Diamond & Related Materials 69 (2016) 81–85

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Effect of modified graphene quantum dots on photocatalytic degradation property

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ARTICLE INFO

Article history:
Received 12 May 2016
Received in revised form 6 July 2016
Accepted 18 July 2016
Available online 19 July 2016

Keywords:
Graphene quantum dots
Organic matter degradation
Photocatalytic property
Polymer-modified

ABSTRACT

The effective use of solar energy in sewage disposal has been extensively investigated. This work focuses on the photocatalytic property of graphene quantum dots (GQDs) and polymer-modified GQDs under visible light. A hydrothermal synthesis route to GQDs was developed by using citric acid as a carbon precursor. The GQDs were modified with polyethylenimine (PEI) and polyethylene glycol (PEG). The obtained GQDs, GQDs-PEIs, and GQDs-PEGs were characterized and their structural information was determined through Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), photoluminescence spectroscopy, and UV–Vis absorption spectroscopy. Results revealed that the GQDs were uniform in size (2–5 nm) and rich in oxygen-containing groups. The GQDs exhibited a strong blue and excitation-independent photoluminescent behavior under excitation wavelengths of 320–420 nm. The photocatalytic performance of these samples was demonstrated on the basis of methylene blue (MB) degradation. The photocatalytic rates of GQDs, GQDs-PEIs, and GQDs-PEGs decreased successively. The polymer-modified GQDs could qualitatively control the degradation rate of MB. Free radical species were generated to oxidize MB under light irradiation. Thus, photocatalytic organic matter degradation, sustained drug release, and tracking can be combined to implement proper sewage disposal.

Prime novelty: The main object of this work is to find out a novel property of graphene quantum dots (GQDs) as efficient nanomaterials for degradation of organic pollutant dyes under visible light irradiation. And, the GQDs exhibited a strong blue and excitation-independent photoluminescent behavior under excitation wavelengths of 320–420 nm. Moreover, the degradation rate could be qualitatively controlled by using different polymer-modified GQDs. Thus, photocatalytic organic matter degradation, sustained drug release, and tracking can be combined to implement proper sewage disposal. Also, the degradation mechanism is discussed.

1. Introduction

Energy shortage and environmental pollution are major problems worldwide. As a newly developed energy source, solar energy is abundant, renewable, and pollution-free. The effective utilization of solar energy for environmental pollution treatment and clean energy conversion was extensively investigated. Functional materials, such as photocatalytic semiconductors, have been highly considered for solar energy applications [1]. These materials can directly utilize solar energy to degrade organic pollutants [2]; however, most of these materials are applicable in the UV region only. Zhou et al. [3] used complex photocatalysts, namely, rutile TiO_2/GQDs and anatase TiO_2/GQDs systems, to harness the visible spectrum of sunlight and thus allow photocatalytic organic matter degradation in visible light. However, insufficient research was performed to synthesize graphene quantum dots (GQDs) with an excitation-independent behavior for the visible light photocatalytic degradation of organic matter [4]. GQDs [5–8] are new types of quantum dots that were widely explored because of their pronounced quantum confinement and edge effects. GQDs display numerous novel physical and chemical properties [9–12], such as stable photoluminescence, thermal conductivity, and enhanced surface grafting; as such, GQDs are considered as promising materials of optoelectronic devices [13,14]. Pan et al. [9] prepared GQDs with bright blue photoluminescence by cutting oxidized graphene sheets through a hydrothermal method. In addition, a simple, reliable, and reproducible approach was developed to directly prepare functional GQDs with uniform size (3–5 nm) and green luminescence [15]. The optical properties and surface modification of GQDs were also examined [14,16].

High concentrations of organic pollutants and microorganisms have been detected in wastewater. Microorganisms are treated using drugs with polymers as a carrier. Polymer-modified GQDs [17] likely combine photocatalytic organic matter degradation, sustained drug release, and tracking. Polyethylenimine (PEI) and polyethylene glycol (PEG) were applied in biopharmaceutical research [18,19] and were used to modify GQDs. This study examined the visible light catalytic degradation property of GQDs and its effects on the photocatalytic degradation property of polymer-modified GQDs. The prepared GQDs exhibit uniform size distribution and excitation-independent photoluminescence [20]. This

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http://dx.doi.org/10.1016/j.diamond.2016.07.008
0925-9635/

study also investigated the structural and optical properties of the GQDs in detail.

2. Experimental

2.1. Synthesis of GQDs, GQDs-PEIs and GQDs-PEGs

Citric acid (2.52 g; TianJin ZhiYuan Reagent Co., Ltd.) and urea (2.16 g; TianJin Guangfu Technology Development Co., Ltd.) were dissolved in 60 mL of deionized water and stirred to form a clear solution. The solution was then transferred to a 100 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was heated to 160 °C in an electric oven and maintained at the same temperature for another 4 h. The final product was collected by adding ethanol to the solution. The resulting solution was then centrifuged at 10,000 rpm for 10 min. Afterward, the solution was concentrated in a lyophilizer (Beijing Boyikang Experimental Instrument Co., Ltd.). PEI and PEG (Mw = 10,000; Aladdin Reagents [Shanghai] Co., Ltd.) were employed as modifying compounds because of their environment-friendly properties [21].PEI (0.2 g) was added to an aqueous solution of GQDs (50 mL, 1 mg/mL) with thorough stirring. The solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, heated to 200 °C, and maintained for 20 h. The colloidal solution was cooled to room temperature, purified, and separated through column chromatography on a silica gel to remove the excess PEI. For comparison, GQDs-PEGs were prepared with the same preparation process used for GQDs-PEIs. However, the solution was autoclaved for 24 h.

