm². Since $\eta = J_{SC} \cdot V_{OC} \cdot FF / P_0$ where $P_0$ is the intensity of incident light, the improvement of PCE in plasmon-enhanced DSSC is mainly due to the increased photocurrent corresponding to enhanced dye absorption by LSP. We further investigated the effect of the concentration of Ag@TiO₂ on the device performance. Figure 3.5b,c show the averaged PCE and $J_{SC}$ changing with concentration of Ag@TiO₂ NPs. When the concentration of Ag/TiO₂ increased from 0 to 0.6 wt%, both $J_{SC}$ and PCE monotonically increased. The decrease of PCE was observed with further increasing Ag@TiO₂ concentration, which was probably due to the increased trapping of photo-generated electrons by Ag and increased light absorption of Ag NPs which transformed part of the incident solar power into heat. Therefore, through enhancing the light absorption and photocurrent, the device performance of DSSCs has been improved by LSP from Ag@TiO₂ NPs. To our knowledge, PCE of 4.4% is the best performance for DSSCs with photoanodes of similar thicknesses.
For practical DSSCs, thicker photoanodes are required to absorb more light. By using LSP, the thickness of photoanodes can be reduced while maintaining the optical absorption of DSSC. As shown in Figure 3.5d, the PCE of DSSCs increases with the thickness for both conventional and plasmon-enhanced DSSCs, but it increases faster with the presence of Ag@TiO\textsubscript{2} NPs in the photoanode. For the devices with the same thickness, the PCE of the plasmon-enhanced DSSC is higher than that of TiO\textsubscript{2}-only DSSC. In addition, to achieve the same PCE, the photoanode thickness of the plasmon-enhanced DSSC is much thinner than that of TiO\textsubscript{2}-only DSSC. For instance, it is observed that the plasmon-enhanced DSSC with 5 \textmu m thick photoanode and TiO\textsubscript{2}-only DSSC with 13 \textmu m thick photoanode possess the same PCE of 6.5%, reducing 62% of materials used for device fabrication without affecting the device performance.

Electron collection is also an important factor to be considered in addition to light harvesting, since light absorption in practical devices is near unity with thicker photoanodes. Although the optical absorption is increased by thicker photoanodes, the carrier collection efficiency is decreased due to longer distance for electron diffusion. In contrast, a thinner photoanode with the same optical absorption, enabled by LSP, is expected to be advantageous to the electron collection as well as the device performance. As shown in Figure 3.5e, the plasmon-enhanced DSSC achieved the highest PCE of 9.0% with a 15 \textmu m thick photoanode, compared to the TiO\textsubscript{2}-only DSSC reaching the highest PCE of 7.8% with a 20 \textmu m thick photoanode. Therefore, by introducing Ag@TiO\textsubscript{2} NPs into the TiO\textsubscript{2} photoanode, the PCE of the DSSC was improved by 15% while the photoanode thickness was decreased by 25%. Considering the near unity optical absorption for the photoanodes of both plasmon-enhanced and TiO\textsubscript{2}-only DSSCs,
the improved PCE mostly arises from increased electron collection efficiency by decreased distance for electron diffusion. In addition, the uniform plasmonic geometry employed enhances the absorption throughout the photoanode, whereas the metal NPs from previous works were located either on the current collector,68-72 or the counter electrode,73 where LSP only affected the thin layer close to the metal NPs.

To investigate the effect of LSP on the spectral response of the solar cells, the incident photon-to-current efficiency (IPCE) measurement was performed Figure 3.6). The IPCE is the product of the light harvesting efficiency, electron injection efficiency and electron collection efficiency. Increasing light absorption will directly improve light harvesting and the IPCE, if electron injection and collection are not affected. As shown in Figure 3.6a, the shape of the IPCE spectrum from the TiO2-only device closely matches the shape of optical absorption of the dye molecules in the thin film; while the IPCE spectrum from the plasmon-enhanced device increases over the whole wavelength range. Moreover, the enhancement is most significant in the range of 400~500 nm with a peak around 460 nm (Figure 3.6b). The similarity between IPCE enhancement of DSSC and the absorption enhancement of thin film indicates that the LSP from core-shell NPs improved the device performance through increased dye absorption.

3.4. Conclusion

We developed a general approach to utilizing LSP to improve the performance of DSSCs. We demonstrated that the enhanced localized electromagnetic field increased the optical absorption of dye molecules in solution and in thin film. By incorporating small Ag NPs coated with a thin TiO2 shell into the TiO2 photoanodes as thin as 1.5 μm, we achieved a
PCE of 4.4%; and the best plasmon-enhanced DSSC in our work had a PCE of 9.0% with reduced photoanode thickness for better electron collection. Our method has advantages of preventing charge recombination at the surface of metal NPs, improving thermal and chemical stability of metal cores and uniformly enhancing optical absorption throughout the photoanode. In addition, the fabrication method for plasmon-enhanced DSSCs is compatible with the large-scale processes, such as printing and jet-spraying.

We believe that the implication of our work will guide the research in utilizing LSP to improve practical DSSC performance, by reducing the photoanode thickness while remaining the near unity absorption, thus improving electron collection and PCE. Moreover, molecular dyes possessing improved charge separation and better stability against water and oxygen in the environment could be employed in DSSC without the requirement of high light extinction due to enhanced dye absorption by LSP. Our approach also enables the utilization of LSP in many other thin-film photovoltaic technologies that require efficient light harvesting and decreased recombination and back reaction, such as quantum dot-sensitized solar cells, organic solar cells and quantum dot/organic hybrid solar cells, and other types of photo-electron conversion devices, such as photo detectors.

3.5. Figures
Figure 3.1. Structures and mechanisms of conventional DSSCs and plasmon-enhanced DSSCs. Device structures of conventional DSSCs (a) and plasmon-enhanced DSSCs (b); plasmon-enhanced DSSCs require thinner film and less materials to achieve same PCE. Illustration for photo-generated electron collection in conventional DSSCs (c) and plasmon-enhanced DSSCs (d); plasmon-enhanced DSSCs avoid electron recombination due to thinner photoanode layer. Mechanisms of plasmon-enhanced
DSSCs using Ag@TiO₂ NPs (e) and Ag NPs (f); while using Ag@TiO₂ NPs, optical absorption of dye molecules is enhanced by LSP, electrons diffuse among TiO₂ NPs and iodide ions regenerate dyes by providing electrons; while using Ag NPs, there is direct contact between Ag and the electrolyte and the surface of Ag NPs serve as recombination sites for the photo-generated electrons and triiodide ions.

Figure 3.2. **Synthesis and characterization of Ag@TiO₂ NPs.** (a-c) TEM and HRTEM images of Ag@TiO₂ NPs. (d) Optical absorption spectra of solutions of Ag NPs stabilized by PVP (molecular weight 10,000 D), TiO₂ NPs and Ag@TiO₂ NPs.
Figure 3.3. XRD patterns of Ag@TiO₂ NPs. as-synthesized at room temperature (a) and after annealing at 500°C for 30 minutes (b). The inverted triangle symbols indicate the XRD patterns from anatase structured TiO₂. (c,d) The XRD patterns based on the JCPDS card for anatase TiO₂ (#21-1272) and Ag (#04-0783) respectively.
Figure 3.4. LSP induced enhancement of optical absorption of dye molecules in solution and thin film. (a) Optical absorption spectra of Ag NPs, ruthenium dye molecules, and their mixture in ethanol solution. (b) Net changes of dye absorption (ΔOD) due to the presence of Ag NPs in solution. (c) Relative changes of effective extinct coefficient of dye (Δα/α) due to the presence of Ag NPs in solution. (d) Optical absorption spectra of Ag@TiO₂ NPs, ruthenium dye molecules, and their mixtures (immediately after mixing and 16 hours after mixing) in ethanol solution. (e) Net changes of dye absorption (ΔOD) due to the presence of Ag@TiO₂ NPs in solution. (f) Relative changes of effective extinct coefficient of dye (Δα/α) due to the presence of Ag@TiO₂ NPs in solution. (g) Optical absorption spectra of Ag@TiO₂ NPs, ruthenium dye
molecules, and their mixtures in the matrix of TiO$_2$ thin film. (h) Net changes of dye absorption ($\Delta$OD) due to the presence of Ag@TiO$_2$ NPs in thin film. (i) Relative changes of effective extinct coefficient of dye ($\Delta\alpha/\alpha$) due to the presence of Ag@TiO$_2$ NPs in thin film. For the calculation of $\Delta$OD and $\Delta\alpha/\alpha$: $\Delta\alpha/\alpha = \Delta$OD(\(\lambda\)) / OD$_{dye}(\lambda)$ = ($OD_{dye,Ag}(\lambda) - OD_{dye}(\lambda) - OD_{Ag}(\lambda)$) / OD$_{dye}(\lambda)$, where $OD_{dye}(\lambda)$, $OD_{Ag}(\lambda)$ and $OD_{dye,Ag}(\lambda)$ are the optical densities at wavelength $\lambda$ of pure dye solution, Ag NP solution and their mixture solution with the same concentrations of dye and Ag NPs, respectively. For the solid state thin films, the net absorption of dye molecule is $OD_{dye}(\lambda) = OD_{dye,TiO_2}(\lambda) - OD_{TiO_2}(\lambda)$.

Figure 3.5. Effect of LSP on the performance of DSSCs. (a) Current density (solid lines) and PCE (dashed lines) of the plasmon-enhanced DSSC (Ag/TiO$_2$=0.6 wt%,
$\eta=4.4\%, \text{FF}=66\%$ and TiO$_2$-only DSSC ($\eta=3.1\%, \text{FF}=64\%$) with the same photoanode thickness of 1.5 $\mu$m; (b,e) the dependence of PCE and $J_{SC}$ on the concentration of Ag@TiO$_2$ NPs in photoanode with the same thickness of 1.5 $\mu$m; (d) the PCE of plasmon-enhanced DSSC and TiO$_2$-only DSSC with photoanodes of different thickness, where the lines are drawn to show the tendency; (e) Current density (solid lines) and PCE (dashed lines) of the most efficient plasmon-enhanced DSSC (Ag/TiO$_2$=0.1 wt%, $\eta=9.0\%, \text{FF}=67\%, 15 \mu$m) and TiO$_2$-only DSSC ($\eta=7.8\%, \text{FF}=66\%, 20 \mu$m) in this work.

Figure 3.6. Spectral responses of TiO$_2$-only and plasmon-enhanced DSSCs. (a) IPCE spectra of the DSSCs with and without the presence of Ag@TiO$_2$; (b) the relative change of the IPCE caused by the incorporation of Ag@TiO$_2$ NPs. $\Delta\text{IPCE/}\text{IPCE}(\lambda) = (\text{IPCE}_{\text{plasmon-enhanced}}(\lambda) - \text{IPCE}_{\text{TiO}_2\text{-only}}(\lambda)) / \text{IPCE}_{\text{TiO}_2\text{-only}}(\lambda)$, where IPCE$_{\text{plasmon-enhanced}}(\lambda)$
and IPCE_{TiO2-only}(\lambda) are the ICPE at wavelength \lambda for plasmon-enhanced DSSC and TiO2-only DSSC respectively.

**Figure 3.7.** TEM images of synthesized Ag@TiO2 NPs with thick TiO2 shells. The average thickness of the shell is around 10 nm.

**Figure 3.8.** The comparison of device performance of TiO2-only DSSC and DSSC incorporated with Ag@TiO2 NPs with thick TiO2 shells. By incorporating Ag@TiO2 NPs with average shell thickness of approximately 10 nm, the PCE was increased from 2.3% of TiO2-only DSSC to 2.6% of plasmon-enhanced DSSC. 13% increase was less than 42% increase while using 2 nm TiO2 shell coated Ag NPs for plasmon-enhanced
DSSCs. This experimental result demonstrates that thinner TiO$_2$ shell is advantageous for maximizing the LSP effect. Current density and PCE of plasmon-enhanced DSSC (Ag@TiO$_2$ NPs with thick shells, $\eta=2.6\%$, FF=68$\%$) and TiO$_2$-only DSSC ($\eta=2.3\%$, FF=69$\%$).

3.6. Experimental

Materials.

Titanium iso-propoxide (TPO, 97$\%$) and polyvinylpyrrolidone with an average molecular weight of 10 kg/mol (PVP-10) were purchased from Sigma-Aldrich; ethanol (99.5$\%$), acetone (99.5$\%$), nitric acid (70$\%$) and ethylene glycol (99.9$\%$) were purchased from Mallinckrodt Chemicals; ammonia (28-30 wt% NH$_3$ in water) was purchased from VWR International Inc. Poly(acrylic acid) (PAA, average molecular weight: 90,000, 25$\%$ aqueous solution) was obtained from Polysciences, Inc. cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (also named N3 or Ruthenizer 535, purchased from Solaronix) was used as 0.5 mM solution in acetonitrile and tert-butanol (volume ratio = 1:1). All chemicals were used as received. All water was deionized (18.2 M$\Omega$, milli-Q pore).

Synthesis of NPs.

The 20 nm sized TiO$_2$ nanocrystals were synthesized using the procedure in literature$^{15}$. Small Ag NPs with a diameter of 20-30 nm were synthesized by a modified polyol process: typically, 0.1 mmol of silver nitrate was added into 25 mL of ethylene glycol solution containing 0.5 g of PVP-10 and the mixture was kept stirring at room
temperature till silver nitrate was completely dissolved. Then the solution was slowly heated up to 120°C and kept at the temperature for 1 hour with constant stirring. After the reaction, the NPs were separated from ethylene glycol by addition of acetone (200 mL of acetone per 25 mL of reaction mixture) and subsequent centrifugation at 3000 rpm. The supernatant was removed and the NPs were washed with ethanol and centrifuged at 3000 rpm, and redispersed in 18 mL of ethanol and 2 mL of 4% ammonia in ethanol (achieved by diluting the 28% ammonia 7 times in ethanol). This solution was stirred and sonicated more than 30 minutes, and divided equally into two parts, and they were directly used for coating TiO₂ shell by adding TPO solution in ethanol while stirring the solution vigorously. Typically, 6 μl of TPO in 1 ml of ethanol was added into the solution, yielding a shell of TiO₂ around 2 nm thick. The reaction mixture was then stirred for 12 hours at room temperature in dark. The Ag NPs in ethylene glycol (as synthesized) or in ethanol (purified) both can be used for synthesis of Ag@TiO₂ NPs with thicker TiO₂ shell. A solution of PAA was prepared by adding 2 g of PAA (25% aqueous solution) into mixed solvent of 1 mL of water and 8 mL ethanol and stirring at room temperature over 1 hour. Then 0.2 mL of PAA solution was added into 12.5 mL of as synthesized Ag NPs in ethylene glycol (containing 0.05 mmol Ag) or into 10 mL of Ag NPs in ethanol (containing less than 0.05 mmol Ag due to the loss during purification), and the solution was kept stirring for over 4 hours and sonicated for 30 minutes at room temperature. Then 1 mL of ethanol solution containing with 20 μL TPO was added into the Ag NPs solution, and the reaction was kept stirring in dark. The TEM images of Ag@TiO₂ NPs after reacting with TPO for 2 hours were shown in Figure 3.7.

Characterization of NPs.
TEM observations of synthesized nanostructures (TiO$_2$, Ag and Ag@TiO$_2$) were performed using JEOL 200CX, JEOL 2011 and JEOL 2010F TEMs with accelerating voltage of 200 kV. The optical absorption spectroscopy measurements were performed using Beckman Coulter DU800 UV-VIS spectrophotometer. 1 μm thick films of TiO$_2$ NPs or TiO$_2$ NPs incorporated with Ag@TiO$_2$ NPs on 2.5x2.5 cm$^2$ fused silica wafers were used for thin-film optical absorption measurements, which were prepared by spin coating (Specialty Coating Systems, 6800 spin coater) and followed by annealing treatment at 500°C for 15 minutes. Then the film thickness was measured using a Dektak 150 surface profiler. These films were immersed into 0.1 mM ruthenium dye solution (volume ratio of acetonitrile to tert-butanol is 1:1) and kept at room temperature for 12 hours. Then the dyed films were immersed in acetonitrile for 5 minutes to remove non-adsorbed dye.

Fabrication of DSSCs.

The fabrication of the 1.5 μm thick photoanodes of both TiO$_2$-only DSSCs and plasmon-enhanced DSSCs is performed by spin coating, the same method used for preparing the thin films for optical absorption measurement. For TiO$_2$-only DSSCs with photoanode thickness larger than 1.5 μm, the fabrication was carried out using the procedure described previously.$^{58}$ The photoanodes incorporated with Ag@TiO$_2$ NPs were fabricated with a modified procedure. The different amounts of Ag@TiO$_2$ NPs in ethanol solution (Ag to TiO$_2$ ratio from 0.02 to 1.2 wt%) were mixed with TiO$_2$ paste (mixture of TiO$_2$ NPs, ethyl celluloses and terpineol), followed by stirring and sonicating. Then ethanol was removed by a rotary-evaporator. After the paste incorporated with Ag@TiO$_2$
NPs was achieved, the fabrication procedure of the photoanodes of plasmon-enhanced DSSCs was the same as that of the TiO₂-only DSSCs. The photoanodes of TiO₂-only and those incorporated with Ag@TiO₂ were immersed into N3 dye solution and kept at room temperature for 24 hours. Then dyed films were immersed in acetonitrile for 5 min to remove non-adsorbed dye.

**Characterization of DSSCs.**

Photovoltaic measurements were performed under illumination generated by an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to 100 mW/cm² by using a reference Si photodiode with a powermeter (1835-C, Newport) and a reference Si solar cell in order to reduce the mismatch between the simulated light and AM 1.5. The $J-V$ curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. A black tape mask was attached to the device in order to prevent irradiations from scattered light. The IPCE spectra were obtained using a computer-controlled system (Mode QEX7, PV Measurements Inc.) consisting of a 150 W xenon lamp light source, a monochromator equipped with two 1200 g/mm diffraction gratings. The incident photon flux was determined using a calibrated silicon photodiode. Measurements were performed in a short-circuit condition, while the cell was under background illumination from a bias light of 50 mW/cm².
Chapter 4. Tunable localized surface plasmon-enabled broadband light harvesting enhancement for high-efficiency panchromatic dye-sensitized solar cells

4.1. Abstract

In photovoltaic devices, light harvesting (LH) and carrier collection have opposite relations with the thickness of the photoactive layer, which imposes a fundamental compromise for the power conversion efficiency (PCE). Unbalanced LH at different wavelengths further reduces the achievable PCE. Here, we report a novel approach to broadband balanced LH and panchromatic solar energy conversion using multiple-core-shell structured oxide-metal-oxide plasmonic nanoparticles. These nanoparticles feature tunable localized surface plasmon resonance frequencies and the required thermal stability during device fabrication. By simply blending the plasmonic nanoparticles with available photoactive materials, the broadband LH of practical photovoltaic devices can be significantly enhanced. We demonstrate a panchromatic dye-sensitized solar cell with an increased PCE from 8.3% to 10.8%, mainly through plasmon-enhanced photo-absorption in the otherwise less harvested region of solar spectrum. This general and simple strategy also highlights easy fabrication, and may benefit solar cells using other photo-absorbers or other types of solar-harvesting devices.

KEYWORDS. Tunable, localized surface plasmon, light harvesting enhancement, panchromatic dye-sensitized solar cells, multiple-core-shell nanoparticles.

4.2. Introduction
Developing efficient and inexpensive solar cells is of paramount importance for preserving non-renewable energy and lowering carbon dioxide emissions. The power conversion efficiency (PCE) of the solar cells is generally governed by the tradeoff between light harvesting (LH) and carrier collection. To break this compromise, strategies of improving either LH or carrier collection while maintaining the other have been successful\textsuperscript{58,79}. However, most photo-absorbing materials possess unbalanced LH in high- and low-absorption wavelength regions ($\lambda_{Hi}$ and $\lambda_{Lo}$, \textbf{Figure 4.1a,b}), which results in another tradeoff. At $\lambda_{Lo}$, long absorption lengths are required, which reduce carrier collection; at $\lambda_{Hi}$, solar energy is fully-absorbed by thin photoactive layers, which inefficiently exploit energy at $\lambda_{Lo}$ (usually the red to near-infrared (NIR) region, \textbf{Figure 4.1c}). Consequently, the ability to achieve broadband balanced LH is desirable for high-efficiency solar cells.

