

Photodetectors based on treated CdSe quantum-dot films

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We demonstrate photodetectors of sandwich geometry active in the visible spectrum in which the active layer is a 200 nm thick film of CdSe quantum dots (QDs). The solution-phase treatment of the QD film with *n*-butylamine after casting greatly increases the exciton dissociation efficiency and charge-transport properties of the film. Under 110 mW/cm² illumination with light at $\lambda=514$ nm, the photocurrent to dark current ratio, $I_{\text{photo}}/I_{\text{dark}}$, is 10^3 at $V=0$ V, and the 3 dB frequency is ~ 50 kHz. At room temperature, we observe zero-bias external quantum efficiencies (EQE) from 0.08% to 0.23% in the wavelength range $\lambda=350$ nm to $\lambda=575$ nm, corresponding to an internal quantum efficiency (IQE) of $0.6\pm 0.1\%$ across the tested spectrum. At $V=-6$ V, EQE ranges from 15% to 24%, corresponding to an IQE of $70\pm 10\%$. © 2005 American Institute of Physics. [DOI: 10.1063/1.2136227]

Colloidal semiconductor nanocrystals, or quantum dots (QDs), have attracted considerable interest for use in optoelectronic devices. QDs can be synthesized using wet-chemical methods, they are solution processable, and their bandgaps can be tuned over a considerable range by varying the particle size. Thin films composed of QDs are thus attractive candidates for light-emitting devices (LEDs) and photodetectors in which large device area, substrate flexibility, and spectral selectivity are important.

One challenge in the incorporation of colloidal QDs in efficient optoelectronic devices is the poor transport properties of neat QD films. QD-LEDs in which a monolayer of QDs is inserted at the interface of organic host layers have been demonstrated to have efficiencies comparable to organic LED counterparts.¹ In this design, QDs do not participate appreciably in charge transport. However, monolayers of QDs have very low optical absorption efficiencies (on the order of 1% at the band edge). Consequently, thicker layers (on the order of 100 nm) have been used in existing reports of QD-based photodetectors and photovoltaics. Although there has been one study of sandwich-geometry devices made from neat films of CdSe QDs,² the general approach for making QD-based photodetectors and photovoltaics has been to use a bulk heterojunction design in which QDs are mixed at a high loading fraction (70% to 90% by weight) with a hole-transporting polymer.³⁻⁵ In this work, we augment the earlier understanding of QD photodetectors (QD-PDs) by demonstrating that QD-PDs containing neat multilayers of QDs, 200 nm thick, can efficiently detect visible light with response frequencies up to 50 kHz when the QD multilayers are chemically treated to increase film conductivity.

Our work builds on recent studies, the first of which were carried out in an electrochemical cell,^{6,7} that have

shown that *n*-type doping or solution-phase chemical treatments of neat QD films significantly increases film conductivity.⁸ Improvement in conductivity observed after treatment with bidentate ligands has been attributed to inter-dot cross-linking,⁷ but treatment with monodentate ligands with amine functionality has demonstrated similar improvement.⁸ Further, scattering data suggest that these treatments cause QD cores to move significantly closer together, facilitating more efficient exciton dissociation and subsequent tunneling of charge.⁸ We note that thermal annealing of neat QD films at high temperatures (~ 350 °C) can also lead to modest improvements in photoconductivity but at the expense of increased dark currents and broadening of the QD absorption spectrum.⁹

