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Magnetic recoverable $MnFe_2O_4$/cellulose nanocrystal composites as an efficient catalyst for decomposition of methylene blue

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ABSTRACT

$MnFe_2O_4$/cellulose nanocrystal ($MnFe_2O_4$/CNC) composites featured high catalytic activities on the decomposition of methylene blue (MB) were prepared by a novel approach, through which the H^+ ions produced during the acid hydrolysis of cellulose are largely consumed. Attributed to their high specific surface areas, small particle size and low band gap, contributing to the generation of large number of reactive hydroxyl radicals from H_2O_2, the magnetic $MnFe_2O_4$ nanoparticles anchoring on CNC demonstrate pronounced improvements of catalytic activities on the decomposition of MB pollutants compared with that of the bare $MnFe_2O_4$. Specifically, the degradation degree of MB catalyzed by $MnFe_2O_4$/CNC composite containing 20 wt% of CNC is 99%, which suggests more than 60% increase than that in the bare $MnFe_2O_4$. More particularly, $MnFe_2O_4$/CNC composites featuring excellent magnetic properties exhibit an excellent recycling catalytic performance, suggesting a great promising candidate in application of environmental pollutant treatment.

1. Introduction

Organic dyes, as the ubiquitous pollutants in the waste water discharged from a variety of industries such as dyeing, printing, textile, leather and so forth, have posed severe detrimental effects on the human health and environmental organisms. As one representative dyes used in cottons, wools and textile coloring, methylene blue (MB) consisting of a monovalent organic cationic quaternary ammonium ionic group is extremely hazardous to the water resource as well as the physiological and respiratory systems of human. Many efforts have been dedicated to dealing with organic dyes in waste water (Zhan et al., 2017; Fu et al., 2017; Yamaguchi et al., 2016; Li et al., 2018). Among those strategies, the catalytic degradation of organic dyes is fairly attractive because of its simplicity, high efficiency and cost effectiveness (Kora and Rastogi, 2018; bin Osman et al., 2018). The hydroxyl radical (•OH) originating from the ozone or peroxide (H_2O_2) with the aid of catalysts can attach themselves to organic dyes, capable of neutralizing and destroying the pollutants. A variety of catalysts, such as TiO_2 (Romero-Sáez et al., 2017; Saravanan et al., 2018b; Rajendran et al., 2018; bin Osman et al., 2018), $Fe_xZn_{1-x}O$ (Dhiman et al., 2017), ZnSe-WO_3 (Kumar et al., 2017), SnO_2 (Gupta et al., 2017), ZnO (Qin et al., 2017), CeO_2 (Saravanan et al., 2018a), Fe_3O_4 (Liao et al., 2016; Yang et al., 2015; Lei et al., 2015), Fe_2O_3 (Han et al., 2014), Fe (Das et al., 2017), $MnFe_2O_4$ (Peng et al., 2016) and MnO_2 (Shayesteh et al., 2017), have been utilized to accelerate the generation of active •OH radicals. Among which, $MnFe_2O_4$ owning outstanding paramagnetic performance points to new opportunities for designing and engineering reusable catalysts for the decomposition of organic dyes, which outperforms previously reported metal oxide such as Fe_3O_4, Fe_2O_3 and MnO_2 (Xiong et al., 2012; Chen et al., 2017).

The outstanding properties enable $MnFe_2O_4$ as an efficient catalyst for removal of organic dyes such as MB and Congo red (Yang et al., 2014). However, free standing nanoparticles tend to severely aggregate due to their high surface energy, which decreases accessible surface areas, compromises catalytic activities and prevents the universal applications of bare $MnFe_2O_4$ nanoparticles. In this context, many strategies have been explored to overcome these issues by the decoration of $MnFe_2O_4$ nanoparticles on the large surface area substrates, which have been testified to be viable manner to maintain chemical activities of nanoparticles (Peng et al., 2016; Yao et al.,2014; Han et al., 2014; Bai et al., 2012). For example, two-dimensional reduced graphene oxide (rGO)/$MnFe_2O_4$ composites fabricated by an environmentally benign

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strategy demonstrate substantially high efficiency (Peng et al., 2016), enabling a completely decomposition of MB in 130 min. Although rGO shows effectiveness on the stabilization of nanoparticles, the fabrication of rGO nanoplatelets suffers from several disadvantages such as high cost, nonrenewable, and rather hazardous to handle, which inhibit their ubiquitous employments as structural and functional substrates adopted in catalysts.