Achieving such broadband balanced LH would lead to panchromatic solar energy conversion, an ideal strategy for maximizing overall LH. As a promising solution-processed photovoltaic technology, dye-sensitized solar cells (DSSCs) have demonstrated PCE exceeding 12\%\textsuperscript{80-85}; to further improve the PCE, several approaches toward panchromatic DSSCs\textsuperscript{86} have been attempted, including the development of panchromatic dyes\textsuperscript{87}, co-adsorbing dyes\textsuperscript{88}, and energy transfer systems\textsuperscript{89}. However, these methods usually require extensive synthesis and optimization for various parameters (\textit{e.g.}, spectral overlapping and spatial arrangement) and are limited to small ranges of materials. Therefore, a general and simple approach for broadband balanced LH and panchromatic DSSCs is required.
Localized surface plasmons (LSPs) are the elementary excitation states in noble metal nanoparticles (NPs), and can improve LH of photo-absorbers\textsuperscript{59,76,79,90-93}. Here, we introduce a general and simple strategy for broadband LH enhancement and panchromatic DSSCs by matching LSP resonance (LSPR) wavelength \( \lambda_{\text{LSPR}} \) of plasmonic NPs with \( \lambda_{\text{Lo}} \) of existing photo-absorbers. Demonstrated by both simulations and experiments, matching \( \lambda_{\text{LSPR}} \) with \( \lambda_{\text{Hi}} \) or \( \lambda_{\text{Lo}} \) affects LH differently (Figure 4.1d).

Although matching \( \lambda_{\text{LSPR}} \) with \( \lambda_{\text{Hi}} \) readily improves LH and PCE for optically-thin photo-absorbing layers, matching \( \lambda_{\text{LSPR}} \) with \( \lambda_{\text{Lo}} \) maximally increases LH and PCE for practical photovoltaic devices with optically-thick layers, through enhancing photo-absorption in the weakly-absorbing region. The multiple-core-shell oxide-metal-oxide plasmonic NPs developed and utilized here are advantageous over other geometries, by featuring: adjustable \( \lambda_{\text{LSPR}} \) of 600-1,000 nm, substantially enhanced near-field electromagnetic (EM) intensity, and preservable plasmonic properties during device fabrication. By matching \( \lambda_{\text{LSPR}} \) with \( \lambda_{\text{Lo}} \) of a common dye (N719), a panchromatic DSSC with broadband balanced LH and a PCE of 10.8\% is achieved (30\% increase comparing to DSSCs without plasmonic NPs).

4.3. Results and discussion

Synthesis and optical characterization are performed for the core-shell (\( d_{\text{core}} \sim 15 \text{ nm}, \ d_{\text{T}} \sim 2 \text{ nm} \)) Ag@TiO\(_2\) (AgT) and Au@TiO\(_2\) (AuT) and multiple-core-shell (\( d_{\text{core}} \sim 15 \text{ nm}, \ d_{\text{Au}} \sim 0-4 \text{ nm}, \ \text{and} \ d_{\text{T}} \sim 2 \text{ nm} \)) TiO\(_2\)-Au-TiO\(_2\) (TAuT) NPs (Figure 4.2a, Figure 4.6, Figure 4.7, Figure 4.8, and Figure 4.9). \( d_{\text{core}}, \ d_{\text{Au}}, \ \text{and} \ d_{\text{T}} \) represent core diameter, gold-shell thickness, and TiO\(_2\)-shell thickness, respectively. When synthesizing the gold-shell of
TAuT NPs, Au seeds gradually cover the core and coalesce to form a continuous layer, which is stable at 500°C (annealing condition for DSSCs). The outer TiO_2-shells impede the metals from promoting recombination in the DSSCs. The $\lambda_{\text{LSPR}}$ of AgT and AuT NPs are 420 and 550 nm respectively, and the $\lambda_{\text{LSPR}}$ of TAuT NPs is continuously tunable from 1,000 to 600 nm by increasing $d_{\text{Au}}$ to 4 nm (Figure 4.2b). Tunable $\lambda_{\text{LSPR}}$ across visible-NIR is thus achieved.

The interaction of the NPs with light was investigated using the finite-difference time-domain (FDTD) method. All plasmonic NPs strongly amplify the near-field EM intensity (Figure 4.2c). Therefore, surrounding dye-molecules would experience a significantly increased light intensity near the LSPR frequency and a higher photon flux ($\phi_{\text{ph}}$), which increases electron-hole pair generation. The enhancement factors (derived by integrating over near-field space, Figure 4.10) of plasmonic NPs as functions of wavelength (Figure 4.2d) show similar results of $\lambda_{\text{LSPR}}$ to those obtained from absorption spectra. The characteristic absorption peak of the TAuT NPs originates from the LSPs arising in the gold-shell structure. By tuning $d_{\text{Au}}$ and $d_T$ of TAuT NPs in 2-6 nm, $\lambda_{\text{LSPR}}$ of 600-800 nm is achieved; as expected, thinner gold- and thicker TiO_2-shells result in longer $\lambda_{\text{LSPR}}$ (Figure 4.2e, and Figure 4.11). Furthermore, an optimum $d_{\text{Au}}$~3 nm maximizes the spectrum-integrated enhancement factor and thicker TiO_2-shells tend to weaken the enhancement (Figure 4.2f, the enhancement factor at $\lambda_{\text{LSPR}}$ is shown in Figure 4.12). The $\lambda_{\text{LSPR}}$ and enhancement factors are also obtained for AgT and AuT NPs, which extend the LSP-enhanced spectral range to vis-NIR. These results represent
the intrinsic near-field enhancement of plasmonic NPs and do not take the spectral response of dye-molecules into account.

The impact on the photo-absorption of surrounding dye-molecules is investigated by comparing the enhancement factors at different wavelengths (Figure 4.2g, and Figure 4.13). At $\lambda_{Lo}=600-800$ nm (for N719), the greatest enhancement occurs by using TAuT NPs (e.g., $d_{Au}$~3 nm and $d_{T}$~2 nm for 700 nm), where $\lambda_{LSPR}$ matches $\lambda_{Lo}$; at $\lambda_{Hi}=400-600$ nm, the maximum enhancement occurs by using AuT and AgT NPs, where $\lambda_{LSPR}$ matches $\lambda_{Hi}$. The overall dye absorption is also maximally improved by AgT and AuT NPs (bottom part of Figure 4.2g). These results and the simulated LSP-enhanced dye absorption ($\lambda_{LSPR}$=400-700 nm, Figure 4.14) suggest that, on the level of individual plasmonic NP, matching $\lambda_{LSPR}$ with $\lambda_{Hi}$ enhances overall LH of dye-molecules more efficiently, whereas matching $\lambda_{LSPR}$ with $\lambda_{Lo}$ balances LH in a broad spectral range.

Moreover, the LSP-enhanced LH of N719-sensitized mesoporous TiO$_2$ films (Figure 4.2h) agrees with the simulation results. AgT and AuT NPs improve LH mostly at $\lambda_{Hi}$, whereas TAuT NPs (TAuT-700 NPs with $\lambda_{LSPR}$=700 nm are used for all thin film LH and device performance characterizations) increase LH at $\lambda_{Lo}$, resulting in balanced spectra. The similar enhancements of simulated EM intensity and LH of thin films around $\lambda_{LSPR}$ confirm that the LH improvement stems from the interaction between dye-molecular dipoles and the LSP-enhanced near field and scattering cross-section of the NPs.

The multiple-core-shell oxide-metal-oxide plasmonic NPs are advantageous over other geometries (e.g. nanorods, nanodisks, and hollow nanoshells) which also possess tunable
\( \lambda_{\text{LSPR}} \) in vis-NIR\(^{95,99}\). Under thermal treatment, the TAuT NPs maintain geometric and plasmonic properties with the rationally-designed templated metal-shell structure, while other geometries melt to spheres or spheroids and the characteristic \( \lambda_{\text{LSPR}} \) blue-shifts (Figure 4.2i, Figure 4.15, and Figure 4.16), severely reducing the ability to enhance LH at \( \lambda_{\text{Lo}} \). In addition, little change in synthesis is required to tune \( \lambda_{\text{LSPR}} \) of TAuT NPs due to their high sensitivity to geometry. Moreover, metal-shell structures (e.g. TAuT, hollow gold-shell (Figure 4.18 and Figure 4.19), and TAgT (Figure 4.20 and Figure 4.21)) possess larger EM field enhancement than spherical solid metal structure (e.g. AuT and AgT). Therefore, the multiple-core-shell plasmonic NPs can benefit many LSP-enhanced applications which require tunable spectral response and high temperature fabrications.

To study the LH of tunable LSP-enhanced DSSCs, different plasmonic NPs-incorporated TiO\(_2\) photoanodes (thickness of 1-20 \( \mu \)m and plasmonic NPs-TiO\(_2\) ratio of 0.01-3.2 wt\%) are assembled into DSSCs\(^{58,79}\). In 1.5-\( \mu \)m-thick optically-thin photoanodes, AgT, AuT, and TAuT NPs increase the incident photon-to-current conversion efficiency (IPCE) at \( \lambda_{\text{max}} \) (maximum absorption wavelength \( \sim \)530 nm) by 45%, 60%, and 50%, respectively (Figure 4.3a-left). Enhancement is maximized when \( \lambda_{\text{LSPR}} \) is closest to \( \lambda_{\text{max}} \). Similarly, at 700 nm, TAuT NPs increase IPCE the most by 80%, whereas AgT and AuT NPs enhance IPCE only by 21% and 22% due to large mismatch between \( \lambda_{\text{LSPR}} \) and \( \lambda_{\text{Lo}} \). By correlating the absorbance, LH efficiency (LHE), and IPCE, we find that the experimental results of absorbance and IPCE enhancement are similar, which indicate that the IPCE improvement mainly arises from LSP-enhanced LH.
While IPCE (specifically LHE) of thin photoanodes is readily increased by LSPs, optically-thick photoanodes (10–15 µm) for practical devices are required to ensure balance between LH and carrier collection for maximized PCE, where the LHE at $\lambda_{Hi}$ and internal quantum efficiency are close to unity. At $\lambda_{\text{max}}$, less than 5% enhancement of IPCE for all plasmonic NPs is observed (Figure 4.3a-middle). In contrast, at $\lambda_{Lo}$, the TAuT NPs increase IPCE by up to 100%, whereas AgT and AuT NPs increase IPCE slightly. Additionally, the IPCE increases monotonically with the concentration of TAuT NPs (Figure 4.3a-right).

Therefore, both experiments and simulations have demonstrated that matching $\lambda_{\text{LSPR}}$ with $\lambda_{Hi}$ or $\lambda_{Lo}$ impacts the spectral response of LH differently. Matching $\lambda_{\text{LSPR}}$ with $\lambda_{Hi}$ enhances LH in already strongly-absorbing region, which benefits optically-thin photoanodes. In contrast, matching $\lambda_{\text{LSPR}}$ with $\lambda_{Lo}$ improves the weakly-absorbed part of solar spectrum, which is of great importance for broadband balanced LH in practical panchromatic solar cells.

The PCEs of tunable LSP-enhanced DSSCs are measured (Figure 4.22) (PCE=$J_{SC}V_{OC}FF/P_{in}$, $J_{SC}$, $V_{OC}$, FF, and $P_{in}$ represent short-circuit current density, open-circuit voltage, fill factor, and incident power density, separately). $J_{SC}$ ($=q \int \text{IPCE}(\lambda) \phi_{ph}(\lambda)d\lambda$) is improved with increasing concentrations of plasmonic NPs (within the concentration range studied); the largest $J_{SC}$ is achieved by incorporating the highest concentration of TAuT NPs (Figure 4.3b). Besides the improved LH, thinner photoanodes for optimized PCEs (the optimized thicknesses for TiO$_2$, AgT, AuT, and TAuT DSSCs are 13.2, 10.9, 10.1, and 11.0 µm) are also responsible for the improved
IPCE and $J_{sc}$, by improving the carrier collection (electron diffusion lengths are not changed significantly, Figure 4.25).

Additionally, $V_{oc}$ is increased by introducing plasmonic NPs (Figure 4.3c). Generally, $V_{oc}$ is limited by the material properties of electronic structure (e.g., the quasi-Fermi level of TiO$_2$ and redox potential of electrolyte); enhancing $V_{oc}$ usually requires exploiting new materials$^{80}$. Two reasons could be responsible for the LSP-induced $V_{oc}$ enhancement: thinner optimized photoanodes reduce the voltage loss from charge recombination; and the quasi-Fermi level is lifted due to the equilibrium between quasi-Fermi level of TiO$_2$ and LSP energy level of plasmonic NPs$^{90,100}$. In addition, we observe that TAuT NPs increase $V_{oc}$ less significantly than AgT and AuT NPs, which is likely due to lower LSP energy level. The different $V_{oc}$ enhancements could assist in the elucidation of the origin of LSP-enhanced $V_{oc}$, and the ability of rationally increasing $V_{oc}$ could further improve PCE.

Since LSPs have a larger effect on enhancing LH than changing $V_{oc}$ and FF (no significant impact on FF is observed, Figure 4.26), the PCEs are improved (Figure 4.3d) with increasing concentrations of NPs (0-3.2 wt%, higher concentrations could reduce performance). Thus, maximum PCEs of 10.1%, 10.3%, and 10.8% are achieved for AgT, AuT, and TAuT NPs-incorporated DSSCs respectively, comparing to 8.3% without plasmonic NPs.

**Light harvesting and achievable $J_{sc}$ (short-circuit current-density).**
Light harvesting (LH), the process of capturing solar energy with electrons, is an important factor of PCE and is directly determined by the bandgap energy ($E_g$) and extinction coefficient ($\varepsilon$) of the materials. LH efficiency (LHE) limits the achievable short-circuit current density ($J_{SC}$) and PCE of photovoltaic devices\(^8\) (Figure 4.4).

**Light harvesting in high- and low-absorption wavelength regions.**

LH materials with low $\varepsilon$ or non-ideal $E_g$ inefficiently exploit the solar spectrum (usually red to near-infrared (NIR) region, Figure 4.1c); $\varepsilon$ is inevitably small (Figure 4.1a,b) when the photon energy is close to $E_g$ or faraway from $\Delta_g$HOMO-LUMO (highest occupied molecular orbital to lowest unoccupied molecular orbital gap).

**Absorption length.**

The absorption length at a wavelength of $\lambda$ is the reciprocal of the absorption coefficient. For a photo-absorbing layer with thickness of the absorption length, the absorbance is 1 and 90% of the light is absorbed.

**The importance of balancing LH at different wavelengths and carrier collection.**

Previous studies discussed the importance of balancing LH and carrier collection. However, in most cases, only the LH at $\lambda_{Hi}$ is balanced with carrier collection, giving an optimized thickness of photo-absorbing layer. In fact, LH at $\lambda_{Lo}$ and carrier collection is not balanced and a thicker photo-absorbing layer is required for the balance. In this thicker film, only a small portion contributes to the LH at $\lambda_{Hi}$. As a result, only balanced LH at $\lambda_{Hi}$ and $\lambda_{Lo}$ can truly optimize the LH and carrier collection.
Deriving the enhancement factor.

In order to arrive at an enhancement factor, the electric-field intensity of the enhanced near field was integrated by fixing the core-shell outer radius \( R_{SC} \) as the characteristic length scale and considering the field contained within a two diameter sphere (indicated by the cyan circles plotted in Figure 4.2c, Figure 4.18, and Figure 4.20) and then divided by the EM field of the incident light over this same volume when the NP is absent. While the NP is present, the EM intensity inside the NP is considered to be zero, because no dye-molecules can access this space. The EM intensity of the rest of the space in the two diameter sphere is calculated from the FDTD simulation. In summary,

\[
\text{Enhancement Factor}(\lambda) = \frac{\vert E_{\text{int}}^2 \vert}{\vert E_0 \vert^2_{\text{int}}} (\lambda) = \int_0^{2\pi} \int_0^\pi \int_0^{2R_{CS}} \frac{\vert E(r, \theta, \phi, \lambda) \vert^2}{\vert E_0 (r, \theta, \phi, \lambda) \vert^2} r^2 \sin \theta \, dr \, d\theta \, d\phi, \]

\[\vert E(r, \theta, \phi, \lambda) \vert^2 = 0 \text{ when } 0 \leq r \leq R_{CS} .\]

Enhancement factors in the figures of the manuscript and Experimental.

There are overall four different ways illustrating the enhancement factors in Figure 4.2f,g, Figure 4.12, and Figure 4.13, which are calculated at specific wavelengths or integrated in specific wavelength regions.

The enhancement factors in Figure 4.12 are calculated at \( \lambda_{LSPR} \) for TAUt NPs with \( d_{\text{core}}=15 \text{ nm}, d_{\text{Au}}=2-6 \text{ nm} \) and \( d_t=2-6 \text{ nm} \), and AuT and AgT with \( d_{\text{core}}=15 \text{ nm} \) and \( d_t=2-6 \text{ nm} \). In fact, since each TAUt NP with different gold and TiO\text{\textsubscript{2}} shell thicknesses has different \( \lambda_{LSPR} \), the enhancement factor at each pixel in this figure is evaluated at a different wavelength, which is partially responsible for the discontinuity observed in the figure. The values on the color scale represent the absolute enhancement factors.
The enhancement factors of Figure 4.2f are calculated by integrating the enhancement spectrum over 300-900 nm (400 wavelengths between 300-900 nm are calculated). The values on the color scale have arbitrary units.

The enhancement factors shown in the top part of Figure 4.2g are calculated at different wavelengths for TAuT NPs with $d_{\text{core}}=15$ nm, $d_{\text{Au}}=2-6$ nm and $d_{\text{T}}=2-6$ nm, and AuT and AgT with $d_{\text{core}}=15$ nm and $d_{\text{T}}=2-6$ nm. The values on the color scale represent the absolute enhancement factors. In the bottom part of Figure 4.2g, the enhancement factors at different wavelengths are multiplied by the normalized optical absorption of N719 and integrated over 300-900 nm (400 wavelengths between 300-900 nm are calculated). The values on the color scale also have arbitrary units. Similarly, in Figure 4.13, the enhancement of overall dye absorption is calculated for TAuT NPs with $d_{\text{core}}=15$ nm, $d_{\text{Au}}=2-6$ nm and $d_{\text{T}}=2-6$ nm, and AuT and AgT with $d_{\text{core}}=15$ nm and $d_{\text{T}}=2-6$ nm.

As described in the manuscript, both the enhancement factors in Figure 4.2f and Figure 4.12 arise from the intrinsic ability of plasmonic NPs to enhance the near field at their characteristic $\lambda_{\text{LSPR}}$ (Figure 4.12) and in the entire vis-NIR spectrum (Figure 4.2f). However, the enhancement factors in Figure 4.2g and Figure 4.13 take the surrounding photo-absorbing dyes into account. The calculated enhancement factors at different wavelengths describe the ability to enhance the photo-absorption of N719 in both strongly-absorbing and weakly-absorbing regions of the spectrum (the top part of Figure 4.2g). The electric field enhancement weighted with the normalized N719 absorption spectrum and integrated over wavelengths between 300 and 900 nm represents
the ability of the plasmonic NPs to enhance the overall LH of N719 (the bottom part of Figure 4.2g and Figure 4.13).

**Maximum enhancement for TAuT NPs occurs at \( d_{Au} \sim 3 \text{ nm}. \)**

In a nanoshell-like gold structure, the enhancement factor at \( \lambda_{LSPR} \) shows an optimum \( d_{Au} \) which is in agreement with other literature. Xu\textsuperscript{101} concluded that, for thin metal shells, the damping due to electron-surface collisions broadens the surface plasmon resonance peak and decreases the field enhancement. However, thick metal shells experience increased absorption, which also diminishes the field enhancement. Tanabe\textsuperscript{102} calculated the enhancement around nanoparticles and dielectric-metal core-shell structures within the quasistatic limit (i.e. \( R_{CS} << \lambda \)) and also saw that the dielectric-metal core-shells had a significantly higher field enhancement compared to metal-dielectric core-shells. They also noticed that an optimum core-shell ratio of \( (R_{core}/R_{CS}) \sim 0.9 \) maximized enhancement. For this work, it is maximized at a value of \(~0.73\).

**Different \( \lambda_{LSPR} \) achieved from simulations and experiments (solution of NPs).**

The \( \lambda_{LSPR} \) achieved from simulations and experiments (solution of NPs) are slightly different, because in the simulation the parameters from crystalline TiO\textsubscript{2} are used, which is different from the amorphous TiO\textsubscript{2} coatings for the (multiple-)core-shell NPs as synthesized in solution, but similar to the crystalized TiO\textsubscript{2} coating (anatase) after annealing at 500°C in the DSSCs. Therefore, although there is a slight difference between the simulation results and the absorption spectra of the solutions, the simulated results are close to the condition used in the actual devices.
Ease of tunability of $\lambda_{\text{LSPR}}$ for TAuT NPs compared to other geometries of plasmonic NPs.

