Supporting information

Flexible photovoltic cell based on graphene-CdSe quantum dot nanocomposite

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1. Experimental procedure

G-CdSe film preparation:

Graphene oxide (GO) was produced by acid oxidation of natural graphite based on the modified Hummers method.[1, 2] The fabrication of mercaptopropionic acid (MPA) capped CdSe QD can be found in our previous work.[3] In brief, oleic acid (OA)-capped CdSe QDs in toluene solution was synthesized by one-pot growth method. In a three-neck flask, a 70 ml octadecene (ODE) solution containing 5.54 g OA and 0.51 g CdO was firstly heated to 180 ºC to form a clear solution under N_2 atmosphere. The solution was then heated up to 260 ºC. TOP-Se solution (1.3 mmol Se powder and 0.5 g trioctylphosphine dissolved in 10 ml ODE, stirred for more than 1 hour) was quickly injected into the flask (within 40 seconds). The reaction was kept for 30 sec, 60 sec and 90 sec, respectively, to obtain 2.7 nm, 3.3 nm and 4.1 nm CdSe QD. Thereafter, methanol and acetone were added to the mixture to precipitate QDs, which were then dissolved in toluene for storage purpose. OA ligand was exchanged with mercaptopropionic acid (MPA) ligand for polarization. 1 mL purified OA-capped CdSe QD in toluene solution containing approximately 50 mg of CdSe QDs in powder form was first mixed with 1 mL MPA and 1 mL acetone in a vial, then stirred continuously for 30-40 min. Ethanol was then added, followed by centrifugation at 3500 rpm for 5 min, and the supernatant fluid was discarded. The resulting precipitate containing MPA-capped CdSe QDs was dissolved in ethanol and some tetramethylammonium hydroxide (TMAOH) in methanol was added in order to get the clear products. Thus, CdSe QDs transform from the nonpolar solvent to polar solvent, which was then mixed with graphene aqueous solution.

The synthesis procedure of poly(diallyldimethylammonium chloride) (PDDA) modified graphene sheets were described as follows.[4] 100 µL of 20 wt% PDDA solution was added into 20 ml of 1.0 mg/ml GO solution and stirred for 30 min. Then the prepared PDDA-GO dispersion was mixed with 200 µL 80% hydrazine hydrate at 95 ℃ for 24 h under stirring. The resulting PDDA modified graphene sheet was obtained through filtration and washing with de-ionized water. Afterwards, the modified graphene solution was mixed with MPA capped CdSe solution with the volumetric ratio of 1:1 under sonication for 1 h. The final product was rinsed with water and isolated through centrifugation.

The synthesized G-CdSe aqueous solution (0.2 mM) was then transferred to a small vial in which polyethylene terephthalate (PET)/indium-tin-oxide (ITO) and Pt substrates were kept at a distance of 5 mm using constant current density of 0.001 mA for 10 min. Finally, the uniform G-CdSe film was coated on the flexible substrate. For further improvement of the cell performance, G-CdSe films were carried out for post deposition treatment of coating by a thin layer of ZnS. Briefly, photoelectrodes were dipped for three cycles of 1 min in 0.1 M aqueous solutions of zinc acetate and sodium sulfide.

Flexible QDSSCs fabrication: QDSSCs were fabricated with Pt sputtered PET/ITO as the counter electrode, a thermal-plastic spacer, and an electrolyte solution, which is composed of 1 M Na_2S and 1 M S. QDSSCs fabricated with 2.7 nm, 3.3 nm and 4.1 nm CdSe QDs were named as cell 2.7, cell 3.3 and cell 4.1, respectively.

Measurement: High resolution TEM images were taken by JEM-2010 (JEOL) with accelerated voltage of 120 kV. The absorption spectra were recorded using a SHIMADZU MPC-2200 UV-vis Spectrometer. XRD patterns of the products were collected out on a X-ray diffractometer with Cu-Ka radiation (λ =1.54056 À). The incident photon to current conversion efficiency (IPCE) was measured with a QE/IPCE measurement kit (Oriel, U.S.A.) in the wavelength range of 300 to 700 nm. Current density-voltage (*I-V*) characteristics were measured with a Keithley 2440 sourcemeter under 100 mW/cm^2 (AM 1.5 G) illumination from a solar simulator (Abet-technologies, U.S.A.).

