Supplementary Information

Incorporation of graphene in quantum dot sensitized solar cell based on ZnO nanorod

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1. Experimental details

Glass substrates (15 mm×30 mm) coated with fluorine-doped tin dioxide (FTO) were ultrasonically cleaned in de-ionized water, acetone, and isopropanol, and were dried at 100 °C in an atmospheric pressure oven. After that, FTO glass were treated with a 3% solution of (aminopropyl) triethoxysilane (APTES) in tolunene at room temperature for 1 h., and dried under a nitrogen stream to 15 form an APTES adhesion layer¹.

Oleic acid (OA)-capped CdSe QDs in toluene solution was synthesized by one-pot growth method.² 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 °C to form a clear solution under N₂ atmosphere. After that, it was heated up to 260 °C. TOP-Se solution (1.3 mmol Se powder and 0.5 g trioctylphosphine dissolved in 10 ml ODE, stirred more than 1 hour) was quickly injected into the flask (within 40 seconds). The heater was

20 removed 1.5 minutes later to stop the reaction. Then methanol and acetone were added to precipitate QDs, which were then dissolved in toluene/acetonitrile for storage. The CdSe toluene/acetonitrile solution (0.2 mM) was transferred to a small vial in which two graphene-ZnO electrodes were kept at a distance of 5 mm, and a dc voltage (35 V) was applied using the Sourcemeter. After 3-4 min, CdSe QDs were loaded on graphene-ZnO electrode.

The ZnO/CdSe photoanode was fabricated for comparison. Pt was sputtered on ITO as the counter electrode, a thermal-plastic 25 spacer applied, and an electrolyte solution consisting of 0.1 M I₂, 0.1 M LiI, 0.5 M terbutylpyridine, and 0.6 M 1-hexyl-3methylimidazolium iodide in methoxy-acetnnitrile was introduced. Herein, QDSSCs consisting of ZnO/CdSe and graphene-ZnO/CdSe are defined as cell A and B, respectively.

2. Instruments.

30 The absorption spectra were recorded using a SHIMADZU MPC-2200 UV-VIS Spectrometer. Current density-voltage (J-V) characteristics were measured with a Keithley 2440 Sourcemeter under 100 mW/cm² (AM 1.5 G) illumination from a solar simulator (Abet-technologies, U.S.A.). Electrochemical impedance spectra (EIS) were measured under open-circuit voltage with an oscillation voltage amplitude of 10 mV for frequencies from 10^{-1} to 10^{6} Hz. Emission lifetimes were measured using the Horiba Jobin Yvon single photo counting system with a 467 nm diode. The morphologies were investigated using a field-emission

as scanning electron microscope (FESEM) and a field-emission gun transmission electron microscope (Tecnai G2 F30).

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3. schematic of the fabrication graphene-ZnO nanorod photoanode



Figure S1. Schematic of the fabrication of graphene-ZnO nanorod photoanode (a) graphene sheets on FTO glass substrate after reduction treatment. (b)ZnO seeds were deposited on graphene sheets by spray pyrolysis (c) ZnO nanorods were grown vertically based on graphene sheets by hydrothermal ⁵ method.

4. Morphology of ZnO nanorod grown on different thickness of graphene film

The morphology of ZnO nanorod on graphene thin film is different from that without graphene. The surface ratio of ZnO nanorod grown on few-layered graphene is higher than that without graphene thin films. The density of ZnO array is obviously decreased with the increased thickness of graphene sheets. The surface morphology of ZnO nanostructure is varied by the growth ¹⁰ substrate. Mono- and few-layered graphene sheets with large surface areas and step edges could provide more nucleation centers for nanorod growth.³ However, when the graphene forms to a thicker film (thickness of ~20 nm), the density of ZnO nanorod is decreased largely due to the lattice mismatch between the ZnO seed and the graphene sheets.⁴



Figure S2 FESEM images of ZnO nanorod grown on graphene thin film with thickness of (a) 0 nm (b) ~2.6 nm (c) ~9 nm and (d) ~20 nm.

5. XRD spectra of graphene-ZnO



Figure S3 XRD spectra of graphene, graphene-ZnO seed, and graphene-ZnO nanorod

Figure S3 shows the XRD spectra of graphene, graphene-ZnO seed, and graphene-ZnO nanorod. From XRD spectra of ⁵ graphene-ZnO seed, the peaks at 20 values of 31.8, 34.4, 36.3, 47.5, 56.6, 62.9 and 68.1° are consistent with the hexagonal phase wurtzite ZnO (JCPDS No. 89–0511). The diffraction peaks at 26.3, 42.4, and 46.3°can be attributed to graphene. After ZnO nanorod was grown, the strongest intensity of the (002) peak confirms the preferential anisotropic growth of ZnO along the [001] direction on the graphene films.