Quantum-dot photodetectors of structure ITO/PEDOT:PSS/QD (CdSe)/Ag were fabricated on precleaned glass substrates with a 115 nm thick layer (lithographically patterned before cleaning) of conductive indium-tin oxide (ITO) of sheet resistance 55 Ω /square. The conductive polymer poly-3,4-ethylenedioxythiophene doped with polystyrene sulfonate (PEDOT:PSS) was used both to planarize and to increase the work function of the ITO electrode. PEDOT:PSS was spin-coated as received (Starck) and baked at 110 °C for 30 min, yielding a 40 nm thick layer. CdSe QDs were synthesized and processed⁸ prior to spin casting on the PEDOT:PSS layer in a nitrogen atmosphere from a concentrated solution in chloroform. QDs were not over-coated because the higher-bandgap shell layer in core-shell structures increases the distance through which charge must tunnel to move from one QD core to a neighbor, decreasing the QD film conductivity. Partial devices with structure ITO/PEDOT:PSS/QD were treated in a solution of 0.1 M *n*-butylamine in acetonitrile.⁸ After treatment, the substrates were baked at 70 °C for 1 h to expel excess solvent, and the resulting CdSe QD film was 200 nm thick.¹⁰ A decrease in mean interparticle spacing from 1.1 nm to <0.5 nm as a result of this treatment has been observed previously.⁸ After

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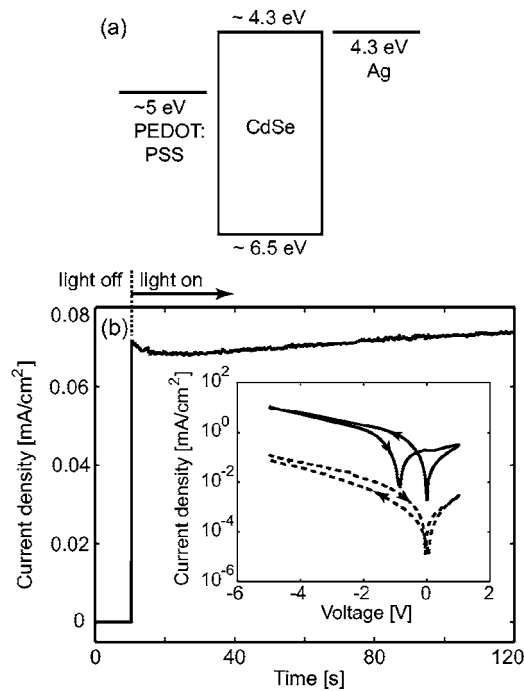


FIG. 1. (a) Energy-level diagram for a single-layer QD-PD. (b) Current response of QD-PD when exposed to 110 mW/cm^2 illumination at $\lambda = 514 \text{ nm}$, showing signal modulation due to charging within $\pm 5\%$. [Inset: Magnitude of current density versus voltage plots for QD-PD in the dark (dotted line) and under 110 mW/cm^2 illumination at $\lambda = 514 \text{ nm}$ (solid line). Positive voltage corresponds to the Ag electrode biased positive with respect to ITO.]

treatment, the Ag electrode (40 nm thick) was evaporated through a shadow mask at a pressure $< 10^{-6}$ Torr without exposing the partial device structure to air. The final device area was 1.22 mm^2 . For the reported measurements, all data were recorded at room temperature and in air.

Figure 1(a) shows the proposed energy-level diagram of our QD-PDs. Though the position of the ionization potential and electron affinity for CdSe QDs relative to vacuum has not previously been measured, the theoretically predicted electron affinity is likely near 4.3 eV ,¹¹ close to the work function of the Ag electrode. The work function of the PEDOT:PSS-coated ITO electrode is significantly larger at $\sim 5 \text{ eV}$,¹² consistent with the asymmetric I - V characteristics shown in the inset to Fig. 1(b). [Not depicted in Fig. 1(a) are the aliphatic ligands of large bandgaps that stabilize the surface of each QD but through which photogenerated charge must tunnel.]

