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Graphene quantum dots decorated rutile TiO_2 nanoflowers for water splitting application

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ABSTRACT

Flower like rutile TiO_2 films were decorated with green-photoluminescent graphene quantum dots (GQDs) and photovoltaic properties were investigated for water splitting application. Rutile TiO_2 nanoflowers (NFs) and GQDs (average width of ~12 nm) synthesized separately using a hydrothermal method and TiO_2 NFs were decorated with various amounts of GQDs solution ($x = 5$, 10, 15 and 20 μL) by spin coating. Optical characterization reveals that GQDs are highly luminescent and absorb UV and visible light photons with wavelengths up to 700 nm. GQDs-x/TiO_2 electrode shows a photocurrent enhancement of ~ 95% compared to pristine TiO_2 NFs for the optimum sample ($x = 15$ μL) at an applied potential of $P = 0$ V using 1 M Na_2SO_4 solution as electrolyte.

1. Introduction

Hydrogen as a candidate alternative to the traditional fossil energy has become the focus of the global attention. Photoelectrochemical hydrogen generation with semiconductor materials constitutes the most attractive approach toward the direct conversion of solar energy [1–7]. TiO_2 has been intensively studied as a photocatalyst to date due to its favorable band-edge positions, high resistance to photocorrosion, excellent physical and chemical stability, nontoxicity, low-cost and abundance [8,9]. However, TiO_2 has some drawbacks such as a large band gap (3.2 eV for anatase and 3 eV for rutile phase) and a negligible light harvesting efficiency in visible light, which limit its quantum efficiency.

Various strategies have been investigated to attack these problems. Doping with interstitial atoms like N [10], S [11], doping with metal or non-metal elements and hydrogen annealing [12] have provided limited success in extending the absorption range of TiO_2. Another common approach relies on sensitization with narrow bandgap semiconductors and generally entails the use of chalcogenide materials (CdS, CdSe, PbS, etc.) which pose environmental problems and exhibit fast photocorrosion in aqueous solutions [13,14].

Graphene quantum dots (GQDs) due to their unique properties, such as ultraviolet and blue to green luminescence, excellent photostability, biocompatibility, chemical inertness, environmentally benign, cost effective preparation and appropriate band positions against TiO_2 band positions (CV and VB bands) are a good candidate for improving disadvantages of TiO_2 and reducing the photoelectrons' loss [15–21]. GQDs show great promise in a wide range of applications such as photocatalysis [22,23], sensing [24,25], light emitting diodes (LEDs) [26], and energy conversion or energy storage devices [27–29]. So far, various methods have been utilized to prepare GQDs, including cage-opening fullerenes [10], mechanical grinding exfoliation [11], rapid thermal annealing [30], electrochemical approach [5], electron-beam lithography [12], chemical oxidation of CX-72 carbon black [13], cutting large graphene oxide sheets via a hydrothermal route [14] and carbonizing suitable organic precursors [15]. However, most of the methods mentioned above suffer from some disadvantages such as difficulty to obtain starting materials, difficulty for functionalization, expensive, low yield and poor optoelectrical properties. For example, methods of the cage-opening fullerenes on the ruthenium surfaces and carving graphite crystallites by high-resolution electron-beam lithography are limited by the low productivity and high cost. Theoretical calculations revealed that interfacial charge transfer can mediate the direct excitation of electrons from GQD into TiO_2 conduction band under visible-light irradiation and electron transfer takes place from GQD to TiO_2 surface in both the physisorption and chemisorption cases [31], leading to hole accumulation that is necessary to water splitting process.

Here we have used rutile TiO_2 nanoflowers (NFs) as a base semiconductor substrate for GQDs because of its large surface area originating from its shape and favorable band-edge positions and a low cost, high yield, one-step facile process method was used

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for preparing GQDs from only glucose powder as precursor in DI water and the obtained GQDs was utilized to sensitize TiO_2 NFs. Explaining the electron transfer mechanism in GQDs/TiO_2 interface and generation of H_2 and O_2 under photoirradiation in a photoelectrochemical cell, could be informative to promote the utilization of GQDs in photovoltaic systems.

2. Experimental

2.1. Synthesis of rutile TiO_2 nanoflowers (NFs)

TiO_2 NFs were grown on the fluorine-doped tin oxide (FTO, F:SnO_2) using a hydrothermal method without TiO_2 seed layer. In a typical synthesis, 12 mL of deionized water was mixed with 6 mL of concentrated hydrochloric acid to reach a total volume of 18 mL in a Teflon-lined stainless steel autoclave (75 mL volume). After addition of 0.6 mL of Titanium Isopropoxide (TTIP), the mixture was stirred under ambient conditions for 5 min. After that, the pieces of FTO substrates (F:SnO_2, 1×1.5 cm^2) were ultrasonically cleaned for 15 min in deionized water and in acetone and put into the autoclave. The hydrothermal synthesis was conducted at 160 °C for 10 h in an oven. After synthesis, the autoclave was cooled to room temperature naturally. The obtained samples were washed with deionized water and dried at 80 °C in air.

2.2. Synthesis of GQDs

The GQDs were prepared by a hydrothermal method using glucose and deionized water as precursors. In a typical synthesis, 0.05 g of glucose was dissolved in 50 mL of deionized water. The mixture was then treated by a one-step hydrothermal method in a Teflon-lined stainless-steel autoclave (75 mL) at 200 °C for 12 h, producing GQDs' dispersions with a good solubility in water after filtration with the qualitative filter paper. The initial liquid sample was transparent (colorless) and it changed to orange after synthesis of GQDs. Under the hydrothermal process, glucose molecules are dehydrated to form C=C, which is the elementary unit of GQDs.