Little change in synthesis is required to tune the $\lambda_{\text{LSPR}}$ of TAuT NPs due to their high sensitivity to geometry. For a 15 nm in diameter TiO$_2$ core, tuning the gold shell thickness from about 1 nm to 4 nm experimentally achieved $\lambda_{\text{LSPR}}$ of 1000-600 nm, which is realized by simply adding different amounts of gold precursor (or reducing agent). However, for gold nanorods\textsuperscript{95}, tuning the $\lambda_{\text{LSPR}}$ from 550 nm to 800 nm requires the aspect ratio of the nanorods changing from 1 to 4, which involves more sophisticated synthesis and more geometric modification than simply changing the gold shell thicknesses in the TAuT NPs. Moreover, for Au nanoplates with cylindrical or triangular shapes, the synthesis is even more complicated and is difficult to control\textsuperscript{103}.

Simulated absorption spectra of N719 enhanced by plasmonic NPs with $\lambda_{\text{LSPR}}$ from 400 to 700 nm.

The simulated absorption spectra of N719 enhanced by plasmonic NPs with different $\lambda_{\text{LSPR}}$ were obtained by multiplying (normalized) absorption spectrum of N719 and the enhancement factors (as a function of wavelength) at each wavelength (the left part of Figure 4.14). The enhancement factors (as a function of wavelength) are represented by the Gaussian distributions with center at 400-700 nm and full-width at half-maximum (FWHM) about 100 nm (the right part of Figure 4.14). The maximum enhancement factors of 2 are considered, and the enhancement factors away from $\lambda_{\text{LSPR}}$ are set to 1, \textit{i.e.}

\[
\text{Enhancement Factor}(\lambda) = e^{-\frac{(\lambda - \lambda_{\text{LSPR}})^2}{2000}} + 1, \text{ where } \lambda_{\text{LSPR}} = 400 - 700 \text{ nm.}
\]
**Calculation of the concentrations of plasmonic NPs.**

For all of TiO₂ (3.9 g cm⁻³ of density), Ag (10.5 g cm⁻³ of density), and Au (19.3 g cm⁻³ of density) core NPs, the particle concentrations were estimated by assuming that (1) the reactions went to completion for the synthesis of core particles and (2) the NP batch was monodispersed with a uniform distribution of ~15 nm particles in diameter. An estimated yield of 80% was used when considering the loss during washing and centrifugation steps after the NPs were coated to form TAuT, AgT, and AuT (multiple-)core-shell NPs.

The plasmonic AgT NPs-TiO₂ ratios in the photoanodes are from 0.01-1.0 wt%, which corresponds to a volume density of 0.003-0.3 ml% and a particle density of 8.4×10¹²-8.4×10¹⁴ cm⁻³, assuming that the porosity of TiO₂ photoanodes is 0.60, as demonstrated in the literature using the same composition of TiO₂ paste⁸³ (including 9 wt% ethyl cellulose as binders and 73 wt% terpineol as solvent).

The total number of NPs is calculated by: \[ \text{total # of NPs} = \frac{\text{total # of moles}}{\text{# of mole per NP}} \] \[ \frac{\text{concentration} \times \text{volume}}{\left(\frac{4}{3}\pi r^3 \times \frac{\rho}{M_w}\right)} \]. In the above equation, \( r \) is the radius of the NP, \( \rho \) is the density, and \( M_w \) is the atomic weight.

Subsequently, for AuT and TAuT NPs, the ranges of plasmonic particle densities in TiO₂ photoanodes are chosen to be the same as AgT-incorporated photoanodes. Considering the different densities of Ag, Au, and TAu NPs, the Au-TiO₂ and TAu-TiO₂ ratios in the photoanodes are 0.018-1.8 wt% and 0.032-3.2 wt%, respectively. For the volume density, AuT NPs have the same range with AgT NPs; considering a TAuT NP with \( d_{\text{Au}}=3 \) nm.
and $d_t=2$ nm, the volume density of TAuT NPs in the photoanode is 0.0069-0.69 vl%. There exists a factor of 2 to 3 comparing the volume densities of TAuT and AgT or AuT NPs, due to the different core radius and shell thickness. We believe that this is not responsible for the different device performance we observed, simply because, even for the same concentration of different plasmonic NPs, the different device performance still exists.

**The possible reasons for $V_{OC}$ enhancement induced by plasmonic NPs-incorporation.**

1. The relationship between $V_{OC}$ and the thickness of the photoanode shows that $V_{OC}$ increases with decreasing the thickness of photoanodes, which is due to less charge recombination. Since the plasmon-enhanced DSSCs feature thinner photoanodes for optimized PCE due to the enhanced LH ability, the $V_{OC}$ of the optimized plasmon-enhanced DSSC is thus larger than the $V_{OC}$ of the optimized DSSCs without plasmonic NPs.

2. In terms of the material properties of electronic structure, the $V_{OC}$ of a DSSC is determined by the difference between the quasi-Fermi level of TiO$_2$ and the redox potential of electrolyte. By introducing plasmonic NPs, the quasi-Fermi level is lifted due to the equilibrium between quasi-Fermi level of TiO$_2$ and LSP energy level of plasmonic NPs$^{90,100}$. The ground states of the electrons in plasmonic NPs are the Fermi level, and the work functions for Ag and Au are 4.7 eV and 5.1 eV, respectively. Considering that the energy difference between the ground state and the surface plasmon state of the electrons is provided by the photo-excitation, this energy difference is 3.0 eV, 2.3 eV, and 1.8 eV, corresponding to 420 nm, 550 nm, and 700 nm of $\lambda_{LSPR}$ for AgT, AuT, and
TAuT NPs, respectively. Therefore, AgT, AuT, and TAuT NPs have the highest to lowest LSP energy levels, which could be responsible for that the TAuT NPs increase $V_{OC}$ less significantly than AgT and AuT NPs. In addition, the different interfaces of metal-TiO$_2$ and different recombination rates induced by metal particles (non-ideal outer TiO$_2$ coating exists) could also be related to the different $V_{OC}$ enhancement.

**Comparing simulated and experimental results of dye LH enhancement at $\lambda_{LSPR}$.**

The simulated enhancement factor of TAuT NPs with $d_{\text{core}}=15$ nm, $d_{\text{Au}}=3$ nm and $d_{T}=2$ nm gives a maximum value of 7.2. As described previously, this enhancement factor is obtained by integrating in a region 8 times the volume of the NP (volume density 12.5%). We assume that the EM intensity is not significantly enhanced by the LSP in the space beyond the two-diameter spherical cutoff. In this case, we can use the above-calculated volume densities of plasmonic NPs to arrive at another enhancement factor, which considers the exact volume density of plasmonic NPs in the photoanodes. The calculated enhancement factor for TAuT NPs with a volume density of 0.69 vl% would be 1.4. Comparing to the enhancement factor obtained from optical absorption spectra (Figure 4.2h), the simulation and experimental results are comparable.

**Correlation of the optical density, light harvesting efficiency, and IPCE.**

It is worth noting that the optical density (OD), LHE, and IPCE are all correlated. LHE relates to OD as $\text{LHE}(\lambda)=1-\text{Transmittance}(\lambda)=1-10^{-\text{OD}(\lambda)}$. The LHE enhancement is achieved as, $\Delta \text{LHE}(\lambda)/\text{LHE}_0(\lambda)=(\text{LHE}_{LSP}(\lambda)-\text{LHE}_0(\lambda))/\text{LHE}_0(\lambda)=(1-10^{-\text{OD}(\lambda)_{LSP}})/(1-10^{-\text{OD}(\lambda)_{0}})-1$. Considering $\text{IPCE}(\lambda)=\text{LHE}(\lambda)\text{CSE}(\lambda)\text{CCE}(\lambda)$ (CSE is charge separation
efficiency, CCE is charge collection efficiency) and CSE and CCE are not affected by LSP as strongly as LHE is, \( \Delta \text{IPCE}(\lambda)/\text{IPCE}_0(\lambda) \approx \Delta \text{LHE}(\lambda)/\text{LHE}_0(\lambda) \). In fact, the experimental results of OD and IPCE enhancement are in agreement, which indicates that the IPCE improvement mainly arises from LSP-enhanced LHE.

For an optically-thin photoanode, assuming an OD of 0.2 at \( \lambda_{\text{max}} \), the light harvested is 1-10^{-0.2}=36.9\%, neglecting reflection by the glass substrate and photo-absorption by the electrolyte. Considering the plasmonic NPs enhance the OD by 100\% (to OD=0.4), the improved light harvesting efficiency is 1-10^{-0.4}=60.2\%, improved by 63\%. For an optically-thick photoanode, assuming an OD of 1 at \( \lambda_{\text{max}} \), the light harvesting efficiency is 90\%. If the OD is also enhanced by 100\% (to OD=2), the light harvesting efficiency would be 99\%, improved only by 10\%. Similar to the discussion in the manuscript, for optically-think photoanodes, the impact of enhancing the photo-absorption in the strong-absorption range of dye-molecules is small, while great enhancement can be achieved by improving the photo-absorption in the weak-absorption range of dye-molecules.

**Difference of IPCE at \( \lambda_{\text{max}} \) for optically-thick films.**

All AgT, AuT, and TAuT NPs improve the IPCE of optically-thick photoanodes at \( \lambda_{\text{max}} \) by less than 5\%. There are several possible reasons. IPCE(\( \lambda \))=LHE(\( \lambda \))CSE(\( \lambda \))CCE(\( \lambda \)). Due to the reason described in the manuscript, for TiO\(_2\)-only photoanodes or plasmonic NPs incorporated-photoanodes, the LHE at \( \lambda_{\text{Hi}} \) (especially \( \lambda_{\text{max}} \)) and CCE should be balanced and are close to unity. However, slight difference still exists for the LHE and CCE due to the thinner photoanodes for optimized PCE for the following reasons. First,
even for the photoanodes with the same optical density, thinner photoanodes would have less loss of incident light due to the optical absorption from electrolyte (e.g., iodine in the electrolyte absorbs visible light). Second, thinner photoanodes have higher CCE due to similar electron diffusion length. In addition, it is possible that the CSE is affected by plasmonic NPs, due to the changed photo-physical processes, e.g. increased radiative recombination rate has been observed as enhancement of photoluminescence. Consequently, the IPCEs at $\lambda_{\text{max}}$ of plasmonic NPs-incorporated optically-thick photoanodes are improved slightly.

**The effect of plasmonic NPs on fill factors.**

There is no significant decreasing or increasing effect of the plasmonic NPs on the fill factors of the DSSCs. However, compared to a small variation of the fill factors of TiO$_2$-only DSSCs, the fill factors of the DSSCs with plasmonic NPs show a similar average but a larger variation. This is probably due to the preparation of plasmonic NPs-incorporated TiO$_2$ paste. Since we prepared the TiO$_2$ pastes for each condition (each type of NPs, each concentration, and for doctor-blading and spin-coating) in a relatively small amount, the quality of the plasmonic NPs-incorporated pastes is not as perfect as the original TiO$_2$ paste, which is prepared in a relatively large amount. The large variation in fill factor is also responsible for the variation observed for the PCEs. However, we believe that, if the plasmonic NPs-incorporated TiO$_2$ pastes are prepared in large quantity, this issue could be easily solved.

**Higher concentrations of plasmonic NPs decrease the device performance.**
As shown in many previous publications\textsuperscript{79,90}, higher concentrations of plasmonic NPs would decrease the device performance due to both saturated effect of LSP-enhancement and increasing defects and impurities incorporated by the plasmonic NPs. In our experiments, although we did not observe obvious decrease using high concentrations of plasmonic NPs, the device performances of the highest and the second highest concentrations of plasmonic NPs are similar, which indicates that the saturation point has been reached at this concentration range.

4.4. Conclusion

The optimized device performance helps distinguish the improvement from different plasmonic NPs. AgT and AuT NPs used here and similar materials in previous studies on LSP-enhanced DSSCs\textsuperscript{76,79,90,91} improve IPCE and PCE, mainly through improved LH at $\lambda_{\text{Hi}}$. However, this approach could not break the compromise imposed by unbalanced LH at $\lambda_{\text{Hi}}$ and $\lambda_{\text{Lo}}$. In contrast, our general and simple strategy of matching $\lambda_{\text{LSPR}}$ with $\lambda_{\text{Lo}}$ balances and optimizes broadband LH, achieves panchromatic DSSCs with the existing dye, and further enhances LH, $J_{\text{SC}}$, and PCE. In fact, the distribution of core sizes and shell thicknesses result in the broad absorption spectrum of TAUt NPs with $\lambda_{\text{LSPR}} - \lambda_{\text{Lo}}$ (Figure 4.2b), which benefits panchromatic LH and carrier collection simultaneously. Our approach toward panchromatic DSSCs can apply to other photo-absorbers and other types of solar cells. Furthermore, since LH is the initial stage of a series of physical, chemical, or biochemical processes in many solar energy conversion devices, our strategy of matching $\lambda_{\text{LSPR}}$ with $\lambda_{\text{Lo}}$ may benefit many other devices\textsuperscript{104} including artificial photosynthesis\textsuperscript{93}, solar heating, solar thermal electricity, and solar fuels\textsuperscript{105}.
4.5. Figures

Figure 4.1. Spectral response of the LH of a solar cell and tunable LSP-enhanced broadband LH. **a,b**, the absorption coefficient of bulk silicon (**a**) and extinction coefficient of N719 (**b**); the shaded areas are low LH regions, which require thicker photoactive layers to achieve efficient LH. **c**, a schematic of the spectral response of a solar cell. The solar energy is less utilized at \( \lambda_{\text{Lo}} \) (usually red-NIR). **d**, illustrations of enhancing EM intensity by AgT (yellow), AuT (purple), and TAUt (blue) plasmonic NPs. \( \lambda_{\text{LSPR}} \) of AgT and AuT overlaps with \( \lambda_{\text{Hi}} \) of N719, maximizing the effect of LSP-enhanced LH. \( \lambda_{\text{LSPR}} \) of TAUt matches \( \lambda_{\text{Lo}} \) of N719, balancing LH at different wavelengths.
Figure 4.2. Synthesis, optical characterization, and FDTD simulation of AgT, AuT, and TAuT plasmonic NPs. 

a, illustrations and transmission electron microscope (TEM) images of AgT, AuT, and TAuT NPs. The scale bars are 5 nm.

b, photograph picture and absorption spectra of AgT, N719, AuT, TAuT-590 ($\lambda_{\text{LSPR}}=590$ nm), TAuT-700, and TAuT-810 in ethanol solutions.

c, simulated EM intensity enhancement ($|E|^2/|E_0|^2$) in near
field at $\lambda_{\text{LSPR}}$ for AgT, AuT, and TAuT NPs. The inner circles (white and yellow) represent different layers of NPs, and the outermost circles (cyan) represent the volume of integration. $d_{\text{core}}$=15 nm (used for all simulations unless specified), $d_{\text{Au}}$=3 nm, and $d_{\text{T}}$=2 nm. d, enhancement factor as a function of wavelength for AgT, AuT, and TAuT NPs with different $d_{\text{Au}}$ ($d_{\text{T}}$=2 nm). e,f, simulated $\lambda_{\text{LSPR}}$ (e) and spectrum-integrated enhancement factor over 300-900 nm (f) for AgT, AuT, and TAuT NPs as a function of $d_{\text{Au}}$ (of TAuT) and $d_{\text{T}}$ (of AgT, AuT, and TAuT). g, enhancement factor at different wavelengths (top) and enhancement of overall dye absorption (bottom) for AgT, AuT, and TAuT with different $d_{\text{Au}}$ ($d_{\text{T}}$=2 nm). h, absorption of N719 in sensitized 3-µm-thick TiO$_2$ films improved by AgT (1.0 wt%), AuT (1.8 wt%), and TAuT (3.2 wt%) NPs. i, absorption spectra and photograph images of thin films of Au nanocage@TiO$_2$ (AuNCT, left) and TAuT-700 (right) on glass substrates after 500°C annealing; TAuT NPs maintain optical properties, whereas $\lambda_{\text{LSPR}}$ of AuNCT blue-shifts toward $\lambda_{\text{LSPR}}$ of AuT NPs.
Figure 4.3. Tunable LSP-enhanced LH and photovoltaic performance of DSSCs. a, IPCE spectra of DSSCs with AgT, AuT, and TAuT NPs-incorporated photoanodes of 1.5 μm thickness (left), of optimized thickness for maximum PCE (middle), and as a function of concentration of TAuT NPs in optimized TAuT-DSSCs (right). b, c, d, $J_{SC}$ (b), $V_{OC}$ (c), and PCE (d) of LSP-enhanced DSSCs with AgT (left), AuT (middle), and TAuT (right)
NPs-incorporated photoanodes, as a function of the concentration of plasmonic NPs (0-3.2 wt%) and thickness of photoanodes (1-20 μm). The particle densities for all plasmonic NPs are the same and in the range of $8.4 \times 10^{12}$-$8.4 \times 10^{14}$ cm$^{-3}$, and the difference in weight percent is due to the different geometries of NPs (Results and discussion).

**Figure 4.4. Light harvesting and the achievable $J_{SC}$.** Photon flux of the AM 1.5 G spectrum at 1000 W m$^{-2}$ (ASTM G173-03) and the calculated accumulated photocurrent (assuming 100% quantum efficiency).
Figure 4.5. Illustrations for previous efforts for panchromatic DSSCs, including the development of panchromatic dyes (broadband-absorbing dye-molecules), co-adsorbing dyes (energy is absorbed by small-bandgap and large-bandgap materials together), and energy relay systems (energy absorbed by small-bandgap materials is transferred to large-bandgap materials and harvested by carrier separation and collection).
Figure 4.6. Zeta-potentials of alternating polymer PAA and PAH-coated TiO$_2$ NPs. All zeta-potentials are measured at pH=3.5.

Figure 4.7. Synthesis of core-shell AgT and AuT and multiple-core-shell TAuT NPs. 

- **a**, illustrations and transmission electron microscope (TEM) images of Ag, AgT, Au, and AuT NPs. 
- **b**, an illustration of multiple-core-shell TAuT structure, and TEM images of TiO$_2$ NPs.
TiO$_2$ core as a template, TiO$_2$ core with Au seeds coating, TiO$_2$ with continuous Au shell, and TAuT NP annealed at 500°C. All scale bars are 5 nm.

Figure 4.8. TEM images of TAuT NPs focused on the gold shell layer (left) and focused on the TiO$_2$ shell layer (right). These TEM images clearly show the multiple-core-shell oxide-metal-oxide structure of the TAuT NPs. All scale bars are 5 nm.
Figure 4.9. Low magnification TEM images of Ag, AgT, Au, AuT, TiO$_2$-Au seeds, and TAuT (bright field and dark field) NPs. The uniform synthesis for all NPs used in this report is illustrated.
Figure 4.10. Schematic illustration for deriving the enhancement factor.

Enhancement Factor(λ) = \frac{|E_{int}^2|}{|E_0|_{int}^2} (\lambda) = \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{R_{CS}} |E(r,\theta,\phi,\lambda)|^2 \frac{r^2 \sin \theta \, dr \, d\theta \, d\phi}{|E_0(r,\theta,\phi,\lambda)|^2}.

|E(r,\theta,\phi,\lambda)|^2 = 0 when 0 ≤ r ≤ R_{CS}.

Figure 4.11. λ_{LSPR} of TAU T NPs as a function of \(d_{Au}\) and \(d_T\).
Figure 4.12. Enhancement factor at $\lambda_{\text{LSPR}}$ as a function of $d_{\text{Au}}$ (of TAuT) and $d_{\text{T}}$ (of AgT, AuT, and TAuT).

Figure 4.13. Enhancement of overall dye absorption as a function of $d_{\text{Au}}$ (of TAuT) and $d_{\text{T}}$ (of AgT, AuT, and TAuT).
Figure 4.14. Simulated absorption spectra of N719 by matching $\lambda_{\text{LSPR}}$ and $\lambda_{\text{Hi}}$ or $\lambda_{\text{Lo}}$.

On the left, simulated absorption spectra of N719 enhanced by plasmonic NPs with $\lambda_{\text{LSPR}}$ from 400 to 700 nm. Each spectrum is normalized by the maximum absorbance in the visible region. On the right, the enhancement factors as a function of wavelength are represented by Gaussian distributions (each curve in the graph has a Y-offset value of 1). When the $\lambda_{\text{LSPR}}$ is between 400 to 550 nm, the optical absorption at strong-absorption range of dye-molecules is enhanced, and the spectral shape is more unbalanced compared to the original optical absorption of N719. When the $\lambda_{\text{LSPR}}$ is between 600 to 700 nm, the optical absorption at weak-absorption range of dye-molecules is enhanced, and the spectral shape is more balanced compared to the original optical absorption of N719.
Figure 4.15. Thermal stability of AgT and AuT NPs. Photograph images and absorption spectra of thin films of AgT (left) and AuT (right) on glass substrates after 500°C annealing; both AgT and AuT NPs maintain their structural and optical properties, as expected.
Figure 4.16. Thermal stability of other geometries of plasmonic NPs. TEM images of gold nanocage@TiO₂, gold nanorod@TiO₂, and silver nanocube@TiO₂ before and after 500°C annealing; after annealing, the gold nanocages and silver nanocubes melt and form spherical structures, and the gold nanorods melt to form spheroidal or spherical structures.
Figure 4.17. TAuT core effect. Enhancement factor as a function of wavelength for TAuT NPs with different $d_{\text{core}}$ ($d_{\text{Au}}=2$ nm, $d_{\text{T}}=2$ nm). Each curve in the graph has a Y-offset value of 5. Comparing to changing $d_{\text{Au}}$ and $d_{\text{T}}$, changing $d_{\text{core}}$ has a smaller effect on the $\lambda_{\text{LSPR}}$ and enhancement factor.

