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Constructing Multifunctional Virus-Templated Nanoporous Composites for Thin Film Solar Cells: Contributions of Morphology and Optics to Photocurrent Generation

Noémie-Manuelle Dorval Courchesne,^{1,2†} Matthew T. Klug,^{2,3†} Kevin J. Huang,⁴ Mark C. Weidman,¹ Victor J. Cantu,¹ Po-Yen Chen,^{1,2} Steven E. Kooi,⁵ Dong Soo Yun,² William A. Tisdale,¹ Nicholas X. Fang,³ Angela M. Belcher,^{2,4,6} and Paula T. Hammond^{1,2*}*

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ²The David Koch Institute for Integrated Cancer Research, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ³Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁴Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁵The Institute for Soldiers Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁶Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States.

† These authors contributed equally to this work.

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ABSTRACT

Biotemplates, such as the high aspect ratio M13 bacteriophage, can be used to nucleate noble metal nanoparticles and photoactive materials such as metal oxides, as well as organize them into continuous structures. Such attributes make them attractive scaffolds for solar applications requiring precise organization at the nanoscale. For instance, thin film solar cells benefit from nanostructured morphologies that aid light absorption and carrier transport. Here, we present a biotemplating strategy for assembling nanostructured thin film solar cells that enhance the generated photocurrent through two features: (1) a nanoporous and continuous M13 bacteriophage-templated titania network that improves charge collection, and (2) the incorporation of metal nanoparticles within the active layer of the device to improve light harvesting. We demonstrate our ability to construct virus-templated solar cells by applying this strategy to depleted titania–lead sulfide quantum dot (PbS QD) bulk heterojunctions. The titania morphology produced by our biotemplate allows charges to be efficiently collected from the bulk of the active material and light that is otherwise poorly absorbed by the QDs to be harvested using metal nanoparticles that exhibit plasmon resonances in the visible range. We show that high aspect-ratio bacteriophages provide a structural template for synthesizing titania networks with tunable porosity, into which PbS QDs are infiltrated to create photoactive nanocomposites suitable for photovoltaics. Upon optimization, the generated photocurrent and power conversion efficiency of the bacteriophage-templated devices demonstrate a 2-fold improvement over control devices made with randomly organized titania nanoparticles. When the virus is complexed with gold nanospheres (Au NPs), silver nanospheres (Ag NPs), or silver nanoplates (Ag NPLs) during assembly, device performance is further improved with Ag NPLs enhancing the short-circuit

current density and power conversion efficiency by 16% and 36.5%, respectively, over virus-based devices without NPs. The observed trends in photocurrent enhancement match well with numerical predictions and the role of the nanostructured morphology on the device optics was computationally explored. The challenges overcome in this work could be extended to other heterojunction devices, such as hybrid systems involving conducting polymers, as well as other biologically-templated electronics.

INTRODUCTION

Strategies for improving solar cells generally fall into one of two categories; the first focuses on synthesizing better materials, while the other focuses on generating architectures that optimize performance. New materials with improved photovoltaic properties are constantly emerging; however, device architectures that can capitalize on a material's strengths, while compensating for its weaknesses are necessary for maximizing the performance of any given solar cell. For instance, the careful selection of materials in heterojunction solar cells can maximize photovoltage and reduce recombination, whereas nanostructured architectures can enhance photocurrent by improving light absorption and carrier collection efficiencies. Such nanostructured morphologies have been shown to improve the performance of several heterojunction types, including organic,^{1 2} inorganic,³ hybrid,^{4 5} and colloidal quantum dot devices.^{6 7 8 9 10} Likewise, optical structures such as gratings,^{11 12} plasmonic nanoparticles,^{13 14 15} and photonic crystals¹⁶ have been used to improve the ability of photovoltaics to harvest light, and thus offer a second pathway for increasing photocurrent. Therefore, a well-designed architecture that complements excellent active materials is required to achieve champion photovoltaic performance.

Biotemplating is a bottom-up approach to constructing nanostructures that uses biological material as a scaffold to nucleate inorganic material. By programming the biotemplate at the genetic level to express proteins with specific functionality, multifunctional composites can be assembled and further mineralized for use in non-biological applications. One of the most well-characterized and versatile biotemplates is the filamentous M13 bacteriophage, which has been used previously to (1) bind a variety of inorganic nanomaterials including carbon nanotubes,¹⁸ graphene,¹⁹ and metal nanoparticles,^{20 21 22} (2) assist in the nucleation and templating of inorganic materials such as metals, semiconductors,^{22 23} polymers,²⁴ and complex metal-oxides,²⁵ and (3) act as building blocks for the assembly of hierarchical structures.^{22 23 24} All of these virus-templated materials exhibit nanowire-like morphologies consistent with the filamentous structure of the individual virions. The availability of surface functional groups allows M13 bacteriophages to be easily cross-linked to generate porous scaffolds, films, and gels suitable for energy applications. As previously demonstrated in dye-sensitized solar cells (DSSCs), virus hydrogels and virus-polymer composites are able to create percolation pathways that improve electron diffusion lengths by acting as a scaffold for the nucleation of titania.^{23 26} Furthermore, genetically encoding the virus to bind with either carbon nanotubes¹⁸ or gold nanoparticles²³ has enhanced device performance by respectively improving either the charge collection efficiency or light harvesting ability of the photoanode.

The aim of this work is to use the M13 bacteriophage to construct solution-processable thin film solar cells that are light weight, solid-state alternatives to the thicker, liquid-based dye-sensitized counterparts. This class of devices uses heterojunctions comprised of either organic or inorganic materials to generate photovoltage and extract charges to the proper electrodes. However, these photoactive materials generally exhibit shorter carrier extraction and absorption

lengths than dye-sensitized solar cells, and thus require thinner films with feature sizes that match these length scales. Therefore, building a virus-templated morphology suitable for use in solution-processed solar devices that are only a few hundred nanometers thick requires synthesis techniques that offer more precise control over device thickness and porosity than the methods previously employed for building DSSC photoanodes. The procedures used to synthesize the tens of microns thick photoanodes necessary for DSSCs resulted in rough films with macroscopic pores that varied in size throughout the film thickness, which are unsuitable for thin film devices. In contrast, we have previously reported a method to assemble nanoporous bacteriophage-based anatase titania films of controllable thickness and uniform porosity by combining a covalent cross-linking process with layer-by-layer (LbL) assembly.²² It was also shown that by binding metal nanoparticles to the virus prior to film assembly, the particles could be evenly distributed throughout the final nanoporous anatase titania film without aggregation. Using this framework, we aim to construct a multifunctional device architecture that is capable of enhancing photocurrent generation in a variety of solution-processed thin film solar devices. As illustrated by Scheme 1, our two-fold approach consists of (1) controllably constructing a M13 bacteriophage-based nanoporous titania nanowire network with nanoscale features to efficiently collect and transport charges from the bulk material, and (2) loading it with plasmonic metal nanoparticles capable of increasing light harvesting via localized surface plasmon resonance (LSPR).

Scheme 1. Illustration of two fold-strategy employed in building a virus-based nanoscale device architecture, as applied to PbS QD solar cells, to enhance the photocurrent generation over a randomly-organized geometry. A. The control device has a disorganized geometry that consists of a layer of PbS QDs infiltrated into a porous layer of titania nanoparticles. The percolation pathways for electrons can be circuitous depending on how the TiO_2 NPs sinter together. B. Virus-templated titania network provides a blended heterojunction morphology that allows photogenerated charges to be collected from QDs that have infiltrated into the network and provides more direct pathways to conduct electrons. C. Metal nanoparticles act as nano-antennas to concentrate light in their near-field region, thereby producing a higher photon flux on nearby QDs and an increased rate of carrier generation.

This strategy is applicable to many different solution-processed solar cell types because (1) anatase titania is popularly employed as the n-type component in hybrid organic-inorganic, colloidal quantum dot, and perovskite systems, (2) nanostructured titania is commonly used to assist in charge extraction in bulk-heterojunction devices and in perovskite solar cells,²⁷ and (3) the resonance position of the plasmonic nanoparticles can be tuned by geometry and material

choice to capture light that is poorly absorbed for any given active material. To evaluate the feasibility of our approach and the suitability of the multifunctional virus-based films for solid-state thin film solar cells, we have chosen to assemble colloidal quantum dot bulk heterojunction solar cells. This is a class of solid-state photovoltaic devices that are low-cost, compatible with solution-processing methods, and have recently demonstrated efficiencies as high as 9.2%.^{6, 28 29}
³⁰ Specifically, lead sulfide quantum dots (PbS QDs) are excellent active materials for solar cells because they are efficient charge transporters, their band gaps can be tuned throughout the infrared spectrum, their band edges can be modified with various ligand molecules,³¹ and they are often paired with anatase titania to form a heterojunction.

Traditionally, PbS QDs are stacked on top of a nonporous titania film to form a depleted heterojunction. In order to extract carriers efficiently in this planar device, the QD film thickness must be thinner than the carrier collection length (~200 to 250 nm), which is the sum of the depletion width and the minority carrier diffusion length.³² On the other hand, complete light absorption requires that the QD film thickness be greater than the absorption length (>1 μm). Instead, a bulk heterojunction structure can be constructed by infiltrating QDs into nanostructured titania, which can extend the width of the depletion region and allow for more light to be absorbed with thicker QD films. However, these structures are more prone to trap-assisted recombination at defects if the conduction pathways are tortuous and if the interfacial surface area is high. For this reason, nanowire-based titania morphologies that provide continuous and direct pathways for charge transport are advantageous over disorganized mesoporous nanoparticle films commonly used in solution-processed solar cells.^{9 29} It has been shown that using an array of titania^{7 8 33} or zinc oxide⁶ nanopillars or nanowires infiltrated with PbS quantum dots enhances the device performance compared to planar oxide layers because the photocurrent increases enabled by

extended depletion zones overcome any undesirable increases in non-radiative recombination that result from a larger interfacial area between the active material and the titania nanostructures.

Our plasmonic virus-templated porous composite is rationally designed to generally compensate for the weaknesses of photoactive materials with relatively short lifetimes. Specifically for titania-PbS QD depleted bulk heterojunctions, our system offers the following advantages: first, the highly porous film allows for substantial infiltration of QDs into the titania networks, thereby extending the depletion region of the device.⁷ Second, compared to a porous film made using a titania nanoparticle paste, the interconnected network of titania nanowires formed by the high aspect ratio viruses provides direct pathways for transporting charges from the bulk of the device to the electrodes. Likewise, forming titania along a high aspect ratio template like the M13 bacteriophage produces a smaller overall surface area compared to a porous film comprised of spherical particles, and is therefore expected to have less surface defects to promote non-radiative recombination. Third, PbS QDs suffer from an absorption spectrum that preferentially absorbs high energy photons. Therefore, it is susceptible to the classic tradeoff in solar cells between light harvesting and carrier collection, where thick active layers are required to absorb light throughout the visible and infrared ranges, but carrier generated in the quasi-neutral region are less likely to diffuse to the depletion region before recombining. By using the M13 bacteriophage to carry and assemble metal nanoparticles with plasmon resonances in the visible range within nanoporous films, photons at poorly absorbed wavelengths can be concentrated in the near-field surrounding the NPs and light harvesting is improved without further increasing the QD film thickness. Lastly, the uniformity and sub-wavelength pore size combined with the ability of the virus to evenly disperse metal nanoparticles throughout the film offers an ideal environment where effective medium theory can be paired with finite-difference time-domain (FDTD)

simulations to theoretically evaluate how several metal nanoparticle types can enhance light absorption in the devices.

This work presents the overall process for constructing virus-based depleted bulk heterojunction PbS QD solar cells, with a focusing on the optimization of various critical steps to maximize device performance, such as (1) PbS QD infiltration into the titania pore network (2) surface preparation prior to assembly, (3) biomineralization time and control of the morphology, and (4) nanoparticle-virus complexation procedures with different nanoparticles including gold nanoparticles (Au NPs), silver nanoparticles (Ag NPs) or silver nanoplates (Ag NPLs). Through this optimization, we were able to diminish parasitic resistances and improve light harvesting in the devices, yielding enhanced photocurrents and power conversion efficiencies. By comparing a nanoparticle paste control device against our virus-based system, we demonstrate significant photocurrent enhancement and separate the contributions due to morphology and plasmon enhancement.

RESULTS AND DISCUSSION

The device assembly process is schematized in Figure 1A. On a patterned fluorine-doped tin oxide (FTO) substrate, a dense and compact layer of titania paste is first spin-coated, and acts as a hole blocking layer to prevent shorting of the device. After annealing this base layer at 500 °C, the viruses or virus-metal nanoparticle complexes are assembled via LbL, as previously described.²² Various methods to functionalize the titania surface and prepare it for virus attachment can be employed, and will be discussed later. Once the virus film is constructed, it is coated with titania using titanium tetrachloride as the precursor, and annealed again to burn off the viruses and generate an anatase crystalline titania nanoporous film. PbS QDs with an average

diameter of 2.9 nm and a first excitonic absorption peak at 905 nm ($E_g = 1.37$ eV) are then infiltrated into the pores of the film via dropcasting or spin-coating to create the titania-lead sulfide composite. Finally, a 25 nm thick hole transporting layer of MoO₃ is thermally evaporated, followed by a 100 nm thick gold electrode. The device area of the resulting solar cells is 0.0547 cm².

