

Assembly of CdSe nanoparticles on graphene for low-temperature fabrication of quantum dot sensitized solar cell

Shengrui Sun, Lian Gao, Yangqiao Liu, and Jing Sun

Citation: *Appl. Phys. Lett.* **98**, 093112 (2011); doi: 10.1063/1.3558732

View online: <http://dx.doi.org/10.1063/1.3558732>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v98/i9>

Published by the [American Institute of Physics](http://www.aip.org).

Related Articles

Development of pulsed laser deposition for CdS/CdTe thin film solar cells

Appl. Phys. Lett. **101**, 153903 (2012)

Simulation of non-linear recombination of charge carriers in sensitized nanocrystalline solar cells

J. Appl. Phys. **112**, 074319 (2012)

Enhanced carrier transport by defect passivation in Si/SiO₂ nanostructure-based solar cells

Appl. Phys. Lett. **101**, 153902 (2012)

Optimization of antireflective zinc oxide nanorod arrays on seedless substrate for bulk-heterojunction organic solar cells

APL: Org. Electron. Photonics **5**, 226 (2012)

Optimization of antireflective zinc oxide nanorod arrays on seedless substrate for bulk-heterojunction organic solar cells

Appl. Phys. Lett. **101**, 153301 (2012)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.

[LEARN MORE](#)

Assembly of CdSe nanoparticles on graphene for low-temperature fabrication of quantum dot sensitized solar cell

Shengrui Sun, Lian Gao,^{a)} Yangqiao Liu, and Jing Sun

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, People's Republic of China

(Received 24 September 2010; accepted 31 January 2011; published online 2 March 2011)

Quantum dot sensitized solar cell (QDSSC) was fabricated in a low-temperature process based on graphene-CdSe composite, which was prepared by the procedures of immobilizing CdSe on graphene oxide (GO) and reduction in GO. It was found that the charge separation between excited CdSe and graphene could be tapped to generate photocurrent from photocurrent measurements, which established the ability of graphene to collect and transport electrons. By optimizing the CdSe-to-GO ratio at 4.5:1, the obtained graphene-CdSe-based cells exhibited significantly higher short-circuit photocurrent and energy conversion efficiency (5.8 mA/cm² and 0.72%, respectively) than the reported values of the C₆₀ or carbon nanotube related QDSSC, demonstrating that the graphene-CdSe composite is an attractive candidate in energy conversion devices. © 2011 American Institute of Physics. [doi:10.1063/1.3558732]

Classical quantum dot sensitized solar cells (QDSSCs), constructed by narrow band gap semiconductor QDs, nanocrystalline metal oxides, electrolytes, and counter electrode, have attracted many researchers' interest because of QDs' tunable absorption spectra, high molar extinction coefficient, and chemical stability.¹⁻³ Although the theoretical efficiency of QDSSCs is as high as 44%,⁴ the practical performance still lags behind that of DSSCs at present. One reason is the existence of surface state in QDs, which can capture photoinduced electrons and lead to recombination of carriers. Moreover, if the surface state is located below the conduction band (CB) of photoanode material, injection of photoinduced electrons into photoanode will be inhibited, therefore limiting the amount of photoinduced electrons collected by conducting substrate and reducing the photocurrent density of QDSSCs. In a word, capturing photoinduced electrons as quickly as they are generated and transporting them to the conducting substrate with an efficient method is the big challenge in QDSSCs system. Kamat and co-workers⁵⁻⁷ have reported that carbon nanotube (CNT) and fullerene (C₆₀) could be used to collect and transport photoinduced electrons in QDSSCs. Compared with CNTs and C₆₀, graphene with high surface areas, low manufacturing cost, and excellent electron mobility have been proved to be more suitable for application as conductive network.⁸⁻¹⁰ Besides, work function of graphene is in the range of 4.42–4.5 eV, which is much lower than the CB of many metal oxide photoanode material such as TiO₂, ZnO, and so on. Therefore, more effective electron injections are expected to occur into graphene than into traditional nanocrystalline metal oxides. In our previous work, we incorporated graphene into TiO₂ as photoanode of DSSCs and found it could effectively improve the photocurrent density of DSSCs by providing fast electron transfer paths and prolonging electron lifetime.¹¹ In this study, we employed the graphene as conducting scaffolds to anchor CdSe QDs for light harvesting and constructed QDSSCs. Considering the excellent exciton generation properties of CdSe and the electron capture and transport charac-

teristics of graphene, we believe graphene-CdSe composite has the potential to show unique photoelectrochemical performance in QDSSCs.