Figure 4.18. Simulated EM intensity enhancement ($|E|^2/|E_0|^2$) in near field at $\lambda_{\text{LSPR}}$ for a hollow gold nanoshell ($d_{\text{inner sphere}}=15$ nm, $d_{\text{Au}}=3$ nm). The inner circles (white
and yellow) represent the inner and outer spheres of the hollow gold nanoshell, and the outermost circles (cyan) represent the volume of integration.

Figure 4.19. Enhancement factor as a function of wavelength for hollow gold nanoshells with different $d_{\text{Au}}$ ($d_{\text{inner sphere}}=15$ nm). Each curve in the graph has a Y-offset value of 3.

Figure 4.20. Simulated EM intensity enhancement ($|E|^2/|E_0|^2$) in near field at $\lambda_{\text{LSPR}}$ for TAgT NPs ($d_{\text{core}}=15$ nm, $d_{\text{Ag}}=3$ nm, $d_{\text{T}}=2$ nm). The inner circles (white and yellow)
represent different layers of NPs, and the outer most circles (cyan) represent the volume of integration.

Figure 4.21. Enhancement factor as a function of wavelength for TAgT NPs with different $d_{\text{Ag}}$ ($d_{\text{core}}=15 \text{ nm}, d_{t}=2 \text{ nm}$). Each curve in the graph has a Y-offset value of 5.

Figure 4.22. $J$-$V$ curves of optically-thick photoanodes of TiO$_2$ without plasmonic NPs, AgT (1.0 wt%), AuT (1.8 wt%), and TAuT (3.2 wt%) NPs blended with TiO$_2$ NPs for optimized PCE under AM 1.5 illumination.
Figure 4.23. Equivalent circuit impedance model of DSSCs. $R_s$: ohmic series resistance of the cell. $R_{CO}$ and $C_{CO}$: contact resistance and capacitance at the interface between the conducting substrate and the TiO$_2$ photoanode film. $R_{SU}$ and $C_{SU}$: charge transfer resistance and double layer capacitance at the substrate/electrolyte interface. $R_{Pt}$ and $C_{Pt}$: charge transfer resistance and double layer capacitance at the counter electrode-electrolyte interface. $Z_{TiO2}$: transmission line impedance of the TiO$_2$ photoanode film consisting of the elements $R_T$ (resistivity of electron transport in the photoanode film), $R_{REC}$ (charge recombination resistance at the TiO$_2$/dye/electrolyte interface), and $C_\mu$ (chemical capacitance of the photoanode film). $Z_{Electrolyte}$: mass transport impedance at the counter electrode.
Figure 4.24. Nyquist diagrams of the electrochemical impedance spectra obtained under dark condition for different devices. Experimental data are presented by symbols, and fitted results using the equivalent circuit in Figure 4.23 are shown as solid lines. The bias applied to all the devices during measurement is 600 mV. EIS spectra of four DSSCs: with only TiO$_2$ NPs, with AgT (1.0 wt%), AuT (1.8 wt%), and TAuT (3.2 wt%) NPs-incorporated photoanodes are measured. The highest concentration for each plasmonic NPs investigated in this report has been utilized for the electrochemical impedance spectra measurement.
Figure 4.25. **Electron diffusion lengths of four DSSCs:** with only TiO$_2$ NPs, with AgT (1.0 wt%), AuT (1.8 wt%), and TAuT (3.2 wt%) NPs-incorporated photoanodes. The highest concentration for each plasmonic NPs investigated in this report has been utilized for the electron diffusion length measurement.
Figure 4.26. Fill factors of tunable LSP-enhanced DSSCs with AgT, AuT, and TAU T NPs-incorporated photoanodes, as a function of the concentration of plasmonic NPs (0-3.2 wt%) and thickness of photoanodes (1-20 μm).

4.6. Experimental

Materials.

Sodium citrate, silver nitrate (AgNO₃), tetra chloroauric acid (HAuCl₄), acetic acid, hydroxylamine (NH₂OH), titanium tetrachloride (TiCl₄), ethyl cellulose, terpineol, acetonitrile, turt-butanol, 1-butyl-3-methylimidazolium iodide, iodine, guanidinium thiocyanate, 4-tert-butyl pyridine, and valeronitrile are purchased from Sigma Aldrich.
Titanium isopropoxide (TPO, 97%), Titanium butoxide (TBO, 98%), polyvinylpyrrolidone with an average molecular weight of 8,000 (PVP-8) and poly (allylamine hydrochloride) (PAH) were purchased from Alfa; ethanol (99.5%), acetone (99.5%), nitric acid (70%), and ethylene glycol (99.9%) were purchased from Mallinckrodt Chemicals; ammonia (28-30 wt% NH₃ in water) was purchase from VWR International Inc. Poly(acrylic acid) (PAA, average molecular weight 5,000, 50% aqueous solution) was obtained from Polysciences, Inc. Cis-diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (also named N719 or Ruthenizer 535-bisTBA, purchased from Solaronix) was used as a 0.5 mM solution in acetonitrile and tert-butanol (volume ratio = 1:1). All chemicals were used as received. All water was deionized (18.2 MΩ, milli-Q pore).

**Synthesis of AgT NPs.**

The Ag NPs of an average diameter of 15 nm were synthesized by a modified polyol process and described in previous publication⁷⁹. Typically, 0.1 mmol of silver nitrate was added into 25 ml of ethylene glycol solution containing 0.5 g of PVP-8 and the mixture was kept stirring at room temperature until silver nitrate was completely dissolved. Then the solution was slowly heated up to 120°C and kept at the temperature for 1 hour with constant stirring. After the reaction, 12.5 ml of the as synthesized Ag NPs in ethylene glycol (containing 0.05 mmol of Ag) was added with 5 ml of 1% PAA aqueous solution. The solution was kept stirring for over 4 hours and then added with 100 ml of acetone and centrifuged at 3,000 r.p.m. Then the supernatant was removed and the Ag NPs were washed again with ethanol, and centrifuged at 10,000 r.p.m.
The Ag NPs were then redispersed in 25 ml of ethanol. After cooling down the solution with ethylene glycol-dry ice bath, 1 ml of ethanol solution containing 10 μl of TBO was added into the solution. The reaction was kept stirring in the dark for 1 hour, and then sonicated in a bath sonicator for 30 minutes, after which the reaction was kept stirring in the dark for a certain time to achieve requested TiO₂ shell thickness (typically 12 hours).

**Synthesis of AuT NPs.**

100 ml of 0.01% HAuCl₄ solution in a 300 ml round-bottom flask was heated to boiling with vigorous stirring. 1.8 ml of 1 wt% sodium citrate aqueous solution was added to the reaction. The solution color turned to blue within 25 seconds; and to red-violet 70 seconds later. The reaction was kept on boiling for another 30 minutes; then the solution was stirred for another 15 minutes while the heating source was removed. TEM image indicated an average diameter of 15 nm for the Au NPs. To the as-synthesized solution, 5 ml of 5% PVP aqueous solution was added and kept stirring for 12 hours. Then, after centrifuging at 18,000 r.p.m., the supernatant was removed and the Au NPs were washed with ethanol and centrifuged again.

The Au NPs were redispersed into 25 ml of ethanol and used for the synthesis of AuT core-shell structure. After cooling down the solution with ethylene glycol-dry ice bath, 1 ml of ethanol solution containing 10 μl of TBO was added into the solution. The reaction was kept stirring in the dark for 1 hour, and then sonicated in a bath sonicator for 30 min, after which the reaction was kept stirring in the dark for a certain time to achieve requested TiO₂ shell thickness (typically 12 hours).
Synthesis of TiO$_2$ NPs.

The 15-20 nm sized TiO$_2$ nanocrystals were synthesized using the procedure in the literature$^{106}$. An amount of 1.2 g (0.02 mol) of acetic acid was added all at once to 5.86 g (0.02 mol) of TPO under stirring at room temperature. The modified precursor was stirred for about 15 minutes and poured into 29 ml water as quickly as possible while vigorously stirring (700 r.p.m.). A white precipitate was instantaneously formed. One hour of stirring was required to achieve a complete hydrolysis reaction. After adding a quantity of 0.4 ml of 70% nitric acid, the mixture was heated from room temperature to 80$^\circ$C within 40 minutes and kept at the temperature for another 75 minutes. Water was then added to the cooling liquid mixture to adjust the volume to a final 37 ml. The resultant mixture was kept in a 57 ml Teflon-lined autoclave and heated at 250$^\circ$C for 12 hours. Following this step, 0.24 ml of 70% nitric acid was added and the dispersion was sonicated to re-disperse in water.

Synthesis of TAuT NPs.

The as-synthesized TiO$_2$ NPs were dispersed in DI water and were positively charged because of the H$^+$ termination. The surface of the NPs was modified by layer-by-layer (LbL) coating of polyelectrolytes$^{107-110}$ (zeta-potentials of the polyelectrolytes-coated NPs are shown in Figure 4.6). To the 50 ml of 5 mM TiO$_2$ NPs aqueous solution, 10 ml of 5% PAA solution was added in order to modify the NPs with a negatively charged polyelectrolyte and incubated for 6 hours at room temperature with stirring. The dispersion was then precipitated by centrifugation at 12,000 r.p.m. and redispersed in DI water (repeated three times) to remove excess PAA. To modify the NPs with a positively
charged polyelectrolyte layer, to PAA-coated NPs aqueous solution, 10 ml of 5% PAH aqueous solution was added and incubated for 12 hours at room temperature with stirring. The NPs were then centrifuged and redispersed in DI water to remove excess polyelectrolyte (repeated three times). Sequentially, another PAA and PAH layers were coated by repeating incubation, precipitation and dispersion in DI water. LbL modified NPs were characterized by zeta-potential measurements. 50 ml of the aforementioned solution containing 100 μmol TiO₂ and 3 ml of 1% HAuCl₄ were mixed and diluted with DI water to 100 ml. The HAuCl₄ precursor was incubated with the PAA/PAH/PAA/PAH coated particles for more than 6 hours for complexation and immobilization on the particle surface at room temperature. Then, the flask of solution was immersed in acetone-iced water bath and the solution was allowed to cool down. Subsequently, 5% hydroxylamine aqueous solution was added dropwise to initiate the surface confined growth of the gold-shell. After the reaction, 10 ml of 5% PAA aqueous solution was added into the solution and incubated for more than 4 hours.

The gold-shell encapsulated particles TAu were obtained, and were centrifuged, washed and redispersed in 25 ml of ethanol for coating TiO₂ outer shell. After cooling down the solution with ethylene glycol-dry ice bath, 1 ml of ethanol solution containing 10 μl of TBO was added into the solution. The reaction was kept stirring in the dark for 1 hour, and then sonicated in a bath sonicator for 30 minutes, after which the reaction was kept stirring in the dark for a certain time to achieve requested TiO₂ shell thickness (typically 12 hours).

**Other geometries of plasmonic NPs.**
The silver nanocubes and gold nanocages are synthesized using previously published method\textsuperscript{111,112}. The gold nanorods (10 nm in diameter and different aspect ratios to achieve $\lambda_{\text{LSPR}}$ between 700 to 800 nm) are purchased from Strem Chemicals, Inc.

**TEM Characterization of plasmonic NPs.**

TEM observations of the synthesized nanostructures (TiO$_2$, Ag, Au, AgT, AuT, TAu, and TAuT) were performed using JEOL 2010, JEOL 2010F, and JEOL 2100F TEMs with an accelerating voltage of 200 kV. TEM samples were prepared by directly dropping nanoparticle solutions to carbon supported copper or nickel grids. To get better contrast image, the high contrast objective aperture was used for all images. The high resolution image was taken under smaller illumination area size by changing the alpha selector. The STEM images were taken by both Gatan High-Angle Annular Dark Field (HAADF) and Bright filed (BF) detectors under 0.2 nm probe size and 12 cm camera length.

**Zeta-potential measurement of alternating polymer PAA and PAH-coated TiO$_2$.**

Zeta-potential were measured at an accumulation time of 10 with 5 measurements per sample at 20 V using DelsaNano (Beckman Coulter). Electrophoretic mobility was calculated using the Smoluchowski approximation.

**Thermal stability of the plasmonic NPs characterized by TEM.**

For the thermal stability observation, the grids with nanoparticles were heated at 450 to 500°C for 15 to 30 minutes in argon atmosphere and followed by fast quenching.

**Optical absorption measurement of the solutions of plasmonic NPs**
For both solutions and thin films of AgT, AuT, and TAuT NPs, the optical absorption measurements were performed using a Beckman Coulter DU800 UV-Vis spectrophotometer.

**Optical absorption enhancement of dye-molecules induced by the incorporation of plasmonic NPs.**

3-μm-thick thin films of TiO₂ NPs or TiO₂ NPs incorporated with plasmonic NPs on 2.5x2.5 cm² fused silica wafers were used for thin-film optical absorption measurements, which were prepared by spin coating (Specialty Coating Systems, 6800 spin coater) and followed by annealing treatment at 500°C for 15 minutes. Then the film thickness was measured using a Dektak 150 surface profiler. These films were immersed into 0.1 mM ruthenium dye solution (volume ratio of acetonitrile to tert-butanol is 1:1) and kept at room temperature for 12 hours. Then the dyed films were immersed in acetonitrile for 5 min to remove non-adsorbed dye molecules. 3-μm-thick films were used because of the small interference and scattering effects in the optical absorption spectroscopy observations at this thickness. The absorbance shown in Figure 4.2h is the absorbance of N719-sensitized different plasmonic NPs-incorporated TiO₂ films subtracted by the absorbance of the TiO₂ films, which describes the absorption of the dye-molecules.

**Thermal stability of the plasmonic NPs characterized by optical absorption.**

Plasmonic NP solutions (AgT, AuT, TAuT, and Au nanocage@TiO₂) were directly drop-casted on the glass slides to form thin films. The thin films were dried at a temperature from room temperature to 80°C. After these thin films were annealed at 500°C for 30
minutes in air, the optical absorption measurements for these thin films were performed using a Beckman Coulter DU800 UV-Vis spectrophotometer.

**Synthesis, optical characterization, and thermal stability of other geometries of plasmonic NPs with tunable \( \lambda_{\text{LSPR}} \) in vis-NIR region.**

Different geometries of plasmonic nanomaterials (gold nanorods, gold nanodisks, and gold hollow shells) were purchased or synthesized using previously published methods. They were coated with TiO\(_2\) thin shells using the same method for coating Ag, Au, and TAu NPs. The TEM and optical characterization for the thermal stability of these geometries of plasmonic nanomaterials were also carried out using the same method for AgT, AuT, and TAuT NPs.

**FDTD simulation of AgT, AuT, TAuT, and other geometries of plasmonic NPs.**

The near-field response of core-shell structures to a plane-wave excitation was evaluated with the finite-difference time-domain (FDTD) method using the software Lumerical FDTD Solutions Version 8.0.0. The two core-shell geometries considered in this paper are (1) a silver or gold spherical nanoparticle with a thin TiO\(_2\) coating (i.e. AgT and AuT) and (2) a spherical TiO\(_2\) nanoparticle with a thin gold coating that is further cladded in an outer TiO\(_2\) coating (i.e. TAuT). Each core-shell type was modeled as a set of two or three concentric spheres, respectively, and was placed in an ethanolic environment with refractive index 1.36 and illuminated by a plane wave. All of the simulations performed modeled the core, regardless of material, as a 15 nm diameter sphere (unless otherwise specified). The shell thicknesses were varied between 2 and 6 nm by increments of 0.2
nm. All simulations were performed with a mesh size of 1 nm and the conformal meshing option “Conformal variant 1” was applied to provide greater accuracy, particularly at the metal-TiO$_2$ interfaces. Each core-shell geometry was subjected to a plane-wave illumination at 400 different wavelengths between 300 and 900 nm. A fourth order polynomial was fitted over this wavelength range to the measured dielectric data of silver and gold as reported by Palik. The refractive index of TiO$_2$ was approximated as 2.34 and taken to be constant over the wavelengths of interest. This value was found by averaging the dispersion relation reported by Kim between the wavelengths of 350 and 950 nm.

In order to generate an enhancement factor that evaluates the nanoparticle’s ability to concentrate light in the near-field zone, the total electric field intensity was integrated over the space between the outermost core-shell surface and a fictitious sphere locate one core-shell radius away and divided by the integral of the incident plane wave’s electric field intensity over the entire volume enclosed by the fictitious sphere, including the nanoparticle volume. This definition is meant to compare the amount of electric energy contained in the near-field surrounding the particle (where the dye molecules are present in the DSSC) to the amount of energy available to the same region under the plane-wave illumination in the absence of the particle.

\[
\text{Enhancement Factor}(\lambda) = \frac{|E|^2_{\text{int}}(\lambda)}{|E_0|^2_{\text{int}}} = \frac{\int_0^{2\pi} \int_0^\pi \int_{R_{\text{CS}}}^{2R_{\text{CS}}} |E(r, \theta, \phi, \lambda)|^2 r^2 \sin \theta dr d\theta d\phi}{\int_0^{2\pi} \int_0^\pi \int_0^{2R_{\text{CS}}} |E_0(r, \theta, \phi, \lambda)|^2 r^2 \sin \theta dr d\theta d\phi}
\]

where $R_{\text{CS}}$ is the outer radius of the core-shell particle, $E$ is the total electric field in the near-field, and $E_0$ is the electric field of the incident plane wave.
Preparation of TiO$_2$ paste for spin-coating and doctor-blading.

Two kinds of pure ethyl cellulose (EC) powders, i.e., EC (5–15 mPas) and EC (30–50 mPas) were dissolved prior to usage in ethanol to yield 10 wt% solutions. 4.5 g of EC (5–15) and 3.5 g of EC (30–50) of these 10 wt% ethanol solutions were added to a round bottom flask containing 1.6 g pure TiO$_2$ (obtained from previously prepared precipitate) and 6.5 g of terpineol and diluted with 8 ml of ethanol to obtain a final total volume of 28 ml. This mixture was then sonicated using an ultrasonic horn. Ethanol and water were removed from these TiO$_2$/ethyl cellulose solutions by rotary-evaporator. The final doctor-blading pastes correspond to 18 wt% TiO$_2$, 9 wt % ethyl cellulose and 73 wt % terpineol. For each doctor-blading process using the scotch-tape, a film of 5-7 µm was formed.

To achieve the spin-coating paste, the doctor blading paste was diluted by terpineol 2 to 3 times. By adjusting the spin-coating speed from 1000 to 3000 r.p.m., the film thicknesses from 3 to 1 µm were obtained.

Fabrication of photoanodes of DSSCs.

The FTO glass (TEC15 2.2 mm thickness, 15 Ω ◦-1, Pilkington, USA) was first cleaned in a detergent solution using an ultrasonic bath for 15 minutes, and then rinsed with water and ethanol. After treatment in an air plasma system for 1 minute, the FTO glass plates were immersed into a 40 mM of aqueous TiCl$_4$ solution at 80°C for 30 minutes and washed with water and ethanol. The fabrication of the 1-4 µm thick photoanodes of both TiO$_2$-only DSSCs and plasmon-enhanced DSSCs was performed by spin coating (for one or two times), the same method used for preparing the thin films for optical absorption.
measurement. For DSSCs with a photoanode thickness larger than 5 μm, the fabrication was carried out using the doctor-blading procedure. A layer of paste was coated on the FTO glass plates by doctor blading, left for 3 minutes to reduce the surface irregularity of the paste, and then dried for 5 minutes at 120°C. This doctor blading procedure with paste (coating, storing, and drying) was repeated to get an appropriate thickness about 5-20 μm for the photoanodes. The film thickness was measured using a Dektak 150 surface profiler. The photoanodes were sintered at 500°C for 30 minutes after the required thicknesses of photoanodes were achieved. The TiO₂ films were then treated with 40 mM of TiCl₄ solution at 80°C for 30 minutes again, rinsed with water and ethanol, and then sintered again at 500°C for 30 minutes. After cooling to 80°C, the TiO₂ electrodes were immersed into a 0.5 mM of N719 dye in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1), and were kept at room temperature for 24 hours. The photoanodes incorporated with plasmonic NPs were fabricated with a modified procedure. The different amounts of AgT, AuT, and TAuT NPs in ethanol solution (plasmonic NPs to TiO₂ NPs ratio ~0.01-3.2 wt%) were mixed with the TiO₂ paste (mixture of TiO₂ NPs, ethyl celluloses, and terpineol), followed by stirring and sonicating. Then the ethanol was removed by a rotary-evaporator. After the pastes incorporated with plasmonic NPs were achieved, the fabrication procedure of the photoanodes of plasmon-enhanced DSSCs was the same as that of the TiO₂-only DSSCs.