A cross-section of the final titania film shows the difference in morphology between the compact titania nanoparticle base layer and the porous virus-templated titania film (Figure 1B). The porous virus-templated titania film exhibits interconnected mesh-like titania structures (See Figure S1 in Supporting Information for additional images), and was designed to be easily infiltrated with quantum dots. In addition, nanowire-like features can be observed in the top virus-based portion of the film, creating direct pathways for electrons to travel in the titania phase. The TEM film cross-section shown in Figure 1C demonstrates that a titania-lead sulfide composite is achieved after QD infiltration. The QDs not only infiltrate completely through the nanoporous virus-template titania network but also form a packed layer above it. Others have previously infiltrated PbS quantum dots into nanowire arrays,^{6, 34, 8} but the inter-spacing of the nanowires (on the order of 50 to 100 nm) was considerably larger than the pores of the virus-templated titania film presented here, which average 8.1 nm in diameter. Elemental mapping shows that a concentration gradient occurs within the infiltrated virus-templated film, and that the fraction of QDs gradually decreases with the film depth. This gradient was quantitatively measured for two successful infiltration methods, spin-coating and dropcasting. X-ray photoelectron spectroscopy (XPS) with depth profiling was used to monitor the atomic concentration of lead and titanium as a function of film depth and these atomic concentrations were converted to volume fraction of PbS using the molecular weight and crystalline densities of titania and lead sulfide. From this data, the

efficiency of pore filling with PbS QDs was calculated as a function of depth in the titania film, using a measured porosity of 42% for the titania film (see Figure 2B), and assuming the maximum possible QD packing density inside the pores is a loose random-packing configuration³⁵ (see supporting information for details). The results are shown in Figure 1D. Dropcasting a dilute PbS solution at 50 mg/mL, followed by slowly drying at room temperature allows for more PbS QDs to infiltrate the film via capillary action, and maintains a high pore filling efficiency that is above 40% throughout the 100 nm thick virus-templated titania film (as opposed to using more dilute solutions or dip-coating methods, which result in a low PbS content within the pores, as shown in Figure S2 of supporting information). However, drying rings are observed on the surface of the film and poor film quality is produced when the dropcasting method is employed. In contrast, spin-coating produces a very smooth and uniform film. The concentration profile of PbS decreases more sharply with film depth, but the QDs still penetrate deeper than 80 nm into the virus-templated titania film. Therefore, a combination of these two methods is used to prepare the photovoltaic devices: PbS QDs are first dropcast onto the surface of the titania film, and then allowed to penetrate the film for 1 min; the solution is then spun off of the substrate at 2500 rpm in order to produce a smooth film, followed by a mercaptopropionic acid (MPA) ligand exchange and rinse. Subsequent layer of PbS quantum dot are then spin-coated and ligand exchanged in a layer-by-layer fashion.

To assess the impact of the virus nanocomposite system on device performance, we fixed the thickness of the titania layers and kept the PbS deposition procedure (concentration, ligand, number of deposited layers) consistent between devices. To determine these parameters, simple planar devices were fabricated using conventional procedures and a commercially available titania paste (Solaronix Ti-Nanoxide HT/SC) to create a compact titania layer. By varying the thicknesses

of both layers, it was established that a total titania thickness of approximately 200 nm is optimal, and that beyond five layers of spin-coated PbS QDs, no improvement is observed (See Figure S3 for details). In order to ensure full infiltration of PbS QDs within the virus-templated titania layer, we fixed the electron transporting compact titania base layer to 100 nm and the virus-templated titania layer to 100 nm, for a total of 200 nm of titania.

A.

B.

C.

D.

Figure 1. Virus-based titania-PbS QD composites are assembled via sequential solution-processing to result in the final solar cells. A. Assembly process for virus-based solar cells via layer-by-layer assembly of viruses, titania nucleation of the virus template using a TiCl_4 precursor, PbS QD infiltration and film deposition, followed by thermal evaporation of MoO_3 and gold top electrodes. B. SEM image of the cross-section of a titania-coated virus film on a compact titania paste base layer. The dash line indicates the interface between the base layer and the virus-templated titania film. C. TEM image with elemental mapping (EDX) of lead sulfide quantum dots infiltrated into a porous virus-templated titania film constructed in a silicon substrate. D. Pore filling efficiency of loose-packed lead sulfide quantum dots as a function of depth in a virus-templated titania film, when the PbS QDs are either spin-coated or dropcast. A depth of 0 nm corresponds to the interface between the top PbS QD layer and the TiO_2 -PbS blend layer.

A critical design step in assembling photoactive materials using biomolecules is controlling the surface chemistry of inorganic components. The chosen surface functionalization method must provide uniform surface coverage with a high loading density of the biotemplate, but it must also involve reagents that can be completely degraded and removed from the device afterwards to avoid interfering with charge transport. In this work, M13 bacteriophages must be adsorbed or covalently attached to the titania base layer as a first step in the virus film assembly. After the film assembly and biomineralization with titania, the bacteriophages are burnt off at a temperature of 500 °C. Therefore, the reagents used for surface functionalization must also burn off at this temperature.

Three surface modifications were considered for functionalizing the titania base layer with a monolayer of viruses: silanization with (3-aminopropyl)trimethoxysilane (APTMS), construction of polymer base layers via electrostatic LbL assembly, and spin-coating a thin layer of a charged short chain polymer. These modifications are illustrated in Figure 2A, and the corresponding performance of each virus-based titania-PbS solar cell is shown in Figure 2B. The silanization method has the advantage of forming covalent amide bonds between the amine groups of the silane molecules and the carboxylic acid groups of the virus through a reaction catalyzed by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). However, APTMS can leave silica, silicon, polysiloxane and other silicon derivative residues after combustion at 500°C. In consequence, high series and low shunt resistances are observed for devices made using silanization, producing low fill factors. The high series resistance is likely due to the presence of insulating residues, such as silica, at the titania-substrate interface while the shunt resistance could be created by the presence of conducting residue, such as silicon, providing alternate pathways for electrons to travel to the compact titania layer.

In contrast, polymers such as poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA), and polyethyleneimine (PEI) are excellent candidates to replace silanes because they burn off at temperatures below 500 °C, with the major combustion product being carbon dioxide in the gas phase.³⁶ Using LbL assembly, cationic PAH and anionic PAA can be layered electrostatically on an oxygen plasma-treated titania surface. We thus assembled 4.5 bilayers of PAH and PAA, ending with a top positively charged PAH layered onto which negatively charged M13 bacteriophages can be electrostatically adsorbed. The virus adsorption was carried out, as described previously, in sodium acetate buffer at pH 4.9 to obtain a dense assembly of viruses.³⁷ This thin polymer base layer film is expected to have a thickness of approximately 10 nm according to literature for a comparable system.³⁷ To further decrease the thickness of the polymer base layer formed, a short branched PEI polymer (1.3kDa) was spin-coated onto a plasma-treated titania base layer surface. The resulting thickness of this positively charged layer is only ~2 nm,³⁸ and similarly, M13 bacteriophage can be electrostatically adsorbed to this surface. Figure 2B shows the improvement in device performance, as (1) the amount of inorganic residues decreases, and (2) the thickness of the base layer decreases. In fact, the short-circuit current is significantly larger for the devices constructed with polymers compared to silanes, and is higher when the 2 nm thin PEI layer is used as opposed to a thicker PAH/PAA film. These results are also consistent with XPS measurements confirming the presence of the polymer layers after deposition, and their subsequent disappearance after annealing at 500 °C (See Supporting Information for details, Figure S4 and Table S2). Although all polymers burn off at high temperatures, the thicker PAH/PAA layer may lead to higher series resistance because it could create a gap in between the compact titania base layer and the bacteriophage-templated titania film, preventing a good contact between the titania layers and potentially promoting film delamination.

Accordingly, the calculated series and shunt resistances are improved when thin polymer films are used (see Figure 2C, and supporting information for calculation details). The series resistance decreases when the silane residues disappear, and the shunt resistance increases, indicating that charges are travelling more efficiently through the titania pathways. All device results presented hereafter employ the optimal PEI spin-coating surface functionalization method.

Figure 2. Series and shunt resistances can be improved by changing the surface functionalization method prior to LbL assembly. A. Three methods for functionalization the surface and allow for bacteriophage attachment, either via covalent bonding or electrostatic adsorption. From left to right, silanization using APTMES, LbL-assembled PAH/PAA base layers, and thin PEI layer. B. Comparison of the device JV curves with the three different surface preparations. C. Normalized series and shunt resistance calculated from the JV curves. The series and shunt resistances are calculated from the slope at zero current and zero voltage respectively, and are normalized by the characteristic resistance of the device.

Biom mineralization time strongly affects the morphology of the virus-templated titania film, and consequently the device performance. M13 bacteriophages are 6 nm in diameter by 880 nm in length, and can therefore create very fine titania nanostructures, as thin as 6 to 7 nm in diameter, after burning them off and sintering the crystallites. The reaction time in a 0.2 M TiCl_4 solution was varied between 1.5 and 2.5 hours, and the morphology, porosity and pore size distribution of the resulting titania network were compared. Figure 3A shows the surface morphology of the virus-templated titania films after 1.5, 2 and 2.5 hours of titania nucleation and subsequent annealing at 500 °C. It is readily observed that the porosity tends to decrease with increasing reaction time and that the diameter of nanowire-like features increase. The structure is highly porous after 1.5 h, and the pores begin to occlude after 2.5h in the reaction mixture. Therefore over time, the nanostructured and porous titania film become less porous and more planar. Image analysis revealed that the porosity decreased from 44.3% to 41.9% and 36.1% after 1.5, 2 and 2.5 hour reactions respectively (see Figure S5 for details). However, the pore size distribution is only slightly affected, with somewhat smaller pores being formed on average for shorter reaction times. A striking change in morphology between 1.5 and 2 hour reaction time is the diameter of nanowire-like features, which increase from an average of 6.2 nm to 11.8 nm.

The highest performing virus-templated device was obtained with a reaction time of 2 h (JV curve shown in Figure 3C). Therefore, the increase in nanowire diameter appears to have strongly affected the efficiency of the device and significantly increased the short-circuit current density, as observed in Figure 3D (see also Table 1). The average short-circuit current density and power conversion efficiency increased by about 2-fold in the devices biom mineralized for 2 h compared to those biom mineralized for only 1.5 h. The fill factor also increased from 1.5 to 2 h,

indicating that thicker nanowires decrease the series resistances by improving the electron conductivity through the titania mesh. The thicker nanowires could improve performance for two reasons: 1) it is less likely that there would be disconnects between neighboring titania crystallites, which would provide more direct pathways for electron collection, and 2) the larger titania crystallites comprising thicker nanowires would reduce the number of grain boundaries photogenerated electrons must travel through before collection at the electrode. Both reasons would minimize the interaction of electrons with grain boundaries, which would reduce the likelihood of non-radiative recombination occurring at defects at the titania surface and result in higher current generation and lower series resistances during operation. It is also expected that the samples mineralized for 1.5 h would have an increased variability between devices as the probability of electrical disconnects occurring along the mesh increases when less titania is allowed to nucleate along the biotemplate. The virus films biomineralized for 2.5 h hours also perform better than the ones reacted for 1.5 h, but the short-circuit current decreases compared to the 2 h biomineralization, likely due to the decrease in titania film porosity, which not only provides less pore volume for QDs to fill but also diminishes their ability to infiltrate into them. In summary, we found that the biomineralization time has a strong effect on device performance and that increasing time to an optimum of 2 h increases both the short-circuit current and the fill factor. For longer times, the efficiency might continue to plateau or decrease due to pore occlusion and flattening of the titania surface. These findings demonstrate that fine tuning the morphology of the titania-PbS layer is critical.

Figure 3. The biomineralization reaction time allows for tuning the feature size and porosity in virus-based devices, which affect device performance. A. Surface morphology of the virus-templated titania film captured by SEM, as a function of reaction time in $TiCl_4$ (1.5, 2 and 2.5 h). B. Pore size distribution, porosity and average nanowire (nw) size for the different reaction times. Values were determined using image analysis. C. JV curve for device with best performance with a 2 h reaction time. D. Average and maximum device performance parameters as a function of the reaction time. Error bars represent standard deviation. Paired t-tests were performed and the statistically significant differences between pairs of results are shown by * for a p-value < 0.05 and ** for a p-value < 0.005. Exact values are reported in Table 1.

In order to demonstrate the advantages of using M13 bacteriophages as a scaffold to construct a continuous and porous titania matrix, our optimized virus-templated device was compared to an analogous device built using a titania nanoparticle paste. A titania paste was prepared using the same $TiCl_4$ precursor at 0.2 M in water and collecting the particles formed after a 2 h hydrolysis reaction (as opposed to using commercially available titania paste that may differ in surface chemistry, solvent and particle size from the titania nucleated on virus-templated films).

