# Efficient polymer-nanocrystal quantum-dot photodetectors

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We have realized highly efficient photodetectors based on composites of the semiconducting polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] and PbSe nanocrystal quantum dots. The external quantum efficiency in these devices is greater than 1 for electric fields $E \sim 7 \times 10^5$ V/cm. The observed photocurrent gain could be attributed to the carrier multiplication in PbSe nanocrystal quantum dots via multiple exciton generation, and the efficient charge conduction through the host polymer material. This photocurrent gain is observed only when the PbSe nanocrystal band gap is at least three times smaller than the optical energy gap of the active polymer material. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1872216]

Conjugated polymers, nanocrystal quantum dots (QDs), and their composites have attracted the attention of researchers for the development of optoelectronic devices, such as light-emitting diodes (LEDs),[1,2] photovoltaics,[3,4] and optical information memory.[5] The tunable band gap of QDs makes them attractive for tailoring the visible and infrared absorption and emission of the light-sensitive layer of optoelectronic devices. Both conjugated polymers and nanocrystals are promising candidates for optoelectronic devices also because of their simple chemical syntheses and the easy processing methods such as spin-coating or doctor-blading.

PbS, CdTe, and CdSe QDs have been investigated in LEDs and solar cells.[1–4,6] Efficient excitation transfer from a conducting polymer to PbS QDs has been reported from photoluminescence measurements.[7] In comparison to CdSe or CdS QDs, the PbSe QDs show stronger quantum confinement due to their large exciton Bohr radius of ~40 nm and low effective hole and electron masses.[8] The band gap of PbSe QDs is tunable from ~0.5 to ~1.6 eV for QD diameters ranging from 9 to 3 nm. Recently, Schaller *et al.* have demonstrated the carrier multiplication in PbSe QDs by monitoring their transient absorption.[9] These transient absorption results have shown that the photogeneration of multiple excitons can occur via impact ionization (the inverse of Auger recombination)[10] for pumping photon energies $\geqslant 3E_g$, where $E_g$ is the band gap of PbSe QDs. For PbSe QDs with the absorption peak of ~1900 nm and diameter of ~8 nm, this corresponds to excitation wavelengths smaller than ~630 nm, still in the visible range. However, for QD sizes $\leqslant$4.5 nm, corresponding to the absorption peak of $\leqslant$1100 nm, the carrier multiplication should not occur for excitations in the visible range. This phenomenon of carrier multiplication can be exploited to realize efficient optoelectronic devices.

In this letter, we describe the fabrication and properties of efficient photodetectors based on the conducting polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and PbSe nanocrystal QDs. The optoelectronic devices made of pure MEH-PPV have limited quantum efficiency due to a low electron and hole mobility compared to those of inorganic materials.[11] When PbSe QDs are dispersed in the polymer host, with the absorption spectrum in the visible range, we observe a dramatic enhancement of the quantum efficiency of the polymer-based photodetectors. We show the photocurrent measurements for several devices consisting of different polymer-nanocrystal mixing ratios with polymer concentrations ranging from 50% to 100% of the total mass. We used two different sizes of PbSe QDs: one with the IR absorption peak at 1100 nm (1.13 eV) and the QD diameter ~4.5 nm, and the second with the absorption peak at 1900 nm (0.65 eV) and QD diameter ~8 nm. For excitation wavelengths from ~400 to 800 nm, quantum efficiencies greater than 1 (i.e., gain) are observed only in devices with the larger PbSe QDs, as expected.

Figure 1 shows the schematic diagram of the fabricated devices. The MEH-PPV/PbSe photodetectors were fabricated

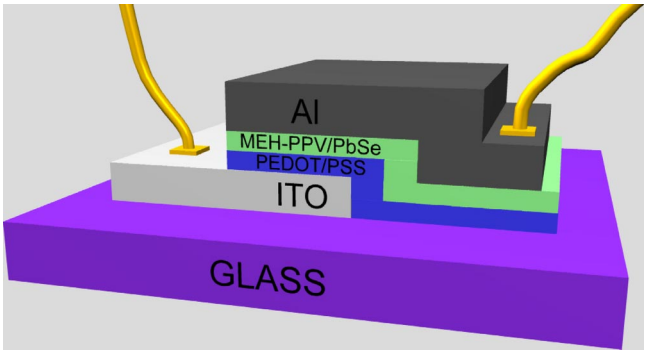


FIG. 1. (Color online) The schematic layout of the ITO/PEDOT:PSS/MEH-PPV:PbSe/Al photodetector on a glass substrate.

