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Original Research Paper

Synthesis of magnetic carbon nanodots for recyclable photocatalytic degradation of organic compounds in visible light

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ABSTRACT

In this study, magnetic carbon nanodots (C-dots) were synthesized by connecting C-dots and magnetic Fe_3O_4 nanoparticles (so called magnetic C-dots) in seeking to understand the photocatalytic activity under visible light and the recyclable ability in wastewater treatment. All of the samples were synthesized by bottom-up procedure at reaction temperatures (T_r) of 140 °C and 180 °C with different reaction times (t_r = 0–18 h). The results indicated that the C-dots gradually attached to Fe_3O_4 nanoparticles with the increase of t_r at T_r = 140 °C, but suddenly approached saturation adsorption on Fe_3O_4 particles at T_r = 180 °C. Microstructural images confirmed that magnetic Fe_3O_4 nanoparticles were surrounded by C-dots 5–10 nm in size. Optical properties illuminated that magnetic C-dots presented a red-shifted emission at λ = 300–450 nm attesting to their photocatalytic ability in visible light. In this study, a higher extent of degradation of the dye was noted in a larger amount of C-dots on a Fe_3O_4 nanoparticle surface. Methylene blue (MB) concentration can be decreased by 83% within 30-min visible light irradiation. A recyclability test evidenced that the magnetic C-dots can further photodegrade large MO concentrations by at least 10-fold or more. Therefore, magnetic C-dots exhibit good degradation ability for MB under visible light, and could be easily recycled by applying a magnetic field after photodegradation, as shown in this study.

1. Introduction

A life of convenience entails a great deal of pollution that can harm our natural environment, as we have witnessed from the 18th century to the present. Massive industrial wastewater has been drained into rivers, thereby infiltrating and contaminating the groundwater system. Industrial wastewater contains organic compounds and metal ions from manufacturing, such as printing, papermaking, dyeing, and the food industry. Industrial wastewater may contain organic pollutants which are colored, toxic, carcinogenic, and teratogenic; if injected into nature without proper treatment, plants, aquatic organisms, and humans will be harmed [1,2]. In addition, these colored substances are hard to remove naturally as the concentration of dye in the effluents is less than 1 ppm in water [3,4]. Adsorption and a technique to head off pollution are usually adopted to treat wastewater; however, only photocatalytic degradation can transfer organic wastewater into CO_2 and H_2O without any intermediate [5,6]; thus, photocatalytic degradation is a promising green material in environmental technology. It is well-known that TiO_2 is a photocatalyst because it is clean and has low toxicity and good degradation ability [5]. The band gap of TiO_2 is about 3.2 eV, implying that only high energy light, e.g. ultraviolet light, can trigger its photocatalytic response [6]. However, high energy light (λ < 400 nm) is obtained in only 5% in the sunlight; the other 95% is visible light and heat [7]. A proper photocatalyst material should work in natural surroundings.

Carbon nanodots (C-dots), part of the carbon family, were discovered in 2004 [8]. C-dots act as an alternative photocatalyst whose photocatalytic response can be triggered by sunlight. C-dots possess not only low toxicity and a unique optical property, but also a large range for absorption in visible light [9]. According to the quantum size effect, small size materials exhibit more effective conversion ability. The average size of C-dots is smaller than 10 nm; hence, C-dots could contribute more effective conversion ability, becoming a potential material to replace the traditional semiconductor photocatalyst. However, it is difficult to remove C-dots from the aqueous phase after putting them in wastewater and finishing the degradation due to the C-dots' lack of polarity; hence, the result is secondary pollution [10]. In order to separate these nanoscale C-dots from wastewater, a costly recyclable procedure is needed due to the C-dots' small particle size. Connecting

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magnetic particles is one promising solution; it is an easy and inexpensive way to replace traditional separation [11]. Nanomagnetite (Fe_3O_4) particles show low toxicity, bio-compatibility [12], high magnetization, and superparamagnetism [13–16]. The mobility of magnetite nanoparticles could be easily controlled by applying a magnetic field. If C-dots can attach to the surface of magnetic Fe_3O_4 nanoparticles, the C-dots would be easily trapped, removed, and recycled by the applied magnetic field after finishing photocatalytic degradation. Hence, in this study, C-dots were fabricated on a magnetic Fe_3O_4 nanoparticle as a new type of photocatalytic material (so-called magnetic C-dots). Our results presented that magnetic C-dots exhibit outstanding photocatalytic activity. More than 80% degradation of dye in the solution was confirmed following 30 min of visible light irradiation. In brief, the magnetic C-dots could be easily trapped, restored, and recycled using an applied magnetic field after photodegradation.

2. Experimental methods

2.1. Materials

Glucose ($C_6H_{12}O_6$), the precursor of C-dots, was supplied by Riedel-de Haën (Morristown, NJ, USA). Sodium hydroxide (NaOH) and acetic acid (CH_3COOH) were obtained from the Macron Fine Chemicals Co. (Center Valley, PA, USA) and the Sigma-Aldrich Co. (St. Louis, MO, USA), respectively. Commercially-available magnetic Fe_3O_4 nanoparticles, with a size of 20–40 nm, were purchased from Nanostructured and Amorphous Materials Inc. (Houston, TX, USA). For the photocatalytic degradation tests, methylene blue (MB), one of the azo dyes which is usually used in industry [17], was purchased from Acros Organics (Geel, Belgium). The chemical formula of MB is $C_{16}H_{18}N_3ClS$.