**Assembly of DSSCs with photoanodes, electrolyte, and counter electrodes.**

The counter electrodes were 100-nm-thick platinum, sputtered on ITO substrates (Delta Technologies). The electrolyte was a solution of 0.6 M 1-butyl-3-methylimidazolium
iodide, 0.03 M iodine, 0.10 M guanidinium thiocyanate, and 0.5 M 4-tert-butyl pyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). The dye-adsorbed TiO$_2$ or plasmonic NPs-incorporated TiO$_2$ photoanodes and Pt counter electrodes were assembled into a sandwich type cell and sealed with a hot-melt Surlyn of 25 μm in thickness (Solaronix). The size of the TiO$_2$ electrodes used was 0.16 cm$^2$ (4 mm×4 mm). The actual active areas of the devices were accurately measured by a photo scanner. The aperture of the Surlyn frame was larger than that of the TiO$_2$ area by 2 mm. Copper tape was adhered on the edge of the FTO outside of the cell. The position of the tape was 1 mm away from the edge of the Surlyn gasket and 4 mm away from the edge of the TiO$_2$ layer.

**Characterization of DSSCs.**

Photovoltaic measurements were performed under illumination generated by an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to 100 mW/cm$^2$ by using a reference Si photodiode with a powermeter (1835-C, Newport) and a reference Si solar cell in order to reduce the mismatch between the simulated light and AM 1.5. The J-V curves were obtained by applying an external bias to the solar cells and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. A black tape mask was attached to the device in order to prevent irradiations from scattered light.

**Spectral response of incident photon-to-current conversion efficiency (IPCE).**
IPCE spectra were measured with a commercial IPCE measurement system (Model QEX7, PV Measurements, Inc.). Under full computer control, light from a xenon arc lamp (150 W) was focused through a grating monochromator, equipped with two 1200 lines/mm diffraction gratings, onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum (from 350 nm to 850 nm) to generate the spectral response of IPCE with a spectral resolution of 10 nm. The incident photon flux was determined using a calibrated silicon photodiode (calibrated by PV Measurements, Inc.). Measurements were performed in a short-circuit condition, while the cell was under background illumination from a bias light of 50 mW/cm². Bias illumination was from the same direction as the monochromatic light, which was from the FTO side. The monochromatic beam was chopped using a computer-controlled shutter at a frequency of 1.33 Hz, and averaging of up to 10 shutter cycles was employed.

**Electrochemical impedance spectroscopy (EIS).**

Electrochemical impedance spectra measurements of DSSCs were performed with a Solartron 1260 frequency response analyzer. The spectra were measured at various forward bias voltages (from -0.85 to -0.45 V) in the frequency range of 0.1 Hz~1 MHz with oscillation potential amplitudes of 10 mV at room temperature. The photoanode was connected to the working electrode. The Pt electrode was connected to the auxiliary electrode and the reference electrode. The impedance measurements were carried out in dark conditions.

**Calculation of electron diffusion length from electrochemical impedance spectra.**
The electron diffusion length, $L_n$, can be calculated from $L_n = L (R_{REC}/R_T)^{1/2}$, where $L$ is the film thickness, $R_{REC}$ is electron recombination resistance, and $R_T$ is electron transport resistance. $R_{REC}$ and $R_T$ were obtained by fitting the measured electrochemical impedance spectra to the equivalent circuit (known as transmission line model, shown in Figure 4.23) with the Z-view software (v3.2b, Scribner Associates Inc.). The transmission line component ($Z_{TiO2}$ in Figure 4.23) in an equivalent circuit is often used to represent the interface resistance and capacitance for a porous structure, which is the case for the photoanodes of DSSCs. During fitting the electrochemical impedance spectra to the transmission line model, the resistance and capacitance at the substrate/TiO$_2$ interface, and the substrate/electrolyte interface were assumed negligible due to good contact between the substrate, the TiO$_2$ NP layer, and the blocking layer of TiO$_2$, achieved by TiCl$_4$ treatment to the substrate. In Figure 4.24, electrochemical impedance spectra from each type of DSSCs, measured at 600 mV, are shown in symbols. The fitted results are shown as solid lines. For more detailed information about fitting electrochemical impedance spectra to the transmission line model and extracting electron diffusion length from fitted electrochemical impedance spectra, refer to references$^{38,50-53}$.

**Calculation of electron collection efficiency from electron diffusion length.**

The electron collection efficiency is$^{38}$, $\eta_{COL} = \frac{-La \cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) + L\alpha e^{-ad}}{(1-e^{-ad})(1-L^2 \alpha^2)cosh\left(\frac{d}{L}\right)}$, where $d$ is the thickness of the TiO$_2$ film, $L$ is the electron diffusion length, and $\alpha$ is the absorption coefficient of dye-sensitized TiO$_2$ film. For the calculation, we assume $\alpha d$ equals to 1, indicating 90% of the incident light is absorbed. We observed very similar electron
diffusion lengths for all types of DSSCs. Thinner photoanodes (smaller $d$ and larger $L/d$) thus result in larger values of $\eta_{\text{COL}}$.

*The FDTD simulation in this project was performed by Mr. Matthew Klug. The analysis of the simulation data was performed by me and Mr. Klug.
Chapter 5. A versatile three-dimensional virus-based template for dye-sensitized solar cells with improved electron transport and light harvesting

5.1. Abstract

M13 virus is a versatile bio-template to generate hybrid materials with unique properties, and the assembled virus complex has been utilized in various device applications. Here, the M13 virus is employed to create a multifunctional three-dimensional scaffold to improve electron collection and light harvesting for efficient dye-sensitized solar cell (DSSC). The DSSC with the virus-templated nanowire-based TiO₂ photoanodes exhibits advantageous electron transport properties, characterized by a longer electron diffusion length compared to the nanoparticle-based DSSC. Moreover, the ability of the virus to bind Au nanoparticles is utilized to increase the light absorption of dye molecules by the localized surface plasmon. Consequently, the virus-templated plasmon-enhanced DSSC achieves an increased efficiency of 8.46% by improving both light harvesting and electron collection simultaneously.

5.2. Introduction

There is a constantly growing demand for fabricating cost-effective energy conversion devices. Biological or polymeric templated synthesis offers an inexpensive, room-temperature and aqueous solution-based synthetic approach, and can provide assembly of hybrid materials with nanoscale precision. In particular, the M13 virus is a filamentous bacteriophage of 880 nm in length and 6.5 nm in diameter, and has been demonstrated as a versatile bio-template to assemble and to nucleate an ordered array of a broad range of
materials, including metals, metal oxides, semiconducting compounds, polymers, carbon nanotubes, and graphene. Through genetic engineering of the surface coat proteins, the targeted materials can be assembled along the phage surface, and used to assemble functional materials into two- and three-dimensional structures for various device applications, including fuel cells, lithium ion batteries, water splitting and photovoltaics.

Dye-sensitized solar cells (DSSCs) are a promising solution-processed photovoltaic technology. The key components of a DSSC are dye-molecules which absorb light and mesoporous titanium dioxide (TiO$_2$) thin films (photoanodes) which collect the photo-generated electrons. The power conversion efficiency (PCE) of DSSCs is determined by light harvesting and electron collection. In general, to efficiently harvest light and collect electrons, different design criteria must be considered. For efficient electron collection, nanostructures of TiO$_2$ with high aspect ratio, such as nanorods, nanotubes and nanofibers, have been proven to be effective, compared to the commonly used architecture of photoanodes composed of randomly-packed nanoparticles (NPs). However, the reduced surface area of one-dimensional (1-D) structures leads to insufficient dye adsorption and thus restricts light harvesting. As a result, achieving sufficient light harvesting requires developing strong-absorbing dye-molecules or various mechanisms to increase optical absorption, e.g. localized surface plasmon (LSP)-enhanced optical absorption by using metal NPs. Therefore, different functional materials are required for electron collection and light harvesting, and an approach that enables the assembly of different functional components into a homogeneously distributed composite with a three-dimensional (3-D) structure particularly attractive.
Here, we report a novel 3-D viral network as a versatile platform for DSSCs which can template TiO$_2$ nanowires for improved electron transport, and can also bind Au NPs and then incorporate them uniformly into the photoanodes for the LSP-enhanced light harvesting of dye-molecules. Templated by a cross-linked virus hydrogel scaffold with tunable porosity, the TiO$_2$ nanowires promote electron transport from the photo-excited dyes to the current collector (Figure 5.1) in the photoanodes, resulting in an increased electron diffusion length compared to conventional NP-based photoanodes. In addition, the M13 virus can bind Au NPs prior to the templated synthesis of TiO$_2$; the resulting TiO$_2$-coated gold nanoparticles incur LSP effects that improve the photo-absorption of dye-molecules adsorbed on the Au@TiO$_2$ nanocomposites (Figure 5.1). As a result, the 3-D LSP-enhanced virus-templated photoanodes exhibit efficient electron collection and improved light absorption simultaneously. An optimized amount (0.8 wt.%) of Au NPs homogeneously distributed in the virus-templated photoanode enhances the short-circuit current density ($J_{SC}$) from 10.97 to 13.72 mA cm$^{-2}$ and improves the PCE from 6.03% to 8.46%. Moreover, the virus-templated nanowire networks are envisioned to serve as a modular, scalable and general design architecture for many other applications, including batteries, catalytic membranes, and sensors.

5.3. Results and discussion

3-D M13 virus-templated photoanodes for improved electron collection.

A virus hydrogel network is first formed on a fluorine-doped tin oxide (FTO) or other transparent conducting substrate using a glutaraldehyde solution as the crosslinking agent (Figure 5.2). The substrate with the virus solution (specific gravity~1) is placed upside
down on the surface of the glutaraldehyde solution (specific gravity~1.1) to create a liquid-liquid interface. As the glutaraldehyde diffuses across the interface and into the virus solution on the top, a virus hydrogel is spontaneously formed due to the covalent crosslinking between the amine groups on the virus coat proteins. After the virus hydrogel is achieved, the virus-templated TiO$_2$ nanowires are formed directly on the substrate by an aqueous phase nucleation method using solutions of TiO$_2$ precursors (e.g. TiCl$_4$, (NH$_4$)$_2$TiF$_6$) which deposit a conformal TiO$_2$ thin layer on the virus template. A final calcination step is then used to remove the sacrificial virus scaffolds and to generate the anatase crystalline phase in the 3-D porous TiO$_2$ film (Figure 5.3A).

It is observed that the virus-templated photoanode is composed of tightly packed TiO$_2$ crystallites forming interconnected nanowires (Figure 5.3B and C). Compared to the size of individual viral particles, the virus-templated TiO$_2$ nanowires are approximately 100 nm in diameter and 2-3 µm in length (Figure 5.3C and D), which suggests that each nanowire in the photoanode is templated by a bundle of viruses. In addition, the mesoporous structure of the interconnected nanowire network persists throughout the thin film, which can provide a directional electron pathway for improved electron transport (Figure 5.3E). Moreover, the permeable matrix with interconnected pores maximizes interfacial contact with the electrolyte and increases the mobility of redox couples, which also minimize back recombination.

To demonstrate the improved electron diffusion length ($L_n$) and carrier collection of the 3-D virus-templated TiO$_2$ photoanode, the electrochemical impedance spectra (EIS) are measured (Figure 5.4A) after the photoanodes are assembled with the electrolyte and
counter electrodes. The DSSC with the virus-templated photoanode shows longer \( L_n \) and thus better electron collection than the commonly used TiO\(_2\) NP-based DSSC. Furthermore, the device performance of the DSSC with virus-templated TiO\(_2\) photoanode is characterized (Figure 5.4B and Table 5.1), which shows a PCE of 6.03\% and a \( J_{SC} \) of 10.97 mA cm\(^{-2}\). Despite the improved electron collection for the virus-templated TiO\(_2\) photoanode, the \( J_{SC} \) and PCE are both lower than those of the TiO\(_2\) NP-based DSSC (6.63\% and 12.31 mA cm\(^{-2}\)). Since the charge separation efficiency approaches unity when the N719 dye and TiO\(_2\) are used, the decreased overall performance results from the reduced surface area, dye adsorption, and thus light harvesting of the 1-D structure of the virus-templated TiO\(_2\) nanowires. In fact, the virus-templated device shows \(~89.1\%\) of \( J_{SC} \) with only \(~73.5\%\) of the adsorbed dye compared to the NP-based solar cell. Therefore, the virus-templated photoanodes composed of interconnected nanowires exhibit efficient electron collection, while the randomly packed NP photoanode is advantageous for light harvesting. In order to compensate for the reduced dye adsorption from the virus-templated TiO\(_2\) nanowire structure, strategies for improving the light harvesting characteristics were designed.

**M13 virus as a versatile tool for improved light harvesting.**

LSPs are the elementary electronic excited states in metal NPs.\(^{112}\) By utilizing LSPs from surrounding Au or Ag NPs, the light harvesting in various photovoltaic technologies has been improved.\(^{64,130}\) The ability of M13 viruses to bind with these noble metal NPs can thus be utilized to improve the optical absorption of the virus-templated photoanode in DSSCs. Once the viruses (Figure 5.5A) and Au NPs (20 nm, transmission electron
microscopy (TEM) images in Figure 5.5B) are bound together through complexation in a colloidal suspension (Figure 5.5C), the same film fabrication process mentioned above is performed with the Au NP-virus complex. The morphology of the resulting virus-templated Au@TiO₂ structures is similar to that of the virus-templated TiO₂ films (Figure 5.9). After the calcination of the virus-templated Au@TiO₂ photoanode, both Au and anatase TiO₂ can be observed in the X-ray diffraction (XRD) pattern (Figure 5.5D). In addition, it is observed in the TEM image (Figure 5.5E) that the ~8 nm TiO₂ crystallites are densely packed around the Au NPs. This encapsulation of the Au NPs with TiO₂ help prevent the Au NPs from promoting electron recombination and also prevent etching of the Au NPs by the electrolyte.⁷⁹

The effect of Au NPs on the optical absorption of dye-molecules in solution and in the network thin films were investigated. The effect of LSP in solution simulates the behavior observed in plasmon-enhanced DSSCs, since the concentrations of Au NPs and dye molecules in solution can be easily controlled and the contribution from light scattering is minimized. The light absorption of dye-molecules increases with the presence of Au NPs in the wavelength range of 450-530 nm with maximum relative enhancement 45% (Figure 5.6A-C), which suggests that the increase in photo-absorption mainly arises from the interactions between dye-molecular dipoles and LSPs from Au NPs. Similarly, the light absorption of dye-molecules in the virus-templated TiO₂ thin films is increased to a maximum 21% at 540 nm (Figure 5.6D-F), which can be attributed to the enhanced near field electromagnetic intensity and scattering cross-section of Au NPs. In addition, the shift of the absorption peak from the Au NP solution
to a longer wavelength results from the high dielectric constant of the thin TiO$_2$ layer surrounding the Au NPs, which also has been observed in previous report.$^{79}$

To investigate the effect of LSPs on the spectral response of the solar cells, the incident photon-to-current conversion efficiency (IPCE) of virus-templated TiO$_2$-only and Au@TiO$_2$ photoanodes are compared (Figure 5.7A-C). The IPCE of the plasmon-enhanced DSSC is increased over the entire wavelength range compared to the TiO$_2$-only DSSC (Figure 5.7A), indicating that the Au@TiO$_2$ structures improve light harvesting of the dye molecules and thus the solar cell. Moreover, the most significant enhancement is in the range of 500-600 nm with a peak around 530 nm (Figure 5.7B and C), in agreement with the absorption enhancement of the thin films.

**Device performance of virus-templated Au@TiO$_2$ DSSC.**

The device performance of the virus-templated Au@TiO$_2$ photoanodes is optimized by varying the concentration of the plasmonic Au NPs ($\sim$0.24 to $\sim$2.40 wt.%) and the thickness of the photoanodes ($\sim$0.5 to $\sim$18.1 $\mu$m) (Figure 5.8A and B). In general, thicker photoanodes tend to absorb more light, and have higher PCEs and $J_{SC}$. The virus-templated Au@TiO$_2$ DSSCs (concentrations of Au NPs, $\sim$0.24 wt.% and $\sim$0.8 wt.%) always show higher PCE and $J_{SC}$ than the virus-templated TiO$_2$-only DSSCs with similar thicknesses of the photoanodes. In other words, to achieve the same PCE (e.g., $\sim$6%), the photoanode of the plasmon-enhanced DSSC (6.6 $\mu$m) is much thinner than that of the TiO$_2$-only DSSC (18.1 $\mu$m), reducing 63.5% of the photoactive materials used. In addition, both PCE and $J_{SC}$ increase monotonically with the concentration of Au NPs from 0 to 0.8 wt.% PCE and in $J_{SC}$ decrease when the concentration of Au NPs is
increased to 2.4 wt.%, probably due to the increased trapping of photo-excited electrons by Au NPs and competing light absorption of Au NPs with dye-molecules, which transform part of the incident light into heat. Thus, the optimal concentration of incorporated Au NPs was found to be 0.8 wt.%.

Figure 5.8C and Table 5.1 show the $J-V$ characteristics of the most efficient virus-templated plasmon-enhanced DSSC and virus-templated TiO$_2$-only DSSC. The plasmon-enhanced DSSC achieves a $J_{SC}$ of 13.72 mA cm$^{-2}$, a 25.1% increase compared to that of the TiO$_2$-only DSSC, 10.97 mA cm$^{-2}$. Also, the plasmon-enhanced DSSC shows higher open-circuit voltage ($V_{OC}$) than the TiO$_2$-only DSSC, which probably results from the reduced charge recombination because of thinner optimized photoanodes and the lifted quasi-Fermi level due to the equilibrium between quasi-Fermi level of TiO$_2$ and the LSP energy level of Au NPs.$^{90}$ In addition, the optimized thickness for the LSP-enhanced photoanode (15.1 μm) is thinner than that for the TiO$_2$-only photoanode (18.1 μm). As a result, by introducing Au@TiO$_2$ nanostructures into the virus-templated photoanode, the PCE (8.46%) of the plasmon-enhanced DSSC was improved by 40.3% compared to that of the virus-templated TiO$_2$-only DSSC, 6.03%, while the photoanode thickness was decreased by 19.9%. The LSP from Au NPs in nanowire-based photoanodes has the ability to increase the light harvesting without affecting the high $L_n$ achieved with the virus nanowire network, and thus maintain efficient electron collection (Figure 5.5A).

5.4. Conclusion

In summary, the M13 virus has been demonstrated as a bio-template to create a dual-functional three-dimensional nanowire-based porous DSSC photoanode for efficient
electron collection and improved light harvesting. The synthesized virus-templated photoanode is composed of TiO$_2$ nanowires, which transport electrons more directionally and achieve a longer $L_n$ compared to the NP-based photoanode. Also, the virus has demonstrated excellent molecular recognition in its ability to bind Au NPs; the Au NP-virus complex can be incorporated into virus-templated photoanodes to improve the optical absorption of dye-molecules by the LSP. We have observed LSP enhancement on the optical absorption of dye-molecules in solution, thin films and on the IPCE of the devices. Consequently, virus-templated plasmon-enhanced DSSC with optimal concentration of incorporated Au NPs (0.8 wt%) achieves an increased efficiency by improving the light harvesting while maintaining the electron collection. This synthetic templating process is expected to be scalable to large area formats. In addition to the ability to rapidly transport electrons and the versatility to incorporate multi-functional materials, the virus-templated nanowire networks have the capability to be assembled into numerous materials engineering applications, e.g. sensors and lithium ion batteries.