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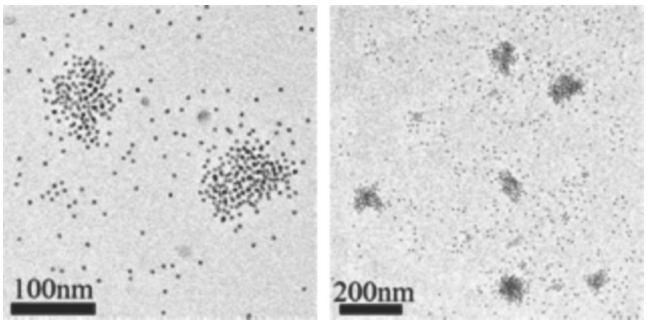


FIG. 2. TEM images of PbSe QDs (1900 nm) in the MEH-PPV host (95 wt % of MEH-PPV). The scale bars in the left and right images are 100 and 200 nm, respectively. Some aggregation of QDs into nonordered clusters is observed.

on 25 mm × 25 mm glass substrates precoated with a 150-nm-thick layer of indium tin oxide (ITO). A 60-nm-thick layer of poly(2,3-dihydrothieno(3,4-b)-1,4-dioxin/poly(styrenesulfonate) (PEDOT/PSS) was spin-cast on the ITO substrate in order to improve the charge transport through the device. The active layer of the photodetector was also spin-cast from the MEH-PPV/PbSe mixed solution. The MEH-PPV, a soluble derivative of poly(p-phenylene vinylene) was used as a host for the PbSe QDs. PbSe QDs were capped with 2-nm-long oleic acid ligands. The MEH-PPV was dissolved in chlorobenzene and purified with a 5 $\mu$m syringe filter. The MEH-PPV and PbSe QDs were mixed to make films with 99.7, 99, 97, 95, 90, 83, and 50 wt % of MEH-PPV. Another device with pure MEH-PPV was fabricated for comparison. The average thickness of polymer-nanocrystal blended films was about 60 nm, as measured by a stylus profilometer (Tencor Alpha Setup 500). The samples were stored in vacuum overnight to completely remove the residue solvent. Finally, an aluminum top electrode was fabricated using thermal evaporation through a shadow mask. The active area of the photodetector was about 0.07 $cm^2$(~3 mm × 2.3 mm).

Figure 2 shows the transmission electron microscope (TEM) images of PbSe QDs dispersed in MEH-PPV. The molecular weight of MEH-PPV ($M_w \approx 86\,000$) indicates that the average degree of polymerization of MEH-PPV is ~334; that is, 334 units in one molecule backbone. One repeating unit of MEH-PPV is ~8 Å.[12] The average molecular length of MEH-PPV is ~267 nm. The size of PbSe QDs is 8 nm and the absorption peak is at 1900 nm. The PbSe QDs were capped with a 2-nm-long oleic acid ligand to prevent aggregation and to provide a good dispersion of PbSe QDs in MEH-PPV host.

The current-voltage characteristics were measured in air with a picoammeter (Keithley 6487) remotely controlled via a general purpose interface bus (National Instrument). The samples were measured immediately after the external leads were attached to the electrodes using a silver paste. The sample degradation in air happens on time scales longer than the time scales of our measurements. The monochromatic light was generated with a monochromator (Thermo Oriel) coming from a 100 W tungsten lamp. The optical power was read with a multifunction optical power meter (Spectra-Physics). The photocurrent densities of MEH-PPV/PbSe (1900 nm; 99.7, 99, 97, 95, 90, 83, and 50 wt % of MEH-PPV) photodetectors and a pure MEH-PPV device in the dark and under the illumination with a 510 nm, 68 $\mu W/cm^2$