2.2. Synthesis of magnetic C-dots

Magnetic C-dots were fabricated by connecting the C-dots and magnetic Fe_3O_4 nanoparticles by a bottom-up procedure. Fig. 1 describes the synthetics process. First of all, glucose (4 g) was added to acetic acid (40 ml), and the solution was stirred for 30 min. Following this, commercial magnetic Fe_3O_4 nanoparticles (0.4 g) were added into the solution. After stirring the solution for 30 min with a magnetic stirring apparatus (the mixture process in Fig. 1(a)), the solution was transferred into a 50 ml Teflon-lined stainless autoclave whose reaction temperature (T_r) was kept at 140 °C and 180 °C. The reaction time (t_r) was varied from 0 to 18 h, where $t_r = 0$ means the solution remained in a mixture state before heating. During the nucleation process (Fig. 1(b)), C-dots precipitated at the surface of Fe_3O_4 particles initially in an autoclave. Continuously extending the t_r, the size of the C-dots grew to about 10 nm, called the growth process in Fig. 1(c). After the reaction, the solution was cooled naturally to room temperature. The produced powders were then separated from the solution using Nd-Fe-B magnets and washed with DI water and ethanol three times, respectively. The washed powders were dried at 70 °C for 12 h in a vacuum oven prior to storage.

2.3. Characteristics of magnetic C-dots

In this study, magnetic hysteresis loops of magnetic C-dots were measured using a vibrating sample magnetometer, VSM (DMS Model 1660, ADE Technologies Inc., MA, USA) in the applied field range of ±10 kOe. Crystal structures of magnetic C-dots were analyzed by a D2 PHASER X-ray diffractometer, XRD (Bruker, Germany) with a scanning region of 2θ from 10° to 70°. Functional groups were measured by Fourier transform infrared, FTIR (PerkinElmer Spectrum 100, PerkinElmer, Massachusetts, USA). Photoluminescence properties used photoluminescence (PL) spectroscopy (OBB Quattro II, Optical Building Blocks, New Jersey, USA). The surface morphology of magnetic C-dots prepared under various conditions was determined by a JEOL scanning electron microscope, SEM (JSM-7800F Prime, Tokyo, Japan). Microstructures and nanobeam compositions of the samples were observed by a JEOL transmission electron microscope, TEM (JSM-2010, Tokyo, Japan) with EDS analysis. The accelerating voltage during the TEM operation was 200 keV.

2.4. Photocatalytic degradation experiments

Photocatalytic degradation of the industrial dye, methylene blue (MB), was investigated by dispersing 50 mg of photocatalyst in 25 ml of a MB dye solution (2×10^{-3} M) and 25 ml of NaOH solution (0.01 M). The hybrid solution was stirred for 60 min under dark conditions for physical adsorption. A xenon lamp (400 W) was the source of visible light providing a cutoff filter ($\lambda > 420$ nm). The concentration of MB was detected using a UV–VIS spectrum with $\lambda_{max} = 663$ nm. After visible light irradiation for 30 min, the photodegraded material was removed from the MB hybrid solution using Nd-Fe-B magnets.

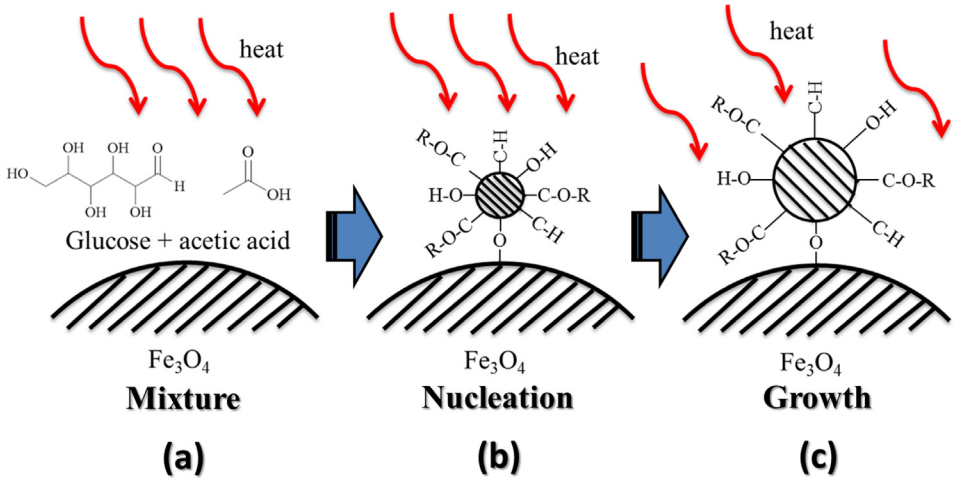

Fig. 1. The synthetic process of magnetic C-dots.

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