2. Raman spectra

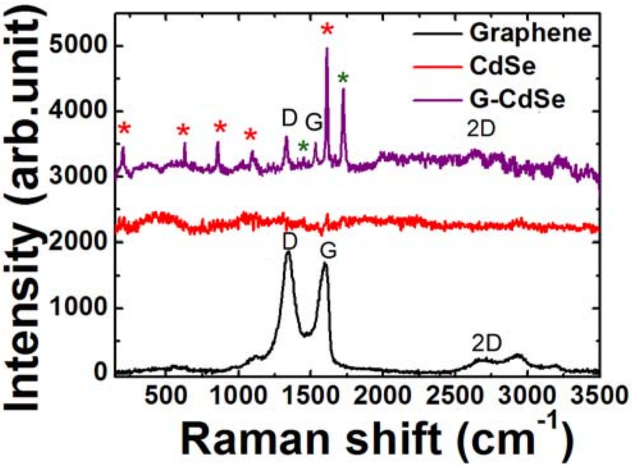

Figure S1. Raman spectra of graphene sheets, MPA-capped CdSe, and G-CdSe film taken using a 514 nm excitation laser. The characteristic peaks for MPA-CdSe QD were indicated in red star and peaks for PDDA in green star.

Raman spectra were used to investigate the interaction between the CdSe QDs and graphene sheets on PET/ITO substrate. An excitation laser of 514 nm was used, which is close to the absorption peak at 562 nm for MPA-CdSe. Thus, the characteristic peaks of MPA-CdSe can not be observed. However, the PL intensity was largely reduced for G-CdSe film. Therefore, peaks for G-CdSe film can be observed. Raman peak of CdSe was found at 201 cm^{-1}, which correspond to the CdSe longitudinal optical (LO) phonon.[5] Raman peaks located at 1091 cm^{-1} ν_s(COO$^-$) and 1609 cm^{-1} ν_{as}(COO$^-$), indicating MPA molecular is chemisorbed CdSe as a carboxylate onto Cd ions on CdSe QD surface. And peaks located at 628 cm^{-1} ν(C-S)$_G$ and 860 cm^{-1} (C-S), indicating the formation of Cd-S-C-C chain.[5] Raman peaks located at 1670 cm^{-1} ν(C-N) and 1440 cm^{-1} for CH_2 bending vibrations, which reflected the presence of PDDA.

The graphene sheets exhibit characteristic peaks located at approximately 1588 cm^{-1} (G band) and 1346 cm^{-1} (D band), which are assigned to the E_{2g} phonon of sp^2 carbon atoms and the breathing mode of κ-point phonons of A_{1g} symmetry, respectively.[6] For G-CdSe film, the G band and D band of graphene shifted to higher wavenumbers of 1592 cm^{-1} and 1349 cm^{-1} due to the CdSe QD was significantly quenched by graphene sheets.

3. AFM analysis

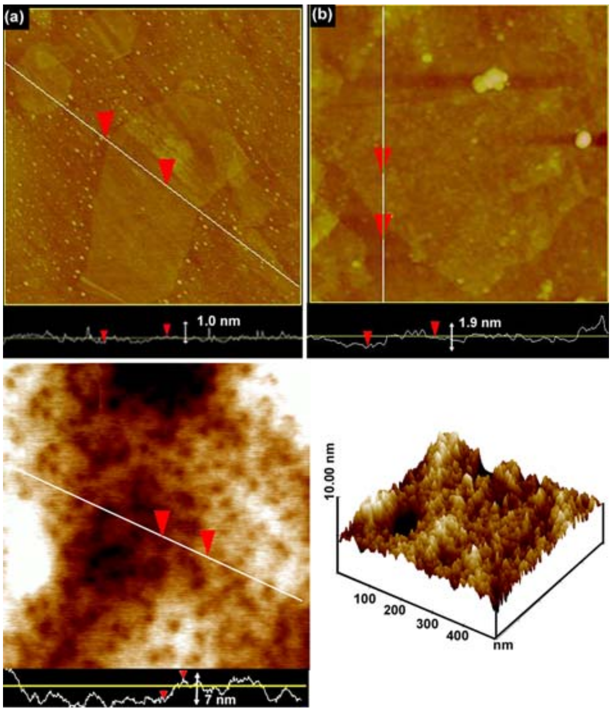

Figure S2. Tapping mode AFM images of (a) graphene sheets; (b) PDDA modified graphene; (c) G-CdSe film; (d) cross-sectional analysis of G-CdSe film. All of the samples were processed by spin-coating method on silicon substrate. The insets in (a)-(c) are the height profiles taken along the white lines marked in the corresponding AFM images.