6. AFM images of graphene thin films with different thicknesses

To investigate the charge transfer properities of graphene in QDSSCs, uniform graphene thin films were deposited on top of the FTO/glass by spin coating and were subsequently reduced. Atomic force microscope (AFM) topography images of graphene thin films of four different thicknesses are shown in Figure S4(a)-(d). The average thicknesses of the four samples were estimated to be ~1 nm, ~1.8 nm, ~2.6 nm and ~9.0 nm with corresponding surface rms roughness values of 0.35, 0.55, 0.73 and 1.54 nm, respectively. With increasing film thickness, micrometer-long wrinkles and creases developed [Figure S4(b)-(d)]. The AFM image of ZnO seeds deposited an graphene thin film (thickness of 1.8 nm) shows a uniform covering of grains with size of ~100 nm [(Figure S4(e)]. The optical transmission spectra of graphene thin films deposited on FTO/glass substrates shown in Figure S4(f) show that graphene does not significantly alter the transparency of the FTO/glass substrate. After deposition of ZnO seeds on graphene thin film, the optical transmission intensity is largely decreased.



²⁰ Figure S4. Tapping mode AFM height images of spin-coated graphene films in a $1 \times 1 \mu m$ field with the thickness of (a) 1.0 nm (b) 1.8 nm (c) 2.6 nm. (d) AFM image of spin-coated graphene films in a $3 \times 3 \mu m$ field with the thickness of 9.0 nm. (e) Tapping mode AFM height images of ZnO seed deposited

on graphene film with thickness of 1.8 nm in a 3×3 μ m field. (f) Corresponding optical transmission spectra of the four graphene films deposited on FTO/glass substrate, and ZnO seed deposited on graphene film with thickness of 1.8 nm.

7.TEM image of graphene

Figure S5 shows the TEM image of graphene sheet and inset shows the corresponding selected area electron diffraction pattern s (SAED). The SAED spot patterns of the graphene layer reveals that the crystalline order of the original graphene lattice is present over at least a few nanometers⁵.



Figure S5.TEM image of graphene, inset shows the SAED pattern

10 8. EDX of ZnO/CdSe

The red line on the TEM image indicates the path of scanning electron beam. With the distance increasing, the concentration of Zn is increased to the maximum value then decreased, while the Cd amount drops slightly at the centre of ZnO nanorod. It is indicated that the CdSe QDs are uniformly attached on the surface of ZnO nanorod.



15 Figure S6. EDX of ZnO/CdSe (a) High angle annular dark field STEM image of ZnO/CdSe. (b) and (c) EDS line-scanning analysis for Zn and Cd element.

9. EIS measurement

Figure S7 shows the typical Nyquist plots for cell A and B. Inset of Figure shows the equivalent circuit and the table shows the resistances results. The obtained impedance spectra were fitted using Z-view software. R_s is a series resistance for the cell; R_1 is the recombination resistance R_r , CPE₁ is a constant phase element representing the chemical capacitance, R_2 represents the charge

- ²⁰ transfer resistance between the counter electrode and the redox couple and CPE_2 takes into account the capacitance of the electrolyte-counter electrode interface. Two semi-circles exist in the high-frequency region and middle-frequency region for both cells. It was reported that the middle-frequency reflects the properties of the photoinjected electrons with the oxide semiconductor.⁶ The semi-circle size in the middle-frequency region for cell B is decreased significantly compared to that for cell A, indicating an increased electron transfer rate at the photoanode. From Figure S6, it can be seen that the series resistance (R_s)
- $_{25}$ value, which is composed of R_s and R_2^{-7} , is highly reduced based on graphene-ZnO photoanode compared to pure ZnO photoanode. Therefore, the FF vlaues for cell B is increased.



Figure S7. Nyquist plots of QDSSCs of cell A and B. Inset is the Bode phase plots.

Table S1. QDSSCs performance (Vac, Jac, FF, PCE) taken from the I-V characteristics under illumination100 mW/cm² (AM 1.5 G).

Graphene thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PC (%
None (cell A)	0.566	3.37	40.9	0.78
1.0 (cell B)	0.598	4.65	61.8	1.72
1.8	0.584	4.44	53.4	1.38
2.6	0.582	3.57	52.2	1.08
9.0	0.572	2.30	47.5	0.63

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Table S2. Triexponential fit parameters.

CdSe film	α_1	$\tau_1(ns)$	α2	$\tau_2(ns)$	α3	τ_3 (ns)	<τ>(ns)
CdSe on glass	0.506	2.34	0.237	14.1	0.58	9.7	10.2
CdSe on ZnO	0.227	1.55	0.826	1.28	0.892	6.1	6.4
CdSe on graphene-ZnO	0.24	0.53	0.44	2.2	0.314	9.99	4.3

The emission decay is multi-exponential because the distribution of the recombination rate constants influences the decay kinetics. Tri-exponential decay kinetics have been reported to reasonably describe carrier lifetimes.⁸

These values were used to estimate the average lifetime of CdSe emission decay using the expression⁸:

 $15 < \tau >= \alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2 / \alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3$

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

$$\begin{split} \kappa_{_{et(ZnO)}} &= 1/\tau_{_{(CdSe/ZnO)}} - 1/\tau_{_{(CdSe)}} \\ \kappa_{_{et(Graphene-ZnO)}} &= 1/\tau_{_{(Graphene-ZnO/CdSe)}} - 1/\tau_{_{(CdSe)}} \end{split}$$

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