2.3. Decorating of TiO_2 NFs with GQDs

Herein, GQDs were used for sensitizing of TiO_2 NFs by spin coating method. Various amounts of GQDs solution ($x = 5$, 10, 15 and 20 µL) was dropped on TiO_2 NFs substrates under rotation speed and deposition time of 3000 rpm and 3 min, respectively. Then to better tenacity of GQDs on the TiO_2 NFs surfaces, the GQDs-x/TiO_2 NF photoanodes were heated for 30 min in an oven at 200 °C.

2.4. Measurement and characterization techniques

Photoluminescence (PL) emission was recorded using PL spectroscopy (Gilden photonics) and optical absorbance measurements were carried out using a spectrophotometer (Unico 4802). Structural morphology of samples was studied using a scanning electron microscope and transmission electron microscope (CM30 300 kV). Steady state current density voltage (J–V) and EIS measurements were carried out using a VSP-300 Multichannel Potentiostat/Galvanostat EIS (Bio-Logic Science Instruments). Fourier Transform Infrared (FTIR) spectroscopy was employed using a FTIR spectrometer (Nicolet Nexus 670). Raman analysis (BRUKER, Germany, SENTERRA) was used for proving of formation of rutile phase TiO_2 and appearance of GQDs on the TiO_2 NFs surfaces. For IV and EIS measurement, three electrode configurations was used, where the TiO_2 NFs and GQDs-x/TiO_2 NFs photo-electrode were connected to the working electrode, and a saturated Ag/AgCl was used as the reference electrode and a Pt wire was connected to the counter electrode. The solution of Na_2SO_4 (1 M, pH 6) was used as the electrolyte, and electrodes were illuminated using a xenon lamp and the light intensity was adjusted with a thermopile to 100 mW/cm^2. CV measurements were performed with a three electrode configuration, i.e. GQDs/glassy carbon as the working electrode, Ag/AgCl as the reference electrode and a platinum wire as the counter electrode in an acetonitrile solution including 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$).

3. Results and discussion

3.1. Characterization study

Fig. 1(a) and (b) shows typical top view SEM images of the TiO_2 NFs films grown at 160 °C for 10 h in two different scales. SEM images reveal that the TiO_2 NFs are perpendicular to the FTO substrate and the entire surface of the FTO substrate is covered uniformly with TiO_2 NFs. Inset in Fig. 1(a) shows a cross section SEM image of the TiO_2 NFs film. According to this picture, TiO_2 NFs are composed from nanorods, with an average diameter determined about 150 nm with a thickness of about 4 µm. Fig. 1(c) shows TEM image of the obtained GQDs, which can be observed to have a uniform dispersion without apparent aggregation with the average size of about 12 nm, and the GQDs decorated TiO_2 NFs are shown in Fig. 1(d).

UV–vis absorption spectra of the glucose and GQDs solutions are shown in Fig. 2(a). Glucose solution has a peak around ~200 nm and primary peak at 230 nm was assigned to π–π^* transitions of aromatic C=C bonds in sp^2 hybridization region and peak at about 300 nm is attributed to the n–π^* transition of C=O bonds [19,32,33]. Thus, the absorption spectrum could also provide the fingerprints of GQD structures. According to this figure, absorption region is recorded at all wavelengths in the spectrum and a strong optical absorption appeared near UV region with a tail extending in the visible range. Absorption at visible regions originates from connected functional groups. Such wide absorption allows excitation with a spectrally wide light source, necessary to perform efficiently in photovoltaic devices. GQDs possess defect, oxygen groups and functional groups on the edge and surface and because of their

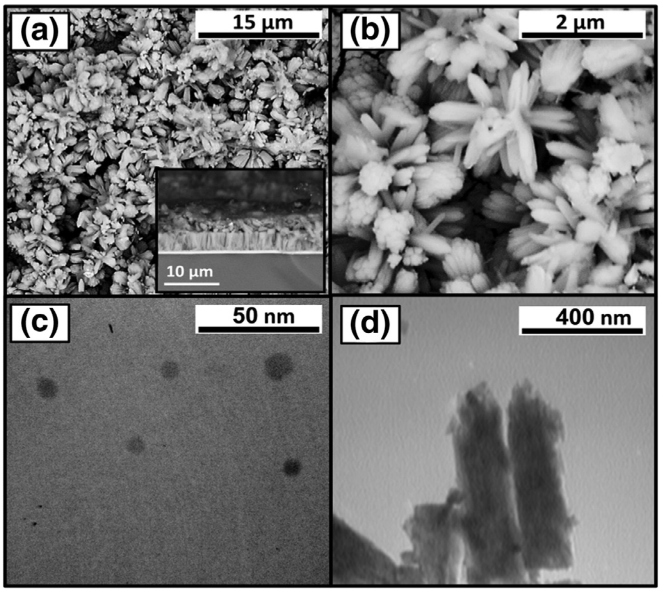

Fig. 1. (a, b) Top-view SEM images of the TiO_2 NFs grown on the FTO substrate at different scales (inset shows the cross section SEM image), (c) TEM image of the GQDs and (d) TEM image of the GQDs decorated TiO_2 NFs.

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