Narrowband Colloidal Quantum Dot Photodetectors for Wavelength Measurement Applications

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ELECTRONIC SUPPLEMENTARY INFORMATION

Materials

All chemicals were of the highest purity available unless otherwise noted and were used as received. Lead oxide (PbO, 99.999%), oleic acid (technical grade 90%), 1-octadecene (ODE, technical grade 90%), bis(trimethylsylil)sulfide (TMS, synthesis grade), tetrabutylammonium iodide (TBAI, 99%) were purchased from Sigma-Aldrich. Sulfur (S, 99%) was purchased from Strem Chemicals. All solvents were anhydrous and were used as received. Acetone (99.8%) was purchased from Merck. Hexane (95%), methanol (99.8%), tetrachloroethylene (99%), and toluene (99.8%) were purchased from Sigma-Aldrich.

QDs synthesis

In a typical synthesis yielding rock salt PbS QDs, 2 mmol of PbO (450 mg) and 6 mmol (1700 mg) of oleic acid were mixed in 10g of 1-octadecene. The mixture was vigorously stirred and deaerated through repeated cycles of vacuum application and purging with nitrogen at about 80 °C. The mixture was then heated to above 100 °C to allow dissolution of PbO until the solution became colorless and optically transparent, suggesting the complete formation of lead(II)-oleate complex(es). The solution was cooled to 80°C and repeatedly subjected to vacuum in the attempt of removing water eventually released upon lead(II)-oleate complex formation. The solution was then heated again under nitrogen flow at 110 °C. When the temperature was stabilized, 1 mmol of the sulfur precursor (bis(trimethylsilyl)sulfide; 210 µL) in 2 mL of octadecene was swiftly injected. The heating mantle was immediately removed and the resulting colloidal dispersion was allowed to cool to room temperature. After the synthesis, PbS QDs were transferred to a nitrogen-filled glove box. The QDs were precipitated using excess acetone (about 1:4 vol/vol), centrifuged at 4000 rpm and then redissolved in toluene. Two additional precipitation-redissolution cycles were performed by using methanol and toluene, respectively; an estimate of solvent volumes (about 4 mL of toluene to dissolve the QD pellet and 2 mL of methanol to precipitate the QDs) is crucial to obtain subtly purified QDs, although inherently empirical. The PbS QD size was varied by changing the amount of oleic acid (from two to sixteen equivalents) added to PbO, keeping constant its total concentration in the reaction flask; eventual dilution yielded larger nanocrystals. Oleylamine (2 mmol) was added to the Pb-oleate precursor to obtain PbS QDs with diameters below 2.5 nm. Stock solutions with QD concentration of ~ 1 mM were prepared and stored at room temperature in the glove box for subsequent use. We synthesized different QDs with diameters ranging from 2.0 nm to 4.7nm, corresponding to excitonic absorption peaks between 700 nm and 1400 nm. Fig. S1 shows the TEM micrographs of the four different QDs, from the smaller (a) to the bigger (d).



Fig. S1. TEM micrographs of the as synthesized QDs. A, b, c, and d panels represent 2.0nm, 2.7nm, 3.2nm and 4.7nm QDs, respectively.

Device and filter fabrication

Photoconductors were fabricated spin-casting the QD dispersion onto the prepatterned substrate at 3000 rpm for 30"; subsequently, a drop of a tetrabutylammonium iodide (TBAI) solution in methanol was deposited onto the substrate for ligand exchange and the exchange reaction was carried out for 1'; finally, the device was rinsed with isopropanol to remove excess ligand and other organic residues. The deposition procedure was repeated 10 times to obtain a QD film with a thickness of ~ 300nm. Finally, devices were annealed at 100 °C for 1h. The whole fabrication procedure was carried out in air. The QD dispersions were also employed for the fabrication of optical filters by drop-casting onto glass substrates. We drop-cast three layers of QDs making the solvent evaporate in vacuum after each deposition. The deposition was carried out on a planar surface and the glass substrate was rotated after every deposition step in order to keep the thickness of the QDs film as uniform as possible over the whole substrate. No ligand exchange and thermal annealing were employed for the fabrication of the filters, thus we expect the QDs in these films to be covered with (Pb-)oleate species. Fig. S2 shows the schematic structure of the fabricated devices together with their responsivity spectra.



Fig. S2. Schematic structure and responsivity spectra of the fabricate devices. Device #1-4 are plain photoconductors, devices #5-14 are photoconductors provided with optical filters.

Characterization methods

TEM images were recorded with a Jeol Jem 1011 microscope operated at an accelerating voltage of 100 kV. Samples for analysis were prepared by dropping a QD solution onto carbon-coated Cu grids and then allowing the solvent to evaporate in a vapor controlled environment. QD diameters were determined by statistical analysis of TEM images of several hundreds of QDs with the ImageJ software.

Optical absorbance measurements of the as synthesized QDs where carried out on QD dispersions in tetrachloroethylene with a Varian Cary 5000 UV-Vis-NIR spectrophotometer.