Current-voltage characteristics and time-dependent photocurrent measurements were recorded with a semiconductor parameter analyzer (Agilent 4156c). Figure 1(b) shows the photocurrent stability of the device at zero bias over a two-minute span. After 10 s, the device was exposed to 110 mW/cm^2 illumination at $\lambda = 514 \text{ nm}$. The photoresponse shows good stability, with charging effects modulating the magnitude of the current response within $\pm 5\%$. Typical I - V characteristics in the dark (dashed line) and under illumination (solid line) are shown in the inset to Fig. 1(b), where the voltage on the abscissa corresponds to the voltage applied to the Ag electrode with respect to the ground ITO electrode. Devices typically experienced irreversible breakdown when the applied bias exceeded the limits of -5 and 1 V . While hysteresis was observed under illumination (with the large V_{oc} seen with the upward voltage sweep), there was appreciable photocurrent in steady-state operation at $V=0 \text{ V}$. The photocurrent to dark current ratio, I_{photo}/I_{dark} , is $\sim 10^2$ and reaches a maximum of 6×10^3 at $V=0 \text{ V}$. The I_{photo}/I_{dark} maximum is due to the very low dark current level at $V=0 \text{ V}$, an indication of poor charge injection from the contacts.

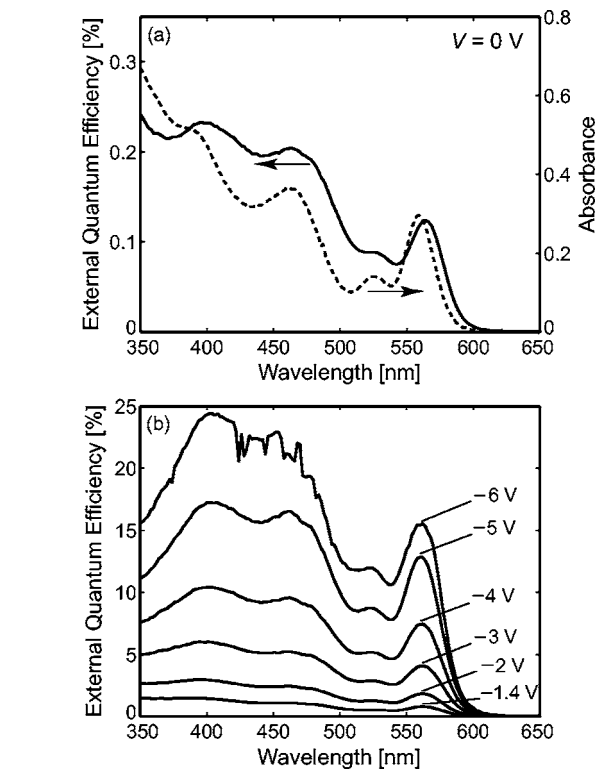


FIG. 2. (a) Plot of the external quantum efficiency (solid line) of a QD-PD at $V=0 \text{ V}$ as a function of wavelength and the absorbance spectrum (dashed line) of the constituent QDs in hexane. (b) EQE spectrum of a QD-PD with different biases applied to the Ag electrode relative to ITO.

The QD-PD external quantum efficiency (EQE) was measured using a lock-in amplifier, a calibrated Si photodetector, and wavelength-scanned monochromatic light generated by a Xe lamp and a monochromator. Figure 2(a) shows agreement between the EQE spectrum and the absorbance spectrum of constituent QDs in hexane, suggesting that the entirety of the photoresponse is from excitation of the QDs and subsequent exciton dissociation. At zero bias, the EQE is 0.13% at $\lambda = 560 \text{ nm}$, which, together with a device absorption (measured *in situ* for a complete device) of $\sim 20\%$ at the band edge peak, implies that the internal quantum efficiency (IQE) is $0.6 \pm 0.1\%$ across the measured spectrum. In Fig. 2(b), a source-measure unit was used to apply bias across the QD-PD, and photocurrent spectra were recorded as in Fig. 2(a). Biases as large as -6 V were applied, resulting in an EQE of 15% at $\lambda = 560 \text{ nm}$ and an IQE of $70 \pm 10\%$. Early signs of device breakdown are evident between $\lambda = 425$ and $\lambda = 475 \text{ nm}$ in the photocurrent spectrum taken at -6 V .