In this letter, 0.7 mmol of Cd(NO₃)₂·4H₂O was added to 120 ml distilled water. A specific amount of graphene oxide (GO) solution prepared by Hummers method¹² was mixed with the Cd(NO₃)₂ solution, by controlling the weight ratio of GO to CdSe at 1: 1.5, 1: 4.5, and 1:9, respectively. Then 0.7 mmol of freshly prepared sodium selenosulfate solution (Na₂SeSO₃) was dripped in with stirring. The pH value was adjusted to 10–14 using NH₄OH. Finally, hydrazine hydrate was added and GO-CdSe was reduced to graphene-CdSe. The composite obtained was denoted as X-CdSe-GR, where X (1.5, 4.5, and 9) referred to the corresponding CdSe /GO weight ratio. Figure 1(a) presents the x-ray diffraction (XRD) result of 9-CdSe-GR composite prepared. The main

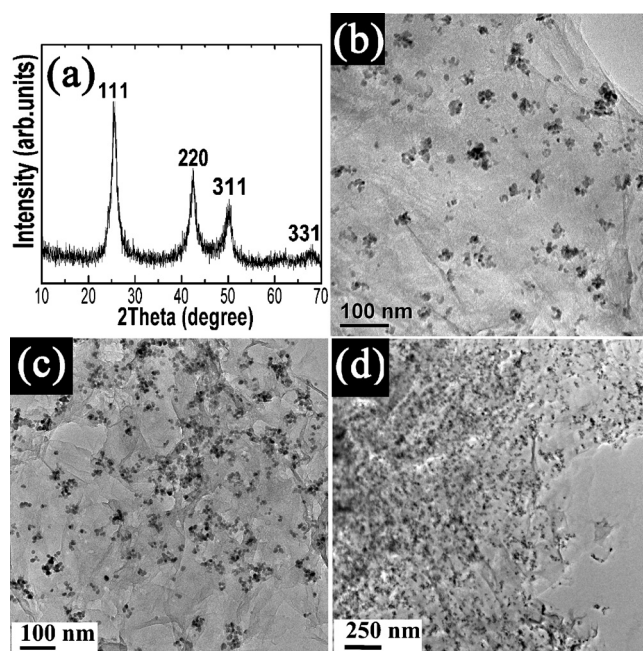


FIG. 1. (a) XRD patterns of 9-CdSe-GR composites. TEM micrographs of (b) 1.5-CdSe-GR, (c) 4.5-CdSe-GR, and (d) 9-CdSe-GR composites.

^{a)} Author to whom correspondence should be addressed. Electronic mail: liangao@mail.sic.ac.cn.

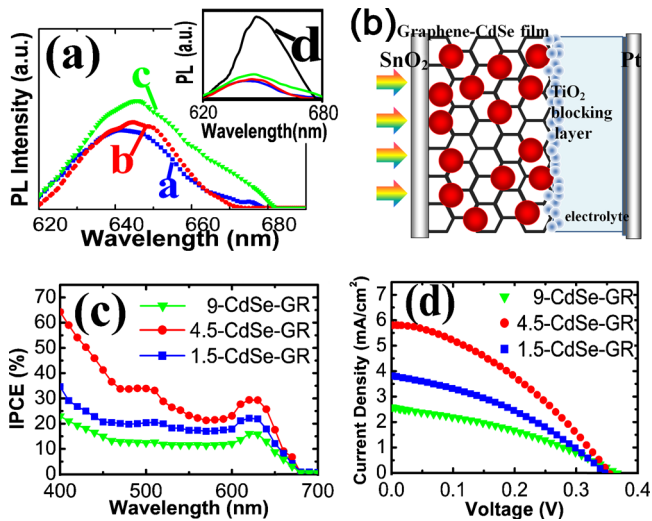


FIG. 2. (Color online) (a) PL spectra of graphene-CdSe composites with a CdSe-to-graphene ratio of 1.5:1 (curve a), 4.5:1 (curve b), and 9:1 (curve c) (excitation wavelength 480 nm). The inset is the PL spectra of CdSe (curve d) and the above composites, (b) structure illustration for QDSSC, (c) IPCE spectrum of, and (d) J-V characteristics of the QDSSCs based on different graphene-CdSe composites.

