Photovoltaics

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Layered Graphene/Quantum Dots for Photovoltaic Devices**

*Chun Xian Guo, Hong Bin Yang, Zhao Min Sheng, Zhi Song Lu, Qun Liang Song, and Chang Ming Li**

To meet the increasing demand of clean energy the harvesting of electricity from solar incident photons with high efficiency at economically viable cost is needed.[1–4] Quantum dot (QD) based solar cells are poised to play a leading role in this revolution owing to their potential in exceeding the Shockley–Queissar limit, their size-tuned optical response, and their efficient multiple carrier generation.[5,6] A major challenge in developing high-performance QD solar cells is the effective separation of photogenerated electron–hole pairs and the transfer of the electrons to the electrode. Strategies that have been tried include the introduction of nanomaterials with a suitable band energy as efficient acceptors.[7,8] Carbon, an environmentally friendly and inexpensive material, exists in a variety of nanostructures ranging from insulator/semiconducting diamond to metallic/semimetallic graphite, conducting/semiconducting fullerenes, and single-walled carbon nanotubes (SWNTs),[9,10] and recently has been widely used in QD solar cells. Particularly, SWNTs[11,12] and stacked-cup carbon nanotubes[13] have been used as efficient acceptors to enhance photoinduced charge transfer for improved performance because of their unique one-dimensional nanostructure and appropriate band energy. However, the efficiency of carbon nanomaterial based QD solar cells reported so far is still low (incident photon-to-charge-carrier conversion efficiency (IPCE) $\leq 5\,\%$ and photocurrent response $\leq 0.4\ \mathrm{mA\,cm^{-2}}$ under light illumination of $100\ \mathrm{mW\,cm^{-2}}$),[13–16] which is still some distance from the requirement for the next generation of solar cells.

Graphene, a new class of two-dimensional carbon material with single-atom-thick layer features different from ball-like C_{60} and one-dimensional carbon nanotubes, has attracted attention in recent years.[17–20] As a result of its high specific surface area for a large interface, high mobility up to $10\,000\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$, and tunable band gap, graphene should be a very promising electron acceptor in photovoltaic devices.[21] In this work, a novel layered nanofilm of graphene/QDs was constructed from all aqueous solutions to fabricate a photovoltaic device using graphene as acceptor, demonstrating the best performance (IPCE of 16% and photoresponse of $1.08\ \mathrm{mA\,cm^{-2}}$ under light illumination of $100\ \mathrm{mW\,cm^{-2}}$) in all reported carbon/QD solar cells. For a better understanding of the mechanism of the graphene in improving the performance of the device, the graphene/QDs and SWNT/QDs photovoltaic devices are compared.

The fabrication of the layered graphene/QDs device is shown schematically in Figure 1. Chemically reduced graphene was used not only because of its unique properties discussed above but also because of its convenient processing in the liquid phase in bulk quantities.[18] CdS QDs were chosen as the model because of their favorable optoelectronic characteristics and easy aqueous processing potential for large-scale fabrication.[15,22] Tapping-mode atomic force microscopy (AFM) was used to characterize the chemically reduced graphene (Figure 2a). From the height profile, it can be seen that the graphene nanosheet has an average thickness of 9.5 Å. Additional evidence for the high quality of the graphene is presented in the UV/Vis spectra in Figure S1 in the Supporting Information. CdS QDs directly synthesized on a graphene layer were characterized by transmission electron microscopy (TEM; Figure 2b,c). CdS QDs with diameters around 5 nm and good crystal structures were uniformly distributed. It is usually very difficult to achieve such a good distribution for SWNT/CdS QDs because SWNTs always exist in a bundle form in solution as a result of their poor

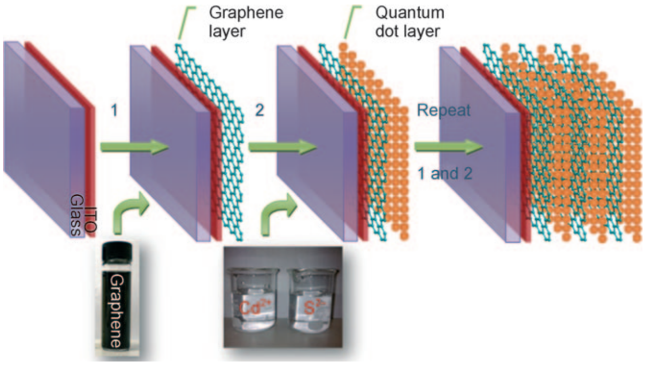

Figure 1. Fabrication of the layered graphene/QDs on ITO glass. 1) Precleaned ITO glass was coated with a thin layer of graphene by electrophoretic deposition from aqueous solution of chemically reduced graphene. 2) Subsequently, a layer of CdS QDs was directly synthesized on predeposited graphene layer by sequential chemical bath deposition from their salt aqueous solutions. The layered graphene/QDs device was fabricated by repeating steps 1 and 2.