The particles were resuspended in a mixture of terpineol containing ethyl cellulose, which acts as a sacrificial polymer to introduce porosity within the film, and the final titania paste was spin-coated onto a silicon substrate to observe its morphology (Figure 4A). The resulting film has a porosity of 40%, which is comparable to that of the phage film biomineralized for 2 h (see Figure S6 for porosity estimation). However, as seen in Figure 4A, the nanoparticles are randomly oriented and particle size is polydisperse. When the phage film is immersed into a TiCl_4 solution, only the crystallites nucleated on the surface of the viruses remain in the film and create the uniform and organized networks of nanowires observed in Figures 1 and 3. In contrast, the paste is formed with all nanoparticles synthesized in solution during TiCl_4 hydrolysis, and cannot be easily purified to exclude larger aggregates that would roughen the final film or disorganize in an organized manner. Although the PbS infiltration profiles measured by XPS depth profiling follow a trend similar to the one observed for the virus films (Figure 4B), the short-circuit current density in the paste device was found to be almost 1.5 times lower than the virus-templated device, as shown in Figure 4C, and on average the performance of the optimized virus-template was two times higher than the paste control (see Table 1). This suggests that organizing titania nanoparticles into an interconnected network of nanowires allows for charges to be transported more efficiently than in a randomly distributed nanoparticle paste film. A nanoporous film composed of sintered nanoparticles likely provides a more circuitous route to electron collection, as is illustrated in Scheme 1, than the nanowire network, which would increase the likelihood of non-radiative recombination, reduce the collected photocurrent, and increase the device's series resistance. Furthermore, the polydispersity of titania nanoparticles in the paste leads to rougher films, which likely contributes to the greater variability in performance observed for this device type.

Figure 4. Randomly organized TiO_2 nanoparticles prepared from the same TiCl_4 precursor result in devices with a lower efficiency. A. Cross-sectional morphology of a TiCl_4 -based TiO_2 paste after annealing. The paste was spun at 2000 rpm onto a silicon substrate. B. PbS QD infiltration profile by dropcasting or spin-coating into the TiO_2 paste film, resembling the infiltration profile in a virus-templated TiO_2 film. A depth of 0 nm corresponds to the interface between the top PbS layer and the TiO_2 -PbS composite film. C. Comparison between the JV curve of a virus-templated TiO_2 film and a randomly organized nanoparticle film.

In addition to improving charge collection via the morphology of the nanoporous titania film, the performance of the solar cells was further improved by enhancing their ability to harvest light with metal nanoparticles (NPs), which concentrate light in the near-field via localized surface plasmon resonance (LSPR). This second approach to device improvement leverages the ability of the M13 bacteriophage to be genetically programmed to exhibit affinity for noble metals, which allows silver and gold nanoparticles to be complexed onto the viruses while in aqueous solution. The complexation process spaces the nanoparticles fairly evenly along the bacteriophages, which avoids aggregation and allows the characteristic absorption peaks of plasmonic particles to be preserved. TEM images of viruses complexed with spherical gold nanoparticles (Au NPs), spherical silver nanoparticles (Ag NPs), and silver triangular nanoplates (Ag NPLs) are shown in Figure 5A. As discussed in our previous report²², the act of binding to the virus causes the characteristic plasmon peak positions of noble metal NPs to be slightly red-shifted compared to

aqueous colloids due to the presence of the virus proteins in the medium directly surrounding the NPs. Figure 5B presents the absorption spectra of all three NP-virus complexes in solution and clearly shows the characteristic dipole peak positions of Au NP at 520 nm, Ag NP at 400 nm, and both the dipole and quadrupole peaks of Ag NPLs at 620 and 400 nm, respectively.

Using our previously reported LbL-assembly process²², Au NPs, Ag NPs, and Ag NPLs were evenly distributed throughout the nanoporous virus films without aggregation with a loading of approximately 0.1 NPs per virus (see Figure S7 for effect of NP concentration on device performance) and subsequently coated with a thin film of titania during the biomineralization process. These plasmonic nanoporous titania films were then used as the n-type component of the heterojunction QD solar cells. All types of nanoparticles improved the overall power conversion efficiency of the titania-PbS devices with the Ag NPLs producing the largest photocurrent enhancement (Figure 5C). The short-circuit current was enhanced in the presence of each nanoparticle type, with statistically significant improvement occurring with Ag NPs and Ag NPLs. In addition, the open circuit voltage (V_{OC}) increased by approximately 50 mV (See Supporting Information, and Figures S18 and S19) and the parasitic resistances improved (See Table S4) when adding any type of metal nanoparticle to the devices. As discussed further in the supporting information, the improvement in V_{OC} is attributed to a natural increase that results from the plasmonic NPs generating a higher photocurrent through LSPR. Likewise, the slight improvement in resistances could be attributed to either local changes in morphology or titania crystallite quality around the nanoparticles that improve charge transport. The improvement in power conversion efficiency (PCE) caused by the metal nanoparticles in the virus-templated devices was calculated to be 22.2% for Au NPs, 25.1% for Ag NPs, and 36.5% for Ag NPLs on average (Figure 5D and

Table 1). The top performing Ag NPL device reached a PCE close to 4%, and its JV curve is compared to a virus-templated device without plasmonic nanoparticles in Figure 5E.

Figure 5. The incorporation of noble metal nanoparticles improves the efficiency of the virus-templated titania-PbS QD depleted bulk heterojunction devices. TEM images (A) and corresponding absorption spectra (B) for virus-nanoparticle complexes that were incorporated into the films. C. Comparison of power conversion efficiency, short-circuit current density and open circuit voltage for devices with naked virus, or for viruses complexed with Au NPs, Ag NPs or Ag NPLs. Paired t-tests were performed and the statistically significant differences between pairs of results are shown by ** for a p-value < 0.005 and *** for a p-value < 0.0005. D. Average percentage improvement in efficiency with addition of metal nanoparticles. E. Comparison of the JV curves for the best device with and without metal nanoparticles. Overall, the nanoparticle device with the highest efficiency contained Ag NPLs. Exact values are reported in Table 1.

Table 1. Solar cell performance parameters for TiO₂ NP paste control device, virus-based device, and plasmonic virus-based devices. Average values and standard deviations are presented for each parameter, as well as the maximum power conversion efficiency (PCE) for each type of device. The averages presented are based on at least 10 to 20 devices of each type.

Device	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)	Max PCE (%)
Paste control	-7.3 ± 2.5	0.53 ± 0.03	0.24 ± 0.03	0.99 ± 0.47	1.99
1.5 h, virus only	-7.4 ± 4.5	0.50 ± 0.04	0.27 ± 0.05	1.06 ± 0.82	2.45
2 h, virus only	-13.2 ± 2.0	0.51 ± 0.04	0.32 ± 0.03	2.18 ± 0.40	2.93
2.5 h, virus only	-11.8 ± 2.2	0.54 ± 0.04	0.31 ± 0.03	1.94 ± 0.52	2.89
2 h, with Au NPs	-14.1 ± 1.6	0.55 ± 0.02	0.35 ± 0.03	2.67 ± 0.36	3.15
2 h, with Ag NPs	-15.5 ± 1.0	0.56 ± 0.01	0.32 ± 0.02	2.73 ± 0.16	3.04
2 h, with Ag NPLs	-15.5 ± 1.2	0.55 ± 0.04	0.35 ± 0.04	2.98 ± 0.58	3.96

It must be noted that significantly higher device performances can be obtained for devices with areas five times smaller (See Figure S10 for details). The higher average performance observed for smaller area devices is likely due to the reduced probability of defects in the film, which significantly increases the short-circuit current and the fill factor for a constant open circuit voltage. We believe, however, that reporting values for larger areas are more valuable since the ultimate goal is to produce large area photovoltaic devices and panels.

The effect of each nanoparticle type on the ability of the devices to harvest light was computationally predicted prior to device fabrication by combining effective medium theory with finite-difference time-domain (FDTD) calculations. As illustrated in Figure 6A, the simulation geometry follows the approximate dimensions of an actual device cross-section, which consists of stacked slabs of homogeneous materials starting with an FTO base layer, a 100 nm thick compact anatase titania layer, a 100 nm thick blended titania-PbS QD layer that contains a single plasmonic

NP, a 100 nm thick layer of random-packed PbS QDs, and a 25 nm thick MoO₃ layer on top. Periodic boundary conditions were placed on both the x and y lateral directions in order to simulate a unit cell of the solar cell slab, which allowed any light scattered out of the sides of the simulated domain to be reabsorbed elsewhere in the unit cell. The extent of the unit cell in the x and y lateral directions was set to 60 nm, which is the estimated approximate distance between nanoparticles in the virus-templated titania film. Finally, the unit cell was illuminated through the FTO layer by a plane wave with wavelengths ranging from 200 to 1200 nm and a three-dimensional power monitor was placed throughout the unit cell to sample the power density of light absorbed at each node in the mesh for each simulated wavelength. Because a nanoparticle can be located at any vertical position within the blend layer, five separate FDTD simulations were performed for each nanoparticle type, each with the nanoparticle center positioned at a different elevation (10, 30, 50, 70, and 90 nm into the blend layer). A sixth simulation was performed with the nanoparticle positioned 10 nm into the QD film layer to account for roughness of the virus film, which would cause a NP located near the top of the blend layer to be surrounded by a higher fraction of QDs. The ensemble average over all six configurations was taken during the analysis to approximate the effect of inherent randomness of homogeneously distributed NPs throughout the thickness of the virus-templated film has upon light absorption.

Aside from the geometry of the model, developing a realistic description of the complex dielectric function of the photoactive materials in the optical model is critical to capturing how light is absorbed as it propagates through the device architecture and how far the near-field generated by the plasmonic NP extends into the active regions. The complex dielectric function of the compact titania, titania-PbS blend layer, and packed PbS QD layers were calculated using effective medium theory in conjunction with values adjusted from previous reports for anatase thin

films³⁹ and PbS quantum dots⁴⁰ (see supporting information for details). When a monodisperse solution of PbS QDs is deposited onto a planar film, the nanospheres will pack into a porous layer with voids existing between them. Because the size of a quantum dot is substantially smaller than the wavelength of light, light cannot distinguish between an individual particle and the air in the voids, rather it perceives an effective dielectric medium that is a blending of the material properties of the two components. Therefore, the dielectric function of a randomly-packed PbS QD layer deposited on top of the nanoporous titania film was calculated using the Maxwell-Garnett effective medium model. Similarly, when the pores of the virus-templated titania film are infiltrated with the PbS QDs, the resulting film is a blend of anatase titania, PbS, and air void-space, which was modelled using the Bruggemann model as an effective homogeneous medium with a dielectric function that depends on the porosity of the virus-templated film (see supporting information for details). For simplicity, it was assumed that the PbS QDs are homogeneously distributed throughout both the blend and QD film layers with a volume fraction of 56% in the spin-coated QD layer and 15% in the blend layer. A value of 56% in the QD film corresponds to a loose random-packing,³⁵ which is considered more appropriate than the 74% value associated with regular close-packed beds because spin-coated films of QDs have been shown to be less-regularly packed with packing densities around 50%.⁴¹ Likewise, a 15% PbS volume fraction in the blend layer was calculated by averaging the infiltration data of spin-coated PbS QDs into the virus film reported in Figure 1D over the film thickness.

By illuminating the simulated device with a flat irradiance across all wavelengths and integrating the absorbed power density over the spatial extent of the photoactive regions of the device, i.e. the titania-PbS QD blend layer and the random-packed QD layer, we predicted how introducing the plasmonic nanoparticles into the solar cell architecture would influence its overall

absorption efficiency, η_a . However, the performance of solar cells depends not only on its ability to absorb photons, but also on how well those photons can be converted into charges and how efficiently those charges can be collected at the electrodes. Therefore, some basic assumptions were applied to build a simple model for charge collection efficiency, η_c , mainly: (1) it is assumed that all of the absorbed power in the blend layer can be converted to charges and collected because it is within the depletion region. Secondly, (2) it is assumed that carriers generated deeper in the close-packed QD layer are less likely to migrate to the titania in the blend layer before recombination occurs than those generated closer to the blend layer interface. Therefore, an exponential decay envelop with a decay length of 30 nm⁴² was applied to the absorbed power density values in the quasi-neutral region in order to capture the fact that carriers generated closer to the blend layer are more likely to diffuse to the depletion region for collection and contribute to the device photocurrent:

$$\eta_c = \begin{cases} 1, & 0 \leq z \leq L_b \\ e^{-(z-L_b)/L_d}, & L_b < z \leq L_b + L_{QD} \end{cases}$$

where L_b is the thickness of the depletion region, L_{QD} is the thickness of the quasi-neutral region, and L_d is the electron decay length in PbS QD films.