5.5. Figures
Figure 5.1. Structures and mechanisms of DSSC with virus-templated TiO$_2$ and Au@TiO$_2$ photoanodes.

Figure 5.2. Schematic illustration of 3-D porous TiO$_2$ photoanode fabrication process, including (1) Hydrogel formation (2) TiO$_2$ nucleation (3) Annealing.
Figure 5.3. Virus-templated TiO$_2$ nanowires and photoanodes. (A) XRD analysis of annealed virus-templated anatase TiO$_2$ photoanodes. SEM images of annealed virus-templated TiO$_2$ photoanodes in (B)-(D) top-view and (E) cross-section.
Figure 5.4. Electron diffusion lengths and device performance. (A) Electron diffusion length analysis. $L_n$ is the electron diffusion length and $L$ is the photoanode thickness. (B) Device performances for DSSCs employing the virus-templated TiO$_2$-only photoanodes. The performance of NP-based DSSC is shown as a reference.
Figure 5.5. Virus templated Au-TiO$_2$ nanowires and photoanodes. TEM images of (A) M13 virus, (B) as-synthesized 20 nm Au NPs and (C) the Au NP-virus complex. (D) TEM image of annealed virus-templated Au@TiO$_2$ photoanode. (E) XRD analysis of virus-templated anatase Au@TiO$_2$ photoanode.
Figure 5.6. LSP-induced enhancement of optical absorption of dye-molecules in solution and in virus-templated TiO$_2$ thin film. (A) Optical absorption spectra of Au NPs, dye-molecules, and their mixture in solution. (B) Net changes of dye absorption ($\Delta$OD) due to the presence of Au NPs in solution. (C) Relative changes of effective extinction coefficient of dye ($\Delta\alpha/\alpha$) due to the presence of Au NPs in solution. (D) Optical absorption spectra of virus-templated TiO$_2$ and Au@TiO$_2$ films and their dye-adsorbed thin films (~0.6 $\mu$m). (E) $\Delta$OD of dye due to the presence of Au NPs in thin film. (F) Relative changes of $\Delta\alpha/\alpha$ of dye due to the presence of Au NPs in thin film. For the calculation of $\Delta$OD and $\Delta\alpha/\alpha$: 

$\Delta\alpha/\alpha = \Delta$OD($\lambda$)/OD$_{dye}$($\lambda$) = (OD$_{dye,Au}$($\lambda$) - OD$_{dye}$($\lambda$) -
OD_{Au}(\lambda))/OD_{dye}(\lambda), where OD_{dye}(\lambda), OD_{Au}(\lambda), and OD_{dye, Au}(\lambda) are the optical densities at wavelength \( \lambda \) of pure dye solution, Au NP solution, and their mixture solution with the same concentrations of dye and Au NPs, respectively. For the solid-state thin films, the net absorption of dye-molecule is OD_{dye}(\lambda) = OD_{dye, TiO_2}(\lambda) - OD_{TiO_2}(\lambda).

Figure 5.7. Spectral responses of virus-templated TiO_2-only and Au@TiO_2 DSSCs. (A) IPCE spectra of the DSSCs with and without the presence of Au NPs. (B) Net change of IPCE (\( \Delta \)IPCE) and (C) relative changes (\( \Delta \)IPCE/IPCE) due to the presence of Au NPs.
\[ \Delta \text{IPCE}(\lambda)/\text{IPCE} = \text{IPCE}_{\text{Au@TiO}_2}(\lambda) - \text{IPCE}_{\text{TiO}_2\text{-only}}(\lambda)/\text{IPCE}_{\text{TiO}_2\text{-only}}(\lambda). \]

\text{IPCE}_{\text{Au@TiO}_2}(\lambda) \text{ and } \text{IPCE}_{\text{TiO}_2\text{-only}}(\lambda) \text{ are the IPCE at wavelength } \lambda \text{ for virus-templated Au@TiO}_2 \text{ and TiO}_2\text{-only DSSCs, respectively.}

**Figure 5.8. Effect of LSPs on the performance of DSSCs.** Dependence of (A) PCE and (B) J_{SC} on the concentration of Au NPs in photoanodes with the different film thickness. (C) Current density of the most efficient virus-templated Au@TiO\textsubscript{2} DSSC (Au weight
percent = 0.8 wt. %, PCE = 8.46%, fill factor (FF) = 74%, ~15.1 μm) and TiO$_2$-only DSSC in this work.

Figure 5.9. SEM images of annealed virus-templated Au@TiO$_2$ photoanodes.

Table 5.1. Relevant solar cell parameters obtained from the devices in Figure 5.4B and Figure 5.8C.

<table>
<thead>
<tr>
<th>Type</th>
<th>Thickness (μm)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>Dye Loading (mmole cm$^{-3}$)</th>
</tr>
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<tbody>
<tr>
<td>Virus-templated TiO$_2$</td>
<td>18.1</td>
<td>801.8</td>
<td>68.6</td>
<td>10.97</td>
<td>6.03</td>
<td>70.92</td>
</tr>
<tr>
<td>Virus-templated Au@TiO$_2$ Nanoparticle</td>
<td>15.1</td>
<td>832.7</td>
<td>74.0</td>
<td>13.72</td>
<td>8.46</td>
<td>68.22</td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>781.1</td>
<td>68.8</td>
<td>12.31</td>
<td>6.63</td>
<td>96.87</td>
</tr>
</tbody>
</table>

5.6. Experimental

Materials.
50 wt.% glutaraldehyde solution, titanium (IV) chloride, hydrogen tetrachloroaurate (HAuCl₄), sodium citrate, acetonitrile, tert-butanol and phosphate buffered saline (PBS) buffer solution were purchased from Sigma Aldrich. Ammonium hexafluorotitanate ((NH₄)₂TiF₆) and boric acid (B(OH)₃) were purchased from Alfa Aesar. Cis(diisothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (also named N719) and TiO₂ NP paste (13/400 nm, Ti-Nanoxide D/SP) were purchased from Solaronix. N719 dye solution was prepared in acetonitrile and tert-butanol (volume ratio 1:1) mixture at 0.5 mM. All reagents were used as received and without further purification. All water was deionized (18.2 MΩ, mill-Q pore). The E3M13 (AEEE expressed on the pVIII major coat protein) virus solution, ~10¹⁴ phage mL⁻¹, was diluted to 5×10¹³ phage mL⁻¹ with PBS buffer.

**Synthesis of Au NPs.**

The Au NP solution was prepared by the following procedure: 10 mg HAuCl₄ was initially dissolved in 100 mL water and the solution was heated to boil. 50 mg sodium citrate was dissolved in 5 mL water and the solution was then added into the boiling HAuCl₄ solution under vigorous stirring. The mixed solution was reacted in boiling for 30 minutes. The synthesized Au NP solution is stored in the 4 °C.

**Binding Au NPs on M13 virus.**

The different amount of phage solution were mixed with Au NP solution and then incubated in dark condition at 4 °C for 12 hours. Then, Au NPs@virus was precipitated through the standard polyethylene glycol and sodium chloride solution to minimize the
impurities. The final pellet was redissolved and diluted to $5 \times 10^{13}$ phage mL$^{-1}$ with PBS buffer. The synthesized Au NPs@virus solution is stored in the 4 °C.

**M13 virus hydrogel.**

On an FTO glass substrate, an area of 1 cm $\times$ 1 cm was defined using a 25-μm-thick Surlyn film (Solaronix Meltonix 1170-25), which was attached onto the FTO substrate by melting at 120°C for 15 minutes. 10 μl of virus solution or Au NPs@virus solution was then dropped on the FTO. The FTO with the virus solution was inverted and put on top of a solution of 50% glutaraldehyde, which served as a crosslinking agent. The crosslinking reaction was allowed to proceed for 2 hours. Afterwards, the resulting virus hydrogels (along with the FTO substrate) were removed from the crosslinking solution and transferred to a PBS buffer to remove excess glutaraldehyde in the hydrogel for 12 hours.

**TiO$_2$ photoanode generation.**

The cross-linked phage hydrogels were immersed in 0.2 M TiCl$_4$ solution for ~6 hours and in a mixture of 30 mM (NH$_4$)$_2$TiF$_6$ and B(OH)$_3$ for 4 hours in 50 °C subsequently for TiO$_2$ nucleation. After the nucleation, the films were rinsed with water and then annealed at 500 °C for 30 minutes. Thicker films were achieved by repeating the fabrication process (crosslinking, nucleation and calcination). For the NP-based photoanodes, layers of commercial TiO$_2$ NP paste were doctor-bladed on the substrates, and then annealed at 500 °C for 15 minutes. Film thickness was monitored using a surface profilometer (Veeco Dektak). Scanning electron microscope (SEM) images of the film morphology were obtained using Helios Nanolab 600 Dual Beam Focused Ion Beam System. TEM
observations of synthesized nanostructures were performed using JEOL 200CX TEMs with an accelerating voltage of 120 kV. The optical absorption spectroscopy measurements were performed using a Beckman Coulter DU800 UV-Vis spectrophotometer.

**Fabrication of DSSCs.**

After calcination, the photoanodes were cooled to 80 °C and immersed in the N719 solution, and kept at room temperature over 24 hours. The counter-electrode was a 100-nm-thick platinum film sputtered on a FTO substrate. The electrolyte employed was a solution of 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich), 0.03 M I₂ (Sigma Aldrich), 0.10 M guanidinium thiocyanate (Sigma Aldrich) and 0.5 M 4-tert-butyl pyridine (Sigma Aldrich) in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). The dyed TiO₂ photoanodes and platinum counter-electrodes were assembled into a sandwich-type cell and sealed with a hot-melt 25 µm Surlyn. The photoanode had dimensions of ~0.16 cm² (4 mm × 4 mm), further determined from a calibrated digital camera image.

**Characterization of DSSCs.**

Photovoltaic measurements were performed using an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to 100 mWcm⁻² by using a reference silicon photodiode with a power meter (1835-C, Newport) and a reference silicon solar cell to reduce the mismatch between the simulated light and AM 1.5. *J-V* curves were obtained by applying an external bias to the cell and measuring the
generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. IPCE spectra were obtained with a computer-controlled system (Model QEX7, PV Measurements, Inc.) consisting of 150 W xenon lamp light source and a monochromator with two 1200 g/mm diffraction gratings. The incident photon flux was determined using a calibrated silicon photodiode (calibrated by PV Measurements, Inc.). Measurements were performed in a short-circuit condition, while the cell was under background illumination from a bias light of 50 mW cm$^{-2}$. EIS of DSSCs were measured using a Solartron 1260 frequency response analyzer. The obtained impedance spectra were fit to the transmission line model with Z-view software (v3.2b, Scribner Associates). The spectra were measured at various forward bias voltages (from 0.85 to 0.45 V) in the frequency range ~0.1 Hz to ~1 MHz with oscillation potential amplitudes of 10 mV at room temperature. The photoanode was connected to the working electrode. The platinum electrode was connected to the auxiliary electrode and reference electrodes. The impedance measurements were carried out at forward bias in dark conditions. The transmission line model was used for fitting the electrochemical impedance data (see Experimental).
Chapter 6. Other projects

6.1. Graphene sheets stabilized on genetically engineered M13 viral templates as conducting frameworks for hybrid energy storage materials

Keywords: Colloidal stability • Conversion reaction materials • Graphene • Lithium ion battery • M13 virus

Introduction

Single-layer graphene sheets have significantly broadened the horizon of nanotechnology with the unique electronic, optical, quantum mechanical and mechanical properties associated with the two-dimensional atomic crystal structure. To best utilize this material for practical applications, it is crucial to prevent the spontaneous aggregation between individual graphene sheets while composite materials are formed. Numerous efforts have been made to stabilize functionalized graphene sheets on molecular or polymeric species. Biomolecules such as DNA and proteins have also been grafted onto graphene planes and used for biosensors, controlled drug-delivery as well as cancer imaging. Besides biomedical applications, graphene sheets can also be hybridized with biomolecules into energy storage devices to increase the conductivity of the active materials that are often insulators. In previous work, ultrasonication or chemical reduction, followed by heat treatment, have been adopted to achieve composites between graphene and various materials (LiFePO₄ and SnO₂). However, due to the non-specific nature of the interactions between the graphene templates and active materials, it is expected that only random and inhomogeneous contacts are created,
leaving the segregation on nano- or even sub-micron levels. Ideally, the performance of these active materials, such as the accessible capacity and the rate capability, can be maximized only if atomic level contacts can be realized between the conductive phase (graphene) and the active phase.

In order to expand the range of graphene based hybrid materials, methods to prevent aggregation around the limit of colloidal stability need to be developed. The stability of aqueous colloidal dispersion of functionalized graphene is usually maintained at high pH and low ionic strength due to the charges on the functionalized surface. Substrate specificity of ligands in biomolecules can improve the colloidal stability of graphene and strengthen the interaction between graphene and functional materials, thereby providing a genetically tunable hybrid building block and a desired conducting frame. The M13 bacteriophage has been demonstrated as a genetically engineerable biological toolkit to develop nanostructured hybrid materials to enhance the performance of energy storage and conversion devices. Here, we show that the non-covalent binding between the engineered M13 virus and graphene increased the dispersion stability of graphene sheets at a pH as low as 3 and an increased ionic strength environment. In addition, using this biological engineering approach, we were able to take a DNA sequence that coded for peptides that could bind graphene and modified this sequence to further broaden the stability window of the aqueous colloid of graphene sheets. With the improved stability of graphene in aqueous media, inorganic nanoparticles nucleated on the M13 virus were able to intimately interface with graphene sheets and fully utilized the excellent electronic conductivity of graphene, although the incorporation of graphene might lower the packing density. As a result, we achieved an efficient conducting matrix throughout the
hybrid material with the genetically engineered M13 virus, which simultaneously stabilizes graphene sheets and mineralizes the active nanoparticles. We also demonstrated that the electrochemical utilization of the originally insulating active materials could be maximized in the composite network consisting of active nanoparticles and conductive graphene sheets.

**Results and discussion**

We utilized an M13 virus to synthesize a graphene/virus complex to function as a building block for a conducting framework. The M13 virus is a filamentous bacteriophage, with a length of ~880 nm and a diameter of ~6.5 nm. The single-stranded DNA encapsulated inside the coat proteins can be modified to express specific peptide sequences on the surface of the virus to enhance the interaction with materials of interest. To fabricate a virus-mediated graphene framework with inorganic nanoparticles, two factors must be addressed; the colloidal stability of graphene and the interface between the active materials and the graphene. In designing an M13 virus, the major coat protein (pVIII) was chosen as a major interacting motif to maximize the attraction between the graphene and the virus, so that every particle templated on the virus was forced to contact the graphene (**Figure 6.1a**). First, the graphene-binding virus, with an 8-mer peptide insert, DVYESALP, fused to the amino-terminus of the pVIII major coat protein (this virus is called p8cs#3), was identified through a bio-panning method using a pVIII library previously reported by this group. The aromatic residue, tyrosine (Y), of the selected sequence is expected to interact with graphene, as well as single-walled carbon nanotubes (SWNTs), through $\pi-\pi$ interaction. In addition to the
aromatic residue, the hydrophobicity plot of the sequence, calculated based on the Hopp-Woods scale with the averaging group size 5, shows a hydrophobic moiety between two hydrophilic regions (Figure 6.1b inset) suggesting that the virus can bind graphene by hydrophobic-hydrophobic interaction. Second, to facilitate the nucleation of nanoparticles, we introduced two additional carboxyl groups on each pVIII protein of p8cs#3 virus, in which the thirteenth amino acid, lysine (K), and the seventeenth amino acid, asparagine (N), were changed to the glutamic acid (E), using site-directed mutagenesis (Figure 6.1b top) (this site-mutated virus is called EFE). Since the thirteenth and seventeenth amino acids of an M13 virus are known to be exposed on the surface and accessible to ligands, these carboxyl groups of glutamic acid can chelate metal ions and catalyze the mineralization. The zeta potential of EFE was measured and compared with that of the control virus, p8cs#3, to confirm the effect of the site-directed mutation on the surface charge of the virus (Figure 6.1b bottom). It was observed that the isoelectric point of the virus shifted to a lower pH by the addition of two glutamic acids on the pVIII protein. The increased negative charges associated with the carboxyl groups have additional advantages in enhancing the colloidal stability of the graphene/virus complex. Finally, the pIII minor coat protein was also engineered to increase the binding affinity between the virus and the graphene (Experimental). We designate this virus clone as FC#2 and use it for further research on stabilizing graphene, nucleating functional materials and improving the performance of lithium ion batteries.

The stability of the graphene/virus complex was tested by adding bismuth nitrate at pH 3. The stability of graphene dispersion by the virus was maintained after 24 hours of incubation with bismuth nitrate as shown in Figure 6.1c. This is in contrast to the control
sample under the same salt concentration and pH without the virus, where the graphene aggregated. We also observed the graphene/virus (FC#2) complex by atomic force microscopy (AFM) (Figure 6.1d). An area with the relatively lower coverage of the virus on the graphene compared to the approximate calculation was selected to clearly visualize the interaction of the virus and the graphene. The thickness of the graphene in the solution was around 0.8 nm as indicated in Figure 6.1d inset.

Leveraging the enhanced colloidal stability of the genetically programmed graphene/virus complex, we assembled bismuth oxyfluoride on the graphene/virus template. Bismuth oxyfluoride is a conversion reaction cathode material with an open circuit voltage of 2.8 V vs Li/Li⁺, a high theoretical specific capacity of 210 mAh g⁻¹ (for BiO₀.₅F₂, from LiF formation) and an attractive volumetric energy density of 5056 Wh l⁻¹ (for BiO₀.₅F₂, higher than LiCoO₂ with 2845 Wh l⁻¹),¹⁵² which can be synthesized in aqueous solution under low pH conditions. Among the candidates of cathode materials for next generation lithium ion batteries, bismuth oxyfluoride was chosen as a model material, since we found the synthetic condition for this material under a weak acidic environment, suitable for demonstrating the improved colloidal stability of the graphene. Since the M13 virus helped maintain the colloidal stability of the graphene during the nucleation of inorganic nanoparticles under low pH, it is now possible to form hybrid nanostructures of the graphene/BiO₀.₅F₂. We first developed an aqueous solution-based approach to synthesize bismuth oxyfluoride nanoparticles on the virus under a weakly acidic condition at room temperature, using LiF as a milder precursor than hydrofluoric acid¹⁵³ and ammonium fluoride.¹⁵⁴ Nanoparticles, thus synthesized, have a diameter of around 40 nm (Figure 6.2a,b). The virus-mediated synthesis increased the reaction yield
(from 17% without virus to 63% with virus, both without graphene) and decreased the particle size of the material compared with the previous report.\textsuperscript{153} To fabricate the nanocomposites of the water-soluble graphene (\textbf{Figure 6.2c}) and bismuth oxyfluoride, the graphene was first complexed and stabilized by the FC\#2 virus, and then bismuth oxyfluoride was grown on the virus/graphene complex. In order to visualize the hybrid structure with graphene, we used a lowered concentration of the precursor to show that more bismuth oxyfluoride was nucleated along the virus than on the surface of graphene (\textbf{Figure 6.2d}). The chemically modified graphene (see Experimental for graphene synthesis) possesses functional groups, which also act as nucleation sites, but the graphene-assisted nucleation is not as efficient as the virus-assisted nucleation. Two control hybrid materials with the graphene were synthesized without using the virus or with a wild type virus (M13KE, denoted in our work as a wild type virus). In addition to the reduced colloidal stability as shown in \textbf{Figure 6.1c}, the yield of bismuth oxyfluoride of the reaction without the virus (42\%) was much lower than the yield of the reaction aided by the FC\#2 (68\%). For the nanocomposites made with the wild type virus, the graphene was initially stabilized by non-specific interaction, but the graphene aggregation and the separation between the graphene and active materials eventually prevailed as the nucleation proceeded (\textbf{Figure 6.2e}). Furthermore, the positive surface charge from the wild type virus under weakly acidic conditions (pH 3) did not facilitate the nucleation of bismuth oxyfluoride and the yield was similar to the reaction without the virus.

The crystal structure of the virus-templated bismuth oxyfluoride was confirmed as cubic (Fm-3m) by high-resolution transmission electron microscopy (HRTEM) (\textbf{Figure 6.2b})
and X-ray diffraction (XRD) (Figure 6.2f), with a lattice parameter of 5.8160(1) Å. From X-ray photoelectron spectroscopy (XPS) elemental analysis, the bismuth-to-fluorine ratio was determined to be 1:2.02 (Table 6.2), giving a chemical formula of BiO$_{0.49}$F$_{2.02}$. The galvanostatic measurement (at a current density of 6 mA g$^{-1}$) further confirmed the composition of fluorine and oxygen based on the fact that oxygen and fluorine in bismuth oxyfluoride react with the lithium at different potentials of 1.8 V and 2.6 V (vs Li/Li$^+$).$^{152}$ In Figure 6.5B, the ratio of discharge capacity in the plateau regions around 2.7 V and 1.9 V was calculated to be 1.95:1.05. Because the ethyl methyl carbonate (EMC) electrolyte is believed to be inert to Bi nanocrystals,$^{155}$ the solid electrolyte interphase formation does not occur under 2 V, therefore does not contribute to the capacity. Since each fluorine atom reacts with one lithium atom and each oxygen atom reacts with two lithium atoms, the galvanostatic measurement gave a chemical formula of BiO$_{0.525}$F$_{1.95}$, in good agreement with the XPS analysis result. Therefore we concluded with a reasonable approximation that the chemical formula of the synthesized bismuth oxyfluoride was close to BiO$_{0.5}$F$_{2}$.