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[*] C. X. Guo, Dr. H. B. Yang, Dr. Z. M. Sheng, Z. S. Lu, Dr. Q. L. Song, Prof. C. M. Li
School of Chemical and Biomedical Engineering &
Center for Advanced Bionanosystems
Nanyang Technological University
Singapore 637 457 (Singapore)
Fax: (+65) 6791-1761
E-mail: ecmli@ntu.edu.sg

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Supporting information for this article (details of the fabrication and characterization of the layered nanofilms, and construction and measurement of the photovoltaic devices) is available on the WWW under http://dx.doi.org/10.1002/anie.200906291.

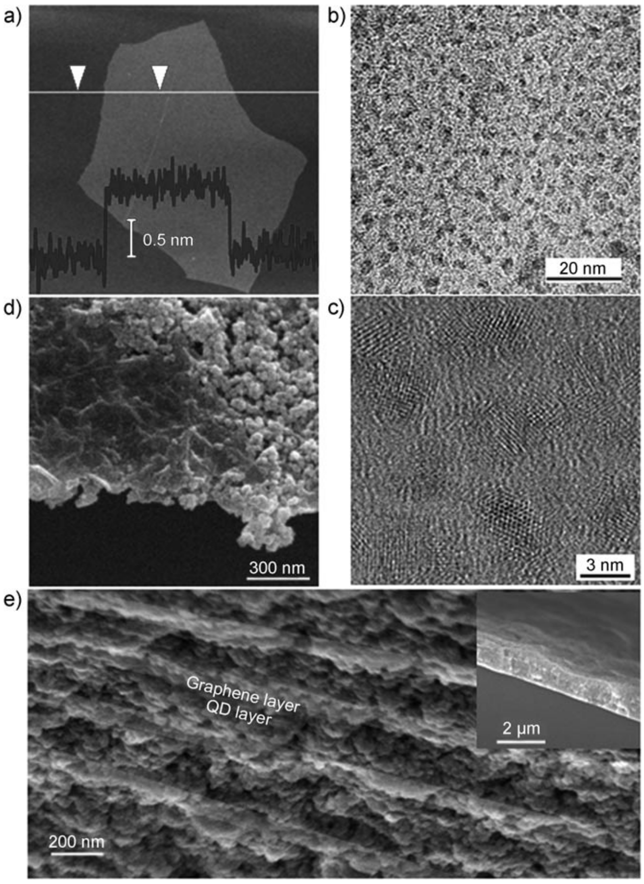

Figure 2. a) AFM image of a graphene nanosheet (2 μm × 2 μm) with a height profile taken along the straight line shown. b) TEM image and c) high-resolution TEM image of QDs on graphene layer. d) SEM image of a $\{graphene/QDs\}_2$ sample occasionally broken during cutting. e) Cross-sectional SEM image of a $\{graphene/QDs\}_{10}$ sample. The inset shows its thickness.

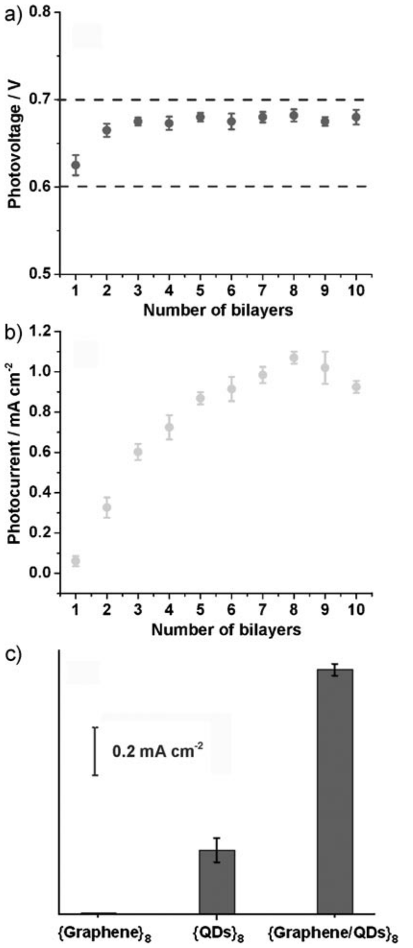

Figure 3. a) Photovoltage and b) photocurrent response versus number of bilayers of graphene/QDs. c) Photocurrent responses of different photoelectrodes. Light: a 150 W Xe lamp (filtered, $\lambda > 300$ nm), 100 mW cm^{-2}. Counter electrode: platinum gauze. Electrolyte: 0.1 м Na_2S.

