Graphene quantum dots as a green photosensitizer with carbon-doped ZnO nanorods for quantum-dot-sensitized solar cell applications

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Abstract. Graphene quantum dots (GQDs), N-doped GQDs (NGQDs) and S, N co-doped GQDs (SNGQDs) were synthesized using hydrothermal methods. All GQDs were attached with carbon-doped ZnO nanorods (C-ZnO NRs) grown on fluorine-doped tin oxide (FTO)-coated glass substrates, for the fabrication of metal-free eco-friendly quantum-dot-sensitized solar cells (QDSSCs). SNGQD-decorated nanorod-based solar cells demonstrated maximum open circuit voltage ($V_{OC} \sim 360$ mV), short circuit current ($J_{SC} \sim 1.84$ mA cm⁻²) and power conversion efficiency ($\eta \sim 0.293\%$) compared to other devices.

Keywords. GQDs; C-ZnO NR; QDSSC.

1. Introduction

Innovative ideas are required to harvest incident solar energy into electrical energy with better efficiency to meet our clean energy demand. The conventional silicon and inorganic thin film solar cells demonstrate power conversion efficiency varying from 10 to 30% [1]. However, such solar cells are quite expensive due to the source materials, high vacuum and elevated temperature fabrication including several lithographic steps. Due to these limitations, intensive research work has been carried out on third-generation solar cells such as dye-sensitized solar cells (DSSCs), organic solar cells and quantum-dot-sensitized solar cells (QDSSCs). These new types of solar cells can achieve the highest theoretical photo-conversion efficiency up to 44.7%, with minimal fabrication cost and easy synthesis procedure [2,3]. Several research studies have been carried out by sensitizing TiO₂ or ZnO nanostructures with low band gap semiconductor QDs such as CdS, CdSe, PbS, PbSe, CdTe etc. [4–6]. To the best of our knowledge, the maximum device performance was obtained with CdSeTe-decorated CdS QD-sensitized TiO₂ nanoparticle films of power conversion efficiency (η) $\sim 9.48\%$ [7]. Although these chalcogenide semiconductors offer excellent size tunable optical band gap, high photoabsorption and favourable band alignment, most of these QDs are hazardous to health due to the presence of highly toxic Cd- or Pb-based elements. On the other hand, environmentally friendly, non-toxic QDs such as CuInS₂, CuInSe₂ and CuInSeS have been utilized as photosensitizers in QDSSCs. The highest reported photoconversion efficiency with such QDs was found to be 11.66% [8].

In recent years, graphene quantum dots (GQDs), have received much attention due to their size tunable optical absorption and emission similar to semiconductor QDs. Such carbon-based zero dimensional (0D) nanomaterials are nontoxic, eco-friendly, chemically inert and can be easily synthesized at minimum cost [9]. Doping is a common method to enhance the photoabsorption and photoinduced charge transport from GQDs to semiconductors. Several kinds of doping elements such as S, N, B, P, F etc. were investigated to modulate optical and electrical properties of the GQDs [10–12]. Instead of using conventional semiconductor QDs, GQD-sensitized solar cells will be attractive for low cost and environmentally friendly solar energy conversion.

In this work, we have fabricated carbon-doped ZnO nanorod (C-ZnO NR) photoanode-based solar cells. GQDs, nitrogen-doped GQDs (NGQDs) and sulphur, nitrogen co-doped GQDs (SNGQDs) were utilized as photosensitizers for QDSSC applications.

2. Experimental

All GQDs were synthesized by a hydrothermal process [13–15]. ZnO NRs were grown on FTO-coated glass substrates by a two-step chemical process. The detailed experimental procedures and growth mechanism are reported elsewhere [14]. C doping was carried out by dipping the ZnO NRs in 0.1 M glucose solutions followed by heating at 120°C. Finally, all samples were annealed at 300°C for 3 h. For the attachment of QDs, nanorods were dipped in GQD, NGQD and SNGQD

Figure 1. Plane view TEM images of (a) GQDs, (b) NGQDs and (c) SNGQDs. High-resolution TEM micrographs are presented in the inset. Full scan XPS spectra of (d) GQDs, (e) NGQDs and (f) SNGQDs.

