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## Chemical processing of three-dimensional graphene networks on transparent conducting electrodes for depleted-heterojunction quantum dot solar cells<sup>†</sup>

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We present a novel chemical procedure to prepare three-dimensional graphene networks (3DGNs) as a transparent conductive film to enhance the photovoltaic performance of PbS quantum-dot (QD) solar cells. It is shown that 3DGN electrodes enhance electron extraction, yielding a 30% improvement in performance compared with the conventional device.

Graphene, with unusual electronic transport properties which follow the characteristics of two-dimensional Dirac fermions and quantum hall effects,<sup>1</sup> has a charge carrier mobility in the order of  $10^6$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>2</sup> It also exhibits ~98% transmittance throughout the entire visible light spectrum, with a flat transmittance from the UV to far IR regions.<sup>3</sup> These electronic and optical properties have attracted growing interest, establishing graphene as a strong candidate for applications in energy harvesting devices.<sup>4</sup> The application of graphene in quantumdot solar cells (QDSCs) has recently been the focus of some studies,<sup>5,6</sup> owing to the fascinating features of these devices such as the low-cost solution processing route, bandgap tenability, and multiexciton generation through harvesting hot electrons and generating multiple carriers.<sup>6-8</sup> In depleted-heterojunction QDSCs, nanocrystals of semiconductor materials (CdS, CdSe, PbS, etc.<sup>9-12</sup>) are utilized as light sensitizers on wide bandgap mesoporous metal oxide layers (TiO<sub>2</sub> and ZnO).

In order to improve the device performance, not only the surface engineering of QDs but also the interface engineering of the device structure should be taken into consideration. In this context, graphene is a potential candidate for improving the QDSC performance as a fast electron funnel.<sup>2</sup> McDonald *et al.*<sup>13</sup>

prepared QD-decorated graphene photoelectrodes and showed that graphene is a good candidate for the collection and transport of photogenerated charges. Recently, we prepared PbS/graphene nanocomposites by the supercritical and hot injection methods to enhance the efficiency of QDSCs.<sup>11,14</sup> Since the effective loading of QDs is limited to a few monolayers, the energy conversion efficiency (ECE) is restricted. In order to balance the graphene loading, without minimizing the absorption of the incident light, Lightcap and Kamat<sup>15</sup> prepared 3D QD-sensitized graphene photoelectrodes to overcome the conductivity problems of QD films. They have shown that the photocurrent response of the prepared solar device is significantly enhanced compared to electrodes without graphene.

In the present work, a facile chemical process is introduced to prepare 3DGNs on transparent conductive electrodes (TCEs). In contrast to the common methods of polystyrene inverse opals<sup>16</sup> and 3D nickel foam scaffolds,<sup>17</sup> the straightforward and all-solution processing route provides a wide pore structure for high loading of QDs for efficient electron transport without reducing the light-harvesting contribution of the nanocrystals.18 Herein, for the first time, we have utilized 3DGN electrodes to fabricate depleted-heterojunction QDSCs by employing PbS nanocrystals as the light absorbing layer. Compared with TiO<sub>2</sub>/QD heterojunctions, an enhanced photo-induced current without an open voltage drop is reported. It is also shown that the 3D graphene electrode improves the quantum efficiency of PbS QD solar cells, which further leads to an enhanced ECE. The results show that we could tackle the fast electron transport of graphene in contact with QDs, while having good interfacial engineering with an n-type TiO<sub>2</sub> layer. Although the attained ECE is lower than the current world record for PbS QDSCs, the prepared 3DGN has potential to further the use of novel graphene-based architectures for advanced photovoltaic devices.

