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Dye-sensitized near-infrared room-temperature photovoltaic photon detectors
Near-infrared photodetector consisting of J-aggregating cyanine dye and metal oxide thin films

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We demonstrate a near-infrared photodetector that consists of a thin film of the J-aggregating cyanine dye, U3, and transparent metal-oxide charge transport layers. The high absorption coefficient of the U3 film, combined with the use of a reflective anode and optical spacer layer, results in a zero-bias external quantum efficiency of 16.1 ± 0.1% (λ = 756 nm) for a device containing an 8.1 ± 0.3 nm-thick U3 film. The specific detectivity (D*) and response speed (f3dB) of a fully optimized device are measured to be (4.3 ± 0.1) × 1011 cm Hz1/2 W−1 and 92 kHz, respectively. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4752434]

Photodetectors (PDs) consisting of organic semiconductors, including solution-processed1,2 and thermally sublimed molecular materials,3 have attracted considerable research interest due to their potential for low-cost processing over large-area substrates and onto arbitrary surfaces.4-6 A promising approach toward realizing high performance in organic photodiodes is to utilize organic semiconductors that are engineered at the supramolecular level.7 The molecular arrangement in such materials may be controlled to realize desirable optical and electronic properties distinct from the molecular constituents. Of particular interest for optoelectronic devices are J-aggregated molecular crystals or “J-aggregates.” The formation of J-aggregates from cyanine dye monomers results in a red shifting and narrowing of the monomeric absorption feature.8 Additionally, peak optical absorption of J-aggregate thin films can be considerably higher than for non-J-aggregated organic semiconductors, with values for the optical absorption coefficient, α, exceeding 106 cm−1.9,10

The narrow and intense absorption features of J-aggregates are highly desirable in photodetector applications where wavelength specificity may be important. Moreover, the variety of available J-aggregate materials can enable PDs to be engineered to operate specifically at desired narrow wavelength ranges,11 spanning the visible and the near-infrared spectrum. Of particular interest in this regard is to realize detectors that operate at near-infrared wavelengths to enable applications such as night-vision imaging and biochemical sensing.12

Special consideration is warranted in the design of photodetectors that incorporate J-aggregate films. Due to their high optical absorption coefficients, very thin active layer films (<10 nm) may be used to absorb nearly all of the incident light. Also, in order to take advantage of the spectral narrowness of J-aggregate absorption, device structures with transport layers that are transparent at wavelengths outside of the J-aggregate peak are desirable. Finally, directionality in the ordering and packing of J-aggregate films may result in highly anisotropic exciton diffusion,13,14 which can have significant implications on the efficiency of donor-acceptor heterojunction devices.

Here, we demonstrate a near-infrared photodetector structure that consists of metal-oxide charge transport layers and that is optically sensitized by a thin film of the J-aggregating cyanine dye, U3 (molecular structure is shown in Fig. 1(a)). J-aggregates of U3 exhibit an absorption peak at wavelength λ = 790 nm and possess excellent photostability relative to other J-aggregating cyanine dyes.15 The structure of our U3 photodetector and its corresponding energy band diagram are shown in Figs. 1(b) and 1(c). ITO acts as both a top and bottom contact, while ZnO and MoO3 act as electron and hole transport layers, respectively. The MoO3 layer also serves to pin the Fermi level of the top contact to facilitate the extraction of holes from the U3 layer.16 The frontier energy levels for the U3 film were determined by cyclic-voltammetry and suggest the formation of a type-II heterointerface between the ZnO and U3 layers, suitable for the transfer of photo-generated carriers. A cyclic-voltammogram and details regarding the calculation of the energy levels are provided in the supplementary material23 (see Fig. S1). The MoO3 and top-ITO layers also constitute a transparent optical spacer between the U3 layer and the silver mirror. The thicknesses of these spacer layers can be chosen such that the U3 layer is situated at the anti-node of the optical electric field, thus maximizing absorption of the incident light.17

Films of U3 (purchased from Ryan Scientific and used without any further purification;CAS Number 202135-09-9) are prepared by dissolving U3 powder in ultrapure water and
spin-casting at 4000 RPM for 60 seconds on top of the ZnO layer. The ZnO surface is pre-treated in oxygen plasma prior to spin-casting. The thickness of the U3 film is varied from 1 nm to 15 nm by varying the concentration of the U3 solution from 2 mg ml$^{-1}$ to 10 mg ml$^{-1}$. Excess material is swabbed away from the edges of the substrate in order to ensure good electrical contact to the ITO electrodes. Further details regarding the fabrication of the U3 photodiode structures are provided in the supplementary material.

