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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 107 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

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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.\(^{23}\) 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 open-circuit 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

\[ \text{FIG. 1.} \text{ (a) Molecular structure of U3. (b) Device structure with direction of illumination indicated with arrows. (c) Energy band diagram of the structure. HOMO and LUMO levels for U3 are determined by cyclic-voltammetry. The remaining energy levels are taken from literature.} \]

\[ \text{FIG. 2.} \text{ (a) Current-voltage characteristic of a typical device in the dark and under illumination of 1.7 mW cm}^{-2}\text{ with }\lambda = 785\text{ nm light. U3 thickness is 10.5 nm and the MoO}_3\text{ thickness is 60 nm. (inset) }J_{SC}\text{ as a function of illumination intensity. A linear fit to the data (scatter plot) is shown in red (solid line). (b) External quantum efficiency of the same device as in (a), shown in red. Also shown are the absorption spectra of monomeric U3 (dotted line), measured in a 3.3 \mu g \text{ ml}^{-1}\text{ solution of ultrapure water, and J-aggregated U3 (black line), measured in a thin film spin-cast from solution with concentration of 8 mg ml}^{-1}\text{.} \]
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 U3 absorption spectrum is attributed to enhanced off-peak absorption due to the optical half-cavity present in the structure, as discussed in the supplementary material. 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\% $\pm$ 0.1\% is obtained in a device consisting of a 60 nm MoO3 film and a U3 thickness of 8.1 $\pm$ 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 material for more details). The peak in IQE of 25.8\% $\pm$ 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 photoactive 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 $\pm$ 0.3 nm.

To quantify the exciton diffusion length and to better understand the dependence of device performance on layer thicknesses, experimental IQE data was modeled using the optical transfer matrix formalism coupled with the one-dimensional diffusion equation. Optical constants for U3 films were measured using a Woollam WVase spectroscopic ellipsometer (see Fig. S4 in the supplementary material), 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 IQE 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 $L_D = 2.0 \pm 0.4$ nm (see Figs. 3(a) and 3(b)). We note that IQE 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 IQE as functions of U3 thickness and MoO3 thickness were fit separately and found to be consistent within the reported error. The theoretical IQE as a function of layer thickness, shown in a contour plot in Fig. 3(c), agrees with our experimental results and suggests that higher IQE 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 detectivity, $D^*$, 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 is normalized to the detector area. It can be calculated using the equation, $D^* = (\sqrt{A_D} \Delta f / I_n) R$, 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 $U_3$ 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 consider is Johnson–Nyquist noise ($i_{J-N} = \sqrt{4k_B T A_f / R_D}$), which results from random thermally-induced current fluctuations. Measurements of $R_D$ for different $U_3$ 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 responsivity occurs with a $U_3$ thickness of 8.1 nm, $D^*$ is found to increase monotonically and plateau for greater $U_3$ thicknesses. The maximum $D^*$ achieved is $(4.3 \pm 0.4) \times 10^{11}$ Jones at $\lambda = 756$ nm for the device consisting of a 15 nm-thick $U_3$ film and a 60 nm MoO$_3$ 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 $U_3$ film is shown in Fig. 4(c). The frequency for which the response is attenuated by 3-dB is found to be $f_{3-dB} = 91.5$ kHz, making the device suitable for a wide range of photodetector applications.

In summary, we demonstrated a photodetector that employs ZnO and MoO$_3$ charge transport layers and that is sensitized at near-infrared wavelengths by a thin film of the J-aggregating cyanine dye, $U_3$. The magnitude of the EQE is found to be highly sensitive to both the thickness of a MoO$_3$ optical spacer in the structure and to the thickness of the $U_3$ film itself. A maximum specific detectivity of $(4.3 \pm 0.4) \times 10^{11}$ at $\lambda = 756$ nm is obtained for a device consisting of a 15 nm-thick $U_3$ film and a 60 nm MoO$_3$ film. Modeling of experimental EQE data as a function of layer thicknesses reveals that photocurrent is limited by the diffusion of photo-generated excitons to the ZnO/$U_3$ hetero-interface, and the exciton diffusion length in the $U_3$ 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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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.