hydrophilicity and the size of the CdS QDs is almost in the same range as the diameters of the SWNT bundles for difficult stacking.[14,15] Such a better distribution of QDs on graphene apparently is favorable for the performance improvement of a photovoltaic device.[6]

The layered structure was probed by using scanning electron microscopy (SEM). The interface of graphene and QDs can be clearly seen from the edge of a two-bilayer sample ($\{graphene/QDs\}_2$) occasionally broken during cutting (Figure 2d). A cross-sectional image (Figure 2e) clearly shows the layered structure. The layer thickness is around 30 and 120 nm for graphene and QDs, respectively. A plot of film thickness versus number of bilayers (Figure S3 in the Supporting Information) indicates that the film thickness linearly increases with the number of bilayers. The composition was checked by energy dispersive X-ray spectroscopy (Figure S4 in the Supporting Information), which further confirmed the compositions of the layered film.

A photoelectrochemical cell consisting of two electrodes was constructed (Figure S5 in the Supporting Information). The generation of photovoltage and photocurrent related to number of bilayers is shown in Figure 3a,b. When the number of bilayers was two or higher, quite constant open circuit voltage (V_{oc}) of 0.68 V was observed. A smaller V_{oc} value (0.62 V) was found for $\{graphene/QDs\}_1$ samples, and the reason might be that some QDs directly contacted with the indium tin oxide (ITO). Actually, a much smaller V_{oc} value (0.58 V) was observed for pure CdS QDs on ITO. The short-circuit photocurrent density (I_{sc}) increases with the number of bilayers, reaches a maximum of 1.08 mA cm^{-2} at $\{graphene/QDs\}_8$, and then decreases as the number of bilayers further increases (Figure 3b). This trend is possibly caused by the competition between photon adsorption and charge recombination. The I_{sc} value of $\{graphene/QDs\}_8$ was compared with that of $\{graphene\}_8$ and $\{QDs\}_8$ alone (Figure 3c). The I_{sc} value of $\{graphene/QDs\}_8$ is four times higher than that of $\{QDs\}_8$ (0.26 mA cm^{-2}), while the I_{sc} value of $\{graphene\}_8$ is negligible. The device stability was also examined. After operation for 36 h, the I_{sc} value of $\{graphene/QDs\}_8$ remained at 92 %, while the I_{sc} value of $\{QDs\}_8$ dropped to only 32 % (Figure S8 in the Supporting Information). These results clearly demonstrate that the performance of CdS QDs solar cells can be significantly enhanced by graphene.

To better understand the roles of graphene and layered structure in QDs solar cells, the performance of {graphene/QDs}$_8$ samples was further compared with that of {SWNT/QDs}$_8$ samples of the same thickness. Reproducible responses to ON–OFF light cycles on both {graphene/QDs}$_8$ and {SWNT/QDs}$_8$ were observed (Figure 4a,b). The V_{oc} value of {graphene/QDs}$_8$ is 0.1 V higher than that of {SWNT/QDs}$_8$. It is interesting that the V_{oc} value of {SWNT/QDs}$_8$ is almost equal to that of pure CdS QDs on ITO. For I_{sc}, the value of {graphene/QDs}$_8$ is more than 2.5 times the value of {SWNT/QDs}$_8$. The origin of photocurrent generation was probed by recording the photocurrent at different excitation wavelengths and the dependence of IPCE (external quantum yield) was recorded (Figure 4c). There was almost no IPCE for {graphene}$_8$, closely following its negligible photocurrent shown in Figure 3c. The shape of IPCE curves for both {graphene/QDs}$_8$ and {SWNT/QDs}$_8$ is similar to that of {QDs}$_8$. Thus, in the experimental conditions, most of the excitation should come from the QDs. The highest IPCE value (16 %) was observed for {graphene/QDs}$_8$. This is far superior to that of other carbon/QD solar cells reported to date (≤ 5 %),[13–16] indicating that graphene is a much better carbon candidate in QD solar cells. Although the IPCE values for {SWNT/QDs}$_8$ (maximum of 9 %) are smaller than that of {graphene/QDs}$_8$, they are much higher than those of reported bulk SWNT/CdS QDs (maximum of 0.45 %).[15] The 20-fold enhancement in IPCE values indicates the nanoscale thin layered structure may help to solve the inherent problems associated with charge collection and transport in QD solar cells. Figure S7 in the Supporting Information shows that the quantum efficiency is strongly dependent on the film thickness, very possibly because of the combination effect of light absorption and charge transport, which has been reported in organic and dye-sensitized solar cells.[23]