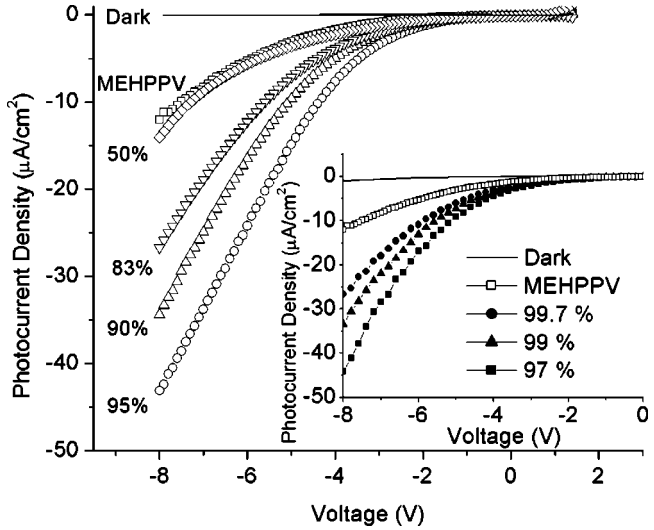


FIG. 3. Photocurrent density of MEH-PPV/PbSe (1900 nm) photodetectors with 95 wt % (circles), 90 wt % (upward triangles), 83 wt % (downward triangles), 50 wt % of MEH-PPV (diamonds), and pure MEH-PPV (squares) under the illumination with 510 nm monochromator light with a power density of 68 $\mu W/cm^2$. The dark current (solid line) for all devices is similar and $<10^{-7}$ A. Inset: Photocurrent density for devices with 97 wt % (dark squares), 99 wt % (dark triangles), 99.7 wt % (dark circles), 100 wt % of MEH-PPV (open squares), and dark current (solid line).

monochromatic light are given in Fig. 3. For all the measured devices, the dark current was $<10^{-7}$A at reverse bias voltages $0 > V > -8$ V; that is, one to two orders of magnitude lower than the photocurrent.

From Fig. 3 we see that there is a range of polymer weights in the mixture, around 95±2 wt %, for which the photocurrent is optimal. This corresponds to ~95 wt % of the polymer and ~5 wt % of the QDs. In contrast, the devices with ~50 wt % polymer and 100 wt % polymer show smaller photocurrents. When the amount of QDs is large (>50 wt %), the photoconduction through the film decreases. We have measured the photocurrent in pure PbSe QDs arrays separately, and it is several orders of magnitude lower than in the polymer-nanocrystal films. The presence of significant amounts of the conducting polymer appears to help the charge transport, while the exciton generation can occur in both the polymer and the QDs. We speculate that the concentration of QDs should be low enough to allow for many QDs to be well separated. Figure 3 (inset) shows photocurrent for four devices from 97 to 100 wt % of polymer. The photocurrent is largest for 97 wt % and decreases as the polymer content is increased to 100 wt %.

The external quantum efficiency (EQE) of a photodetector is defined as $EQE = hcI/e\lambda P$, where $I$ is the photocurrent, $P$ is the power of monochromatic light with wavelength $\lambda$ falling on the photodetector, $h$ is Planck's constant, $e$ is the electron charge, and $c$ is the speed of light in vacuum. In Fig. 4 we show the EQEs of MEH-PPV/PbSe (1900 nm) and MEH-PPV/PbSe (1100 nm) composite photodetectors with the same polymer weight percentage (95 wt %), but two different QD diameters. The maximum EQE of the MEH-PPV/PbSe (1900 nm, 95 wt % of MEH-PPV) composite at −8 V is ~150%, more than three times higher than the maximum EQE of a pure MEH-PPV device (see Fig. 4). The maximum EQE of the MEHPPV/PbSe (1900 nm, 95 wt % of MEH-PPV) composite at −4 V is 30%. The gain (i.e., EQE greater than 100%) at −8 V applied to the ITO electrode was ob-

