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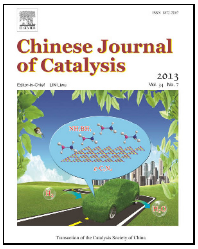

Article

Recyclable Fe_3O_4@SiO_2-Ag magnetic nanospheres for the rapid decolorizing of dye pollutants

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ABSTRACT

A simple electroless plating method using non-toxic, cost-effective precursors to fabricate Fe_3O_4@SiO_2-Ag nanospheres for catalytic reduction of dye pollutants is developed. Incorporating the individual advantages of Ag and Fe_3O_4 nanoparticles, the Fe_3O_4@SiO_2-Ag nanospheres exhibit enhanced catalytic reduction efficiency for rhodamine B and eosin Y compared with those of pure Ag or Fe_3O_4 nanoparticles, and can also be rapidly separated from aqueous solution using a magnet. The catalytic reaction rate is strongly dependent on both reaction temperature and Fe_3O_4@SiO_2-Ag dosage. The presence of surfactants and inorganic salt (Na_2SO_4) influences the catalytic activity of the Fe_3O_4@SiO_2-Ag nanospheres. Fe_3O_4@SiO_2-Ag nanospheres show great promise for the treatment of industrial dye pollutants.

1. Introduction

Dyes are among the most common organic industrial pollutants. Methods used to dye textiles, paper, plastics, leather, food, and cosmetics are major sources of toxic species in the form of colored wastewater. It is estimated that over 700000 tons of dyes are commercially produced annually, 15% of which are discharged in wastewater during the dyeing process [1,2]. These colored species can disturb photosynthesis in aquatic plants because they reduce light penetration [3,4]. Many methods have been developed to decolorize/detoxify dyes, such as adsorption, degradation, oxidation, and catalytic reduction [5–11]. All are technically viable clean-up processes for dyes but are limited by disadvantages including energy cost, safe operation, and secondary pollution. Therefore, it is highly desirable to develop a safe, non-toxic, and energy-efficient process to decolorize/detoxify dyes in aqueous solution under mild conditions. Noble metal nanoparticles (NPs), in particular silver (Ag) NPs, are efficient catalysts in many redox reactions, such as the reduction of *p*-nitrophenol, because they efficiently release electrons from bulk metal to nanoregions [12,13]. However, Ag NPs catalysts encounter an obstacle when applied in practice owing to the difficulty of recycling these nano-sized catalysts using traditional methods [14–17]. In addition, the aggregation of the Ag NPs restricts and reduces their catalytic efficiency.

To address these problems, surface modification using polymers, complex ligands or surfactants is frequently used to stabilize metal catalysts [18–21]. However, polymers or surfactants may interact with the catalysts and coat their surfaces, reducing the accessibility of the Ag NPs to reacting molecules and thereby decreasing catalytic activity. It is therefore desirable both to develop novel routes to remove and recycle nanosized catalysts after use and also to find ways to minimize

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their aggregation.

Recently, magnetic catalysts have emerged as a new generation of materials for dye reduction because magnetic separation is an effective, economical way to recycle magnetic NPs. Iron oxide (Fe_3O_4)/Ag magnetic catalysts have been synthesized [22–24], but unfortunately these hybrids are usually unstable because of the aggregation of Ag NPs. Moreover, the Fe_3O_4 cores tend to be oxidized or dissolved under acidic conditions during catalysis. Silica is reported to be an ideal protective layer for Fe_3O_4 NPs not only because of its high chemical and thermal stability but also because it provides a suitable supporting matrix to immobilize Ag NPs [25]. Therefore, a Fe_3O_4@SiO_2 core-shell nanostructure, which combines the advantages of magnetic separation and stability, is proposed as a novel, efficient substrate to immobilize Ag NPs.

Significant effort has already been devoted to the preparation and application of Fe_3O_4@SiO_2-Ag nanohybrids. For example, Fe_3O_4@SiO_2-Ag nanohybrids have been used as an antibacterial material, surface-enhanced Raman scattering substrate, and in environmental Cr(VI) analysis [25–27]. However, no attempts to use Fe_3O_4@SiO_2-Ag nanohybrids to decolorize the dye pollutants rhodamine B (RhB) and eosin Y (EY) have been reported.