solutions for 2 h. The samples were thoroughly rinsed with DI water after attachment and annealed at 120°C for 3 h under an air atmosphere. The surface topography and elemental analysis of C-ZnO NRs and ZnO NRs were studied using a NOVA NANO (FEI, USA) scanning electron microscope (SEM). Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2100F microscope. To study the chemical bonding of GQDs and C-ZnO NRs, X-ray photoelectron spectroscopy (XPS) study was performed using a PHI 5000 Versa Probe II (ULVAC-PHI, Inc., Japan) instrument. UV-Vis absorption spectra of the GQDs were recorded using a PerkinElmer Lambda 950 spectrometer. To fabricate QDSSCs, GQD-sensitized NRs were used as working electrodes and platinum-coated FTO substrates were used as counter electrodes. The iodine-based electrolyte solution (Iodolyte Z-50, Solaronix) was introduced in between the two electrodes. The current-voltage (J - V) characteristics of the QDSSCs were measured using a source meter (B2912A, Agilent, USA) under illumination of 100 mW cm⁻² light (AM 1.5) from a solar simulator (Enlitech, Taiwan).

3. Results and discussion

Figure 1a–c presents the plane view TEM micrographs of GQDs, NGQDs and SNGQDs. The average size of GQDs,

Figure 2. UV-Vis absorption spectrum of GQDs, NGQDs and SNGQDs.

NGQDs and SNGQDs estimated from the micrographs are 5.2, 4.5 and 4 nm, respectively. The corresponding high-resolution TEM images of all GQDs are presented in the inset of figure 1a–c, respectively. Interestingly, all GQDs are highly

Figure 3. SEM micrographs of (a) ZnO and (b) C-ZnO NRs. Chemical mapping of both NRs is shown in the inset. XPS full scan spectra of (c) ZnO and (d) C-ZnO NRs. C1s electronic peaks before and after surface cleaning are presented in the inset.

crystalline with interplanar spacing of ~ 0.34 nm, which is similar to the (002) facet of graphitic carbon [14]. The full range XPS spectra of GQDs, NGQDs and SNGQDs are shown in figure 1d–f, respectively. The major binding energy peaks at 283.2 and 531.2 eV are attributed to the presence of C1s and O1s electrons, which are the key elements of GQDs. In addition to C1s and O1s peaks, an extra peak at 399.2 eV has been observed in NGQDs, which is ascribed to N1s electrons. Similarly, XPS spectrum of SNGQDs shows two more peaks at 167.3 and 399.4 eV, which are denoted as S2p and N1s electrons. Our XPS study confirmed the doping of N atoms in NGQDs and S, N atoms in SNGQDs.

Figure 2 shows the UV–Vis absorption spectra of GQDs, NGQDs and SNGQDs. The absorption spectra of all GQDs show two major peaks at wavelength 215 and 338 nm for GQDs, 238 and 334 nm for NGQDs and 222 and 333 nm for SNGQDs, respectively. The origin of such UV absorption at 215–222 nm is attributed to $\pi \rightarrow \pi^*$ transition of C=C bonds and at 338–333 nm corresponds to $n \rightarrow \pi^*$ transition of C=O bonds in GQDs, respectively [13–15].

Figure 3a and b presents the top view SEM micrographs of ZnO NRs before and after C doping. The nanorods were grown uniformly on FTO substrates and no significant microstructural modification has been observed after doping. The average diameter and density of nanorods estimated from the micrographs are found to be ~ 130 nm and $\sim 1.85 \times 10^9$ cm $^{-2}$, respectively. The chemical mapping confirmed the presence of the key elements zinc and oxygen in ZnO and C-ZnO NRs (inset of figure 3a and b). The presence of a significant amount of carbon in C-ZnO NRs (inset of figure 3b) confirmed the doping. However, existence of a small amount of carbon content in pristine ZnO is due to contamination during sample treatment. Figure 3c and d presents full range XPS spectra of ZnO and C-ZnO NRs. Both spectra describe the presence of zinc and oxygen peaks which arises from ZnO NRs. However, we have also observed a detectable peak at ~ 284.4 eV, which is attributed to the presence of C1s electrons in both nanorods. In our study, the C peak may arise either from surface contamination or impurity doping. To verify the origin of C peak, high-resolution XPS spectra