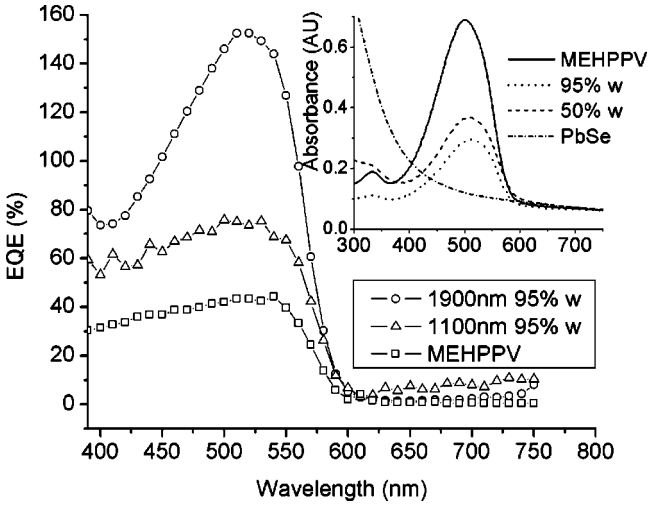


FIG. 4. Comparison of external quantum efficiencies of the MEH-PPV/PbSe QD photodetectors at −8 V: pure MEH-PPV (squares), MEH-PPV/PbSe (1100 nm) (triangles), and MEH-PPV/PbSe (1900 nm) (circles). Inset: UV-visible absorption spectrum of MEH-PPV:PbSe blended films on glass slides with 95 wt % (dots), 50 wt % (dashed line), pure MEH-PPV film (solid line), and PbSe QDs in solution (dash-dot line).

served in the devices with MEH-PPV/PbSe 99, 97, 95, and 90 wt % of MEH-PPV, and not in devices with 99.7, 83, and 50 wt % of polymer. It is assumed that in the MEH-PPV, one photon generates only one exciton. If the photon energy is larger than the optical band gap of the polymer, the excess energy will not contribute to the generation of additional charge carriers. An EQE greater than 1 indicates that the gain could be due to carrier multiplication via multiple excitons in PbSe QDs. This is in agreement with recent results in Ref. 9. In MEH-PPV/PbSe (1900 nm, 95 wt % of MEH-PPV) composite photodetectors the EQE reaches a maximum value of ~150% at 510 nm, close to the reported threshold[9] for formation of triple excitons.

Figure 4 (inset) shows the optical absorption of the pure MEH-PPV film, the MEH-PPV/PbSe QD blended films, and of the solution of the pure PbSe QDs measured with a UV-visible spectrophotometer (Agilent Technologies). The absorption peak of MEH-PPV is ~498 nm. The absorption peaks of all MEH-PPV/PbSe (1900 nm) composites are red-shifted to ~505 nm (shift of ~35 meV on energy scale), due to the presence of PbSe QDs.

In order to confirm that the observed photocurrent gain could result from the appropriate choice of nanocrystal diameters, we have fabricated MEH-PPV/PbSe photodetectors with smaller PbSe QDs. For these devices, we used QDs with diameters ~4.5 nm, corresponding to the main absorption peak at ~1100 nm. Because the estimated onset energy for carrier multiplication in these QDs is ~2.38 eV or ~367 nm, the photocurrent gain should not exist for the light excitations in the wavelength range from ~370 to ~800 nm. In Fig. 4 we show the experimental results confirming that the efficiency is less than 100% for the MEH-PPV/PbSe (1100 nm, 95 wt % of MEH-PPV) composite photodetectors. We observed similar results for devices with 90, and 83 wt % of the polymer. The EQE of all the devices (1100 nm) with the polymer weight percentages of 95, 90, and 83 is significantly less than 100%, so that no gain is observed.

In conclusion, we have realized efficient polymer-nanocrystal QD photodetectors for visible light based on a semiconducting polymer and QDs, with absorption in the visible and infrared ranges, respectively. By choosing a suitable size of QDs, we can tailor the photoresponsivity spectrum of the composite devices in the visible range.

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