Catalysis Communications 74 (2016) 104–109

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Graphene quantum dots prepared from chemical exfoliation of multiwall carbon nanotubes: An efficient photocatalyst promoter

Shu Wei [a,b], Ran Zhang [a], Yan Liu [c], Hong Ding [d], Yong-Lai Zhang [a,*]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[b] College of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, Jilin 130022, China
[c] Key Laboratory of Bionic Engineering, Ministry of Education, Jilin University, Changchun 130012, China
[d] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form 8 November 2015
Accepted 13 November 2015
Available online 15 November 2015

Keywords:
Graphene quantum dots
Multiwall carbon nanotubes
Exfoliation
Visible-light photocatalysts

ABSTRACT

We report here a facile preparation of graphene quantum dots (GQDs) by chemical exfoliation of multiwall carbon nanotubes (MWCNTs) using a modified hummers' method. The resultant GQD samples possess strong electronic property, revealing great potential for photocatalyst design. As an efficient promoter, GQDs/P25 nanocomposites have been successfully prepared by simple wet impregnation and subsequent thermal annealing at 200 °C. In the tests of photocatalytic degradation of organic dyes under visible-light irradiation, the GQDs promoted P25 samples which shows much higher photocatalytic activity compared to the pure P25, indicating the crucial roles of GQDs.

1. Introduction

Recently, zero-dimensional carbon materials, represented by fullerene and carbon dots, have attracted enormous research interests due to their unique physical/chemical properties [1–10]. Especially, carbon quantum dots (CQDs) including graphitic nanoparticles, amorphous carbon dots, and graphene quantum dots (GQDs) have reveal great potential for a wide range of applications, such as fluorescent probes [11], photovoltaic devices [12], photocatalysis [13–14], light-emitting diodes [15] and bioimaging [16–18]. As compared with conventional semiconductor quantum dots, CQDs exhibit a series of unique advantages. For instance, CQDs are generally nontoxic and thus biocompatible, since they consist of only carbon and some oxygen functional groups. Additionally, they could be excited over a broad spectral range from the visible to near IR region, and usually show clear up-conversion PL properties, thus CQDs have been considered as a promising candidate for rational design of novel visible-light driven photocatalysts [19–20]. Moreover, CQDs are excellent electron donors and acceptors in photoexcited states; which makes them promising for various optoelectronic devices [21].

The exceptional superiorities continuously stimulate the rapid progress of methodologies for CQDs preparation. Generally, the preparation strategies could be classified into two broad categories: top-down and bottom-up approaches. The former route usually generate ultra-small fragment of carbon materials (e.g., graphite, graphene, carbon soot and fullerene) using laser ablation, ultra-sonic treatment, electrochemical etching and hydrothermal cutting; whereas, the later method resorts to carbonization or organic molecules, or graphitization of polycyclic aromatic hydrocarbon [22–27]. However, despite the rapid development of synthetic methodologies, current preparation methods still suffer from serious problems with respect to complex procedures, the requirement of special equipment, incontrollable morphology and size, as well as low yields, which significantly limits their broad applications in various scientific fields. In this regard, novel methods for allowing facile preparation of high quality CQDs/GQDs with high-yield are highly desired.

Herein, we present a facile chemical exfoliation of multiwall carbon nanotubes (MWCNTs) for preparation of GQDs via a modified hummers' method [28]. The resultant GQDs were very uniform in size, and possess strong electronics property. Using our GQDs as photocatalyst promoters, we demonstrate the design and preparation of GQDs/P25 (TiO_2) nanocomposites, which show significantly promoted photocatalytic performance for the degradation of organic dyes under visible-light irradiation.

2. Experimental section

2.1. Preparation of GQDs from CNTs

GQDs were prepared from chemical exfoliation of purified MWCNTs by a modified hummers' method. In a typical synthesis, 200 mg of MWCNTs were immersed in 46 mL conc. H_2SO_4 and then 6 g of $KMnO_4$ was added slowly in small quantities under mild stirring while

* Corresponding author.
E-mail address: yonglaizhang@jlu.edu.cn (Y.-L. Zhang).

http://dx.doi.org/10.1016/j.catcom.2015.11.010
1566-7367/

the temperature was maintained between 0 and 5 °C by using an ice bath. After the complete addition of $KMnO_4$, the mixture was heated to 37 °C and kept at this temperature for about 1 h. Then, distilled water (92 mL) was added slowly. The temperature of the mixture was raised to 95 °C and maintained for about 12 h. The mixture was further diluted with 280 mL of water and later 20 mL of 30% H_2O_2 was added. The resultant mixture was purified by following procedure: firstly, low-speed centrifugation was done at 4000 rpm for 15 min about 3–5 times to the removal of the unexfoliated MWCNTs and some water-soluble by-product. Secondly, high-speed centrifugation was implemented at 12,000 rpm for 15 min to collect GQDs samples. Then, the precipitates were redispersed in water with mild sonication and then the remainder mixture was dialyzed in a dialysis bag for 48 h to ensure the complete removal of residual metallic impurities and acid.

2.2. Preparation of GQDs/P25 nanocomposites

In a typical preparation of GQDs/P25 nanocomposites, 200 mg of P25 fine powder was added into 50 mL as-synthesized GQDs aqueous solution with a concentration of 2 $mg \cdot mL^{-1}$ with the aid of ultrasound. Then, water in the mixture was evaporated under stirring in an uncovered beaker at room temperature. The resultant composite was designated as GQDs/P25. To further reduce the GQDs, the composite was annealed at 200 °C for 2 h; and the resultant was designated as GQDs/P25-R.