diffraction peaks of (111), (220), and (311) crystal planes could be detected in the pattern, which correspond well with the values of cubic CdSe (JCPDS 19-0191). Figures 1(b)–1(d) show the transmission electron microscope (TEM) images of graphene coated by QD CdSe. The graphene sheets are thin and contain wrinkles and rolled edges on surface. The coated QDs CdSe has uniform size and spherical shape with average diameters of 7 nm. With the weight ratio of CdSe to GO changing from 1.5 to 9, an increased coating density was observed. The graphene sheets are only partly coated in Figs. 1(c) and 1(d) and the CdSe QDs are mono-dispersed on the surface of graphene. This structure makes full use of graphene network with large surface areas to connect QDs CdSe particles as much as possible. Then, the amount of linked CdSe on graphene network further increases when the ratio of CdSe/GO is 9. And some of CdSe QDs form certain aggregates. Although a higher surface coverage of QDs on graphene surface can improve the efficiencies of QDSSCs, this aggregate caused by CdSe packing indicates the presence of additional internal carriers recombination losses,¹³ which is undesired.

TEM images of graphene-CdSe composites show graphene is dispersed into the matrix of CdSe to form the large two-dimensional network. In order to investigate the effect of the network, we studied the charge transfer of the graphene-CdSe composites following band gap excitation by photoluminescence (PL) spectra and the results are shown in Fig. 2(a). Peng and co-workers³ have reported that CdSe QDs with size of 7 nm exhibit absorption in the visible and show excitonic transition at ~ 640 nm. When excited at 480 nm, the CdSe QDs exhibit strong band edge emission while the PL emissions are significantly quenched in graphene-CdSe composites, just as shown in the inset of Fig. 2(a), corresponding to the expected electron injection from CdSe to graphene. For 9-CdSe-GR, the aggregate of CdSe with unavoidable internal recombination losses gives birth to relatively intensive PL peak at ~ 640 nm. Then increasing the amount of graphene, it shows a decreased emission for 4.5-CdSe-GR and 1.5-CdSe-GR. These quenching of the PL

intensity are related with the depression of photoinduced charge carriers' recombination.^{14,15} As an alternative transport pathway for photoinduced electrons, more graphene implies that the recombination of carriers is suppressed. It is consistent with the expected electron injection from excited CdSe to graphene. The result suggests that graphene network could serve as a good conducting scaffold to capture and transport photoinduced charge carriers.

The above results pave the way for graphene-CdSe composites used in photovoltaic applications. We prepared graphene-CdSe photoanode films according to the method proposed by Wu *et al.*¹⁶ Amorphous TiO₂ (A-TiO₂) nanoparticles prepared by the hydrolysis of titanium(IV) isopropoxide and the graphene-CdSe composites were dispersed in distilled water, respectively, and sequentially filtered using the ester membranes until a thin film was formed on the membrane. Then the film-on-membranes were transferred onto fluorine-doped SnO₂ (FTO) substrates and dried in vacuum at 60 °C for 12 h. After washing with acetone and dried at 60 °C, sandwiched FTO/graphene-CdSe/A-TiO₂ structured films were obtained and used as the photoanodes. Finally, they were assembled into QDSSCs with counter electrode of Pt sputtered on FTO and electrolyte consisting of 0.5 M LiI, 0.05 M I₂, and 0.5 M TBP in CH₃CN. The structure is presented in Fig. 2(b). Different from the traditional QDSSCs, a working electrode was constructed by sensitizers of QDs CdSe and conductive paths of graphene. And there is a layer of A-TiO₂ between the CdSe and the electrolyte, working as blocking layer to protect QDs from corrosive by electrolyte.¹⁷ We used the incident photo to current conversion efficiency (IPCE) and photocurrent density-voltage (J-V) curves to study the energy conversion properties of the QDSSCs.

IPCE was measured with spectral response measuring equipment (CEP-1500, Japan) and the curves obtained with 1.5-CdSe-GR, 4.5-CdSe-GR, and 9-CdSe-GR show similar trends from 400 to 700 nm and exhibit peak at ~ 630 nm, as shown in Fig. 2(c). Considering the absorption spectra corresponding to the QDs with 7 nm³, the characteristic peak indicates the sensitized effect of QDs in light harvesting and exciton generation. For 9-CdSe-GR, the quantum efficiency of the peak is 16.0%. Then it increases to 29.4%, at the same time the quantum efficiencies are considerably enhanced over the whole spectral range for 4.5-CdSe-GR. With the ratio of QDs CdSe to GO decreased to 1.5, the value decreases to 22.1%.