2.2. The photocatalytic activities of the samples

The photocatalytic activities of the samples were evaluated on the basis of methylene blue (MB; Tianjin HengXing Reagent Co., Ltd.) degradation at room temperature. GQDs, GQDs-PEIs, and GQDs-PEGs (1 mL, 2 mg/mL) were added to MB aqueous solution (50 mL, 10 mg/L). The suspension was protected from light and magnetically stirred for 1 h to reach adsorption equilibrium. A 300 W Xe lamp was used as a light source with a 400 nm cutoff filter to provide visible light irradiation. The distance between the light and the solution was approximately 15 cm. At given intervals, the UV–Vis absorption spectra of the three samples were obtained. MB was determined spectrophotometrically at $\lambda_{max} = 664$ nm. The photocatalytic degradation rate of MB was calculated by using the following equation: $E = (A0 - A)/A0 \times 100\%$, where A0 is the adsorption equilibrium absorbance of MB and A is the absorbance of the MB solution at irradiation time.

2.3. Characterization methods

The photoluminescence (PL) spectra of the samples dispersed in deionized water were obtained with a FluroMax-4 fluorescence spectrophotometer (Horiba Jobin Yvon, Japan). Absorption measurements were performed using a Hitachi U-3900 UV–Vis spectrophotometer (Hitachi, Japan). Morphological analysis was conducted with a high-resolution transmission electron microscope (HRTEM, JEM-2010). The FT-IR spectrum of the samples was obtained with a Bruker Tensor 27 Fourier transform infrared spectrometer (Bruker, Germany).

3. Results and discussion

The TEM image (Fig. 1a) shows that the collected GQDs are monodispersed with a mean diameter of 3.34 nm. The discernible lattice structures of the GQDs in the TEM images indicate that the resultant nanoparticles exhibit a graphitic nature. A representative HRTEM image (Fig. 1c) displays a lattice spacing of approximately 2.5 Å, which is very near to that of graphene (1120) facets [22]. These results suggest that the nanoparticles may be composed of nanocrystalline cores of graphene sp^2 carbon atoms.

The solutions of GQDs, GQDs-PEIs, and GQDs-PEGs emit blue luminescence when they are excited with a 365 nm UV beam. Fig. 2a shows the UV–Vis spectrum of the as-prepared GQDs, GQDs-PEIs, and GQDs-PEGs. The UV–Vis spectrum reveals a clear absorption band at 218 nm that can be attributed to the π-π* electron transition of C═C. This result is similar to that of GQDs prepared by a hydrothermal

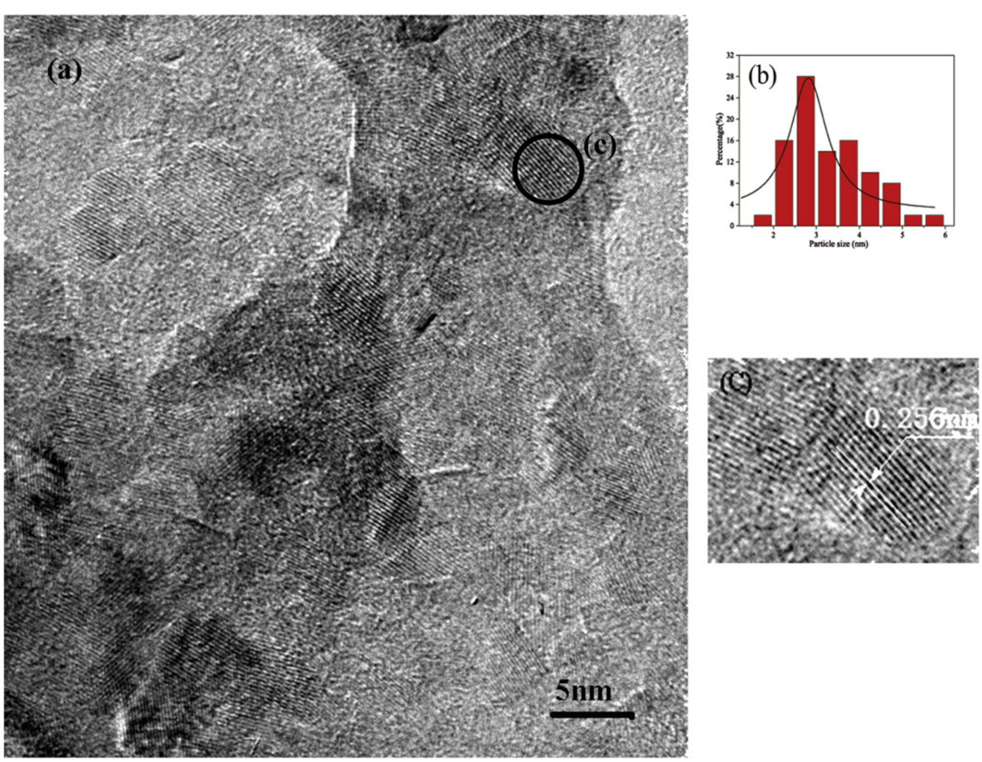

Fig. 1. (a) TEM image of the GQDs, (b) the corresponding size distribution, and (c) high-resolution TEM image of single GQD.