The product of the absorption and collection efficiencies provides an estimate of the external quantum efficiency (EQE) spectra for each device, which quantifies how efficiently incident photons of a given wavelength are converted into collected charges. Figure 6B and C, respectively, show the computed and measured EQE spectra for devices loaded with each type of silver plasmonic particle. The overall shape of the simulated and measured EQE spectra for the devices without nanoparticles are remarkably similar, with a main peak arising around 375 nm followed by a slowly decaying profile at higher wavelengths. The simulations predict a clear

plasmon-induced performance enhancement starting around 400 nm for Ag NPs and 525 nm for Au NPs, which is in good agreement with the observed regions of power enhancement in the actual devices..

In contrast, the predictions for Ag NPLs dramatically underestimate the observed performance increase in devices. This is likely due to the Ag NPLs changing shape and size during the device fabrication process. First, monitoring their shape and absorption spectrum during LbL assembly indicated an evolution from triangular nanoplates to circular nanodiscs and nanoparticles (Figure S8). Second, it is expected that the nanoplates originally incorporated into the films transformed into a polydisperse population of nanospheres during the device annealing process performed to crystallize the titania network. It has been observed that colloidal nanoplate solutions tend to stack upon one another when dried on TEM grids (Figure S9). It is possible that during the LbL process used to build the virus films, free nanoplates could stack upon those that have been already bound to the virus, which later convert into various sizes of silver nanospheres during annealing. A polydisperse nanosphere population would result in a broader enhancement wavelength range consistent with the wide region of enhancement demonstrated by the EQE measurement shown in Figure 6C. This hypothesis was also investigated computationally by running simulations using Ag nanospheres whose volume is conserved from stacks of 1, 2, or 3 Ag NPLs. Averaging the results produces a corrected simulated EQE spectrum that is much closer to the measurements made for devices originally made using Ag NPLs.

Although a metal nanoparticle absorbs light, the power contained within its interior does not contribute to the photogeneration of carriers and is generally lost as heat. Only light concentrated in the NP's near-field that extends into the surrounding active layer will contribute to photocurrent enhancement. Placing a NP inside the blend layer occupies volume that would

have otherwise been filled with a blend of titania and QDs in its absence, therefore the near-field generated by the NP must overcome this loss. Thus, enhancement is only expected to occur at wavelengths where LSPR occurs and performance is expected to be slightly reduced at off-resonant wavelengths because less QDs are physically present in the model to absorb photons at these energies. This is the reason why the simulated EQE spectra of the plasmonic devices are slightly reduced from the devices without NPs at short wavelengths. Discrepancies between the predicted and measured EQE spectra are likely due to local spatial variations in the effective complex dielectric function of the media in the device arising from (1) PbS QDs not being homogeneously distributed throughout the actual blend layer thickness, and (2) roughness at the interfaces between layers. In actuality, a QD concentration gradient exists as is shown in Figure 1D, which is not explicitly considered by the model. Similarly, roughness at the interface between the blend layer and the random-packed QD layer would cause a nearby NP to sense an effective medium comprised of a higher fraction of PbS than a NP buried within the blend layer. The result of both cases is to broaden the wavelength range of plasmon enhancement as metal nanoparticles located at different positions in the actual active layers would experience different effective local dielectric functions of the surrounding medium, thereby producing LSPR peaks at different wavelength positions and broadening the spectra of the ensemble average. Since the idealized model presented herein is sufficient to capture the observed trends in the measurements, any further modeling of local variations in geometry and material properties is considered to be beyond the scope of this report.

The presented model clearly demonstrates for the Ag nanosphere case that the wavelengths between 400 and 600 nm where significant EQE enhancement occurs can be explained by LSPR acting to concentrate light in the near-field region surrounding the noble metal nanoparticles. This

increases the photon flux incident on QDs located within the near-field, thereby increasing their rates of charge carrier generation. The ability of a plasmonic NP to enhance photocurrent generation in a solar cell can be quantified by defining an enhancement factor, EF , which compares the predicted short circuit current density (J_{sc}) resulting in the unit cell geometry that contains a NP to the prediction of the J_{sc} in the same unit cell without the NP:

$$EF = \frac{J_{sc} \text{ from Unit Cell with a NP}}{J_{sc} \text{ from Unit Cell without a NP}} = \frac{\int \left(\int_{\text{volume in active region outside NP}} p_{abs}(\vec{x}, \lambda) \eta_c(z) d^3x \right) \frac{\lambda}{hc} M_{AM1.5}(\lambda) d\lambda}{\int \left(\int_{\text{volume in active region}} p_{abs}^o(\vec{x}, \lambda) \eta_c(z) d^3x \right) \frac{\lambda}{hc} M_{AM1.5}(\lambda) d\lambda}$$

where p_{abs} is the absorption efficiency density as a function of position and wavelength for a unit cell containing a plasmonic NP, p_{abs}^o is the absorption efficiency density as a function of position and wavelength for the same unit cell without a NP, $M_{AM1.5}$ is the solar irradiance for the AM1.5 global solar spectrum, h is Planck's constant, c is the speed of light, and η_c is the carrier collection probability. The enhancement factor can be directly compared to the ratio of the short circuit current density, J_{sc} , for a unit cell with NPs to that without, $J_{sc}^{NP} / J_{sc}^{noNP}$, which is presented in Figure 6D. The measured devices demonstrate higher photocurrent enhancement than the simulations predicted with the measured enhancement being 6.2%, 16.3%, and 16.5% for solar cells with Au NPs, Ag NPs, and Ag NPLs respectively, whereas simulations predicted 3.8, 10.9, and 4.2%. When the photocurrent is calculated for a polydisperse population of Ag NPs that have been transformed from Ag NPLs, the predicted enhancement rises to 11.3%. Although the predictions were lower than observed photocurrent enhancement, the trend is clearly captured. It is worth noting that devices with Ag NPs in both the simulated and measured devices produce a photocurrent enhancement roughly three times larger than devices with Au NPs.

The model presented can only explicitly account for enhancement of the device photocurrent and cannot account for any differences in parasitic resistances and the fill factor between devices, which fortunately do not change significantly between virus-based solar cells with and without plasmonics NPs. However, the increase in V_{oc} that is observed in plasmonic devices likely arises directly from their corresponding increase in photocurrent due to enhanced light harvesting. The standard diode equation model for solar cells couples the current and voltage together; therefore, the open circuit voltage of a device will change if it can output a higher photocurrent. By fitting each of the measured JV curves for virus-based devices with and without plasmonic NPs to the standard diode equation for solar cells, it was revealed that the V_{oc} increase observed for the device with Ag NPLs (Figure 5E) corresponds to the V_{oc} predicted by the standard solar cell model if the virus-based device without plasmonic NPs happened to experience an increase in photocurrent equal to that observed in the virus-based device with Ag NPLs (see supporting information for details). Therefore, the effect of LSPR conveniently causes both the J_{sc} and V_{oc} to rise in the plasmonic devices, causing the observed overall enhancement in PCE to be even higher.

Figure 6. FDTD simulations we used to rationally design and predict the plasmon enhancement in devices containing metal nanoparticles. **A.** Geometry of simulations. **B.** Predicted and **C.** Measured EQE spectra for devices containing Au NPs, Ag NPs or Ag NPLs, compared to virus-only devices. Experimental EQE curves with metal nanoparticles were adjusted based on measured average short-circuit current values for each type of device. **D.** Predicted and measured photocurrent enhancement compared to virus-templated devices without nanoparticles. **E.** Predicted plasmon decay length for different nanoparticles embedded in the blend and random-packed QD layers.

Lastly, as demonstrated in Figure 6E, blending the PbS QDs with the titania nanoporous network provides an effective medium that allows the near-field surrounding the metal NPs to propagate further into the blend layer than they would if incorporated into the random-packed QD layer. This is a direct result of the effective complex index of the blend layer being lower than the random-packed QD film by virtue of its lower volume fraction of PbS. This is useful from a practical standpoint because the larger the extent of the near-field, the greater the chance a PbS QD can experience a higher photon-flux and exist in a defect-free region that can efficiently generate and transport charge carriers.

CONCLUSIONS

In conclusion, we demonstrate that the high aspect ratio M13 bacteriophage can serve as a template to form nanocomposites that are suitable for thin film solar devices. However, in order to make an effective device, many processing parameters had to be optimized to maximize device efficiency. First, we found that a short chain PEI polymer was the optimal surface functionalization molecule to adsorb the bacteriophages to the titania base layer because it could form a very thin layer that was minimally insulating. Second, we showed that the biomineralization time could be optimized to allow for the thickening of the nanowire-features while maintaining the film porosity. Third, the best method for infiltrating PbS QDs into the pores was found to be a combination of dropcasting and spincoating as determined by XPS depth profiling measurements. Although the pores are on average 10 nm in size, the 2.9 nm diameter QDs could substantially infiltrate throughout the virus-templated titania film. Last, we determined the optimal amount of plasmonic nanoparticles that would maximize the enhancement in photocurrent.

Compared to a randomly organized nanoparticle paste control, we confirmed that the virus-based titania morphology had a significant impact on the photocurrent of the device. A two-fold improvement in device efficiency suggests that the high aspect ratio of the virus improves charge transport within the active layer. Devices with AuNP, Ag NPs, and Ag NPLs incorporated into the active layers of solar cells showed an improved light harvesting ability in the EQE spectra near the expected LSPR peak positions and subsequent enhancement in the J_{sc} , V_{oc} , and PCE, with PCE enhancements reaching 36.5% over virus-based control devices with Ag NPLs. How the virus-templated nanoporous morphology affected the propagation of light through the solar cells was numerically computed by modelling the nanostructured device layers with effective medium

theory and using the FDTD method to calculate how power is absorbed throughout the devices. The main features of the predicted EQE spectra and photocurrent enhancement for devices with Au NPs, Ag NPs, and Ag NPLs were in good agreement with the trends observed in measurements, indicating that LSPR is primarily responsible for the observed improvements in light harvesting and photocurrent in plasmon-enabled solar cells. Furthermore, the simulations indicate that generating a blended titania-PbS active layer produces a larger near-field compared with the random-packed QD layer, thereby increasing the chance that light concentration occurs at a point without structural or electronic defects that impair charge generation and transport. Therefore, the virus-templated geometry not only improves the ability of the device to collect and transport charges from the bulk of the device, but also the practical ability of plasmons to enhance light harvesting.

Finally, it is expected that combining our plasmon-enhanced virus-based titania nanotemplate with new ligand molecules and interface engineering techniques that are currently being developed could further improve the efficiency of titania-quantum dot photovoltaic devices. Furthermore, our strategy is intended to be a platform that could be applied to other solution-processable thin film solar systems such as hybrid organic-inorganic solar cells and photocatalytic platforms. Our optimized procedures for assembling and mineralizing the nanoporous virus-based film could be extendable to other biotemplates and find use in any system that interfaces electronic components with biological materials.

ASSOCIATED CONTENT

Supporting Information. Supplementary figures and method details can be found in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Angela M. Belcher (Belcher@mit.edu) and Paula T. Hammond (Hammond@mit.edu)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. N.-M.D.C., M.T.K., A.M.B. and P.T.H. conceived the idea. N.-M.D.C. and M.T.K. designed the experiments and analyzed the data. N.-M.D.C. assembled and characterized the thin films, fabricated and tested the solar cells. M.T.K. synthesized the metal nanoparticles. M.T.K. and N.X.F. performed and analyzed the simulations. V.J.C. and P.-Y.C. assisted with substrate and thin film preparation. K.J.H, M.C.W. and W.A.T. synthesized and characterized the PbS quantum dots. S.E.K. prepared a cross-sectional TEM sample, and D.S.Y. performed elemental mapping of the sample.

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ABBREVIATIONS

APTMS, (3-aminopropyl)trimethoxysilane; EDC, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide; FDTD, finite-difference time-domain; FTO, fluorine-doped tin oxide; LbL, layer-by-layer; LSPR, Localized surface plasmon resonance; MPA, mercaptopropionic acid; NPs, nanoparticles; NPLs, nanoplates; PAA, polyacrylic acid; PAH, polyallylamine hydrochloride; PEI, polyethyleneimine; QDs, quantum dots; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy.

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Supporting Information

Constructing Multifunctional Virus-Templated Nanoporous Composites for Thin Film Solar Cells: Contributions of Morphology and Optics to Photocurrent Generation

Noémie-Manuelle Dorval Courchesne,^{1,2†} Matthew T. Klug,^{2,3†} Kevin J. Huang,⁴ Mark C. Weidman,¹ Victor J. Cantu,¹ Po-Yen Chen,^{1,2} Steven E. Kooi,⁵ Dong Soo Yun,² William A. Tisdale,¹ Nicholas X. Fang,³ Angela M. Belcher,^{2,4,6} and Paula T. Hammond^{1,2*}*

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ²The David Koch Institute for Integrated Cancer Research, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ³Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁴Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁵The Institute for Soldiers Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139, United States. ⁶Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States.

† These authors contributed equally to this work.