2.3. Photocatalytic tests

Photocatalytic degradation of rhodamine B (RhB) was carried out in 80 mL quartz cuvette containing 20 mL (10 $mg \cdot mL^{-1}$) RhB solution and a suitable amount (20 mg) P25 nanoparticles, GQDs/P25, or GQDs/P25-R nanocomposites as catalyst. A 350 W xenon lamp was used for illumination. Photocatalytic degradation of methyl orange (MO) was carried out under the same condition.

2.4. Characterization

Transmission electron micrographs (TEM) and high-resolution TEM (HR-TEM) images were obtained with a JEOL JEM-1011 transmission electron microscope and a Hitachi H-7650 transmission electron microscope, respectively. Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer. UV–vis spectra were measured with a PE Lambda 20 spectrometer. Fluorescence spectra were measured with a Shimadzu RF-5301PC spectrofluorimeter. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. Spectra were baseline corrected using the instrument software. Thermogravimetric (TG) curves were carried out on a NETZSCH STA 449C with a heating rate of 20 °C·min^{-1} from room temperature to 800 °C.

3. Results and discussion

3.1. Characterization of GQDs

Fig. 1a shows the TEM image of both pristine MWCNTs. The diameter of our MWCNTs was about 15 nm, and the wall thickness is ~5 nm. The diameter of CNTs is very important for the size control of the resultant GQDs, thick CNTs would significantly broaden the size distributions of the resultant GQDs. Fig. 1b shows the TEM image of typical GQDs; it reveals that the monodisperse GQDs are very uniform in size, about

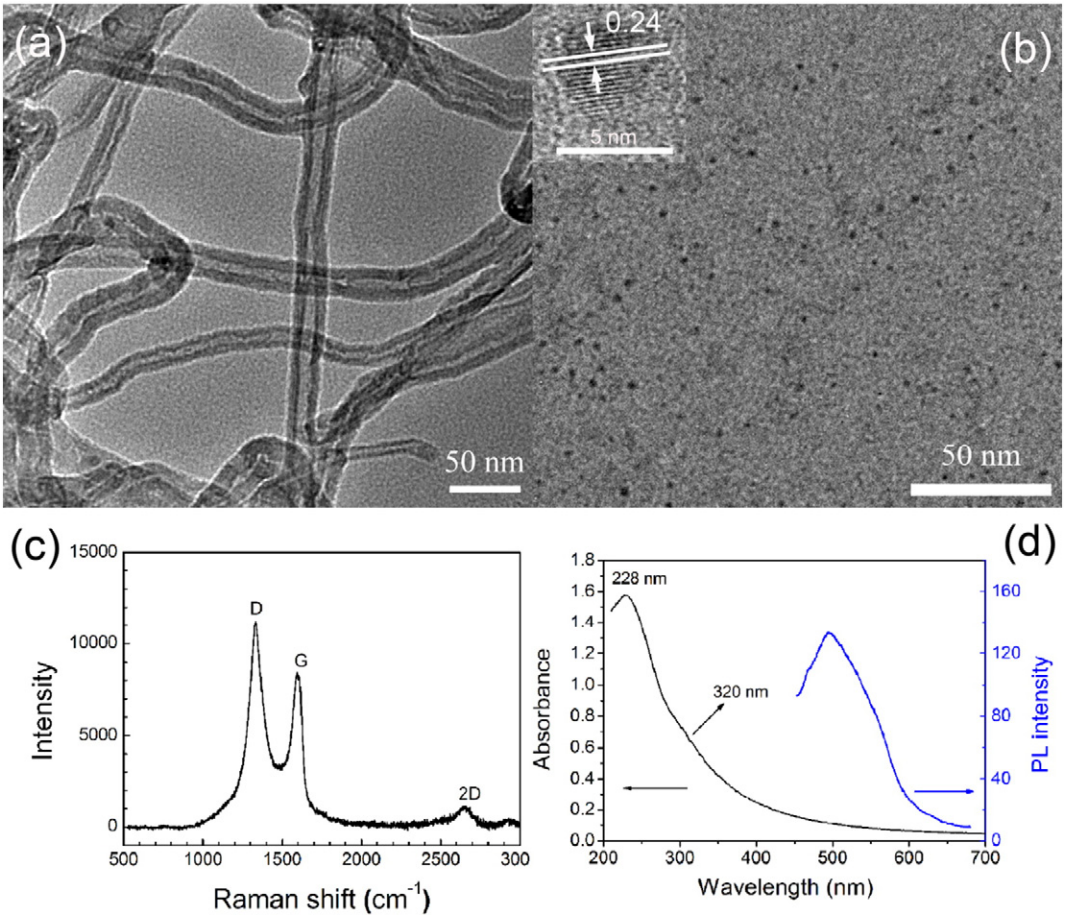

Fig. 1. (a) TEM images of MWCNTs with diameters under 20 nm, (b) TEM images of GQDs with diameters under 5 nm (inset: HR-TEM image of a typical GQDs), (c) raman spectrum of GQDs, and (d) UV–vis absorption and photoluminescent (PL) emission spectra of an aqueous dispersion of GQDs.