In order to fabricate 3DGNs, firstly hybrid ZnO/graphene QDs were synthesized according to the procedure explained in ref. 18. Chemically exfoliated graphene oxide nanosheets (Fig. S1, ESI<sup>†</sup>) were synthesized by a modified Hammers' method and mixed with zinc acetate dihydrate in DMF. The following reaction

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proceeds to form ZnO QDs of  $\sim 4$  nm size, which are wrapped with an ultrathin layer of graphene.

$$Zn(CH_3COO)_2 \cdot H_2O + (CH_3)_2NC(O)H \rightarrow$$
  
$$ZnO + (CH_3COO)_2CHN(CH_3)_2 + H_2O$$
(1)

TEM studies (Fig. 1a and b) and EDAX analysis (Fig. S2, ESI<sup>+</sup>) support the formation of the quasi core/shell structure of zinc oxide/graphene, in agreement with previous studies.<sup>12,19</sup> The interatomic spacing of the graphene nanoshell and interplanar spacing of ZnO QDs are 0.14 nm and 0.26 nm (for (002) planes), respectively. The XRD pattern and Raman spectrum of the prepared ZnO/graphene QDs are shown in Fig. 1c and d. The diffraction peaks of crystalline ZnO (JCPDS no. 36-1451) and ultrathin graphene layers  $(2\theta = 25.8^{\circ}, 43.5^{\circ})$  supports the formation of the hybrid QDs. The Raman spectra also indicate that the G peak splits into two sub-bands, namely  $G^+$  (1592.7 cm<sup>-1</sup>) and G<sup>-</sup> (1566.6 cm<sup>-1</sup>), mostly caused by strain.<sup>20</sup> The mechanism of the hybrid QD formation is explained based on the reaction of Zn<sup>2+</sup> ions with the GO functional groups to form local Zn–O–C bonds.<sup>20</sup> During this process, the chemical exfoliation of GO occurs and partially wrapped ZnO QDs with GO or a quasi-coreshell structure are formed.12

In order to prepare 3DGNs, the synthesized ZnO/graphene QDs are treated with a hydrochloric acid solution (5 wt%) for 90 min at room temperature with aggressive stirring, as schematically shown in Fig. S3 (ESI†). This treatment leaches out the ZnO core while the wrapped graphene shell is partially unfolded, forming a cluster (Fig. 2a). The clusters are porous and composed of several ultrathin films (Fig. 2b) of graphene with an interatomic spacing of 0.14 nm (Fig. 2c). EDAX analysis in some selected areas (marked A in Fig. 2b) shows that the complete removal of the ZnO core occurs without leaving impurities. This finding is further supported by XPS analysis



**Fig. 1** The characterization of ZnO/graphene QDs. HRTEM images show the (a) hybrid ZnO/graphene nanostructure and (b) the lattice scale fringes of the graphene nanoshell and ZnO core. (c) The XRD pattern and (d) Raman spectrum of the particles determine the formation of ZnO nanocrystals during the *in situ* chemical processing in the presence of graphene oxide nanosheets.



**Fig. 2** HRTEM images and EDAX analysis of graphene nanoclusters formed after acid leaching. The clusters are composed of ultrathin graphene layers with a nano-porous structure. EDAX analysis of the clusters in selected regions (marked A in b) indicates the complete removal of zinc from the hybrid structure.

(Fig. 3a). The peaks located at 284.6 eV and 531.8 eV are assigned to the peaks of C1s and O1s. Notably, the peak intensity of O1s is considerably reduced after leaching, which can be related to the dissolution of ZnO as well as the reduction of oxygen agents on the graphene nanolayers.

The Raman spectrum of the graphene clusters is shown in Fig. 3b. 3DGN illustrates a peak at 1578.5 cm<sup>-1</sup> (G band), which is related to the vibration of sp<sup>2</sup>-bonded carbon in the hexagonal structure. The presence of the D-band at 1346.4 cm<sup>-1</sup> points out the existence of defects and disorders in the graphitic sheets, imposed by removing the ZnO core from the ZnO/graphene QDs. As shown in Fig. 3b, the higher level of disorder of the 3DGN layer results in an increase in the  $I_D/I_G$  ratio. Furthermore, 3DGN does not have any peak at 2668 cm<sup>-1</sup> (2D band), which means that there is no monolayer of graphene in the 3DGN structure.<sup>2</sup>



**Fig. 3** The characterization of the 3DGN film. (a) XPS spectra of ZnO/ graphene and 3DGN films, (b) Raman spectrum of the 3DGN film, and (c) UV absorption of ZnO/graphene and 3DGN.