The advantage of incorporating well-dispersed graphene into lithium ion battery cathodes was demonstrated by making electrodes with the graphene/bismuth oxyfluoride nanocomposites assembled with a biologically engineered virus. With a small amount (2.4 wt%) of graphene incorporated into the bismuth oxyfluoride, the specific capacity of the virus-templated bismuth oxyfluoride was increased from 124 mAh g$^{-1}$ to 174 mAh g$^{-1}$ at a current density of 30 mA g$^{-1}$ (C/7) (Figure 6.3a and Figure 6.3b). The second cycle capacity (206 mAh g$^{-1}$, at C/7) of the virus templated bismuth oxyfluoride with 2.4 wt% of graphene in Figure 6.7 corresponds to 98% of theoretical capacity, which is the
highest reported for this material to date. Moreover, the rate performance was also improved, showing a specific capacity of 131 mAh g\(^{-1}\) (corresponding to 711 W kg\(^{-1}\), with an energy density of 316 Wh kg\(^{-1}\), 2718 Wh l\(^{-1}\)) at a current density of 300 mA g\(^{-1}\) (1.4 C) compared to 67 mAh g\(^{-1}\) for the virus-templated bismuth oxyfluoride without graphene. These results represent a significant improvement in the electrochemical performance of bismuth oxyfluoride compared to the previous report, as indicated by the increased active mass loading in the electrode (from 50 wt% to 70 wt%) and the improved specific capacity at a 20 times higher current density. In addition, the presence of the graphene also significantly decreased the voltage hysteresis between the charge and the discharge profiles (Figure 6.7), which became more pronounced at a higher discharging rate (Figure 6.3a). This reduction in the electrode overpotential stems from the excellent electric wiring achieved at the atomic level by graphene sheets, which connects active nanoparticles with the cell current collector through a homogeneously distributed percolating conductive network.

To study the beneficial effect of specific interaction between the genetically engineered virus and the graphene in the formation of a conducting framework, control experiments have been done with graphene/bismuth oxyfluoride nanocomposites synthesized in the absence of the virus or in the presence of the wild type virus. The bismuth oxyfluoride synthesized in the control experiments had the same chemical and crystallographic properties as that formed with FC#2 (Figure 6.8 shows XRD patterns for each composite). As shown in Figure 6.3a, c and d, the specific capacity (174 mAh g\(^{-1}\) at C/7) of nanocomposites using FC#2 was higher than that of nanocomposites using the wild type virus (145 mAh g\(^{-1}\) at C/7) and without the virus (102 mAh g\(^{-1}\) at C/7). Moreover,
the superior electrochemical performance of the nanocomposites using FC#2 was more apparent at a high rate of 600 mA g⁻¹ (110 mAh g⁻¹ for FC#2, 67 mAh g⁻¹ for the wild type virus and 64 mAh g⁻¹ without the virus), indicating accelerated electrode kinetics for the cell reactions in those nanocomposites benefiting from the specific interaction between the graphene and FC#2 virus. The poor electrochemical activities of the nanocomposites in the presence of the wild type virus and in the absence of the virus are caused by the agglomeration of graphene during the active material synthesis. Based on these observations, we conclude that the increased interaction of graphene with the active material particles aided by the genetically engineered virus results in an efficient conducting network. This was made possible by maintaining the colloidal stability of complex during the synthesis. Moreover, we achieved both higher capacity utilization of the active materials and a much reduced kinetic barrier between charge and discharge reactions, as compared with the previous report.¹⁵²

The superior formation of a percolating network with two-dimensional conducting sheets enabled by the genetically engineered virus has also been demonstrated by comparing the effects of graphene and SWNTs on the electrochemical performance of bismuth oxyfluoride. The SWNTs were evenly dispersed inside the electrode by the virus complexation method and bismuth oxyfluoride was synthesized on this template. When the same amount of graphene and SWNTs (0.5 wt%) were incorporated into the nanocomposites, the specific capacities of 128 mAh g⁻¹ for the SWNTs/bismuth oxyfluoride nanocomposites and 181 mAh g⁻¹ for the graphene/bismuth oxyfluoride nanocomposites were obtained respectively, at a current density of 30 mA g⁻¹ (Figure 6.3e). The graphene improves the kinetics of the conversion reaction more effectively
than SWNTs. Although the SWNTs are known to be advantageous for constructing a percolating network because of their high aspect ratio\textsuperscript{156}, when a small quantity of carbon is used, the interconnectivity between the one-dimensional SWNTs could be limited compared to the two-dimensional graphene. In the bismuth oxyfluoride system, the graphene appears to be more effective in facilitating the electrochemical reaction.

**Conclusion**

In summary, using a genetically engineered M13 virus, we broadened the stability window of graphene in aqueous media, which enabled an environment-friendly approach to establish a graphene/virus nanotemplate. By designing the M13 virus for simultaneously stabilizing the graphene and nucleating bismuth oxyfluoride, we fabricated the graphene/bismuth oxyfluoride nanocomposites in which both phases were intimately interwoven. The graphene/virus complex formed a homogeneously distributed conducting framework and the kinetics of electron transfer inside the battery electrodes was improved, demonstrating the increased specific capacity of bismuth oxyfluoride at a high current density (131 mAh g\textsuperscript{-1} at 300 mA g\textsuperscript{-1}) and the reduced overpotentials for both charging and discharging cell reactions. This study demonstrates the importance of well-dispersed graphene in aqueous media for synthesizing composite materials and this general method could be extended to other materials for applications including biosensors, supercapacitors, catalysts and energy conversion applications.

**Figures**
Figure 6.1. The graphene/M13 virus complex with the enhanced colloidal stability for the hybrid graphene/nanoparticle nanocomposites. a) Scheme of the inorganic nanoparticle nucleation on the graphene/virus template. The virus enables a close contact between inorganic nanoparticles and the graphene. b) Top: The peptide sequence of pVIII protein of p8cs#3 and EFE. Bottom: The zeta potential of EFE and p8cs#3. Inset: The hydrophobicity plot of the pVIII major coat proteins of p8cs#3 virus as a function of the
amino acid location. c) The left vial is the graphene solution after 24 hours of incubation with bismuth nitrate, showing the aggregation of graphene on top. The right vial is the graphene/FC#2 complex solution after 24 hours of incubation with bismuth nitrate without any aggregation. d) AFM image of the graphene/virus (FC#2) complex. Inset: The height profile of line A showing the thickness of graphene as ~0.8 nm.

Figure 6.2. Characterizations of the bismuth oxyfluoride nucleated on the graphene/virus complex. a) TEM image of bismuth oxyfluoride nucleated on FC#2. b) HRTEM image of a bismuth oxyfluoride nanoparticle with the Fm-3m crystal system, (200) d=2.9 Å (left arrow) and (220) d=2.1 Å (right arrow). c) TEM image of the chemically reduced graphene with a selected area electron diffraction (SAED) pattern. d) TEM image of the bismuth oxyfluoride/graphene nanocomposites with FC#2 virus for battery electrodes. The bismuth oxyfluoride/FC#2 virus complexes are shown exclusively on the graphene. Inset: Catalyzed nucleation of bismuth oxyfluoride on FC#2 virus was
observed by lowering the precursor concentration in the composite synthesis with a scale bar of 400 nm. Background is the graphene in the inset. e) TEM image of the bismuth oxyfluoride/graphene nanocomposites formed with the wild type virus showing the separation of graphene and bismuth oxyfluoride. f) XRD pattern of bismuth oxyfluoride nanoparticles.
Figure 6.3. The power performance of the graphene/bismuth oxyfluoride nanocomposites with the genetically engineered M13 virus. a-d) The first discharge of bismuth oxyfluoride at different current densities; a) the bismuth oxyfluoride/graphene
nanocomposites with FC#2, b) the bismuth oxyfluoride templated on FC#2 without graphene, c) the bismuth oxyfluoride/graphene composites in the absence of virus, d) the bismuth oxyfluoride/graphene composites in the presence of the wild type virus. e) Comparison between the graphene and SWNTs: The first discharge of the bismuth oxyfluoride/graphene composites and the bismuth oxyfluoride/SWNTs composites formed with FC#2 viruses having the same mass percentage of carbon (0.5 wt% of electrodes) at a 30 mA g\(^{-1}\) of current density.

Figure 6.4. Zeta potential data (A) and AFM image (B) of water-soluble graphene, the size of the AFM image is 2 \(\mu\)m by 2 \(\mu\)m.
Figure 6.5. TGA and galvanostatic analysis of bismuth oxyfluoride. (A) Thermogravimetric (TGA) analysis of bismuth oxyfluoride grown on FC#2 showing that virus accounts for 11 wt% of the final hybrid nanowire. (B) Galvanostatic data of bismuth oxyfluoride/graphene nanocomposites (2.4 wt% of graphene addition) under constant current density (6 mA g\(^{-1}\)) until 1.5 V.

Figure 6.6. TGA of bismuth oxyfluoride-graphene and XRD pattern after discharging to 1.5 V. (A) TGA data for the analysis of virus mass inside the graphene-bismuth oxyfluoride nanocomposites formed by FC#2 (before adding 2.4 wt% of additional graphene), which shows the similar quantity as bismuth oxyfluoride grown on virus. (B) XRD patterns of the bismuth oxyfluoride-graphene nanocomposites (2.4 wt%
addition) electrode after discharging to 1.5 V with constant current density of 6 mA g\(^{-1}\). Bi metal is detected, however, Bi\(_2\)O\(_3\) was not observed and this could be due to small particle sizes.\(^{152}\)

**Figure 6.7.** First (straight) and second (dashed) cycles of bismuth oxyfluoride/graphene (2.4 wt\%) nanocomposites with FC# 2 and bismuth oxyfluoride on FC#2 at a current density of 30 mA g\(^{-1}\).

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Figure 6.8. XRD patterns of various bismuth oxyfluoride samples: (A) bismuth oxyfluoride/graphene nanocomposites formed with FC#2, (B) bismuth oxyfluoride/SWNTs nanocomposites formed with FC#2, (C) bismuth oxyfluoride-graphene composites formed without the virus, (D) bismuth oxyfluoride-graphene nanocomposites formed with the wild type virus.
Figure 6.9. The first five cycles galvanostatic data of bismuth oxyfluoride/graphene (2.4 wt%) nanocomposites (BOF-GP) with FC# 2 (A) and control samples: (B) bismuth oxyfluoride/graphene (2.4 wt%) nanocomposites without virus, (C) bismuth
oxyfluoride/graphene (2.4 wt%) nanocomposites with wild type virus under constant current (30 mA g⁻¹).

Table 6.1. XRD peaks table for synthesized bismuth oxyfluoride from 20~70 degree (2 Theta) with Rietveld refinement results for compound.

<table>
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<tr>
<th>(h k l)</th>
<th>2T(cal)</th>
<th>2T(cor)</th>
<th>2T(obs)</th>
<th>Delta</th>
<th>d(cal)</th>
<th>d(cor)</th>
<th>d(obs)</th>
<th>Del-d</th>
<th>I%</th>
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<tr>
<td>(1 1 1)</td>
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<td>26.547</td>
<td>26.609</td>
<td>0</td>
<td>3.3549</td>
<td>3.355</td>
<td>3.3472</td>
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<td>100</td>
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<tr>
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<td>30.747</td>
<td>30.809</td>
<td>0.001</td>
<td>2.9054</td>
<td>2.9055</td>
<td>2.8998</td>
<td>0.0001</td>
<td>42.2</td>
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<tr>
<td>(2 2 0)</td>
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<td>44.042</td>
<td>44.101</td>
<td>-0.001</td>
<td>2.0545</td>
<td>2.0544</td>
<td>2.0518</td>
<td>0</td>
<td>62.7</td>
</tr>
<tr>
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<td>52.221</td>
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<td>1.7503</td>
<td>0</td>
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<td>1.6775</td>
<td>1.6759</td>
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</tr>
<tr>
<td>(4 0 0)</td>
<td>64.044</td>
<td>64.038</td>
<td>64.093</td>
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<td>1.4527</td>
<td>1.4528</td>
<td>1.4517</td>
<td>0.0001</td>
<td>7</td>
</tr>
</tbody>
</table>

(cal=Calculated, obs=Observed, cor=Corrected)

Table 6.2. Atomic concentration (%) of bismuth oxyfluoride by XPS analysis.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>23.09</td>
</tr>
<tr>
<td>F</td>
<td>46.79</td>
</tr>
</tbody>
</table>

Experimental

FC#2 gene construction

The p8cs#3 clone was selected by a bio-panning method with a pVIII library previously reported by this group. Using QuikChange Lightning site-directed mutagenesis kit (Stratagene, catalog#210518), K was first mutated to E, and N to D then to E, producing EFE virus. The primer sequences used to change K to E are 5’ CAG GGA GTT AAA
GGC CGC TTC TGC GGG ATC CGG CAG CGC 3’ and 5’ GCG CTG CCG GAT CCC
GCA GAA GCG GCC TTT AAC TCC CTG 3’; for N to D, primers of 5’ GTC GCTGA
GGCTT GCAGG GAGTC AAAGG CCGCT TTTGC GGG 3’ and 5’ CCC GCAAA
AGCGG CCTTT GACTC CCTGC AAGCC TCAGC GAC 3’ were used; for D to E,
primers, 5’ GC TGA GGC TTG CAG GGA CTC AAA GGC CGC TTC TGC 3’ and 5’
GCA GAA GCG GCC TTT TAT TCT CAC TCT GAT ATG CCG CGT ACT
ACT ATG TCT CCG CCG CGT GGT GGA GGT TC 3’ and 5’ [Phos]’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
ACT ATG TCT CCG CCG CGT GGT GGA GGT TC 3’ and 5’ [Phos]’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
ACT ATG TCT CCG CCG CGT GGT GGA GGT TC 3’ and 5’ [Phos]’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
Previously reported SWNT-binding peptide MC#2, was fused to pIII of EFE virus. The
oligonucleotides used to introduce SWNT-binding functionality to the minor pIII coat
protein are 5’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
ACT ATG TCT CCG CCG CGT GGT GGA GGT TC 3’ and 5’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
ACT ATG TCT CCG CCG CGT GGT GGA GGT TC 3’ and 5’ GTA CCT TTC TAT TCT CAC TCT GAT ATG CCG CGT ACT
AGA GTA GGA AAG ACC TCC ACC ACG CGG CGG AGA CAT AGT AGT ACG CGG CAT ATC
AGA GTG AGA ATA GAA AG -3’ and they were annealed to form a DNA duplex. The
cloning vector was extracted from EFE virus using standard miniprep kit (QIAGEN) and
was digested with Eag I and Acc65 I enzymes, dephosphorylated, and purified with
agarose-gel. Purified vector and DNA duplex were ligated using T4 DNA ligase at 16°C
overnight, and electrotransformed to XL-1 blue cells. Transformed cells were incubated
for one hour, plated, and incubated at 37°C overnight.

**Synthesis of water-soluble graphene**

Graphene oxide (GO) was synthesized by Hummer’s method. 75 mg of GO was
dispersed in 75 ml of water by bath-sonication for one hour followed by centrifugation
(3,000 rpm). The pH was adjusted to 10 with 5 wt% sodium carbonate (Sigma-Aldrich)
solution. Then 600 mg of sodium borohydride (Sigma-Aldrich) in 15 ml of water was
added to partially reduce GO at 80°C for one hour followed by centrifugation (20,000 rpm). After washing with water, the partially reduced GO was dispersed again in 75 ml of water by sonication. The diazonium salt for sulfonation was made with 46 mg of sulfanilic acid (Alfa-Aesar) and 18 mg of sodium nitrite (Alfa-Aesar) in 10 ml of water and 0.5 ml of 1 M HCl solution in an ice bath. The diazonium salt solution was added to the partially reduced GO in an ice bath for 2 hours. To completely reduce the sulfonated graphene, 2 g of hydrazine (Acros) in 5 ml water was added kept at 100°C for 24 hours. 1 ml of 5 wt% sodium carbonate solution was then added into the mixture to precipitate the graphene. After centrifuging (25,000 rpm) and washing with water, the lightly sulfonated graphene was dried under vacuum at room temperature for 24 hours.

**Characterization of graphene.**

The water-soluble graphene was characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). For TEM, JEOL 2010F TEM was used with accelerating voltage of 200 kV. For AFM, the graphene on mica (Ted Pella) substrate was achieved by drying graphene dispersion and Veeco Nanoscope IV under tapping mode was used.

**Zeta potential measurement of virus and graphene.**

The concentration of virus solution was $10^{12}$ ml$^{-1}$ in water with 10 mM NaCl. The stock solution of virus ($\sim 10^{14}$ ml$^{-1}$) was initially dissolved in 10 mM Tris, 15 mM NaCl before diluting in 10 mM NaCl in $dH_2O$. The amount of solution used to generate curve was 30 ml. The ionic concentration of the solution was set to 10 mM NaCl for all samples to
minimize the fluctuation of ionic strength during pH adjustment. The pH was then adjusted using NaOH until the pH was around 10. For graphene, the concentration was 40 mg ml\(^{-1}\) in water and the pH of graphene dispersion was adjusted to around 11 by NaOH. The zeta potential of both virus and graphene were then measured at an accumulation time of 10 with 5 measurements per sample at 20 V using DelsaNano (Beckman Coulter). Electrophoretic mobility was calculated using the Smoluchowski approximation (used for particles larger than 0.2 \(\mu\)m in 1 mM or greater salt solution). The pH of solution was then adjusted with HCl.

**Synthesis of bismuth oxyfluoride powders, bismuth oxyfluoride and graphene nanocomposites for FC#2 virus, wild type virus and without virus:**

FC#2 viruses (2\(\times\)10\(^{13}\)) were incubated with the graphene solution (64 ml, 2.3 \(\mu\)g ml\(^{-1}\)). Bi(NO\(_3\))\(_3\)\(\cdot\)5H\(_2\)O (200 mM, dissolved in 10% HNO\(_3\)) was added to this mixture to make the final solution (400 ml, 0.2 mM). LiF solution (171 ml, 50 mM) was added and stirred at room temperature for 3 hours. Graphene solution (40 ml, 50 \(\mu\)g ml\(^{-1}\)) was further added into the nanocomposites. The final products were filtered, washed and dried under vacuum at 50°C overnight. With the same method, wild type viruses were used for bismuth oxyfluoride/graphene nanocomposites and virus addition and incubation steps were excluded for composites without virus.

**Synthesis of bismuth oxyfluoride and SWNTs nanocomposites:**

The SWNT/FC#2 complexes were constructed by dialyzing the mixture of FC#2 (2\(\times\)10\(^{13}\)) and SWNTs (0.094 mg in 2 wt% sodium cholate aqueous solution) against D.I. water
with gradual increase of salt (KCl) concentration of media from 10 mM to 80 mM, while maintaining pH 9 using NaOH for two days. Bismuth oxyfluoride was synthesized by adding Bi(NO₃)₃·5H₂O (0.8 ml, 200 mM, dissolved in 10% HNO₃) to complex solution giving final volume to 400 ml. After an hour, LiF (171 ml, 50 mM) was added and rested for 2 hours. The final products were washed and dried under vacuum at 50°C overnight.

**Calculation of yield of synthesized products.**

The mass of final products of each synthesis was measured and the yield of products was calculated as

\[
\text{Yield (\%) } = \frac{\text{mass of BiO}_{0.5}\text{F}_2 \text{ without virus mass}}{\text{number of moles of bismuth precursor} \times \text{molecular weight of BiO}_{0.5}\text{F}_2} \times 100
\]

**Characterization of bismuth oxyfluoride and graphene nanocomposites by XRD, XPS and TGA.**

The crystal structure was confirmed by X-Ray Diffraction (PANanalytical Multipurpose Diffractometer, Cu Kα radiation) and Rietveld refinement was conducted by changing the atomic occupancy of oxygen and fluorine. Since oxygen can take a place in fluorine site, we changed the occupancy of fluorine positions (F1: 0.5,0.5,0.5 and F2: 0.25,0.25,0.25) to fit the calculation to the data. For the electrode discharged to 1.5 V, the coin cell was disassembled inside Ar-filled glove box and the discharged electrode was covered by Kapton® tape to prevent any air contamination. X-ray photoelectron spectroscopy (XPS, Kraots AXIS) was conducted with pass energy 20 eV and step size 0.1 eV and the atomic ratio between bismuth and fluorine were measured. To quantify the
virus mass of the composites, thermogravimetric analysis (TGA, Q50 TA instrument) was used with increasing temperature with rate of 10°C min⁻¹ under nitrogen.