Figure 4. (a) Schematic representation of a typical GQD-sensitized C-ZnO NR-based QDSSC. (b) Current density vs. voltage (J - V) characteristics of pristine ZnO NR, C-ZnO NR, GQD/C-ZnO NR, NGQD/C-ZnO NR and SNGQD/C-ZnO NR-based QDSSCs under 100 mW cm^{-2} white light illumination (AM 15). (c) Schematic representation of charge transportation and separation mechanism in a typical NGQD-sensitized solar cell.

of C1s electrons were recorded after surface cleaning of the NRs using Ar ions. Interestingly, after cleaning, the C peak at $\sim 284.4 \text{ eV}$ for pristine ZnO NRs disappeared (inset of figure 3c). But, the C1s peak in C-ZnO NRs remained unchanged and confirmed the successful insertion of carbon atoms in the ZnO lattice (inset of figure 3d).

To explore the potential use of GQDs as a photosensitizer, solar cells were fabricated after attachment of GQDs, NGQDs and SNGQDs with C-ZnO NRs separately. Figure 4a depicts the schematic representation of QDSSC device structure. The current-voltage (J - V) characteristics of GQD, NGQD and SNGQD-decorated C-ZnO NR photoanodes are presented in figure 4b. The J - V characteristics of pristine ZnO NR and C-ZnO NR photoanodes are also shown in the same figure. All measurements were carried out under illumination of 100 mW cm^{-2} simulated solar radiation. The solar cell parameters such as short circuit current (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (η) for all samples are listed in table 1. It is

obvious that, pristine ZnO NRs showed very poor J_{SC} ($\sim 0.38 \text{ mA cm}^{-2}$), V_{OC} ($\sim 0.31 \text{ V}$) and η ($\sim 0.039\%$). However, after carbon doping, the overall device performance was improved and power conversion efficiency (η) was boosted 2.2 times than the pristine NR-based sample. Such superior photovoltaic behaviour is attributed to higher carrier concentration and better visible photoabsorption in C-ZnO NRs [16,17]. More importantly, the η value increases 3.3 times for GQD, 6.3 times for NGQD and 7.5 times for SNGQD-sensitized C-ZnO NRs compared to ZnO NRs. SNGQD-sensitized C-ZnO NRs demonstrated maximum solar cell performance with $V_{OC} \sim 360 \text{ mV}$, $J_{SC} \sim 1.84 \text{ mA cm}^{-2}$ and $\eta \sim 0.293\%$. Carrier generation and transportation mechanism in a typical NGQD-sensitized solar cell under illumination of light is schematically shown in figure 4c. The optical band gap of C-ZnO NRs and lowest unoccupied molecular orbital-highest occupied molecular orbital gap of NGQDs were measured based on our previous reports [14,18]. The superior photoconversion efficiency

Table 1. Solar cell parameters (V_{OC} , J_{SC} , η) of GQD-sensitized QDSSC devices.

Photoanodes	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	FF (%)	η (%)
FTO/ZnO NRs	310	0.38	33.95	0.039
FTO/C-ZnO NRs	380	0.51	44.37	0.086
FTO/GQD-sensitized C-ZnO NRs	370	0.87	40.38	0.129
FTO/NGQD-sensitized C-ZnO NRs	370	1.51	42.95	0.247
FTO/SNGQD-sensitized C-ZnO NRs	360	1.84	45.28	0.293

in SNGQD-sensitized solar cells is attributed to strong visible photoabsorption, favourable band alignment and low interfacial resistance at SNGQD/C-ZnO NR interfaces [18].

4. Conclusions

In summary, we have synthesized nontoxic, environmentally friendly GQDs by a low cost hydrothermal method. QDSSCs were fabricated by attaching GQDs, NGQDs and SNGQDs with C-ZnO nanorods. SNGQD-decorated ZnO NR-based solar cells showed superior $V_{OC} \sim 36$ mV, $J_{SC} \sim 1.84$ mA cm⁻² and $\eta \sim 0.293\%$ compared to other devices. The present study demonstrated the potential use of GQDs as a new kind of metal-free green photosensitizer for QDSSC application.

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