Fig. 3c shows the optical absorption of the graphene clusters. A blue shift in the absorption peak from 375 mm (for the hybrid ZnO/graphene) to 268 nm (for the graphene cluster) is observed. This proves that the ZnO core is removed from the core-shell structure.

To prepare the counter electrode for PbS QDSCs, the colloidal graphene clusters (0.5 wt%) were deposited on TCE by cathodic electrophoretic deposition. Top-view and cross-sectional SEM images of the electrodes are shown in Fig. 4a and b. The electrode is composed of an FTO substrate covered by a thin layer of dense TiO<sub>2</sub> (40 nm) with a top of 3DGN (70 nm). The graphene network is porous with open channels to yield a high surface area. The transitivity of the 3DGN electrode is shown in Fig. 4c and is compared with FTO/TiO<sub>2</sub> substrates. It was seen that the 3DGN electrode blocked the light to some extent compared with the TiO<sub>2</sub> electrode and we found that a 70 nm thickness of this layer is beneficial for photovoltaic applications.

To fabricate QDSCs, PbS nanocrystals were synthesized by the hot injection method. Cadmium doping was also applied, as discussed in the experimental part. The characterizations of PbS nanocrystals are presented in the ESI,† Fig. S4-S6. Detailed analyses determined that crystalline lead sulfide particles, with an average size of 3 nm, were synthesized. The particles had a narrow size distribution with an absorption peak at 950 nm (corresponding to 1.3 eV optical bandgap). The PbS nanocrystals were deposited on the electrodes through a layer-by-layer deep coating combined with a solid-state ligand exchange (see ESI 1.6<sup>†</sup>). The thickness of the QD film was 300 nm. To complete the device fabrication, the top contacts (MoO<sub>3</sub>/Au) were thermally evaporated on the active layer at a rate of  $\sim 0.8$  Å s<sup>-1</sup>. A crosssectional SEM image of the PbS QDSCs is shown in Fig. 5a and Fig. 5b depicts the cross-sectional SEM image and the schematic architecture of the prepared devices, respectively. The result of the current density-voltage (J-V) measurement under simulated AM 1.5G solar irradiation is illustrated in Fig. 5c. For comparison, the J-V curves for PbS QDSCs utilizing common FTO/TiO2 and ZnO/graphene electrodes are also shown. Table 1 reports the figures of merit for the prepared devices (averaged over 10 runs



Fig. 4 SEM images of the 3DGN structure; (a) top view, (b) cross sectional view, and (c) the transmission of 3DGN and  $TiO_2$  electrodes.



**Fig. 5** Characteristics of bulk heterojunction PbS QD solar cells based on 3DGN acting as a fast electron extraction layer. (a) Cross-sectional SEM image of the device, (b) the schematic of the PbS QD solar cell fabricated on the 3DGN film, (c) J-V curves under AM 1.5G indicate the photovoltaic performance of the heterojunction devices, (d) EQE spectra determine the role of the 3DGN layer on the quantum efficiency of the PbS QD film, (e) band diagram of PbS QDs based on 3DGN, (f) the 3DGN and TiO<sub>2</sub> work functions measured using the ultraviolet photoelectron spectrum (UPS), (g) time-resolved PL spectra of the PbS QD layer deposited on the 3DGN (black curve) and pristine (red curve) sample.

on different/separate specimens). As seen, the power conversion efficiency is increased from 4.1% to  $\sim 5.3\%$  by employing 3DGNs. Furthermore, by removing the ZnO core from the ZnO/ graphene electrode, the PCE is improved up to 13% due to the enhancement of the connection between PbS QDs and the electron transfer layer, however the fill factor of the device with 3DGN is reduced to some extent due to the large surface area, and as a result of surface recombination.<sup>12,14</sup> To further support this finding, the external quantum efficiency (EQE) of the cells was recorded (Fig. 5d). The higher current density highlights the effect of the 3DGN layer on the extraction of charged carriers. The steady photoluminescence of PbS/3DGN and PbS/ZnO films are shown in Fig. S7 (ESI<sup>†</sup>). It is clear that the PL intensity drops a lot in the presence of the 3DGN layer due to the quenching effect. As a result, the transportation of the carriers becomes faster than before and the possibility of recombination is decreased.<sup>12,14,19</sup> This is supported by the EQE results in Fig. 5d. The band diagram for the device prepared with the 3DGN electrode is illustrated in Fig. 5e. The work function of the 3DGN and TiO<sub>2</sub> layers was measured by ultraviolet photoelectron spectroscopy (UPS) (Fig. 5f).