The device area, as defined by the anode-cathode overlap, is 1.2 mm$^2$. Current density-voltage ($J$-$V$) measurements are recorded by a Keithley 6487 picoammeter both in the dark and under illumination. For $J$-$V$ measurements under illumination, a Newport LPM-785 laser diode ($\lambda = 785$ nm) is directed through a beam expander, resulting in an illumination intensity of 1.7 mW cm$^{-2}$. For external quantum efficiency measurements, the sample is illuminated with optically chopped light from a monochromator that underfills the device area. The resulting AC photocurrent is measured with a SRS-830 lock-in amplifier.

A representative $J$-$V$ curve for a device containing a 10.5 nm-thick U3 film and a 60 nm-thick MoO$_3$ film is shown in Fig. 2(a). $J$-$V$ characteristics under dark conditions and fits to the generalized Shockley equation$^{18}$ for devices with different thicknesses of U3 are provided in Fig. S2 of the supplementary material.$^{23}$ The differential resistance ($R_D$), which is defined as the slope of the $J$-$V$ curve about zero-bias, is measured to be 170 k$\Omega$ cm$^2$. A high differential resistance is desirable, as it results in lower electrical noise and, consequently, a higher signal-to-noise ratio for a given value of responsivity. Under illumination at $\lambda = 785$ nm, we measure an opencircuit voltage, $V_{OC}$, of 0.4 V, a short-circuit current density, $J_{SC}$, of $1.12 \times 10^{-4}$ A cm$^{-2}$, and a fill factor of 0.43, making the device suitable for operation as a photodetector without an applied bias. The magnitude of $J_{SC}$ is found to follow a linear relationship with illumination intensity (see inset), which is also desirable in photodetector applications.

These performance characteristics are found to be highly sensitive to the thickness of the U3 film. For example, $R_D$ varies with the thickness of the U3 film from $5.8 \pm 1$ k$\Omega$ cm$^2$ for devices consisting of a 1 nm U3 film to $780 \pm 160$ k$\Omega$ cm$^2$ for devices consisting of a 15 nm-thick U3 film. Moreover, devices with a U3 film thickness of $<8.1$ nm exhibit a considerable reduction.
in $V_{OC}$ (see inset of Fig. 3(a)). These observations indicate that the presence of a high-quality U3 film is integral in this structure to realize high rectification as well as a photovoltaic response, both of which are critical to photodetector performance.

To characterize the photosensitivity of the device, we conducted spectrally-resolved measurements of external quantum efficiency (shown in Fig. 2(b)). Broadening of the U3 EQE peak relative to the J-aggregated quantum efficiency (shown in Fig. 2(b)). This broadening results in a blue-shift in the peak EQE from $\lambda = 790$ nm to $\lambda = 756$ nm. The magnitude of the peak EQE is found to be sensitive to the thicknesses of both the MoO3 optical spacer layer and the U3 film (see Figs. 3(a) and 3(b)). A maximum EQE of 16.1% ± 0.1% is obtained in a device consisting of a 60 nm MoO3 film and a U3 thickness of 8.1 ± 0.3 nm. The peak in EQE magnitude is observed to trail off for increasing thickness of U3 and MoO3 due to optical interference effects. The downward trend in EQE for thinner U3 film thicknesses (Fig. 3(a)) can be attributed to the reduction in film quality and the associated reduction in the photovoltaic performance, as shown in the inset of Fig. 3(a).

The peak internal quantum efficiency (IQE) is calculated by dividing the EQE measured in completed photodetector devices by the fraction of light absorbed in the U3 film (see supplementary material23 for more details). The peak in IQE of 25.8% ± 3% suggests that there is a substantial loss of photocurrent in the device. This loss is attributed to fast non-radiative recombination processes within the U3 film. More specifically, however, this loss can be related to the generation of excitons too far from the photactive region of the U3 film (further than $L_D$ from the ZnO/U3 interface). Such excitons will recombine before they are able to migrate to the donor-acceptor interface, thus preventing them from contributing to photocurrent. This implies that the exciton diffusion length in the direction normal to the U3 film is very low, since the total U3 film thickness is only 8.1 ± 0.3 nm.

To quantify the exciton diffusion length and to better understand the dependence of device performance on layer thicknesses, experimental EQE data was modeled using the optical transfer matrix formalism coupled with the one-dimensional diffusion equation.19,20 Optical constants for U3 films were measured using a Woollam WVase spectroscopic ellipsometer (see Fig. S4 in the supplementary material24), and calculations were performed using a custom MATLAB code. The model takes into account optical interference effects within the structure as well as exciton diffusion to an idealized U3/ZnO dissociating interface, as described by a parameter for the U3 exciton diffusion length ($L_D$). Exciton diffusion lengths were fitted from experimental EQE data using a least-squares algorithm as a function of both U3 and MoO3 thickness. We determine the exciton diffusion length within the U3 film to be $L_D = 2.0 ± 0.4$ nm (see Figs. 3(a) and 3(b)). We note that EQE data for devices consisting of the two thinnest U3 films were omitted from this fit as the low performance of these devices is related to degradation of diode rectification (and correspondingly high reverse-bias leakage current), which is not accounted for by our simple model. The data sets representing peak EQE as functions of U3 thickness and MoO3 thickness were fit separately and found to be consistent within the reported error. The theoretical EQE as a function of layer thickness, shown in a contour plot in Fig. 3(c), agrees with our experimental results and suggests that higher EQE could be obtained if U3 thickness could be reduced further without sacrificing the photovoltaic performance of the device.