**Characterization of bismuth oxyfluoride and graphene/bismuth oxyfluoride nanocomposite by electron microscope.**

The bismuth oxyfluoride was characterized by high-resolution TEM (HRTEM) using JEOL 2010F TEM with an accelerating voltage of 200 kV. The graphene/bismuth oxyfluoride nanocomposites were characterized by TEM and scanning electron microscopy (SEM) using a Helios Nanolab 600 dual beam focused ion beam system possessing both scanning transmission electron microscopy (STEM) detector for bright field and high annular angle dark field (HAADF) mode TEM imaging and TLD detector for secondary electron (SE) mode SEM imaging; and the electron beam for both TEM and SEM imaging has an accelerating voltage of 30 kV. The graphene/bismuth oxyfluoride nanocomposites were also characterized by using JEOL 200CX TEM operating at an accelerating voltage of 120 kV.

**Geometrical quantification of graphene and virus (FC#2)**

The total mass of graphene is 64 ml × 2.3 µg ml⁻¹ = 147.2 µg. For 2 × 10¹³ viruses, there is 147.2 µg / (2 × 10¹³) = 7.36 × 10⁻¹⁸ g of graphene per virus, corresponding to 7.36 × 10⁻¹⁸ g / 12 g mol⁻¹ × 6.02 × 10²³ mol⁻¹ = 3.7 × 10⁵ carbon atoms. Considering a hexagonal packed structure of carbon atoms, each carbon atom contribute to an area of 0.5 × (0.142 nm)² × sin(π/3) × 3 = 0.0262 nm². Also considering the graphene thickness is around 0.8 nm, which is close to the thickness of a two-layer graphene, each virus covers an area of
graphene of $0.0262 \text{ nm}^2 \times 3.7 \times 10^5 = 9.7 \times 10^3 \text{ nm}^2$. The cross section area of a virus is $6.5 \text{ nm} \times 880 \text{ nm} = 5720 \text{ nm}^2$. Thus, the coverage of virus on graphene is expected to be $5720 \text{ nm}^2 / 9700 \text{ nm}^2 = 59\%$. This calculation is based on the assumption that every single virion of virus binds graphene.

**Electrochemical tests**: Active materials were mixed mechanically with Super P (TIMCAL, SUPER P® Li) for 20 minutes and polytetrafluoroethylene (PTFE) was added. (Active materials : virus : graphene : Super P : PTFE (mass ratio) = 68.8 : 8.8 : 2.4 : 15 : 5). Mixed powders were rolled out and punched in $4.08 \text{ mg cm}^{-2}$ and dried under vacuum at $120^\circ\text{C}$ overnight. Inside the Ar-filled glove box, the electrodes were assembled into coin cells with Li metal foils as the counter electrodes and 1 M LiPF$_6$ in EMC was used as the electrolyte. Three layers of microporous polymer separator (Celgard 2325) were used. Assembled coin cells were tested with a Solatron Analytical 1470E potentiostat at room temperature.

*This project was performed in collaboration with Ms. Dahyun Oh, who performed the battery assembly and measurements.*
6.2. M13 bacteriophage-templated synthesis of perovskite nanomaterials for solar energy conversion

Keywords: biomineralization · perovskite · nanomaterials · solar energy · conversion

Introduction

Biological systems provide an ideal environment for synthesizing natural minerals with control of morphology and crystal structure; expanding biological synthesis to non-natural materials while maintaining such control has been the focus of recent study. M13 bacteriophage is a diverse bio-template that has been genetically engineered for synthesizing nanomaterials that can be used to make functional devices. Particularly, metal, metal alloy, and semiconductor nanowires have been assembled and nucleated on M13 viruses. However, biological synthesis of ternary metal oxide nanomaterials is challenging as it requires matching reaction rates of multiple precursors.

As a special case of ternary metal oxides, perovskite materials have attracted wide-spread attention due to their catalytic, ferroelectric, and ferromagnetic properties as well as their application in superconductors, thermoelectrics, and fuel cells. Nanoscaled perovskite materials exhibit improved properties over bulk materials, and their unique characteristics are under investigation. However, using conventional methods to synthesize perovskite nanomaterials of small size and high crystallinity is difficult, and preparing them with different morphologies under environmentally friendly conditions presents an even greater challenge. A general method for biomimetic mineralization of perovskite nanomaterials would present unique opportunities.
Herein, we present a synthetic method of using genetically engineered M13 virus to mineralize perovskite nanomaterials, particularly strontium titanate (STO) and bismuth ferrite (BFO). The filamentous body of M13 virus comprises about 2700 identical copies of the major coat protein pVIII (Figure 6.10). Genetically engineered viruses (amino acid sequence AEEE expressed at the N-terminus of each pVIII yielding high charge density to interact with cationic metal precursors) provide effective templates for perovskite nanomaterials. The virus-templated nanocrystals are small in size, highly crystalline, and show photocatalytic and photovoltaic properties. Virus-templated STO nanowires produce hydrogen gas efficiently under both UV and visible (with dye-sensitization) irradiation, whereas photovoltaic performance of virus-mineralized BFO nanoparticles is investigated for the first time.

Results and discussion

In the biotemplated synthesis of STO nanowires, virus solution was first incubated with strontium titanium ethylene glycolate (SrTi(EG)) precursors. The interaction between viruses and precursors was demonstrated by using transmission electron microscopy (TEM) (Figure 6.11a) which shows staining of the virus with electron dense metal cations. Then the pH of the solution was changed to pH 10 and the temperature was raised to 80°C, allowing for the hydrolysis and condensation of STO nanowires on the virus. The virus-templated STO nanowires were characterized by high resolution transmission electron microscopy (HRTEM) (Figure 6.11b-d). Each STO nanoparticle was only around 5 nm in diameter and with cubic crystalline structure. High negative charge density provided by carboxylate ions on the surface of virus favors the formation
of small nanoparticles. The highly crystalline structure was also confirmed by X-ray diffraction (XRD) (Figure 6.11e).

Biotemplated synthesis of STO was optimized in terms of temperature, concentration of the precursors, and pH. At low temperatures (50°C and 60°C), no crystalline structure was found. The cubic crystalline structure of STO was formed at 80°C, which is the critical temperature to both accelerate the condensation and start STO nanocrystal nucleation and growth. The concentration of SrTi(EG) precursor for successful nanowire formation was between 0.1 mM and 1 mM. When the concentration of precursor was higher than 1 mM, homogeneous nucleation occurred and out-competed the virus-templating. The effect of the pH was also investigated. The zeta-potential of virus showed that the pI (isoelectric point) of AEEE virus was around 4 (Figure 6.15). At pH lower than 4 the surface of the virus was positively charged, when incubated with SrTiEG precursors no stained viruses were formed indicating that there was no interaction between viruses and precursors. At pH higher than 4, the electrostatic interaction between viruses and precursors was demonstrated by increased electron density visualized on the viruses. However, at pH 5~7, due to the low hydrolysis reaction rate, both STO and strontium carbonate were observed with or without addition of oxidants (hydrogen peroxide) (Figure 6.16 and Figure 6.17). At pH 10, the virus-templated nanowires showed only the perovskite structured STO. As the control experiments, we examined the growth of STO using non-genetically modified M13 virus (wildtype) and also performed the reactions without the addition of the virus. Figure 6.19 and Figure 6.20 clearly show discrete nanoparticles grown on wildtype virus, which are different from AEEE virus templated STO. Wildtype virus contains fewer carboxyl
groups and is less effective at nucleating STO, resulting in nanoparticles that are larger than those prepared on genetically modified virus template (AEEE). On the other hand, in the absence of the virus (Figure 6.21 and Figure 6.22), nanoparticles are polydisperse and do not show wire-like assembly. Compared with several studies that showed the carboxyl groups act as the reaction sites for mineralization of perovskite materials using the ethylene glycol precursors,\textsuperscript{171-173} our results demonstrated that the AEEE-genetically modified virus, rich in carboxyl groups, serves as an ideal template for the formation of nanowires of perovskite materials.

To synthesize BFO nanoparticles, the virus solution was incubated with bismuth iron ethylene glycolate (BiFe(EG)) precursor. The interaction between viruses and precursors was demonstrated by TEM (Figure 6.12a). Then the BiFe(EG)-incubated virus was heated at 600°C allowing formation of BFO nanoparticles. HRTEM (Figure 6.12c) and XRD (Figure 6.12d) confirmed the formation of R3c crystalline structure of BFO (JCPDS no. 86-1518). The resulting virus-templated nanoparticles were between 10 and 30 nm in diameter (as measured by both TEM and XRD) which is a difficult size to obtain by conventional methods. The magnetic properties of BFO nanoparticles were characterized using superconducting quantum interference device (SQUID) (Figure 6.23). The saturation magnetic moment (Ms) at 300K was 0.877 emu g\textsuperscript{-1} at 30,000 Oe. The nanoparticles showed coercivity at 5K, with a coercive field of ± 1,500 Oe.

We have demonstrated virus-templated synthesis of STO nanowires and BFO nanoparticles in aqueous solution, with small particle size, different morphologies, and high crystallinity. This biotemplate technique is distinguished from the conventional
methods for synthesizing perovskite nanomaterials, such as sol-gel, coprecipitation, hydrothermal, and surfactant-assisted synthesis, most of which involve the use of alkoxide precursors in organic solvents and do not adequately control the size and morphology. The nanoparticles synthesized by these previous methods are amorphous, or their surfaces are passivated by surfactants. In order to make highly crystalline materials, calcination at high temperatures is applied, sometimes resulting in an increase of particle size, thus a decrease in catalytic activity. Since our reactions are done in aqueous medium using ethylene glycol ligands to bind metal cations which reduces their auto-hydrolysis and matches their reaction rates, the synthesis takes place exclusively on the virus. The small size and high crystallinity of the virus-templated nanocrystals show the advantage of the biotemplate assisted synthetic method.

Recently the photocatalytic and photovoltaic performance of STO and BFO have been investigated. Single crystal STO is a wide-bandgap photocatalyst for producing hydrogen with a high conduction band level and good chemical stability. To investigate photocatalytic water reduction of biotemplated STO nanowires, the hydrogen evolution experiments were conducted using methanol as a hole scavenger and Pt nanoparticles as a co-catalyst. After STO absorbs UV light, the excited electrons in the conduction band of STO reduce hydrogen ions to produce hydrogen gas at the Pt particle active sites, whereas the holes on the valence band of STO were recovered by methanol. The amount of evolved hydrogen was measured by gas chromatography (GC) at several time points (Figure 6.13b). The hydrogen evolution rate of STO nanowire is 370 µmol g⁻¹ hour⁻¹, which is around ten times higher than that of titania (Degussa, P-25), and commercial STO nanopowders (Wako Pure Chemical Industries, Ltd.) (37 and 46 µmol
g\(^{-1}\) hour\(^{-1}\) respectively). We believe that the improved performance of virus-templated STO nanoparticles is from the smaller particle size providing a larger surface to volume ratio and the high crystallinity preventing excited charge recombinations at lattice defect sites. To produce hydrogen under visible light irradiation, Eosin Y dye\(^{185}\) was used to sensitize STO nanowires loaded with Pt nanoparticles (Figure 6.13a). The photo-electrons are excited to the lowest unoccupied molecular orbital (LUMO) of the dye and then transfer to the conduction band of STO. Hydrogen is produced at the Pt particle active sites. Diethanol amine is used to regenerate the electron deficient dye.

While STO is ideal for photocatalytic water reduction, BFO is a promising material for photovoltaic applications.\(^{182,183}\) Most perovskite materials primarily absorb UV light, harvesting solar energy inefficiently. In contrast, BFO has attracted increasing attention due to a direct bandgap corresponding to the wavelength of visible light. The photovoltaic properties of single crystal and thin film BFO have been observed. However, the photovoltaic effect of BFO nanoparticles has not been investigated. The absorption spectrum of virus-templated BFO nanoparticles shows a broad feature with peak around 550 nm (Figure 6.18), absorbing visible light effectively. Photovoltaic properties of virus-templated BFO nanoparticles were characterized by fabricating liquid junction solar cells (see methods) (Figure 6.14a). Under illumination of AM1.5 solar simulator at 100 mW cm\(^{-2}\), an open circuit voltage of 0.578 V and a short circuit current density of 0.735 mA cm\(^{-2}\) were observed (Figure 6.14b), achieving solar power conversion efficiency of 0.17% (the fill factor of the device was 0.40). The BFO-liquid junction photovoltaic device is the first report of BFO nanoparticles based solid-liquid junction PV devices.
Conclusion

In summary, we have demonstrated a novel and general approach to synthesize perovskite nanomaterials in an aqueous system using the genetically engineered M13 virus. STO and BFO nanoparticles were successfully templated on the viruses, achieving small particle size and high crystallinity compared to conventional techniques. We believe that our general method will extend the scope of biotemplated synthesis to ternary metal oxides as well as more complex materials. Furthermore, the virus-templated perovskite nanomaterials have shown photocatalytic and photovoltaic performance. This also extends the applications of solar energy conversion to utilizing multiferroic perovskite materials. Particularly, employing the spontaneous electric polarization of virus-templated BFO nanoparticles is a promising approach to solve the challenging problems of charge separation for photovoltaic devices.

Figures
Figure 6.10. Schematic of M13 virus-assisted synthesis of perovskite nanomaterials. Carboxylate ions on the surface of virus chelate with Ti\(^{4+}\) ions (shown in yellow) and electrostatically interact with Sr\(^{2+}\) ions (shown in blue). At 80°C, crystalline STO was formed.
Figure 6.11. Virus-templated STO nanowires. (a) TEM image of SrTi(EG) precursor-incubated viruses. (b, c) TEM images, (d) HRTEM image and (e) XRD pattern of virus-templated STO nanowires (JCPDS card no. 35-0734).
Figure 6.12. Virus-templated BFO nanowires. (a) TEM image of BiFe(EG)-incubated viruses before heat treatment at 600°C. (b,c) HRTEM images, and (d) XRD pattern of virus-templated BFO nanoparticles after heat treatment at 600°C.

Figure 6.13. Hydrogen evolution analysis of virus-templated STO nanowires. (a) Energy band diagram for hydrogen production of dye-sensitized STO under visible light irradiation. (b) Hydrogen gas production by water-splitting utilizing virus-templated STO
nanowires deposited with Pt nanoparticles under UV irradiation (red line) and visible light irradiation with dye-sensitization (blue line).

Figure 6.14. Photovoltaic measurement of virus-templated BFO nanowires. (a) Schematic diagram for a liquid junction solar cell made of BFO nanoparticles. (b) Photovoltaic properties of a solar cell using virus-templated BFO nanoparticles as photoanode.

Figure 6.15. Zeta potential of the AEEE virus at different pH.
Figure 6.16. XRD pattern of virus-templated STO nanowires synthesized at pH 5 without adding hydrogen peroxide, containing impurities of SrCO₃.

Figure 6.17. XRD pattern of virus-templated STO nanowires synthesized at pH 6 without adding hydrogen peroxide, containing impurities of SrCO₃.
Figure 6.18. Optical absorption of virus-templated BFO nanoparticles.

Figure 6.19. TEM image of wildtype M13 virus-templated STO nanoparticles.
Figure 6.20. XRD pattern of wildtype M13 virus-templated STO nanoparticles.

Figure 6.21. TEM image of free STO nanoparticles without M13 virus.
Figure 6.22. XRD pattern of STO nanoparticles without M13 virus.

Figure 6.23. Magnetic properties of virus-templated BFO nanoparticles at 5K and 300K.

Experimental

Strontium chloride (SrCl₂·6H₂O), titanium chloride (TiCl₄), bismuth nitrate (Bi(NO₃)₃·5H₂O), iron nitrate (Fe(NO₃)₃·9H₂O) and ethylene glycol (EG) were purchased from Sigma Aldrich. Deionized water (DI water) was used to prepare all solutions.
To prepare SrTi(EG) precursor, equal molar ratio of SrCl\textsubscript{2} and TiCl\textsubscript{4} were dissolved into ethylene glycol under continuous stirring. To prepare BiFe(EG) precursor, equal molar ratio of Bi(NO\textsubscript{3})\textsubscript{3} and Fe(NO\textsubscript{3})\textsubscript{3} were dissolved into ethylene glycol under continuous stirring. STO nanowires were synthesized by addition of SrTi(EG) precursor into virus solution. In a typical synthesis, 0.1 ml of the precursors were mixed with 10 ml of 10\textsuperscript{12} pfu (plaque forming units or number of virus particles) of virus solution at neutral pH, and then sodium hydroxide was further added to the solution and heated at 80°C for 4 hours. In a typical synthesis of BFO, 0.1 ml of the BiFe(EG) precursor was added to 10 ml of 10\textsuperscript{12} pfu of virus solution. The solution was incubated for at least one day. Then the reactant of BiFe(EG)-incubated virus was heated at 600°C for one hour.

**Preparation of STO nanoparticles with wildtype M13 virus templates and without templates**

The preparation of both wildtype M13 virus-templated STO nanoparticles and STO nanoparticles without virus were followed the same procedure for the synthesis of AEEE-M13 virus-templated STO nanowires. Briefly, the final concentration of SrTi(EG) precursor in the solution were adjusted in the range of 0.1 mM and 1 mM. The pfu of wildtype M13 virus in the solution was used in the range of 10\textsuperscript{10} and 10\textsuperscript{12}. The pH of the solution containing both precursor and wildtype virus was first adjusted to neutral, and then two fold amount of sodium hydroxide relative to titanium chloride was further added to the solution and heated at 80°C for 4 hours. In the synthesis of STO nanoparticles without virus, the above concentration of SrTi(EG) in the solution without viruses was used. The rest of the procedure was same.
Magnetic properties of bismuth ferrite (BFO) nanoparticles, was measured in the range of magnetic field from 30,000 Oe to -30,000 Oe at two different temperatures, 5K and 300K by superconducting quantum interference device (SQUID).

Zeta potential measurement: The concentration of virus solution was prepared in 0.01 M NaCl solution. The pH was adjusted to 10.5 using 0.1 M NaOH. Zeta potential measurements were then made at an accumulation time of 10 with 5 measurements per sample at 20 V using DelsaNano (Beckman Coulter). Electrophoretic mobility was calculated using the Smoluchowski approximation (used for particles larger than 0.2 µm in 1 mM or greater salt solution). pH was then adjusted with 0.1 M HCl.

Optical absorption measurement: Absorption spectra were obtained on a DU 800 spectrometer (Beckman Coulter) at ambient temperature with a 0.8-cm path-length quartz cuvette.

X-ray diffraction (XRD), was done using Cu Kα radiation and a Rigaku (50 kV, 200 mA) powder diffractometer.

Transmission electron microscopy (TEM): was done under accelerating voltage of 200 kV using JEOL 200CX TEM and JEOL 2010F TEM.

Hydrogen evolution test: Photodeposition method was applied to reduce platinum ions on the surface of STO nanowires using UV-lamp. 0.5 wt% of chloroplatinic acid was added to STO dispersed ethanol solution. Then the mixture was exposed to UV-lamp (100 watts) under stirring condition. 1) Under UV light: 0.05 g of STO nanowires co-deposited with platinum nanoparticles (0.5 wt%) was added to 60 ml of the mixture of methanol
and water (volume ratio 1:1.4). 2) Under visible light: 0.06 g of STO nanowires co-
deposited with platinum nanoparticles (0.5 wt%) was added to 30 ml of 15% diethanol
amine aqueous solution containing 0.5 mM Eosin Y. Then, the solution was purged with
argon for at least 30 minutes. Before irradiation, gas chromatography (Angilent, 7890A,
TCD, Ar carrier) was utilized to confirm the absence of oxygen and hydrogen gas in the
head space. At each injection, 250 µl of gas was tested after irradiation with varied time
using mercury lamp (100 watts). For visible light irradiation, a UV cut-off filter was used
to block wavelengths shorter than 400 nm.

**Photovoltaic performance:** thin film of BFO nanoparticles (10 µm thick) was
constructed by doctor-blading technique. The counter-electrode was 100-nm-thick
platinum, sputtered on an ITO substrate (Delta Technologies). The electrolyte was a
solution of 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich), 0.03 M I₂
(Sigma Aldrich), 0.10 M guanidinium thiocyanate (Sigma Aldrich) and 0.5 M 4-tert-butyl
pyridine (Sigma Aldrich) in a mixture of acetonitrile and valeronitrile (volume ratio,
85:15). I-V curves of the films were measured under dark and light illumination with an
AM1.5 light source (100 mW cm⁻²).
References

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