*Corresponding authors: Hammond@mit.edu, Belcher@mit.edu

Film Morphology

Figure S1 presents additional scanning electron microscopy (SEM) images that highlight the interconnected mesh-like morphology of virus-templated titania thin films.

Figure S1. Virus-templated titania films have an interconnected continuous morphology. SEM images showing A. the cross-section of a virus-templated titania film constructed on top of a compact titania paste layer, B. the surface morphology of a virus-templated titania film also containing silver nanoparticles, and C. a high resolution image of the surface morphology of a virus-templated titania film containing gold nanoparticles.

Pore Filling and XPS Depth Profiling

Pore Filling Efficiency Calculation

X-ray photoelectron spectroscopy (XPS) with depth profiling was used to monitor the atomic concentration of lead and titanium as a function of film depth and these atomic concentrations were converted to lead sulfide/titania molar ratios and subsequently to volume fractions using the molecular weight and crystalline density of anatase titania and lead sulfide. First, the mole fractions of lead (Pb) and titanium (Ti) are equal respectively to the mole fractions of lead sulfide (PbS) and titania (TiO₂) and can be taken as the atomic concentrations measured by XPS.

$$n_{PbS} = n_{Pb} \text{ and } n_{TiO_2} = n_{Ti} \quad (S1)$$

$$x_{PbS} = \frac{n_{PbS}}{n_{PbS} + n_{TiO_2}} \times 100\% \quad (S2)$$

$$x_{TiO_2} = \frac{n_{TiO_2}}{n_{PbS} + n_{TiO_2}} \times 100\% \quad (S3)$$

where x_{PbS} and x_{TiO_2} are the mole fractions of lead sulfide and titania respectively, n_{PbS} , n_{Pb} , n_{TiO_2} and n_{Ti} are the number of moles of PbS, Pb, TiO₂ and Ti respectively.

Then, from the known crystalline volumes of anatase titania and lead sulfide, relative volumes of titania and lead sulfide can be calculated on a 100 mol basis.

$$V_{TiO_2} = V_{TiO_2 \text{ molecule}} \times x_{TiO_2} \quad (S4)$$

$$V_{PbS} = V_{PbS \text{ molecule}} \times x_{PbS} \quad (S5)$$

where V_{TiO_2} and V_{PbS} are the relative volumes of bulk titania and lead sulfide within the film, and $V_{TiO_2 \text{ molecule}}$ and $V_{PbS \text{ molecule}}$ the known volume of a molecule of TiO₂ and PbS in their crystalline phases, respectively.

From this data, the pore filling efficiency, or the percentage of the pores in the titania film that are filled with PbS QDs, was calculated as a function of depth in the titania film. This calculation was done using a measured porosity of 42% for the titania film (see Error! Reference source not

found.B), and assuming that the maximum possible QD packing density insides the pores is a loose random-packing configuration of 56%. A total value for the volume of the blend layer film (including the titania, the loosely-packed PbS and air) can be determined, as well as the volume of the pores within the titania film before infiltration:

$$V_{total} = \frac{V_{TiO_2}}{(1 - \rho_{TiO_2})} \quad (S6)$$

$$V_{pores} = \rho_{TiO_2} x V_{total} \quad (S7)$$

where V_{TiO_2} is the volume of TiO_2 derived from XPS measurements; ρ_{TiO_2} the known porosity of the titania film; V_{total} the total film volume including TiO_2 , loosely-packed PbS and air; and V_{pores} the volume of the pores within the TiO_2 film before infiltration.

From the packing density of PbS, the volume of loosely-packed quantum dots at each film depth can be calculated, as well as the pore filling fraction, which is simply the ratio of the loose-packed QD volume over the volume of the pores in the titania film.

$$V_{l-pPbS} = \frac{V_{PbS}}{f_{PbS}} \quad (S8)$$

$$\eta_{filling} = \frac{V_{l-pPbS}}{V_{pores}} x 100\% \quad (S9)$$

where f_{PbS} is the packing fraction of the quantum dots; V_{PbS} the volume of PbS particles derived from XPS measurements; V_{l-pPbS} the volume of loosely-packed quantum dots; and $\eta_{filling}$ the pore filling efficiency or, in other words, the fraction of the initial volume of the pores in the TiO_2 film that is now filled with PbS QDs taking into account their packing density.

Below is an example of calculated values for the PbS QDs spincoated onto porous titania as presented in Figure 1D (spin-coat). Table S1 shows the numerical values for each calculation steps, and an example of calculation is shown below.

Table S1. Pore filling efficiency is calculated from XPS data by converting the atomic fractions to mole fractions and volumes. The data presented here is for the “spin-coat” curve of Figure 1D. The etching rate was determined to be approximately 1.67 nm per minute from a sample with a known thickness. The film depth of zero corresponds to the interface between the top layer of PbS QDs and the porous titania film infiltrated with QDs. The measured data are colored in grey. The volumes of PbS and TiO₂ were calculated using the crystalline density of the materials (PbS: 7.6 g/cm³ and 239.3 g/mol equivalent to 52.28 Å³ per PbS molecule, TiO₂: 136.27 Å³ for a unit cell composed of 4 molecules equivalent to 34.07 Å³ per TiO₂ molecule).

Etching time (min)	Film depth (nm)	Pb (%)	Ti (%)	n_{PbS} (mol)	n_{TiO_2} (mol)	x_{PbS} (%)	x_{TiO_2} (%)	V_{PbS} (Å ³)	V_{TiO_2} (Å ³)	V_{total} (Å ³)	V_{pores} (Å ³)	V_{l-pPbS} (Å ³)	$\eta_{filling}$ (%)
...													
12	3.34	3.05	14.6	3.05	14.6	17.3	82.7	905.4	2817.0	4857.0	2039.9	1616.8	79.26
14	6.68	2.63	15.5	2.63	15.5	14.5	85.6	755.8	2914.5	5025.1	2110.5	1349.6	63.95
16	10.02	2.28	16.0	2.28	16.0	12.5	87.5	625.9	2981.6	5140.7	2159.1	1165.8 43	54.00
18	13.36	2.08	16.8	2.08	16.8	11.0	89.0	576.2	3031.5	5226.8	2195.2	1029.0	46.87
20	16.7	1.85	16.7	1.85	16.7	10.0	90.0	522.6	3066.4	5286.9	2220.5	933.5	42.04
...													

Step by step, for the first data point,

$$n_{PbS} = 3.05 \text{ mol and } n_{TiO_2} = 14.6 \text{ mol}$$

$$x_{PbS} = \frac{3.05 \text{ mol}}{14.6 \text{ mol} + 3.05 \text{ mol}} \times 100\% = 17.3 \%$$

$$x_{TiO_2} = \frac{14.6 \text{ mol}}{14.6 \text{ mol} + 3.05 \text{ mol}} \times 100\% = 82.7 \%$$

$$V_{TiO_2} = 34.07 \text{ Å}^3 \times 17.3 = 2817.0 \text{ Å}^3$$

$$V_{PbS} = 52.28 \text{ Å}^3 \times 82.7 = 905.4 \text{ Å}^3$$

$$V_{total} = \frac{2817.0 \text{ Å}^3}{(1 - 0.42)} = 4857.0 \text{ Å}^3$$

$$V_{pores} = 0.42 \times 4857.0 \text{ Å}^3 = 2039.9 \text{ Å}^3$$

$$V_{l-pPbS} = \frac{2817.0 \text{ \AA}^3}{0.56} = 1616.8 \text{ \AA}^3$$

$$\eta_{filling} = \frac{1616.8 \text{ \AA}^3}{2039.9 \text{ \AA}^3} \times 100\% = 79.26\%$$

Low Efficiency Infiltration Methods

A first infiltration study was carried out via dip-coating, with or without ligand exchange (Figure S2A). When the QDs were coated ten times onto a titania film without ligand exchange, very little infiltration occurred, and the QDs did not penetrate further than 30 nm in depth. When an exchange of the oleic acid ligands to benzene-1,3-dithiol (BDT) was performed, the infiltration slightly increased, but a thick PbS QD layer formed on top of the titania film. The adherence of the QDs was thus improved by the exchange with BDT, but the infiltration was marginally affected. A third sample was prepared by dip-coating a titania film that was previously incubated overnight in a 1% mercaptopropionic acid (MPA) solution. This treatment allowed for a deeper infiltration than the control, but since only one dip was done, the pore filling fraction was not improved. Next, an infiltration study was carried out by dropcasting the PbS QDs onto titania films and air-drying the samples (Figure S2B). With and without ligand exchange with MPA, the PbS content within the titania film increased compared to the dip-coat method. With MPA exchanges after each dropcast, the PbS QDs were, again, able to infiltrate deeper into the film. Based on these observations, spincoating and dropcasting methods were compared for a more concentrated PbS QD solution, and with MPA ligand exchange, which yielded the most efficient infiltrations that are presented in Figure 1D. Infiltration methods shown in Figure S1 are less efficient in terms of both PbS content and infiltration depth.

Figure S2. Infiltrating PbS QDs in porous bacteriophage-templated titania films by dip-coating, or dropcasting with a very dilute solution does not result in high PbS content within the titania film. Pore filling efficiencies as a function of film depth calculated from XPS depth profiling results for A. Thin films dip-coated in a 5 mg/mL PbS solution with or without ligand exchange. A sample was first incubated in MPA overnight and then dipped in the PbS QD solution for 1h. The other two samples were dipped successively 10 times in the PbS QD solution with or without exchange with BDT between each dip. B. PbS QDs dropcast onto titania films at 5 mg/mL 10 times with or without exchanging the ligands with MPA between each dropcast.

Thickness Optimization

Device thickness was optimized using planar controls constructed using commercial paste to produce a compact titania layer. The results are shown in Figure S3. These devices differ from the porous titania paste control used for comparison against porous virus-templated devices. Here, the titania layer is compact. No sacrificial polymer was used to create porosity in the structure, and therefore, the resulting device architecture should be approximately planar. No infiltration of PbS QDs within the titania layer is expected here.

Figure S3. Device performance as a function of the thickness of the titania and PbS layers for a planar device. Maximum and average power conversion efficiency as a function of A. thickness of titania, and B. number of layers of PbS QDs spin-coated.

Surface Functionalization and Series/Shunt Resistances

Polymer Base Layer Removal upon Annealing

Figure S4 and Table S2 respectively show the XPS surveys scans measured before and after annealing, and the resulting atomic composition of the titania surface. When the polymers are deposited, peaks for nitrogen can be observed due to the presence of amine groups in PEI and in PAH. For the samples with PEI, the nitrogen signal is weak and titanium atoms can still be detected, indicating that that PEI layer is, as expected, thinner than 10 nm (maximum detection depth by XPS). For the samples with PAH/PAA base layers, the nitrogen signal is stronger, as well as the carbon signal, but no titania is detected on the surface. This observation confirms that the PAH/PAA base layers are 10 nm thick or greater. Then, after burning off the polymers at 500 °C, the nitrogen peak disappears from all samples, revealing a clear titania surface. It has to be noted that oxygen and carbon are present in all samples (including the titania surface before any polymer is deposited) because of natural oxidation and contamination with carbon.

Figure S4. Polymer base layers completely burn off after annealing at 500 °C. XPS surface analysis for a thin PEI layer and PAH/PAA base layers deposited onto compact titania paste. A. Survey scans. B. N1s region of the survey scan showing the disappearance of nitrogen after annealing.

Table S2. Atomic composition of the surface of compact titania or titania with polymer layers gives insights about the presence and thickness of polymer layers. Atomic concentrations of titanium, oxygen, carbon and nitrogen determined by XPS before and after annealing at 500 °C.

Sample	Ti	O	C	N
	(%)	(%)	(%)	(%)
Titania base layer	23.2	59.9	16.8	0
Titania with PEI	21.2	54.0	20.7	4.1
Titania with PEI burnt off	21.8	60.2	18.0	0
Titania with PAH/ PAA	0	31.0	62.5	6.5
Titania with PAH/PAA burnt off	20.1	54.4	25.6	0

Normalized Series and Shunt Resistance Calculation

Series and shunt resistances were calculated from the inverse of the slope of the JV curve at $V = 0$ V and $J = 0$ mA/cm² respectively. The resistances were normalized to the characteristic resistance of the cell, R_{CH} , which is calculated as follows:

$$R_{CH}[\Omega/\text{cm}^2] = \frac{V_{OC}[V]}{J_{SC}[A/\text{cm}^2]} \quad (\text{S10})$$

where V_{OC} is the open circuit voltage and J_{SC} is the short-circuit current density.

Dividing the series and shunt resistances by the cell resistance gives the normalized resistances:

$$r_{SH}[-] = \frac{R_{SH}[\Omega/\text{cm}^2]}{R_{CH}[\Omega/\text{cm}^2]} \quad \text{and} \quad r_{SR}[-] = \frac{R_{SR}[\Omega/\text{cm}^2]}{R_{CH}[\Omega/\text{cm}^2]} \quad (\text{S11})$$

where r_{SH} and r_{SR} are the normalized shunt and series resistances, and R_{SH} and R_{SR} the shunt and series resistances, respectively.