We emphasize that the low exciton diffusion length extracted from our model applies for diffusion in the direction normal to the plane of the J-aggregate film. A high exciton diffusion length (>10 nm) is generally expected in J-aggregate...
materials due to the high degree of crystalline order relative to
disordered organic materials. A recent study of exciton-exciton annihilation within a different J-aggregate material, for
example, identified $L_D$ in the lateral direction to be greater than
100 nm. The low value for $L_D$ in the present case may be due
to a high degree of directionality in $L_D$ that arises from the
lamellar arrangement of the film, with diffusion in the more
ordered lateral direction being much more favorable. We note
that if J-aggregate systems that possess both large exciton
diffusion lengths in the direction normal to the film and high
optical absorption coefficients can be identified, IQEs
approaching 100% should be readily achievable in the simple
planar architecture described here.

To characterize the performance of this structure for
photodetector applications, we calculate the specific detec-
tivity, $D^*$, which is measured in units of cm Hz$^{1/2}$ W$^{-1}$ or
“Jones.” $D^*$ is a metric that describes the signal-to-noise
ratio of a photodetector and that is normalized to the detector
area. It can be calculated using the equation, $D^* = \left(\frac{\sqrt{A_D \Delta f}}{I_n}\right) \frac{R}{R_D}$, where $A_D$ is the active area of the device,
$I_n$ is the noise current, $\Delta f$ is the bandwidth over which the
noise current is measured, and $R$ is the responsivity. The
responsivities for devices of varying U3 thickness are shown in
Fig. 4(a). Since the present device is characterized with no
external bias, the only internal source of noise that we con-
consider is Johnson–Nyquist noise ($I_{J-N} = \sqrt{4kT \Delta f / R_D}$),
which results from random thermally-induced current fluctu-
ations. Measurements of $R_D$ for different U3 thicknesses are
also plotted in Fig. 4(a). The resultant calculations for $D^*$ are
shown in Fig. 4(b). Despite the fact that the peak responsivi-
ty occurs with a U3 thickness of 8.1 nm, $D^*$ is found to
increase monotonically and plateau for greater U3 thick-
nesses. The maximum $D^*$ achieved is $(4.3 \pm 0.4) \times 10^{12}$
Jones at $\lambda = 756$ nm for the device consisting of a 15 nm-
 thick U3 film and a 60 nm MoO3 film. This performance in
photosensitivity approaches that of comparable inorganic
technologies. For example, commercially available silicon
p-n photodiodes exhibit specific detectivity $>10^{12}$ Jones in
the near infrared wavelength range.

Finally, we characterize the response speed of the device.
A Newport LQA-785 diode laser (3.1 mW cm$^{-2}$ at $\lambda =
785$ nm) is modulated with a square wave from a function
generator, and the response from the device is recorded on a
Tektronix TDS3054B oscilloscope. The frequency roll-off at
zero applied bias for a device employing an 8.1 nm U3 film
layer thicknesses are shown in Fig. 4(a). The frequency for which the response is
attenuated by 3-dB is found to be $f_{3\text{dB}} = 91.5$ kHz, making the
device suitable for a wide range of photodetector applications.

In summary, we demonstrated a photodetector that
employs ZnO and MoO3 charge transport layers and that is
sensitized at near-infrared wavelengths by a thin film of the
J-aggregating cyanine dye, U3. The magnitude of the EQE is
found to be highly sensitive to both the thickness of a MoO3 opti-
cal spacer in the structure and to the thickness of the U3 film
itself. A maximum specific detectivity of $(4.3 \pm 0.4) \times 10^{12}$ at
$\lambda = 756$ nm is obtained for a device consisting of a 15 nm-thick
U3 film and a 60 nm MoO3 film. Modeling of experimental
EQE data as a function of layer thicknesses reveals that photo-
current is limited by the diffusion of photo-generated excitons
to the ZnO/U3 hetero-interface, and the exciton diffusion length
in the U3 film was determined to be $L_D = 2.0 \pm 0.4$ nm. This
work provides insights relevant to the use of J-aggregating dyes
in photodetector and photovoltaic applications and highlights
the importance of engineering the optical field profile within
such structures in order to maximize performance.

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![Graph](image-url)
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23See supplementary material at http://dx.doi.org/10.1063/1.4752434 for additional details regarding fabrication of the U3 photodiode structures, for the determination of frontier energy levels with cyclic voltammetry, for fitting J-V characteristics to an ideal diode equation, and for measurements of absorption and internal quantum efficiency.