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Synthesis of carbon quantum dots/TiO_2 nanocomposite for photo-degradation of Rhodamine B and cefradine

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ABSTRACT

Pure TiO_2 and carbon quantum dots (CQDs)-doped TiO_2 nanocomposite (CQDs/TiO_2 nanocomposite) were prepared by a sol-gel approach for photocatalytic removal of Rhodamine B and cefradine. Analyses by Transmission electronmicroscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), UV–visible spectroscopy and X-ray powder diffraction (XRD) confirmed the successful formation of CQDs/TiO_2 heterostructure. The as-prepared TiO_2 and CQDs/TiO_2 composite possessed small particles, spherical-like shape, and anatase crystal form. Meanwhile, Rhodamine B and cefradine were chosen to evaluate the photocatalytic activity of TiO_2 and CQDs/TiO_2 composite. Results revealed that with the facile decoration of CQDs, the absorption of photocatalyst was extended into visible light region and photocatalytic activity was improved in comparison with pure TiO_2. Furthermore, the mechanism for the improvement of the photocatalytic performance of the composites was discussed on the basis of the results. CQDs play an important role in the photocatalytic process, due to their superior ability to extend the visible absorption and produce more electrons and electron–hole pairs for the degradation of pollutants. In all, the paper offers further insights into the development of CQDs/TiO_2 nanocomposite as photocatalyst for the degradation of antibiotics.

1. Introduction

As one of the most promising photocatalysts for large scale production, TiO_2 has been widely studied during the decades on account of their low cost, favorable chemical stability and low toxicity [1]. The key step of photocatalytic process is to generate highly active photoexited e^-/h^+ pairs and increase the utilization of photogenerated charge carriers for photocatalytic reaction. However, the band gap of TiO_2 (anatase: 3.2 eV; rutile: 3.0 eV) irradiated only by 3–5% UV light of solar spectrum has limited its widespread application [2]. Various attempts have been made to modify TiO_2 nanoparticles to enhance its photocatalytic activity by coupling with other materials, such as semiconductor materials, metal ions, dyes and nonmetal elements. These materials can form the energies of the intermediate states in the band gap [3,4]. N doped TiO_2 was firstly reported to improve photocatalysis of TiO_2 in the visible light range, and then follow by C, S, Fe and F elements [5–7]. Yet, the combination of charge carriers generated by TiO_2 doped heteroatoms irradiated will be accelerated inside TiO_2, due to the increase of massive binding sites introduced by heteroatoms and defects.

Carbon nanomaterials have been demonstrated as efficient means to enhance the photocatalytic reactions on account of their superior conductivity, capacitance,absorption of visible light and chemical stability. For instance, carbon-based TiO_2 was prepared to degrade the cytotoxin released from cyanobacteria, such as microcystin-L, cylindrospermopsin, geosmin, and 2-methylisoborneol [8–10]. However, carbon nanotubes and graphene are easy to aggregate and inconvenient to react with charge carriers of TiO_2, which will limit their photocatalysis application [11–13]. To avoid the aggregation, multiwalled carbon nanotubes coated with TiO_2 were prepared by a sol-gel method and loaded on heat-pretreated silica gel for photocatalytic removal of NO. The result revealed that optimal denitration efficiency of MWCNTs/TiO_2 was 46% [14]. Recently, Dionysiou group have developed ceramic membranes coated with partially reduced graphene oxide/TiO_2 composite (GOT) to remove the organic dyes [15]. Results demonstrated that the photocatalytic membrane reactor has higher pollutant removal efficiency and lower energy consumption, comparing with standard nanofiltration. The team also utilized the TiO_2-RGO composites for the disinfection of water under real sun conditions, which have achieved good results [16]. Carbon quantum dots (CQDs) as a kind of novel and environmental carbon nanomaterial, have been drawn much attention due to their multiple synthesis methods, favorable biocompatibility and unique photo-induced electron transfer [17]. Among the various applications of CQDs, some researchers have focused on the photocatalysis of CQDs. For instance, Au/CQDs composite were