Calculated Resistances for Different Surface Functionalization Methods

Table S3 presents the characteristic resistance, shunt and series resistances for devices constructed using silanes, PAH/PAA base layers of a thin PEI layer as surface functionalization prior to virus film assembly. These values were used to calculate normalized resistances presented in Figures 2C.

Table S3. Calculated characteristic, shunt and series resistances, and normalized resistances for different titania surface functionalization methods.

Surface functionalization	R_{CH} [Ω/cm^2]	R_{SR} [Ω/cm^2]	R_{SH} [Ω/cm^2]	r_{SR}	r_{SH}
Silane	90.1	97.7	95.4	1.08	1.06
PAH/PAA base layers	62.7	42.3	89.6	0.68	1.43
Thin PEI layer	53.8	35.9	88.1	0.67	1.64

Calculated resistances for best optimized devices with or without metal nanoparticles

Table S4 present the resistances calculated for each optimized virus-based devices with or without nanoparticles, and for the paste control device.

Table S4. Calculated characteristic, shunt and series resistances, and normalized resistances for the best optimized devices of each type.

Device	R_{CH} [Ω/cm^2]	R_{SR} [Ω/cm^2]	R_{SH} [Ω/cm^2]	r_{SR}	r_{SH}
Paste control	49.8	27.1	116.9	0.55	2.35
1.5 h, virus only	37.0	26.2	77.2	0.71	2.09
2 h, virus only	34.4	18.0	128.1	0.52	3.73
2.5 h, virus only	37.1	27.0	104.4	0.73	2.82
2 h, with Au NPs	35.7	19.2	163.5	0.54	4.58
2 h, with Ag NPs	33.9	23.9	173.7	0.71	5.12
2 h, with Ag NPLs	33.8	16.5	176.4	0.49	5.21

Estimating Porosity with ImageJ

Figure S 5. Image analysis for the estimation of porosity, pore size distribution and size of nanowire-like features. The analysis was performed using the ImageJ software. The contrast between the pores and the titania was enhanced (top row), and the area corresponding to the pores was calculated (area in red in the bottom row). To calculate the equivalent diameter of a pore, the area was converted into diameter assuming a circular pore. The red arrows show nanowire features in each image. To determine the average nanowire size, several nanowires were measured in each enhanced-contrast image and the measurements were averaged.

Figure S6. Image analysis of the TiCl_4 -derived TiO_2 paste film. The analysis was performed with the ImageJ software to estimate the film porosity as described in Figure S1.

Silver Nanoplates: Morphology and Effects on Device Performance

Figure S7. Effect of silver nanoplate concentration on power conversion efficiency in bacteriophage-templated devices. Optimal surface functionalization and biomineralization conditions were used for this study. The highest efficiency is observed for a 0.1 NPL/phage ratio.

Figure S8. Evolution of the optical properties and morphology of silver nanoplates during the LbL assembly process. Three different ratios of Ag NPLs/phage were used (0.1, 0.2 and 0.4), and the

absorption spectra and morphology of the Ag NPL-bacteriophage complexes were monitored initially, and after 82, 188, 284 and 325 bilayers. A. Normalized absorption spectra of Ag NPL-bacteriophage complexes through the process. The spectra are blue shifted as the number of bilayer increases as indicated by the arrows. B. Change in peak positions as a function of the number of bilayers. The peak positioned around 625nm corresponds to the dipole resonance of the NPLs. As the corners of the NPLs become more rounded, this peak shifts towards shorter wavelengths. The 390 nm peak position corresponds to the dipole peak of silver nanospheres. This indicates that during the LbL process the morphology of the NPLs change into spheres or discs as the particles interact with the virus proteins and likely lose the protective citrate ions that preserve the triangular shape. Higher NPL loadings of the virus results in more spheres as indicate by an increase in the 390nm peak, whereas lower loadings result in the NPLs becoming cylindrical discs. C. TEM images showing the morphology of the NPLs as a function of the number of bilayers for 0.4 NPL/phage.

Figure S 9. Evidence of Ag NPL stacking, as shown by a TEM image of Ag NPLs dropcast from solution.

Performance of Smaller Area Devices

Figure S10 compares the performance of virus-based devices containing Au NPs with a 0.0547 cm^2 area (as reported throughout this work) and for areas approximately 5 times smaller at 0.0121 cm^2 . Higher currents and fill factors are obtained with smaller area devices. The best small area device reached an efficiency of 4.7 %.

Figure S10. Smaller area devices can reach higher efficiencies. A. Best JV curves and B. Average power conversion efficiency, short-circuit current, open circuit voltage and fill factor, for virus and Au NPs device with areas of 0.0547 cm^2 or 0.0121 cm^2 (small area).

Optical Property Calculations using Effective Medium Theory

Modeling the power absorption throughout the solar cells requires the development of effective complex dielectric functions for the nanostructured active layers of the devices (*i.e.* the virus-templated network infiltrated with PbS QDs, and the PbS QD film layers). Properly modeling the optical material properties is critical for accurately predicting how light propagates and is absorbed throughout the solar cell volume. This section describes the methods used to perform this task.

Pure Anatase Titania

The complex dielectric function for pure anatase titania, ϵ_{TiO_2} , was calculated from the values reported by Kim *et al.*¹ for a 16% porous thin film (84% anatase volume fraction) using Bruggeman effective medium theory:²

$$\epsilon_{TiO_2} = \epsilon_{film} \frac{2 \left(\frac{f_{film} - 1}{f_{film}} \right) \left(\frac{\epsilon_{air} - \epsilon_{film}}{\epsilon_{air} + 2\epsilon_{film}} \right) + 1}{\left(\frac{1 - f_{film}}{f_{film}} \right) \left(\frac{\epsilon_{air} - \epsilon_{film}}{\epsilon_{air} + 2\epsilon_{film}} \right) + 1} \quad (S12)$$

where ϵ_{film} is the complex dielectric function of the 16% porous anatase film reported by Kim *et al.*,¹ f_{film} is the volume fraction of anatase titania in this film (84%), and ϵ_{air} is the dielectric function of air (taken to be 1.000). The complex index of refraction can be calculated from the dielectric function by:

$$n + i\kappa = \sqrt{\epsilon_1 + i\epsilon_2} \quad (S13)$$

where $\epsilon = \epsilon_1 + i\epsilon_2$ is the form of the complex dielectric function, n is the real part of the refractive index, and κ is the imaginary part. The complex index of refraction for pure anatase used for the computations is plotted in Figure S11.

Figure S11. Real (blue) and imaginary (red) components of the index of refraction for the 16% porous anatase TiO_2 film reported by Kim *et al.* (dotted lines) and the estimated function for pure anatase films (*i.e.* 0% porous films, solid lines) as predicted by Bruggeman effective medium theory.

Blend Layer (58% Anatase TiO₂, 15% PbS QDs, 27% Air)

The complex dielectric function of pure PbS QDs was adjusted from the values reported by Moreels *et al.*³ to have an absorption peak that matches the measurement of 904nm for the PbS QDs used in the devices (see Figure S13).

In reality, a *pure PbS QD* film can never be achieved because void space will always exist between the QDs when the spheres pack into a film. Therefore, effective medium theory must be used to estimate the effective index of the virus-templated titania network when PbS QDs are infiltrated into its pores (referred to as the *blend layer*) and for the packed QD film that was spincoated to form a layer on top of the blend layer (referred to as *random-packed PbS QD layer*). For simplicity the blend layer was model as a homogeneous planar slab with an effective index resulting from a blending of anatase titania (corresponding to virus-templated titania nanowires, comprising 58.1% of the film volume) with the PbS QDs and air occupying the pore space of the virus-templated network. The volume fraction of PbS in the blend layer was determined to be 15% by averaging the PbS concentration profile reported in Figure 1D of the manuscript over the 50 nm thickness of that film. Although assuming a homogeneous distribution of PbS is a simplification of the system, by using the average PbS concentration measured for the actual films, the total amount of light absorbed by the PbS QDs in the idealized slab will be equal to that absorbed in the actual film. This can be proven using the Beer-Lambert law for light absorption, where light with intensity, I_0 , is incident on a slab with a 1-D concentration gradient, $c(z)$, of PbS QDs with a molar absorptivity of ϵ . The intensity at any position within the slab, $I(z)$, is:

$$I(z) = I_0 \exp\left(-\epsilon \int_0^z c(z) dz\right) \quad (\text{S14})$$

For a slab of thickness L , the intensity of light after passing through the entire film is:

$$I(L) = I_0 \exp\left(-\epsilon \int_0^L c(z) dz\right) = I_0 \exp(-\epsilon \bar{c} L) \quad (\text{S15})$$

where $\bar{c}$ is the average PbS QD concentration and is equal to:

$$\bar{c} = \frac{1}{L} \int_0^L c(z) dz \quad (\text{S16})$$

A volume fraction of 15% PbS in the blend layer corresponds to a 35% fill fraction of the pores. Therefore, the effective index of the overall blend layer was calculated in two steps. First, the Maxwell Garnett effective medium theory² was used to determine the effective dielectric function of the material in the pores, ϵ_{eff}^{pores} , which is taken to be a 35% fill fraction of PbS QDs with the balance being air:

$$\epsilon_{eff}^{pores} = \epsilon_{air} \left[1 + \frac{3f_{PbS}^{pores} \left(\frac{\epsilon_{PbS} - \epsilon_{air}}{\epsilon_{PbS} + 2\epsilon_{air}} \right)}{1 - f_{PbS}^{pores} \left(\frac{\epsilon_{PbS} - \epsilon_{air}}{\epsilon_{PbS} + 2\epsilon_{air}} \right)} \right] \quad (S17)$$

where ϵ_{PbS} is the dielectric function of pure PbS QDs and f_{PbS}^{pores} is the volumetric fill fraction of PbS QDs in the pore material (35%).

The second step once again uses effective medium theory to blend the anatase titania with the effective medium developed for the pores, ϵ_{eff}^{pores} . The Maxwell Garnett model was not used for this blending because it is only strictly valid for spherical inclusions. Thus, the Bruggeman model was chosen because it applies to a completely randomly inhomogeneous medium. The effective dielectric function of the blend layer, ϵ_{eff}^{blend} , can be found by numerically solving the following transcendental equation:²

$$f_{TiO_2} \frac{\epsilon_{TiO_2} - \epsilon_{eff}^{blend}}{\epsilon_{TiO_2} + 2\epsilon_{eff}^{blend}} + (1 - f_{TiO_2}) \frac{\epsilon_{eff}^{pores} - \epsilon_{eff}^{blend}}{\epsilon_{eff}^{pores} + 2\epsilon_{eff}^{blend}} = 0 \quad (S18)$$

where f_{TiO_2} is the volumetric fill fraction of anatase titania in the blend layer (58.1%) and ϵ_{TiO_2} is the dielectric function of pure anatase titania calculated earlier with Equation S12. Figure S12 plots the real and imaginary parts of the complex refractive indexes calculated for pure anatase, the effective medium in the pores, and the final blend layer comprised of anatase titania, PbS QDs, and air.

Figure S12. Real (Left) and imaginary (Right) parts of the complex refractive index computed for pure anatase titania (blue lines), the 35% PbS QD 75% air mixture in the pores of the blend layer (red lines), and the final blend layer (black lines) consisting of a 58% volume fraction of anatase titania, 15% PbS QDs, and 27% air.

PbS QD Layer (56% PbS QDs, 44% Air)

When the PbS QD solution is spincoated on top of the blend layer, the nanospheres will pack into a film that consists only of PbS and air. The densest possible packing density for a bed of equal size spheres is 74%, which corresponds to perfect close-packing. In practice, this upper limit is not achieved, rather studies of QD films assembled by spincoating colloidal solutions indicate that packing densities are closer to 50%.⁴ Therefore a PbS volume fraction of 56% was chosen for modeling the spincoated PbS QD film, which corresponds to a typical value used for a loose random-packing of equal spheres.⁵ The effective dielectric function, ϵ_{eff}^{film} , of this layer can be calculated by using the Maxwell Garnett effective medium model presented in Equation S17, but substituting f_{PbS}^{pores} with f_{PbS}^{film} (56%):

$$\epsilon_{eff}^{film} = \epsilon_{air} \left[1 + \frac{3f_{PbS}^{film} \left(\frac{\epsilon_{PbS} - \epsilon_{air}}{\epsilon_{PbS} + 2\epsilon_{air}} \right)}{1 - f_{PbS}^{film} \left(\frac{\epsilon_{PbS} - \epsilon_{air}}{\epsilon_{PbS} + 2\epsilon_{air}} \right)} \right] \quad (S19)$$

The effective dielectric function resulting from this calculation is plotted in Figure S13.

Figure S13. Real (blue) and imaginary (red) components of the complex dielectric function for the pure PbS QDs modified from Moreels *et al.*³ for 904 nm QDs (solid lines) and the estimated effective function for a spincoated film of loosely random-packed PbS QDs (56% volume fraction of PbS QD and 44% air) as predicted by Maxwell Garnett effective medium theory.