From Figure S2, it can be seen that the morphology of graphene changes significantly after modifying with PDDA. Some small and uniformly distributed island-like nanostructures appear. Moreover, the thickness of graphene has a significant increase after modifying with PDDA. The height of the CdSe deposits varied from 5 to 7 nm as determined by AFM height scans.

4. Electron transfer rate constant analysis

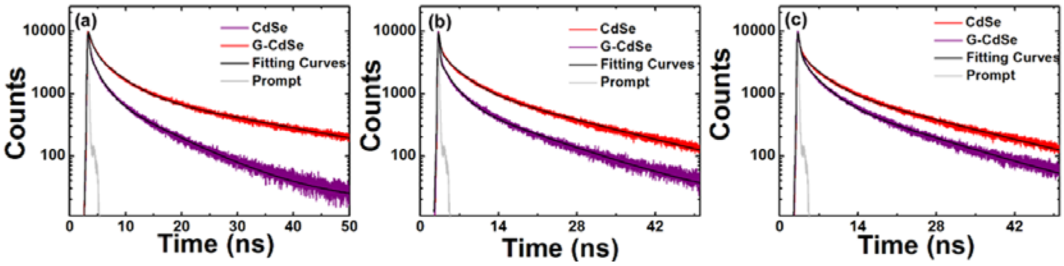

Figure S3. Emission decay of CdSe films cast on glass and G-CdSe films cast on ITO glass with CdSe QD sizes of (a) 2.7 nm (b) 3.3 nm and (c) 4.1 nm, respectively, using 373 nm excitation.

Table S1 Triexponential fit parameters.

Size	Film	α_1	τ_1 (ns)	α_2	τ_2 (ns)	α_3	τ_3 (ns)	<τ> (ns)
2.7 nm	CdSe	683.79936	3.80381	131.58852	7.50992	3607.57091	0.3771	3.6
	G-CdSe	861.40296	1.62158	986.01447	0.40301	3083.82949	0.33295	0.98
3.3 nm	CdSe	1691.024	1.039276	374.8916	0.556827	70.87779	12.18225	4.4
	G-CdSe	1231.598	1.769913	1871.552	0.362393	28.49445	4.256528	1.6
4.1 nm	CdSe	1154.486	1.91865	429.965	8.191	1604.256	0.42128	5.2
	G-CdSe	265.824	7.19558	1130	1.83095	1760	0.53841	3.7

These values were used to estimate the average lifetime of CdSe emission decay using the expression:[7]

$$< \tau >= \alpha_1\tau_1^2 + \alpha_2\tau_2^2 + \alpha_3\tau_3^2 \Big/ \alpha_1\tau_1 + \alpha_2\tau_2 + \alpha_3\tau_3$$

The average rate constant for the electron transfer can be estimated by the expression:

$$\kappa_{et} = 1\big/\tau_{G-CdSe} - 1\big/\tau_{CdSe}$$

The multiexponential decay shows that the average emission lifetimes of CdSe alone for 2.7 nm, 3.3 nm and 4.1 nm diameter particles are 3.6 ns, 4.4 ns and 5.2 ns, respectively. A decrease in the average emission lifetime was observed for G-CdSe film with corresponding average lifetimes of 0.98 ns, 1.6 ns, and 3.7 ns for 2.7 nm, 3.3 nm, and 4.1 nm diameter CdSe QDs, respectively. Thus, an average electron transfer rate constant from 6.4×10^8~7.8×10^7 s^{-1} as varying the sizes of QDs from 2.7 nm to 4.1 nm can be calculated.

References

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