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The fabrication of bio-renewable and recyclable cellulose based carbon microspheres incorporated by $CoFe_2O_4$ and the photocatalytic properties

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ABSTRACT

The bio-renewable cellulose based carbon microspheres through a one-step hydrothermal process (CMS) and a two-step hydrothermal plus pyrolysis process (pCMS) were prepared in the present study, respectively. The prepared carbon microspheres were then hybridized with magnetic $CoFe_2O_4$ to prepare recyclable photocatalyst composites. The impact of pyrolysis step on the photocatalysis performance of the composites were then investigated through degrading rhodamine B dye. The results indicated that the incorporation of both CMS and pCMS could significantly enhance the photocatalytic efficiency of the pristine $CoFe_2O_4$. Since the pyrolysis carbonization process led to a higher graphitization degree to the pCMS, the pCMS-$CoFe_2O_4$ exhibited higher photocatalytic properties than the CMS-$CoFe_2O_4$. Moreover, due to the existence of the magnetic $CoFe_2O_4$, the prepared photocatalysts could be easily separated from the water and readily reused for more cycles, achieving the goal of cleaner production through avoiding secondary pollution lead by the photocatalyst. The present study could open up a new thinking of preparing environmentally sustainable photocatalyst using bio-renewable biomass in the field of wastewater treatment.

1. Introduction

Photocatalysis technology has attracted enormous research interest recently in solving water contamination problems, especially the degradation of organic pollutants due to its merits of high efficiency, high reaction rate, low toxicity, etc. (Dhiman et al., 2017; Gan et al., 2016a, 2016b; Reddy et al., 2011). Moreover, the photocatalysis technology has been thought as an environment-friendly wastewater treatment approach since it utilizes light source as the energy (Ananpattarachai and Kajitvichyanukul, 2016). During the photocatalytic process, the photocatalysts harness the photo energy from the irradiation light to form electron-hole pairs, and produce active radicals which will further drive chemical reactions to decompose organic pollutants (Hadnadjev-Kostic et al., 2017; Xu et al., 2017). In the past few decades, many semiconductors, such as TiO_2, ZnS and CdS, which demonstrated efficient photocatalytic properties, have been well investigated (Meng et al., 2013; Pozo-Antonio and Dionísio, 2017; Reddy et al., 2015, 2016). However, on account of the limitation of wide band gaps, say normally higher than 3.0 eV, these semiconductors can only absorb UV range light, resulting in a relatively low potency in utilization of solar energy (Achouri et al., 2016; Ahmad et al., 2013). Thus, numerous studies have been conducted to develop high-efficient photocatalysts with narrower band gaps which could effectively utilize the incident light and generate redox reactions (Ao et al., 2014; Priyadharsan et al., 2017).

Amongst them, the ferromagnetic photocatalysts, which are chemically and thermally stable magnetic materials, have been studied intensively since they provide desirable optical absorption with relatively narrow band gaps (~2 eV) (Choi et al., 2015; Gan et al., 2015a; Reddy et al., 2008a). Moreover, desirable magnetic

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properties can also provided by the ferromagnetic photocatalysts, which facilitate easy separation from wastewater by magnetic field, and achieves the goal of cleaner production through avoiding secondary pollution to the natural water bodies (Della Pina et al., 2015). Besides, the separated photocatalysts can be recycled for further use, which can be considered as environmentally sustainable materials for wastewater treatment. Thus, the ferromagnetic photocatalyst is considered as a promising alternative to the traditionally used UV-activated catalysts. Meanwhile, it has also been found in many studies that the combination of carbonaceous materials and photocatalysts could simultaneously reduce the band gap and decrease the recombination rate of electron and hole pairs of the photocatalysts, resulting in a higher photo energy conversion rate (Fu et al., 2012; Hassan et al., 2014; Hu et al., 2015). However, most of these carbonaceous materials, such as graphene, carbon nanofibers, are mainly derived from the gradually declining oil resources (Reddy et al., 2008b, 2014), which will induce energy crisis in the long term. Recent studies have shown that being pyrolyzed at oxygen-limited conditions, the naturally abundant biomass could be turned to carbon-enriched biochar materials, and these biomass derived carbonaceous materials could serve as desirable carbon alternatives (Dunnigan et al., 2018; Pi et al., 2015). As a representative, the cellulose is a natural biomass with the advantages of being abundant, ecofriendly, cheap, sustainable and renewable (Laadila et al., 2017; Wan et al., 2015). It has been shown that after hydrothermal process integrated with pyrolysis treatment, the cellulose based carbon microspheres with high specific surface areas, large pore size and low densities could be fabricated (Wu et al., 2015a, 2015b). Previous studies also have indicated that semiconductors loaded microsphere photocatalysts showed enhanced photocatalytic properties since high specific surface areas and large pore size of the microsperes could facilitate the adsorption of organic pollutants, which could improve accelerate the following photo-degradation process (Wang et al., 2017). However, limited studies have investigated the photocatalytic properties of the cellulose carbon microsphere based composite photocatalysts. Furthermore, few studies have discussed the recovery and recycling of these microsphere based photocatalysts until recently.