Recently, cellulose nanocrystals (CNC) demonstrate great potential to enable both physico-chemical adsorption and catalytic reduction of organic dyes, owing to their high surface area, bio-renewable and abundant surface chemistries (Li et al., 2017; Wu et al., 2013; Bossa et al., 2017; Góes et al., 2016). CNC have been composited with metals or metal oxides to fabricate a number of advanced nanocomposites. Wu et al. (Wu et al., 2013) fabricated CNC supported palladium nanocomposites used for organic dyes adsorption and degradation, and attributed their high performance to the high surface areas and stabilization effect of CNC, contributing to increase the accessible active sites of palladium nanoparticles. Dhar et al., (2017) fabricated a nontoxic biocatalyst composed of zerovalent iron nanoparticles decorated on CNC, demonstrating high efficacy on the decomposition of MB in wastewater. The current approaches to fabricate CNC arise from acid hydrolysis of natural cellulose leading to inevitable generation of H^+ ions, which poses a great challenge to water resource (Tang et al., 2017).

Here, we fabricate $MnFe_2O_4$/CNC nanocomposites with magnetically recoverable catalytic performances, which were achieved by anchoring magnetic $MnFe_2O_4$ nanoparticles on CNC supports through a hydrothermal strategy. As one of the main precursors used in the hydrothermal reaction, manganese carbonate ($MnCO_3$) not only provides manganese source of $MnFe_2O_4$, but also reacts with H^+ ions produced during the acid hydrolysis of natural cellulose. Furthermore, the addition of CNC allows to decrease the band gap and increase the active surface areas of $MnFe_2O_4$ nanoparticles, resulting in enhancing catalytic activities compared with those of bare $MnFe_2O_4$. Such $MnFe_2O_4$/CNC composites fabricated in this work suggest a great potential to work as renewable catalyst for the removal of organic dyes from aqueous solution.

2. Experimental

2.1. Materials

Medical purified cotton, concentrated sulfuric acid (H_2SO_4) and manganese carbonate ($MnCO_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Methylene blue (MB) was supplied by Tianjin Fuchen Chemical Reagents Factor (China). Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH) and methanol (CH_3OH) were all purchased from Chendu Kelong Chemical Reagent Company (China). All materials are used without further purification.

2.2. Preparation of CNC solution

CNC was fabricated by acid hydrolysis of medical purified cotton by following the previous reports (Das et al., 2017; Wu et al., 2013; Kloser and Gray, 2010). Briefly, medical purified cotton (4 g) was mixed with 70 mL of H_2SO_4 solution (64 wt%), and the mixture was stirred vigorously at 45 °C for 45 min. Finally, the suspension was diluted ten times to stop the hydrolysis, and CNC solution at concentration of 0.3 wt% was obtained. Notably, H_2SO_4 added in the suspension was not removed to reduce environmental pollution.