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used as a photocatalyst for selective oxidation of cyclohexane in the presence of H_2O_2 under visible light [18]. Result showed that the conversion efficiency was 63.8% and selectivity was 99.9% for the oxidation of cyclohexane to cyclohexane. Similarly, CQDs can realize the transformation from benzyl alcohol to benzaldehyde with high selectivity (100%) and conversion (92%) under NIR light irradiation [19]. As for the photocatalytic degradation of dye, CQDs doped with ZnO and HA respectively to degrade the methylene blue (MB) under visible-light irradiation [20,21]. Both of them revealed that the degradation efficiency of MB by composites reached the maximum value of 80%–90%, which enhanced by about 3 times with respect to that of single nanoparticles. Remarkably, CQDs have been embedded in various microstructures of TiO_2, and then used to enhance the photocatalysis of degrading azo-dye, methylene blue and catalyzing hydrogen evolution in the previous studies [22–24]. Tian and his colleges reported good performance of CQDs/hydrogenated TiO_2 in the degradation of methylene orange in aqueous solution upon UV, visible, and NIR light irradiation [22]. Moreover, CQDs/TiO_2 composites also can be utilized for H_2 evolution under UV–Vis light irradiation, which showed photocatalytic H_2 evolution rate was 4 times higher than that of pure P25 [25]. These literatures proposed that CQDs with NIR up-conversion activity might serve as an intermedium to generate strongly oxidative holes and reductive electrons, which is the key factor in enhancing the photocatalytic activity [26].

In recent years, organic dyes and antibiotics which are important pollutants released from human activities, have been widely concerned by people. These environmental pollutions are persistent and bioaccumulative, and then will bring great damage to ecological environment if their concentrations greatly exceed the level of environment self-purification. So much effort has been made on the removal of organic dyes and antibiotics from water [27,28]. As for the degradation of antibiotics, pure TiO_2 and metallic nanoparticles supported on TiO_2 have been used to degrade antibiotic in water, showing auspicious results [29,30]. Giraldo-Aguirre and his colleagues reported the complete degradation of oxacillin after 120 min of UV light (150 W) irradiation using TiO_2 nanoparticles [31]. Similarly, a previous report described the complete photodegradation of chloramphenicol after 18 min of UV light irradiation using silver-doped TiO_2 nanoparticles [32]. Chung et al. reported the complete degradation and mineralization of ciprofloxacin within 180 min of UV-C light irradiation using TiO_2 modified with mono-(Au, Ag and Cu) and bi-metallic (Au–Ag and Au–Cu) nanoparticles [33]. Though studies related to photocatalytic degradation on antibiotics using pure TiO_2 and TiO_2 doped metallic nanoparticles are cited in the literature, the photocatalytic degradation of antibiotics using CQDs/TiO_2 composite has been rarely reported [29,34].

Herein, we demonstrated a convenient sol-gel method to synthesize TiO_2 doped CQDs heterostructure for enhancing the photocatalytic degradation of Rhodamine B and cefradine which is a semi-synthetic first-generation cephalosporin antibiotic used in human and veterinary medicine worldwide. Meanwhile, optimized parameters of photocatalytic degradation on cefradine and mechanism of photocatalytic degradation were also investigated. For the best of our knowledge, this is the first study using CQDs deposited on TiO_2 for the removal of cefradine in water, which broadened the photocatalytic application of CQDs/TiO_2 composite.