Table 1 Figures of merit for the prepared PbS QD solar cells based on 3DGN, ZnO/graphene electrodes and the conventional device (n = 10)

Device	$V_{\rm oc}$ (V)	$J_{ m sc}~({ m mA~cm^{-2}})$	Fill factor (%)	PCE (%)
Conventional device	$0.58\pm0.04$	$13.7\pm1.1$	$52\pm3$	$4.1\pm0.2$
Device based on ZnO/graphene	$0.58\pm0.04$	$16.1 \pm 1.1$	$51\pm4$	$4.7\pm0.3$
Device based on 3DGN	$0.59\pm0.07$	$18 \pm 1.7$	$50\pm4$	$5.3\pm0.1$

He I (21.2 eV) was utilized as a photon source for the UPS measurement. The established diagram indicates that the 3DGN layer is energetically matched with the absorbing layer and the underlying TiO<sub>2</sub> film. Therefore, photo-generated electrons can be separated and collected by the counter electrode more efficiently than the reference sample (pristine TiO<sub>2</sub>); hence, an improved EQE is attained. This is because of the high conductivity of the 3DGNs and the facilitated electron transport from the conduction band of PbS ODs to the LUMOs of the 3DGN, which results in an efficient charge transfer through a hopping mechanism.<sup>13,14</sup> In addition, the 3DGN layer has a large surface area *i.e.* a three-dimensional nanostructure which can increase the light absorption due to the light trapping effect, however the large surface area can increase the surface recombination at the same time. As a result, there is a balance between these two parameters. In fact, the fast extraction of the carriers is the most important role of the 3DGN layer.<sup>11,12</sup> The results of the time-resolved photoluminescence (TRPL) measurement for the PbS QD film with and without the 3DGN layer are presented in Fig. 5g. Table S1 (ESI<sup>+</sup>) shows the fitting parameters of the corresponding PL decay curves. As can be seen, the lifetime, based on 3DGN, dropped a lot ( $\sim$  80%) compared with the TiO<sub>2</sub> electrode. Quenching in the presence of 3DGN is primarily directed towards charge transfer reactions and static quenching. Despite dynamic quenching, when the donor and acceptor materials are in the ground state, static quenching occurs and thus, it can improve the extraction of charge carriers. The electron transfer also occurs much faster than the charge recombination process using 3DGN, as evidenced by the TRPL measurement.

In summary, we introduce a new and all-solution process to prepare 3DGNs on TCE electrodes in order to reduce fast electron recombination at the surface states of TiO<sub>2</sub>/QD junctions in PbS QDSCs. The method is based on the preparation of quasi core/shell zinc oxide/graphene QDs by a facile solution method followed by dissolution of the ZnO core in acidic solutions and electrophoretic deposition of clusters of ultrathin graphene layers. Infiltration of PbS QDs (3 nm) in the 3DGNs with a wide pore structure results in an enhanced charge transfer and lower recombination rate, hence, a higher short circuit current ( $J_{sc}$ ) of QDSCs (>35%) compared with the planar TiO<sub>2</sub>/PbS heterojunctions is attained. External quantum efficiency measurements also suggest that the light absorption and scattering properties of graphene flakes in the visible region and auxiliary transport (in addition to the TiO<sub>2</sub> layer) influence ECE. On the other hand, the lower work function of graphene than the conduction band of the PbS QDs may offer an energetic arrangement that favours the transfer of photo-induced electrons to graphene with high conductivity. Although the attained PCE (5.3%) is lower than that of the world record for PbS QDSCs, our results suggest that 3DGNs could serve as a good conducting structure to capture and transport charge carriers.

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