In this work, we demonstrate that recyclable Fe_3O_4@SiO_2-Ag nanohybrids can be used to rapidly decolorize dye pollutants RhB and EY. The Fe_3O_4@SiO_2-Ag nanohybrids show excellent catalytic performance in the reduction of dye pollutants and are also readily separated and reused. These properties show that Fe_3O_4@SiO_2-Ag nanohybrids have the potential to form a new generation of catalysts for the treatment of wastewater.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$), anhydrous sodium acetate (CH_3COONa), ethylene glycol ($C_2H_4(OH)_2$), ammonium hydroxide (NH_4OH, 28%), and anhydrous sodium sulfate (Na_2SO_4) were purchased from Beijing Chemical Reagent Co. Ltd. Sodium borohydride ($NaBH_4$, 99%), silver nitrate ($AgNO_3$, 99.8%), *n*-butylamine ($C_4H_{11}N$, 99%), RhB, and EY were obtained from Sinopharm Chemical Reagent Co. Ltd. Tetraethoxysilane (TEOS), poly(oxyethylene) iso-octyl phenyl ether (TX-100), sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB, 99.5%) were provided by Tianjin Chemical Reagent Factory. All reagents were analytical grade and used without further purification. Deionized water was used for all experiments.

2.2. Synthesis of Fe_3O_4@SiO_2 magnetic nanoparticles (MNPs)

Fe_3O_4 MNPs were prepared using a solvothermal method [28]. Silica was coated on the surface of Fe_3O_4 MNPs via a modified Stöber sol-gel method [29]. In a typical process, Fe_3O_4 MNPs (0.10 g) were added to an aqueous solution of HCl (0.1 mol/L, 50 ml) and ultrasonicated for 10 min. The sample was thoroughly washed with deionized water and then dispersed in a mixture of ethanol (80 ml), deionized water (20 ml) and ammonia (1.0 ml). Finally, TEOS (0.4 ml) was added dropwise into the solution, which was stirred at room temperature for 6 h. After washing with ethanol and water several times, the isolated Fe_3O_4-SiO_2 MNPs were dried under vacuum at 60 °C.

2.3. Synthesis of Fe_3O_4@SiO_2-Ag nanohybrids

A simple electroless plating process was carried out to deposit Ag NPs on the surface of Fe_3O_4@SiO_2 [30,31]. $AgNO_3$ (0.034 g) was dissolved in ethanol (150 ml) by ultrasonication in a polypropylene flask, and then a solution of Fe_3O_4@SiO_2 MNPs (0.12 g) in ethanol (50 ml) was added. The mixture was stirred for 50 min at 50±1 °C with a magnetic stirrer, and then a solution of *n*-butylamine (0.015 g/ml, 1.0 ml) in ethanol was added to reduce Ag^+ to Ag NPs on the surface of Fe_3O_4@SiO_2 MNPs. The ratio of *n*-butylamine to $AgNO_3$ was maintained at 1:1. The mixture was stirred for 3 h at 50 °C. Finally, the products were magnetically separated, washed several times with ethanol and dried at 60 °C under vacuum.

2.4. Characterization

UV-Vis absorption spectra were measured by a UV-Vis spectrometer (TU-1901, Beijing, China). The magnetic properties of the catalysts were investigated using a vibrating sample magnetometer (Lakeshore 7304, Lakeshore, USA). The morphology and size of the particles were analyzed using field-emission transmission electron microscopy (TEM, FEI Tecnai-G^2-F30). Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2000 diffractometer using Cu K_α (wavelength λ = 0.1514178 nm) radiation in the 2θ range of 10°–80°. X-ray photoelectron spectroscopy (XPS) was measured on a K-α-surface Analysis system with monochromatic X-rays.

2.5. Catalytic reduction of dyes

In a typical reduction experiment, Fe_3O_4@SiO_2-Ag nanospheres were dispersed in an aqueous solution containing RhB or EY (3.0 ml, 2.0×10^{-5} mol/L) at room temperature. Freshly prepared $NaBH_4$ solution (1.0 ml, 1.0×10^{-2} mol/L) was rapidly added, and then the solution was quickly subjected to UV-Vis measurement. Absorption spectra were measured at different durations. To investigate the effects of surfactants and inorganic salt (Na_2SO_4) on the catalytic activity of Fe_3O_4@SiO_2-Ag, surfactants or Na_2SO_4 were added to the mixture before the addition of dye; all other conditions were kept unchanged.

After the catalytic reaction was complete, the nanocatalysts were separated using a magnet, and then the process was repeated to evaluate the recyclability of the catalysts. The recyclability of the catalysts was determined by measuring the maximal UV-Vis absorption (λ_{max}) of dye solution at the end of each catalytic reaction.

3. Results and discussion