FDTD Simulations

In order to computationally predict how a PbS QD solar cell would perform with and without plasmonic metal nanoparticles, the finite-difference time-domain (FDTD) method was used to determine how light would propagate and become absorbed throughout an idealized device. The simulations were carried out with the software Lumerical FDTD Solutions, Version 8.9.163.

Model Geometry and Materials

The model geometry consists of stacked planar slabs of material starting with 50 nm of FTO at the bottom followed by 100 nm of pure anatase titania, 100 nm of the virus-templated blend layer that has been infiltrated with PbS QDs (58% volume fraction of TiO₂, 15% PbS, 27% Air), 100 nm of PbS QD film (56% PbS, 44% Air), and 25 nm of MoO₃ on top. The complex dielectric functions developed for pure anatase titania, the virus-built titania-PbS QD blend layer, and the random-packed QD film layers using effective medium theory in the previous section were assigned to the corresponding slabs of the model geometry. The lateral extent of the slabs in the x - and y -directions was fixed to be 60 nm, which is the estimated approximate distance between NPs in the solar cells. Three different types of nanoparticles were considered in the plasmon-enhanced solar cells: gold nanosphere (Au NP), silver nanosphere (Ag NP), and silver nanoplate (Ag NPL). The radius of the nanospheres was taken to be 10 nm whereas the cylindrical silver nanoplates had a radius of 10 nm and a thickness of 6 nm. The complex dielectric function reported by Johnson and Christy⁶ was used for gold, whereas the function reported by Palik⁷ was used for silver. Periodic boundary conditions were placed on each of the lateral x - and y - faces of the model in order to simulate an infinite slab with periodically spaced NPs. Likewise, this allows any light that is scattered obliquely from a NP through the lateral faces to re-enter the simulation volume. Six different configurations were performed for each nanoparticle type, each with the nanoparticle positioned at a different location throughout the thickness of the active materials. Because the nanoparticles were built into the blend layer using the layer-by-layer assembly method with the M13 virus, the NPs can be located anywhere within this layer. Five configurations consider a nanoparticle located within the blend layer (10, 30, 50, 70, or 90 nm from the bottom of the blend layer slab). However, in an actual device, the interfaces between the blend and random-packed QD layers is not expected to be smooth, rather the virus-templated titania nanowire film is expected to be rough. Therefore, a NP that exists near the top of the film could almost be considered to be embedded within the random-packed QD film layer. Thus, a sixth configuration was considered where the metal NP was located 10 nm into the random-packed QD film layer. Because the Ag NPL is not spherically symmetric, its orientation to the incident light will impact the nature of its plasmon resonance; thus, for each vertical position, three separate orientations were considered with the NPL located at 0°, 45°, and 90° to the incident field (*i.e.* 18 total cases were considered for the Ag NPL geometry and 6 cases for the Au NPs and Ag NPs.).

The model geometry was illuminated from the FTO side with a plane-wave source at 400 different wavelengths between 200 and 1200 nm to fully capture the incident solar spectrum of interest. All simulations were performed with a refined mesh size of 1 nm in the region around the metal NP and used conformal meshing option “Conformal Variant 1” to provide greater accuracy in elements where multiple materials are present. A three-dimensional power absorption monitor was placed throughout the active regions of the solar cell to capture how much power was absorbed at each point in the solar cell. A cross-section of the mesh through the NP center is shown in Figure S9A for the nanosphere case and Figure S14B shows the mesh configuration for all three orientations of the nanoplate cases.

Figure S14. The mesh, materials, and geometry of each simulated configuration performed with the FDTD method. A. All six of the different positional configurations of metal NPs. Five configurations exist for a NP within the blend layer and 1 in the random-packed PbS QD film layer. B. Because silver nanoplates are not spherically symmetric, their orientation within the blend layer will change the way light is concentrated in the near-field surrounding them. Therefore, at each of the six positional configurations shown in A, three orientational configurations were considered with the NPL positioned at 0°, 45°, and 90° with respect to the faces of the material slabs (18 total cases performed for the NPL device).

As discussed in the manuscript, the silver nanoplates are believed to transform into a polydisperse population of silver nanospheres during the annealing process the virus-templated titania film undergoes to convert the nanowires from amorphous to crystalline titania. The simulations performed to test this hypothesis are exactly the same as those done for the Ag NPs except that nanospheres of radius 8.2, 10.4, and 11.9 nm were considered, which conserve the volume of a stack of 1, 2, and 3 NPLs.

Calculating Power Absorption, External Quantum Efficiency, and Photocurrent Enhancement

Upon completion of the simulation, the power absorption monitor provides the source-normalized power density that has been absorbed at each node throughout the mesh for each illumination wavelength. This can be thought of as a measure of *absorption efficiency density*, p_{abs} , which is how efficiently a given element can absorb photons of a particular wavelength that are incident upon the solar cell per unit volume (units of m^{-3}). By integrating this measure over the spatial extent of active regions in the solar cell, the total absorption efficiency of the solar cell can be determined as a function of wavelength. It must be noted that when metal NPs are incorporated into the model, any light that is absorbed in the NP interior cannot contribute to enhancing solar cell performance because the power it absorbs either goes into producing the near-field or is lost as heat. Only the light that is concentrated by the LSPR of the NP in the active material directly surrounding it can contribute to photocurrent enhancement. Therefore, when determining the total amount of power absorbed by the solar cell with the goal being to estimate the photocurrent the device can produce, only the power absorbed in the active media should be considered. The external quantum efficiency, EQE , of the solar cell, which quantifies how many photons of a given wavelength incident on the solar cell are converted into collected charges, can be estimated by:

$$EQE(\lambda) = \eta_c \eta_a(\lambda)(1 - R(\lambda)) \quad (S20)$$

where η_a is the absorption efficiency, η_c is the charge collection efficiency, and R is the reflectance of the solar cell. For simplicity the following assumptions are made in the solar cell.

1. It is assumed that none of the incident light is reflected: $R = 0$.
2. It is assumed that the PbS QDs in the blend layer are fully depleted by the nanoporous virus-templated titania film. Therefore, any carriers generated within the blend layers will be efficiently transported by drift due to the built-in field in this region. This, it is assumed $\eta_c = 1$ within the blend layer.
3. For simplicity, it is assumed that the depletion region only encompasses the blend layer and does not extend in to the random-packed QD layer above. The basis of this assumption is that there are less quantum dots and titania present in this layer than in a bilayer geometry, which causes the depletion width to be shorter than the typical value of ~ 150 nm. Therefore, the random-packed QD layer is assumed to be within the quasi-neutral region of the heterojunction where diffusion governs charge extraction. Therefore, electrons that are generated deeper in the PbS QD film above the blend layer are less likely to diffuse to the depletion region for efficient collection. To capture this effect, an exponential decay envelop with a decay length of 30 nm, corresponding to the diffusion length of electrons in the PbS QD film, is used for the charge collection efficiency in the random-packed PbS QD film layer. Therefore:

$$\eta_c(z) = \begin{cases} 1, & 0 \leq z \leq L_b \\ e^{-(z-L_b)/L_d}, & L_b < z \leq L_b + L_{QD} \end{cases} \quad (S21)$$

where L_b is the thickness of the titania-PbS QD blend layer, L_{QD} is the thickness of the close-packed QD layer, and L_d is the decay length (*i.e.* 30 nm).

The absorption efficiency, η_a , is determined by integrating the absorption efficiency density, p_{abs} , over the volume of the active layers:

$$\eta_a(\lambda) = \int_{\substack{\text{Active} \\ \text{Material} \\ \text{Volume}}} p_{abs}(x, y, z, \lambda) dx^3 \quad (\text{S22})$$

The EQE can be estimated from the FDTD simulations by multiplying the normalized power absorption density provided by the 3D power monitor, *i.e.* p_{abs} , by the η_c given in Equation S21, and integrating over the volume of the active layer that contains the blend material or the random-packed PbS QD layer active materials (we exclude the power absorbed in the metal NP volume from consideration):

$$EQE(\lambda) = \int_{\substack{\text{Active} \\ \text{Material} \\ \text{Volume}}} \eta_c(z) p_{abs}(x, y, z, \lambda) dx^3 \quad (\text{S23})$$

To account for the different geometrical configurations that the NP and NPL can have in the actual devices, the simulated EQE reported in the manuscript is the ensemble average over all of the cases considered for that device type (*i.e.* 6 cases for No NPs, Au NPs, and Ag NPs; 18 cases for Ag NPLs). For the corrected Ag NPL predictions, which instead simulate three differently sized nanospheres, a total of 18 cases are considered and the ensemble average is taken over this set.

Once the ensemble average quantum efficiency has been determined, the photocurrent enhancement for a given device type (*i.e.* no NPs, Au NPs, Ag NPs, Ag NPLs) can be calculated by comparing the estimated short circuit photocurrent densities of the devices with metal NPs to that without. The short circuit current density can be predicted by:

$$J_{sc} = q \int_{\lambda_{min}}^{\lambda_{max}} EQE(\lambda) b_s(\lambda) d\lambda = \frac{q}{hc} \int_{\lambda_{min}}^{\lambda_{max}} EQE(\lambda) M(\lambda) \lambda d\lambda \quad (\text{S24})$$

where q is the charge on an electron, b_s is the photon flux of the AM 1.5 solar spectrum, M is the spectral irradiance of the solar spectrum (which can be related to b_s by: $M(\lambda) = \frac{b_s(\lambda)}{E(\lambda)} = \frac{\lambda b_s(\lambda)}{hc}$), h is Planck's constant, c is the speed of light, and $\lambda_{min} = 200$ nm and $\lambda_{max} = 1200$ nm for the simulations.

Therefore, the photocurrent enhancement factor, EF , is defined to compare the photocurrent produced in the plasmonic devices to that generated in the same device without metal NPs:

$$EF = \frac{J_{sc}^{NP}}{J_{sc}^{No\ NP}} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} EQE_{NP}(\lambda) \lambda M(\lambda) d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} EQE_{No\ NP}(\lambda) \lambda M(\lambda) d\lambda} \quad (S25)$$

Calculating Plasmon Decay Length

The distance over which the near-field generated by the metal nanoparticles via LSPR can penetrate into the surrounding active media was determined by analyzing line profiles of the absorbed power density taken through the center of the NP while at resonance. The resonance wavelength was determined as the simulated illumination wavelength that produced the largest absorbed power value outside the metal NP core. Figure S15 shows a contour plot of the absorbed power density of each NP device case at resonance taken through the center plane of the metal NP.

Figure S15. Contour plots of source-normalized absorbed power density, p_{abs} [m^{-3}], throughout the simulated solar cell cross-section at a plane through the center of the A. Au NP at $\lambda=564$ nm, B. Ag NP at $\lambda=440$ nm, and (C) Ag NPL at $\lambda=571$ nm. The dotted yellow line indicates the position where the line profiles are taken to determine the plasmon decay length.

The influence of illumination wavelength on the penetration length of the near-field generated by the metal NP into the active media was investigated by sampling the absorbed power density along a line through the center of the metal NP (indicated by the yellow dotted line in Figure S15). Figure S16 plots this line profile for every simulated wavelength for all three NP types. It can be observed that although plasmon resonance increases the absorbed power most strongly at the LSPR wavelength, enhancement occurs over a spectral range of about 100 nm for the nanospheres and 200 nm for the nanoplate cases. It should also be noted that the spatially flat absorption line around wavelength 350 nm corresponds to the main absorption peak of the PbS QD rather than plasmon resonance of the metal NP.

Figure S16. Line profile plots of source-normalized power density, p_{abs} , as a function illumination wavelength for A. Au NP, B. Ag NP, and C. Ag NPL (horizontal configuration). The dotted horizontal yellow line indicates the LSPR wavelength and the dotted vertical white lines indicate the edges of the metal NP. The area between the dotted white lines represents the power absorbed in the interior of the metal NP, whereas the area outside represents the power absorbed in the blend layer of the solar cell.

In addition to performing simulations with the metal NPs located within the blend layer, simulations were also performed with the metal NPs located within the random-packed PbS QD film layer in the absence of the blend layer (device structure: FTO (50nm)\Random-Packed PbS QD Layer (100 nm)\MoO₃). Figure S17 shows the power absorption density line profiles through the NP centers at the LSPR resonance peak and normalized to the maximum value within the active medium for each NP type embedded in both the blend (Figure S17A) and random-packed PbS QD layer (Figure S17B). The dotted line indicates that location where the normalized value reaches $1/e$, which corresponds to the decay length.

Figure S17. Line profile plots of absorbed power density normalized to the maximum value outside of the metal NP core for each of the NP types at the LSPR wavelength. The decay profile for the metal NPs embedded in the blend layer is shown in part A. Part B. shows the decay profiles when the metal NPs are embedded in the random-packed PbS QD layer of a device without the blend layer (a simple bilayer). The horizontal dotted black line represents the value $1/e$, which corresponds to the decay length, indicated by the vertical dotted lines. The printed value L_d is the decay length, *i.e.* the distance from the NP surface when a normalized value of $1/e$ is reached. Note that profiles appear slightly asymmetric due to the way the simulation domain was meshed.