J-V curves of the QDSSCs based on different graphene-CdSe composites are presented in Fig. 2(d), carried out using 100 mW/cm² (AM 1.5) simulated light irradiation (YSS-80A, Japan) with a scan rate of 10 mV/s. The light source was Xe lamp equipped with infrared filter. In addition, we prepared films of graphene and CdSe QDs on SnO₂ substrate, whose related photovoltaic parameters are listed in Table I. It is observed that the short-circuit photocurrent density (J_{sc}) for graphene-CdSe composites is markedly greater than that of graphene and CdSe QDs. The enhanced photocurrent confirms that it is not a simple additive effect for graphene and CdSe QDs, but rather a result of the significant ability for graphene in capturing and transporting photoinduced electrons of CdSe QDs. Therefore J_{sc} further increases from 2.61 to 5.80 mA/cm² with the ratio of GO to QDs CdSe increasing from 1: 9 to 1:4.5. However, further increas-

TABLE I. Photovoltaic parameters of QDSSCs based on different graphene-CdSe composites, graphene and CdSe QDs.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	Eff (%)
1.5-GR-CdSe	3.83	0.346	36.73	0.487
4.5-GR-CdSe	5.80	0.354	36.91	0.76
9-GR-CdSe	2.61	0.365	35.06	0.33
Graphene	0.15	0.192	32.13	0.009
CdSe	0.06	0.423	64.34	0.016

ing the ratio of GO to QDs CdSe, the cell with 1.5-CdSe-GR shows J_{sc} decreasing to 3.83 mA/cm². This phenomenon may be due to the serious competitive light harvesting by too much graphene. The J-V measurement was repeated four times with an interval length of 1 min and it shows similar results, indicating the graphene-CdSe composites in the QDSSCs are photostable.

Compared with the C₆₀ and CNTs-related cells with low overall energy conversion efficiency ($\eta < 0.1\%$) and $J_{sc} (< 0.5 \text{ mA/cm}^2)$ reported previously,^{5,6} the graphene-CdSe nanocomposite film in our work shows a greater enhancement in J_{sc} and η , which reach 5.80 mA/cm² and 0.72% for the cell prepared with 4.5-CdSe-GR, respectively. The great improvement results from two reasons. On one hand, work function of graphene is lower than the CB of QDs CdSe. This energetic arrangement favors the photoinduced electron transfer from excited CdSe to graphene, just as shown in Fig. 3. On the other hand, graphene has an electron mobility of 10⁴ cm²/(V s) at room temperature¹⁸ and a low conductive percolation threshold of about 0.1 vol %.¹⁰ Hence, in our QDSSCs system, an excellent conductive network of graphene with large electron transfer rate was obtained to extend electron mean free paths and escape charge recombination, ensuring electrons can be collected effectively by SnO₂ substrate to produce photocurrent. In a word, the efficiency of graphene in capturing and transporting electrons from QDs CdSe is more remarkable than other carbon nanostructures, confirmed by the above results. For A-TiO₂ blocking layer, though the position of the valence band (VB) edge are not exactly known, some similar situation have been reported^{17,19} and confirmed that A-TiO₂ layer could work as a blocking layer to protect QDs without blocking hole injection from QDs into electrolyte. It is probable that the VB of A-TiO₂ is located close to the QDs ground-state level,¹⁷ so hole can be extracted from CdSe to electrolyte, keeping the transmigration of electron and improving the stability of QDSSCs.