2. Experimental section

2.1. Materials

Hydrogen peroxide (30%, Nanjing Chemical Reagent Co., Ltd., AR) and acetic acid (Nanjing Chemical Reagent Co., Ltd., AR) used to synthesize the CQDs were purchased from Nanjing chemical reagent corporation. Tetrabutyl titanate (98%, Shanghai Macklin Biochemical Co., Ltd., AR) and nitric acid (65–68%, Nanjing Chemical Reagent Co., Ltd., AR) were used to synthesize TiO_2 nanoparticles and carbon quantum dots/TiO_2 composite materials. Methanol (HPLC) and acetonitrile (HPLC) were purchased from CINC High Purity Solvents (Shanghai) Co., Ltd. The other reagents including Rhodamin B (RhB), cefradine and dehydrated alcohol were analytical grade reagents and used as received. High-purity water was used in the experiments.

2.2. Synthesis of CQDs, TiO_2, CQDs/TiO_2 composite

CQDs were prepared by chemical oxidation treatment of starch according to our previous report. Briefly, carbonized starch as carbon source was dissolved in the distilled water. Then the solution was refluxed with acetic acid and hydrogen peroxide based on certain scale (1:1:2) for 2 h at 120 °C [35]. Finally, the CQDs were obtained after the purification by dialysis. To synthesize CQDs/TiO_2 composite, 56 mL ethanol was added slowly into 14 mL CQDs aqueous solution (dissolved 10 mg, 20 mg, 40 mg CQDs powder respectively) under stirring [36]. Then the solution was adjusted to pH = 2.5 with HNO_3 and put into a round-bottomed flask (250 mL), follow by water bath heating at 70 °C with the mechanical stirring. 8.5 mL tetrabutyl titanate was injected into the reaction solution and heated for 24 h. After that, the crude products were washed with absolute ethanol and distilled water for several times and then dried in an oven at 80 °C for 8 h. The synthetic process of TiO_2 was the same as that of CQDs/TiO_2 except that CQDs were not used.

2.3. Characterizations

Transmission electronmicroscopy (TEM) was carried out using JEM-2100 operated at an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) pattern of catalysts were collected on a ARL X'TRA X-ray diffractometer using Cu Kα radiation in the 2θ range of 15–85 °C. Scanning electron microscopy (SEM) was used to characterize the morphologies and size of the synthesized TiO_2 and CQDs/TiO_2 composite. The chemical composition was investigated via energy-dispersive X-ray spectroscopy (EDS). UV–vis spectroscopy was carried out with a Shimadzu UV-2100 UV/vis spectrometer. HPLC (BACKMAN Spectra 100) was used to measure the concentration of cefradine. The detailed chromatographic conditions were as follow. The sample was eluted by the buffer solution of acetonitrile and acetic acid (12:88) with constant liquid flow rates (1.0 mL/min) to go through a chromatographic column (Baseline C18 (150 × 4.6 nm, 5 μm). XPA photocatalytic reactor (Xujiang Machine Factory, Nanjing, China) was used for the photocatalytic degradation of RhB and cefradine [37].

2.4. Photocatalytic activity studies

The photocatalytic activity of the CQDs/TiO_2 composite materials was investigated by the photodegradation of Rhodamin B (RhB) and cefradine under the irradiation of an 8 W UV lamp(λ = 365 nm). For degradation of RhB, 1 mg/mL solution of CQDs/TiO_2 composite synthesized by various amounts of CQDs(10 mg, 20 mg, 40 mg) were added in 200 mL RhB (5 mg/L) solution respectively. Then, the suspensions were treated by ultrasound for 10 min to ensure the photocatalyst was fully contacted with RhB. After that, the solution was exposed to UV-irradiation under stirring (400 rpm) at 20 °C for 120 min. During the measurement process, a certain amount of the solution was sampled at certain time intervals and centrifuged (10,000 rpm, 3 min) to remove the photocatalyst particles. The supernatant was analyzed to measure the concentration of RhB by using a Shimadzu UV-2100 UV/vis spectrometer (peak center: 554 nm). The calibration curve presents a linear relation within the range of 0.1–10 mg/L and relationship coefficient was 0.9998 (Fig. 1(a)). Eventually, the conversion was defined as follows:

$$\text{conversion}(\%) = \frac{C_0 - C}{C_0} \times 100$$