Fitting Measured JV Curves to Standard Solar Cell Model

It was hypothesized that the reason the solar cells with plasmonic NPs produced an increased open-circuit voltage, V_{oc} , was simply a natural result of the solar cells producing a higher photocurrent. The intuition behind this notion is that the standard diode model of solar cells couples together the bias voltage and the photocurrent. Therefore, it would be expected that if the same device would somehow generate a higher current (for instance due to improved light harvesting by LSPR), then the open-circuit voltage would also increase accordingly. Figure 5E in the manuscript shows that the measured JV curves of the virus-based solar cell without NPs has a similar shape to that of the virus-based solar cell that has been assembled with Ag NPLs, and one could imagine that the curve for the Ag NPL device might be almost reproduced if the virus-only curve was translated along the y-axis to match the short-circuit current values. This hypothesis was tested by fitting the measured JV data to the standard diode equation for solar cells that includes parasitic resistances:

$$J = J_{sc} - J_0 \exp\left(\frac{q(V + JAR_{sr})}{mkT}\right) - \frac{V + JAR_{sr}}{R_{sh}} \quad (\text{S26})$$

where J is the current density, J_{sc} and J_0 are the short-circuit current densities for the light and dark current, respectively, q is the charge on an electron, V is the applied voltage bias, m is the ideality factor (which is a function of bias, V), k is Boltzmann's constant, T is device temperature (assumed to be room temperature, 298 K), R_{sr} is the series resistance, R_{sh} is the shunt resistance, and A is the illuminated area of the device.

The series and shunt resistances were determined by calculating the inverse of the slope of the measured JV curves near the x -intercept and y -intercept, respectively. Likewise, the dark and light short-circuit current densities were determined from the measured light and dark JV curves for each of the devices by finding the current density when the applied bias voltage is equal to zero.

The ideality factor, m , characterizes how far the actual solar cell behavior deviates from an ideal diode ($m = 1$) while under illumination. This factor was determined for each applied bias by rearranging Equation S25:

$$m(V) = \frac{q(V + JAR_{sr})}{kT} \left[\ln \left(\frac{J_{sc} - J - \frac{V + JAR_{sr}}{R_{sh}}}{J_0} \right) \right]^{-1} \quad (\text{S27})$$

The calculated ideality factor for illuminated devices are plotted in Figure S18 for the devices made from TiO₂ paste (no virus), the virus-film device without metal NPs, and the virus-film device with Ag NPLs.

Figure S18. The ideality factor as a function of applied voltage bias, as determined from the measured JV curves while illuminated (*i.e.* the *light ideality factor*).

The advantage of the standard model described by Equation S25 is that every term represents a physical characteristic of the solar cell. Thus, changes in solar cell performance can be predicted by adjusting some of these terms and solving the equation. Now that the parasitic resistances and the ideality factor have been determined from the measured light JV curves, it can be predicted how a given device would perform if it were able to somehow generate a different photocurrent. By taking the values for R_{sr} , R_{sh} , and $m(V)$ determined for the *virus-film solar cell without plasmonic nanoparticles* and plugging them into the standard model (Equation S25), but now substituting the J_{sc} and J_0 values measured for the *virus-film solar cell with Ag NPLs*, the JV curve can be predicted for how the non-plasmonic virus-based solar cell would perform if it could suddenly generate the current measured in the virus-based device with Ag NPLs. This was accomplished by numerically solving the transcendental Equation S25 with these values; the result is plotted in Figure S19. The fact that the predicted V_{oc} is so close to that measured for the virus-based device with Ag NPLs strongly indicates that the increase in open-circuit voltage shown by

the plasmonic solar cells is a natural result of the increase in photocurrent that results from the improved light harvesting in the device via LSPR by the metal NPs. It could be argued that any difference between the measured curve for the *virus-based device with Ag NPLs* and the curve predicted from the *non-plasmonic virus solar cell* is due to slight variations in the device morphologies that produce slightly different series and shunt resistances.

Figure S19. The measured light JV curves for the *virus-film solar cell without plasmonic NPs* (solid blue line) and the *virus-film solar cell with Ag NPLs* (solid red line), with the open circles indicating the predicted curve that has been fit to the standard solar cell equation given in Equation S25. The black line represents the predicted JV curve from Equation S25 of the *non-plasmonic virus-film solar cell* (solid blue line) if it generated the short-circuit photocurrent produced by the virus-based device with Ag NPLs.

Materials and Methods

Materials

1-octadecene (technical grade, 90 %) (ODE), oleic acid (technical grade, 90 %) (OA), lead (II) oxide (technical grade, 99.999 %), cadmium chloride (99.99 %), hexamethyldisilathiane (synthesis grade) (TMS-S), titanium tetrachloride, (3-aminopropyl)trimethoxysilane (APTMS), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), gold(III) chloride ($\geq 99.99\%$ trace metal basis), silver nitrate, coumalic acid, hydrogen peroxide (Perdrogen, 30% solution), sodium borohydride, glycerol, and branched PEI (1.3kDa) were purchased from Sigma (St-Louis, MO). 1-tetradecylphosphonic acid (98%) (TDPA) and sodium citrate dihydrate were purchased from Alfa Aesar (Ward Hill, MA). Oleylamine (80-90 %) was purchased from Acros (Fair Lawn, NJ). N-hydroxysulfosuccinimide (sulfo-NHS) was purchased from Pierce Biotechnology Inc. (Rockford, IL). TEC 15 FTO-coated glass substrates were purchased from Pilkington Glass (Northwood, OH). Polyallylamine hydrochloride (PAH, 120000 to 200000 g mol⁻¹) and polyacrylic acid (PAA, >250000 g mol⁻¹) were purchased from Polysciences Inc. (Warrington, PA). Titania paste (HT/SC, 8-10 nm particles) was purchased from Solaronix SA (Switzerland).

M13 Bacteriophage

The E3 M13 bacteriophage variant was amplified by infecting exponentially growing *Escherichia coli* bacteria. The bacteriophage was separated from cell debris via centrifugation and further purified with two cycles of polyethylene glycol-sodium chloride precipitation and centrifugation. The final product was diluted in a PBS buffer, and the EEE peptide displayed on each pVIII protein was confirmed with DNA sequencing.

For metal nanoparticle binding, the p8#9 variant was used, and amplified as described above. The VSGSSPDS peptide displayed on the pVIII proteins was confirmed with DNA sequencing.

Gold Nanoparticle (Au NP) Synthesis

Gold nanoparticles with ~20 nm diameters were synthesized following the Turkevich method.⁸ In summary, 95 mL of deionized water and 2.6 mL of 50 mM gold(III) chloride were combined in a 250 mL round-bottom flask and brought to a boil while stirring in a silicone oil bath. While boiling,

10 mL of 1% wt sodium citrate dihydrate was quickly added while vigorously stirring. The color of the solution quickly turned black and then ripened into a deep ruby red. The solution was kept boiling and stirring for an additional 20 minutes. The solution was cooled to room temperature and stored without further purification.

Silver Nanoparticle (Ag NP) Synthesis

Silver nanoparticles were synthesized following a modified Turkevich method.⁸ In summary, 95 mL of deionized water and 4 mL of 30 mM silver nitrate were combined in a 250 mL round-bottom flask and brought to a boil while stirring in a silicone oil bath. While boiling, 10 mL of 5% wt sodium citrate dihydrate was quickly added while vigorously stirring. After stirring for a minute, 6 mL of 100 mM coumalic acid was quickly added. The color of the solution slowly ripened into a deep yellow-brown color. The solution was kept boiling and stirring for an additional 20 minutes. The solution was cooled to room temperature and stored without further purification.

Silver Triangular Nanoplate (Ag NPL) Synthesis

Silver nanoparticles were synthesized by modifying the method previously reported by Zhang *et al.*⁹ In a 1 L Erlenmeyer flask, 240 mL of deionized water was combined with 5 mL 50 mM silver nitrate and 5 mL 750 mM sodium citrate dihydrate while stirring at room-temperature, followed by 6 mL of 30% hydrogen peroxide stock solution. While stirring at room-temperature, 10 mL of freshly prepared 100 mM sodium borohydride was added dropwise to the solution. The color of the solution should change from yellow to brown to amber-red within about fifteen minutes. Once the color has stabilized, add 3 mL of 30% hydrogen peroxide solution. Repeat addition of hydrogen peroxide, if necessary, until the solution has changed color and stabilized to a deep blue. Add 1 mL of glycerol to stabilize the solution for long-term storage.

PbS Quantum Dot Synthesis

PbS quantum (QD) synthesis followed previously published methods.^{10 11} A metal halide precursor was first prepared by dissolving 0.3 g CdCl₂ and 0.033 g of TDPA in 5 mL of oleylamine in a three-neck flask and degassed at 100 °C under vacuum. The metal halide solution was then kept at 80 °C under nitrogen.

In a separate three-neck flask, 0.45 g of PbO, 1.5mL of oleic acid, and 18 mL of ODE were degassed under vacuum at 125 °C. A sulfur precursor was prepared by mixing 0.18g of TMS-S (weighed out in an argon atmosphere glovebox) with 10mL of degassed ODE. The sulfur precursor solution was then rapidly injected into the reaction flask at 125 °C. Immediately after injection, the reaction mixture was removed from heat and allowed to cool down to room temperature. When the mixture cooled down to 60-70 °C, 1 mL of the metal halide precursor solution was rapidly injected. Once the entire mixture reached room temperature, the QDs were purified and isolated through several centrifugation wash cycles. The QDs were first precipitated with acetone and isolated by centrifugation. The QDs were subsequently re-dispersed in toluene and precipitated again with excess acetone and methanol, followed by centrifugation. Finally, the QDs were washed several more times with methanol and stored as a dry powder.

Device Assembly

Patterned FTO substrates were cleaned sequentially in soap, water, acetone and isopropanol with sonication. After drying with N₂ gas, the substrates were plasma treated for 2 min, and a base layer of titania paste (Solaronix, HT/SC) was spun at 2000 rpm and annealed at 500 °C for 1 h.

The titania paste layer was functionalized either with aminopropylsilanetriol and by attaching a first layer of viruses with EDC as previously described,¹² or by functionalizing the surface either with 4.5 bilayers of PAH/PAA or with a branched PEI (1.3kDa) spincoated at 0.1 w% in water at 5000 rpm, and electrostatically adsorbing the first layer of viruses in a NaOAc buffer (pH 4.9) at 50 °C for 45 min. After each functionalization, the films were rinsed with milli-Q water and dried with N₂ gas. Virus films were assembled via covalent layer-by-layer, as described previously.¹² To remove any residual salts or organics, the films were rinse in milli-Q water for at least 30 min after LbL.

Titania was nucleated onto the virus films using a 0.2 M TiCl₄ solution in water. The hydrolysis occurred at 80 °C for 1.5, 2 or 2.5 h. The films were then sonicated for a few seconds in milli-Q water, and rinsed for at least 30 min. The titania-coated virus films were annealed at 500 °C for 1h.

Oleic acid-capped PbS QDs at 50 mg/mL in octane were dropped onto the titania films for 1 min, and then spun at 2500 rpm for 10 s. Ligand exchange was performed with MPA (1 % in methanol), which was spun for 10s, then rinsed with methanol and spun for 10s, and rinsed with octane and spun for 10s. The cycle was repeated a total of five times.

Patterned electrodes of MoO_x (25 nm) and Au (100 nm) were thermally evaporated onto the PbS film. The resulting area of each device was 0.0547 cm².

Thin Film Characterization

The thickness of the films was determined using a Veeco Dektak 150 profilometer. The cross-section and surface morphology of the films were observed by scanning electron microscopy (SEM) using a Helios Nanolab 600 Dual Beam Focused Ion Beam Milling System. The porosity, pore size distribution and nanowire size were estimated from the SEM images using the Image J software. The cross-sectional TEM sample was prepared using a JEOL 9320-FIB, and the mapping of Ti and Pb was performed with a JEOL 2100 FEG TEM (EDX, X-MAX 80 mm²). XPS with depth profiling was used to determine the atomic concentration of PbS and TiO₂ through the film depth and was converted to volumetric fractions using the molecular weight and the density of the materials. The XPS used was a PHI Versa-Probe II X-ray photoelectron spectrometer with a scanning monochromated Al source (1,486.6eV; 50 W; spot size, 200 μm), and an argon source was used for sputtering, with zalar rotation at 1 rpm.

Device Testing

A solar simulator (150 W Newport 96000 xenon arc-lamp, with AM1.5G filter and diffuser lens) was calibrated to 100 mA cm⁻² using a silicon reference cell. J-V curves were obtained by applying an external bias to the devices and measuring the resulting photocurrent, with a Keithley 6487 picoammeter. External quantum efficiency (EQE) spectra were obtained from 300 nm to 1100 nm without bias illumination, and the useful range of data from ~ 300 nm to 900 nm was presented.

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