2.3. Preparation of $MnFe_2O_4$/CNC nanocomposites

$MnFe_2O_4$/CNC nanocomposites were fabricated by following the procedure illustrated in Fig. 1. First, a calculated amount of $MnCO_3$ was dispersed in 10 mL of the above CNC solution by using ultrasonic bath agitation (KQ3200 V, 40 KHz, Kunshan Ultrasonic Instrument CO., Ltd, China) until no bubble formation was observed. The resulting suspensions were then mixed with appropriate amount of $FeCl_3{\cdot}6H_2O$. NaOH solution (1.0 mol L^{-1}) was added to maintain the pH at 12 under ultrasonic agitation. After 1 h ultrasonic irradiation, the mixture was extensively rinsed with deionized water until the pH value was 7. The resulting mixture was then transferred and sealed into Teflon-lined stainless-steel autoclave, heated at 150 °C for 4 h, and cooled to room temperature. The obtained precipitates were collected and rinsed thoroughly with deionized water. After freezing drying, $MnFe_2O_4$/CNC nanocomposites were gained. The inset photo in Fig. 1 displays that $MnFe_2O_4$/CNC nanoparticles attach on the inner wall of a bottle under magnetic attraction, implying their outstanding magnetic performance. Table 1 lists the detailed composition for $MnFe_2O_4/CNC_x$, where x represents the mass percentages of CNC in $MnFe_2O_4$/CNC nanocomposites. For comparison, bare $MnFe_2O_4$ was also synthesized by following the similar procedure without the step of ultrasonic dispersion in CNC solution.

2.4. Characterization

Field emission scanning electron microscope (FE-SEM) observation was conducted by using a Zeiss Ultra 55 apparatus at an accelerating voltage of 10 KV. X-ray diffraction measurements (XRD) were examined by a PANalytical Empyrean diffractometer equipped with nickel-filtered Cu Kα radiation (λ = 0.1542 nm) source. The spectra were collected in transmission mode with 2θ ranging from 5° to 80° at 40 kV. X-ray photoelectron spectroscopy (XPS) was carried out on an XSAM800 (Kratos, Britain) with a pressure of 2×10^{-7} Pa in the analysis chamber during the measurement. Nitrogen adsorption isotherms and BET specific surface area were measured at −196 °C on an NOVA 4000e surface area & size analyzer (Quantachrome, USA). Prior to adsorption measurements, all samples were outgassed under vacuum at 100 °C for 2 h. The light absorption properties of $MnFe_2O_4$ and $MnFe_2O_4$/CNC composites were measured using UV–vis absorption spectrophotometer (Shimadzu, UV-3600) with a wavelength range of 200–800 nm. The magnetic properties were measured using a Vibratory Sample Magnetometer (MPMS SQUID-VSM, Quantum Design, USA) at room temperature with an applied field of -20,000 to 20,000 Oe.

2.5. Catalytic experiments

The catalytic experiments were conducted at 293 K by adding certain mass of $MnFe_2O_4$/CNC into the mixture solution containing 75 mL of MB solution (20 mg L^{-1}) and 18 mL of H_2O_2. All solutions were ultrasonically treated and exposed to natural sunlight by following the method reported by Dhiman and their co-workers (Dhiman et al., 2017). In fact, to reasonably evaluate the photocatalytic performance of $MnFe_2O_4$/CNC, the catalytic experiments should be performed in an illuminant with stable and uniform irradiance. However, due to the lack of solar simulator equipped with AM1.5 filter, the photocatalytic activities of $MnFe_2O_4$/CNC were only studied by comparing the degradation degree of MB tested in natural sunlight and in darkness respectively. The decolorization degree of MB at different time was measured by using a UV–vis spectrophotometer at the wavelength of 664 nm. The influence of $MnFe_2O_4$/CNC dosage on the decomposition of MB was studied by varying the catalyst concentration from 0.11 to 0.33 mg mL^{-1} in the mixture solution with 75 mL of MB solution (20 mg L^{-1}) and 18 mL of H_2O_2. In order to study the effect of H_2O_2 content on the decomposition of MB, H_2O_2 (6 mL, 12 mL and 8 mL) were added into the mixture with 75 mL of MB solution (20 mg L^{-1}) and 30 mg of catalyst, Also, the influence of initial MB concentration was studied by the addition of MB solution (75 mL) with different initial concentration in the mixture of $MnFe_2O_4$/CNC (30 mg) and H_2O_2 (18 mL). Moreover, in order to study the recyclability of catalysts, after