Herein, two kinds of carbon microspheres were prepared using a one-step hydrothermal process (CMS) and a two-step hydrothermal plus pyrolysis (pCMS) process. The prepared CMS and pCMS were further hybridized with the ferromagnetic cobalt ferrite ($CoFe_2O_4$) to prepare the photocatalyst composites. The structure and morphology of the prepared composites were then investigated in detail. Afterwards, the photo-degradation performance of the prepared composites were examined through degrading rhodamine B (RhB) dye. Specifically, the impact of CMS and pCMS on the photo-degradation efficiency of the composites were studied in detail. Finally, a mechanism was also proposed subsequently. To realize cleaner production, the objectives of this study are to provide application potentials of biorenewable biomass derived carbon materials in wastewater treatment, and to prepare magnetic recyclable photocatalyst which could be reused for cycles for the degradation of organic pollutants.

2. Experimental

2.1. Materials

Sodium carboxymethylcellulose (CMC), ferric nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$) and cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) were purchased from Sigma (USA). Rhodamine B dye (RhB) was purchased from Nanjing Chemical Reagent Co., Ltd. (China). Commercial Degussa P25 was purchased from Beijing Yonge Water Biological Technology Co., Ltd. (China). Other chemicals and solvents were all of analytical grade and used as received (Nanjing Chemical Reagent Co., Ltd., China). Distilled water was used exclusively in this study.

2.2. Preparation of the CMS and pCMS

In a typical experiment, CMC (1.5 g) was first dissolved in distilled water (40 mL). The clear CMC solution was then transferred into a Teflon autoclave, which was heated in the oven at 210 °C for 12 h. The resultant solid was washed with water and ethanol for three times, respectively. After being dried at 60 °C for 12 h, the CMS was obtained. Then the CMS was pyrolyzed at 800 °C for 4 h under nitrogen atmosphere, and the p-CMS was obtained.

2.3. Preparation of the CMS-$CoFe_2O_4$ and pCMS-$CoFe_2O_4$ composites

The CMS-$CoFe_2O_4$ and pCMS-$CoFe_2O_4$ composites were prepared using a coprecipitation method mentioned as follows. Based on the previous studies, the amount of carbon microspheres was set at ~20 wt% (Fu et al., 2012; Gan et al., 2015a). Typically, 4.0 g of Fe $(NO_3)_3\cdot 9H_2O$ (10 mmol) and 1.5 g of $Co(NO_3)_2\cdot 6H_2O$ (5 mmol) were added into 20 mL of distilled water. After all the solids were dissolved, 200 mg of CMS or pCMS was added into the solution. The mixture was further sonicated for ~2 h under ambient temperature before NaOH solution (1 M) was added dropwise to adjust the pH of the solution to ~10.0 under continuous mechanical stirring. After being mechanically stirred for another 1 h, the mixture was put into a Teflon-lined autoclave and kept at 180 °C for 12 h. The precipitate was then washed with 2 × 50 mL of distilled water, 2 × 50 mL of ethanol and 2 × 50 mL of acetone, respectively. After being dried at 80 °C for 24 h, the as-prepared CMS-$CoFe_2O_4$ and pCMS-$CoFe_2O_4$ composites were finally obtained. For comparison, pure $CoFe_2O_4$ without the introduction of CMS and pCMS were also prepared following similar procedures. The preparation steps were illustrated in Fig. 1.

2.4. Characterizations

Fourier transform infrared (FT-IR) spectra were recorded by a Perkin Elmer 100 spectrophotometer at wavenumbers ranging from 4000 to 450 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans. The X-ray diffraction (XRD) was conducted using a Rigaku Smartlab XRD instrument with the Cu-Kα as the radiation source (1.54 Å). Raman spectra were performed using a Thermo DXR532 Raman spectrometer, which was equipped with an Ar laser (532 nm, 180 mW) as the excitation light source, and a microscope. The morphology of the prepared composites was observed by scanning electron microscopy (SEM) using the FEI Quanta 200 equipped with energy dispersive spectroscopy (EDS). Nitrogen adsorption/desorption isotherms at 77 K were performed with a Quantachrome v3.0 instrument, and the data was analyzed by a multipoint Brunauer–Emmett–Teller (BET) method. The diffuse reflectance spectra (DRS) were conducted by a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer. The photoluminescence (PL) spectra of the microspheres were conducted by Perkin-Elmer LS55 spectrofluorometer with a Xe Lamp as the excitation source. The excitation wavelength was selected as 350 nm. The magnetic measurement was conducted with a Quantum Design vibrating sample magnetometer.

2.5. Adsorption capability test of the prepared CMS-$CoFe_2O_4$ and pCMS-$CoFe_2O_4$ composites

In a universal bottle, 20 mg of the samples was immersed in 25 mL of RhB solution. The bottle was placed in a thermostatic shaker with water bath kept at 25 °C. After a certain period of time,