Optical absorbances of the QD filters on glass were measured with a custom monochromator setup, measuring the intensity of the impinging, reflected and transmitted optical radiation. The absorbance was calculated according to eq. 1, where A is the absorbance and I_{ν} I_{R} and I_{T} are the impinging, reflected and transmitted optical intensities.

$$A = -\ln\left(\frac{I_{T} - (I_{I} - I_{R})}{I_{R} - I_{I}}\right)$$
(1)

The current-voltage and responsivity-voltage characteristics of the photodetectors where acquired with a Keithley Source-Measure Unit (SMU2602B) and illuminating the devices with a focused laser radiation at 632.8nm (HeNe laser). In order to measure the responsivity vs. optical power characteristics, the intensity of the laser radiation was varied by means of a series of calibrated optical filters.

The responsivity-wavelength characteristics were measured illuminating the devices with the light coming from a monochromator. Light was modulated by means of a mechanical chopper and the photocurrent signal was amplified with a custom-made trans-impedance amplifier and read out with a Stanford Research SR830 lock-in amplifier.

Devices and filters characterization

We characterized the QD dispersions in terms of optical absorbance; fig. S3a shows the normalized absorbance on the first excitonic peak. Optical measurements were carried out on QD dispersions in tetrachloroethylene with a UV-Vis NIR spectrophotometer. As expected, the absorption edge of the as-

synthesized QDs is strongly dependent on their size and ranges from 750 nm to 1400 nm. QD diameter was determined by electron transmission microscopy imaging.



Fig. S3. Normalized absorbance of the as-synthesized CQD solutions (a) and deposited on glass substrates (b)

We also measured the absorption spectra of the QD-on-glass optical filters (fig. S3b). After the deposition process no significant shifts of the position of the excitonic peaks have been observed, confirming that, during the filter fabrication, no appreciable QD size or surface chemistry modification occurs.

Evaluation of the wavelength-meter performance

We tested several different filter types for the evaluation of the performance of the wavelength-meter system. The responsivity spectra of the 14 devices could be effectively combined to obtain different types of filter as shown in fig. S4. In particular, we tested ideal high-pass, ideal low-pass, ideal band-pass and gaussian band-pass filters. The performance of the different filters were evaluated in terms of mean and maximum error in the determination of the peak wavelength of a quasi-monochromatic radiation. Results are shown in fig. S5 and table S1.



Fig. S4. Ideal (blue line) and calculated (red line) R_{eq} for three different filter types. Ideal high-pass (a), ideal band-pass (b) and gaussian band-pass (c). The gaussian band-pass filter has σ²=10nm.



Fig. S5 Calculated peak wavelength vs. theoretical peak wavelength.

Filter type	Mean absolute error	Max absolute error	Mean % error
LP	14nm	93nm	0.87%
HP	14nm	94nm	0.87%
Ideal BP	17nm	103nm	1.1%
Gaussian BP	14nm	95nm	0.87%

Table S1. Calculated errors for the peak wavelength identification.

Nonlinear responsivity normalization

In the 10nW-10⁴nW power range, the R-P characteristics can be accurately described by a power law as shown in eq. 1, where α and γ are constant values, depending only on the type of QDs employed for the realization of the active layer of the photodetector, and P is the impinging optical power.

$$R = \alpha P^{\gamma} \tag{2}$$

Thus, the wavelength dependent responsivity of each one of the 14 photodetectors can be expressed as in eq. 3, where Rn is the normalized reponsivity.

$$R(\lambda) = R_n(\lambda)\alpha P^{\gamma}$$
(3)

In turn, the total optical power impinging onto a photodetector and participating to the photocurrent generation process can be estimated as in eq. 4 representing the overlap integral of the power density spectrum $S(\lambda)$ and the responsivity spectrum, where λ_M is the maximum wavelength at which Rn>0.

$$P_0 = \int_0^{\lambda_M} R_n(\lambda) S(\lambda) d\lambda$$
(4)

Where δ is a Dirac delta and λ_0 is the peak wavelength. The total photogenerated current can be expressed as in eq. 5.

$$I_{ph} = \int_{0}^{\lambda_{M}} R(\lambda) S(\lambda) d\lambda$$
(5)

Substituting eq. 3 and 4 in eq. 5 we obtain eq. 6.

$$I_{ph} = \int_{0}^{\lambda_{m}} R_{n}(\lambda) \alpha \left(\int_{0}^{\lambda_{M}} R_{n}(\lambda) S(\lambda) \delta \lambda \right)^{\gamma} S(\lambda) d\lambda = \alpha \left(\int_{0}^{\lambda_{M}} R_{n}(\lambda) S(\lambda) \delta \lambda \right)^{\gamma} \int_{0}^{\lambda_{M}} R_{n}(\lambda) S(\lambda) d\lambda$$
(6)

From which we can express the photocurrent as in eq. 7.

$$I_{ph} = \alpha \left(\int_{0}^{\lambda_{M}} R_{n}(\lambda) S(\lambda) \delta \lambda \right)^{\gamma + 1}$$
(7)

A normalized photocurrent, independent of the impinging optical power, can be calculated from eq. 7, resulting in eq. 8.

$$I_{norm} = \exp\left(\frac{\ln\left(I_{ph}\right) - \ln\left(\alpha\right)}{\gamma + 1}\right) = \int_{0}^{\lambda_{M}} R_{n}(\lambda)S(\lambda)\delta\lambda$$
(8)