In a previous report, sandwich-geometry CdSe QD photodetectors displayed a persistent photocurrent of significant magnitude for hundreds of seconds after exposure to the excitation source ceased.² As a result of the reduced charge trapping of the chemically treated QD films, our devices display no such persistent photocurrent. QD-PD bandwidth was measured in the frequency domain using light ($\lambda = 514 \text{ nm}$) sinusoidally modulated in intensity with an acousto-optic

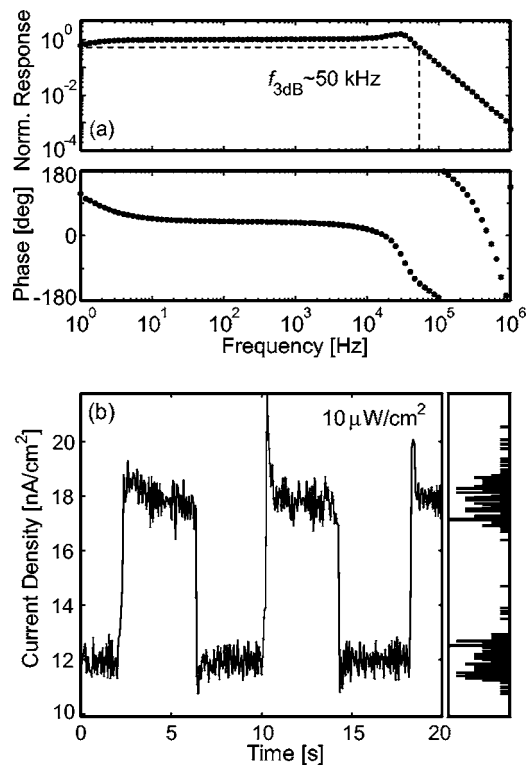


FIG. 3. (a) Normalized photocurrent (top) and phase (bottom) response at $V=0$ V as a function of frequency of sinusoidally modulated incident light at $\lambda=514$ nm. The 3 dB rolloff occurs at ~ 50 kHz. (b) Device response under manually modulated light ($\lambda=514$ nm) at $10 \mu\text{W}/\text{cm}^2$, measured with a parameter analyzer. A histogram of detected values is plotted at the right.

modulator and a lock-in amplifier (bandwidth >1 MHz). Figure 3(a) shows the normalized photocurrent (top) and phase (bottom) response from 1 Hz to 1 MHz for a device at $V=0$ V. The 3 dB rolloff occurs at ~ 50 kHz. Using a capacitance bridge, the capacitance of the device was measured to be 370 pF. The RC time constant of our device is likely limited by the carrier recombination lifetime within the QD film.

The detection limit of the system (device and measurement electronics) was determined at $V=0$ V, where we found $I_{\text{photo}}/I_{\text{dark}}$ to be highest. Using a parameter analyzer, the current response as a function of time was measured while manually modulating the incident light ($\lambda=514$ nm) at <1 Hz. We determined the detection limit to be $\sim 10 \mu\text{W}/\text{cm}^2$ using the $3\text{-}\sigma$ metric,

$$i_{\min} = \bar{i}_{\text{dark}} + 3\sigma_{\text{dark}}, \quad (1)$$

where i_{\min} is the minimum detectable signal and \bar{i}_{dark} and σ_{dark} are the mean and standard deviation of device readings in the dark, respectively. Figure 3(b) displays the response of the device to modulated $10 \mu\text{W}/\text{cm}^2$ light, and a histogram at the right shows that the photo signal and dark signal distributions are separated by roughly three standard deviations.

In summary, we have developed a method to produce CdSe QD photodetectors of sandwich geometry. These devices are solution processable and have the potential to be made large in area and on flexible substrates. The active layer is a close-packed film of QDs, and solution-phase chemical treatments of these films enables devices to be operated at room temperature with high quantum efficiency and bandwidth. The simple design of the present QD-PD structure provides a platform for studies of more complex QD-PD structures in both the visible and IR regions of the spectrum.

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