The energy-level diagrams of graphene/QDs and SWNT/QDs photoelectrodes are shown in Figure 4d. As reported, the calculated work function for graphene is 4.42 eV,[21,24] and that for SWNT bundles is known to be 4.8 eV.[15] CdS QDs with diameters around 5 nm have the conducting band around −3.8 eV and a band gap of approximately 2.25 eV.[25] The V_{oc} value in photovoltaic devices is often determined by the Fermi level difference between the sensitizer and acceptor nanomaterial.[2] In the present study, the upper limit of V_{oc} should be around 1.5 and 1.2 V for graphene/QDs and SWNT/QDs, respectively. The smaller V_{oc} values observed for both graphene/QDs and SWNT/QDs might be caused by factors such as processing conditions and altered work function by interacting with QDs. This may imply that the performance of these devices can be further improved by optimizing the fabrication process. As shown in Figure 4d, the conducting band of QDs is smaller than work functions of graphene and SWNT, such that charge transfer from the QDs to both graphene and SWNT is energetically favorable. Similar mechanisms are also reported for charge transfer between carbon nanotube and CdSe in QD solar cells[13] as well as between graphene and a polymer in organic photovoltaic devices.[21] ITO with a work function of around 4.8 eV can also facilitate the fast capture of electrons from graphene, whereas this does not occur to SWNTs. It is also known that a better distribution of semiconductor crystals is crucial for maximizing the photoconversion efficiency.[6] CdS QDs with good crystal structures can distribute well on graphene (Figure 2b,c), whereas, as discussed, it is usually difficult for them to achieve such a good distribution on SWNTs.[14,15] Additional evidence can also be found from SEM images (Figures S2 and S6 in the Supporting Information). The good distribution of QDs on graphene together with the favorable work function of graphene could make it effective for separation of the photogenerated electron–hole pairs and transfer of the electrons to the electrode surface, thus resulting in higher performance of graphene/QD solar cell. Other factors can also contribute to the enhanced performance in layered graphene/QD solar cells. Studies of these effects are being carried out in our laboratory for a better understanding of the mechanism by functionalizing graphene with different functional groups and semiconductors. Introducing a blocking layer such as TiO_2 to prohibit the possible recombination of the charge carriers at the interface of graphene–QDs may further improve the device performance.

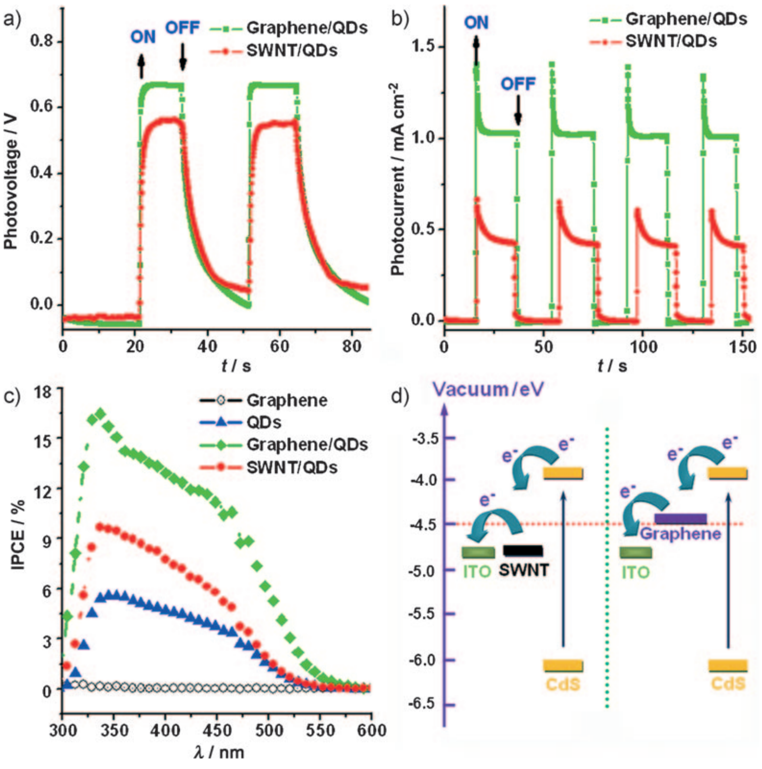

Figure 4. a) Photovoltage and b) photocurrent responses of {graphene/QDs}$_8$ and {SWNT/QDs}$_8$ versus time profiles. c) Dependence of the incident photon conversion efficiency (IPCE, external quantum yield) on the incident wavelength of different photoelectrodes. d) Energy-level diagram of the bilayer system.

In summary, a simple bottom-up approach was used to create a novel layered graphene/QD based electron transfer system. The significantly improved photoresponses, especially photocurrent, achieved herein confirm that graphene is a good candidate for the collection and transport of photogenerated charges, and the layered nanofilm can provide a new and promising direction toward developing high-performance light-harvesting devices for the next generation solar cells.

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