Although we optimized the ratio of graphene to CdSe in this work, we believe that the QDSSCs performance may be

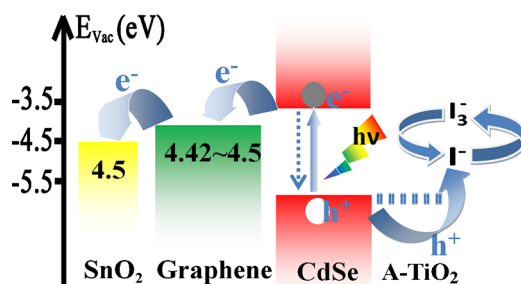


FIG. 3. (Color online) Schematic diagrams for the energy level matching.

substantially improved by optimizing factors such as size of QDs for better energy level alignment, reduced resistance between the substrate and graphene-CdSe film, and more favorable electrolyte. In addition, some previous work referring QDs sensitizers have been carried out to immerse electrode film into QDs solution to absorb them onto electrode²⁰ or with the method of chemical and electrophoretic deposition.^{5,6,17} Compared with those, the way preparing films in our work can control the amount of sensitizers conveniently and increase the surface coverage of QDs effectively. Meanwhile, it is processed at low temperature which might be explored for QDSSC with flexible conductive substrate.

In summary, graphene-CdSe composite has been prepared with the method of chemical bath deposition and used to fabricate graphene-CdSe films at low temperature for assembly of QDSSC without traditional wide band gap semiconductor material. Through a study of TEM images and PL spectra, we found that increasing the amount of graphene could decrease the aggregation of QDs CdSe and inhibit charge recombination. In QDSSC system, graphene network could work as an excellent conducting scaffold to capture and transport photoinduced charge carriers, which has been proven by IPCE and J-V measurements. This study also optimized the weight ratio of GO to CdSe and found that J_{sc} and η increased to 5.80 mA/cm² and 0.76%, respectively, for the QDSSCs with 4.5-CdSe-GR. The low temperature fabrication process greatly benefits the preparation of flexible solar cells.

The project was supported by the National Basic Research Program (Grant No. 2005CB623605), National Natural Science Foundation of China (Grant No. 51072215), and the Shanghai Institute of Ceramics (Grant No. SCX200709).

¹A. P. Alivisatos, *Science* **271**, 933 (1996).

²P. V. Kamat, *J. Phys. Chem. C* **112**, 18737 (2008).

³W. W. Yu, L. H. Qu, W. Z. Guo, and X. G. Peng, *Chem. Mater.* **15**, 2854 (2003).

⁴V. I. Klimov, *J. Phys. Chem. B* **110**, 16827 (2006).

⁵P. Brown and P. V. Kamat, *J. Am. Chem. Soc.* **130**, 8890 (2008).

⁶B. Farrow and P. V. Kamat, *J. Am. Chem. Soc.* **131**, 11124 (2009).

⁷I. Robel, B. A. Bunker, and P. V. Kamat, *Adv. Mater. (Weinheim, Ger.)* **17**, 2458 (2005).

⁸C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj, *Angew. Chem., Int. Ed.* **48**, 7752 (2009).

⁹J. B. Wu, H. A. Becerril, Z. N. Bao, Z. F. Liu, Y. S. Chen, and P. Peumans, *Appl. Phys. Lett.* **92**, 263302 (2008).

¹⁰T. Wei, G. L. Luo, Z. J. Fan, C. Zheng, J. Yan, C. Z. Yao, W. F. Li, and C. Zhang, *Carbon* **47**, 2296 (2009).

¹¹S. R. Sun, L. Gao, and Y. Q. Liu, *Appl. Phys. Lett.* **96**, 083113 (2010).

¹²W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* **80**, 1339 (1958).

¹³I. Mora-Seró, S. Gimenez, F. Fabregat-Santiago, R. Gomez, Q. Shen, T. Toyoda, and J. Bisquert, *Acc. Chem. Res.* **42**, 1848 (2009).

¹⁴C. Harris and P. V. Kamat, *ACS Nano* **3**, 682 (2009).

¹⁵M. Feng, R. Sun, H. Zhan, and Y. Chen, *Nanotechnology* **21**, 075601 (2010).

¹⁶Z. C. Wu, Z. H. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, *Science* **305**, 1273 (2004).

¹⁷M. Shalom, S. Dor, S. Ruhle, L. Grinis, and A. Zaban, *J. Phys. Chem. C* **113**, 3895 (2009).

¹⁸K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).

¹⁹M. Shalom, J. Albero, Z. Tachan E. M.-Ferrero, A. Zaban, and E. Palomares, *J. Phys. Chem. Lett.* **1**, 1134 (2010).

²⁰P. R. Yu, K. Zhu, A. G. Norman, S. Ferrere, A. J. Frank, and A. J. Nozik, *J. Phys. Chem. B* **110**, 25451 (2006).