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Article

Recyclable Fe₃O₄@SiO₂-Ag magnetic nanospheres for the rapid decolorizing of dye pollutants

SUN Lijuan^a, HE Jiang^{a,*}, AN Songsong^a, ZHANG Junwei^b, ZHENG Jinmin^a, REN Dong^a^a State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, Gansu, China^b Key Laboratory of Magnetism and Magnetic Materials of Ministry of Education, Lanzhou University, Lanzhou 730000, Gansu, China

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ABSTRACT

A simple electroless plating method using non-toxic, cost-effective precursors to fabricate Fe₃O₄@SiO₂-Ag nanospheres for catalytic reduction of dye pollutants is developed. Incorporating the individual advantages of Ag and Fe₃O₄ nanoparticles, the Fe₃O₄@SiO₂-Ag nanospheres exhibit enhanced catalytic reduction efficiency for rhodamine B and eosin Y compared with those of pure Ag or Fe₃O₄ 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 Fe₃O₄@SiO₂-Ag dosage. The presence of surfactants and inorganic salt (Na₂SO₄) influences the catalytic activity of the Fe₃O₄@SiO₂-Ag nanospheres. Fe₃O₄@SiO₂-Ag nanospheres show great promise for the treatment of industrial dye pollutants.

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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

* Corresponding author. Tel: +86-931-8912591; Fax: +86-931-8912582; E-mail: hejiang@lzu.edu.cn

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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 ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), anhydrous sodium acetate (CH_3COONa), ethylene glycol ($\text{C}_2\text{H}_4(\text{OH})_2$), 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 ($\text{C}_4\text{H}_{11}\text{N}$, 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-G2-F30). Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2000 diffractometer using $\text{Cu } K\alpha$ (wavelength $\lambda = 0.1514178$ 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

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids

The morphology of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids was analyzed by TEM. Figure 1(a) shows a representative TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles, revealing a clear core-shell structure of uniform size with a smooth surface. The dark area in the core of individual particles is Fe_3O_4 , which exhibits significant electron scattering, and the outer grey area is SiO_2 .

After the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles were decorated with Ag NPs (Fig. 1(b)), many Ag NPs with a mean diameter of 5 ± 1 nm were found bonded to the surface of individual $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs, forming a structure resembling “fried glutinous rice balls with sesame” [32]. This silica coating acted as a supporting base to prevent the aggregation of Ag NPs. The contrast of incoherent high-resolution high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images depends directly on the sample atomic number Z and the thickness of the material. In the image of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ particles, the Ag and Fe_3O_4 particles show the expected high contrast compared to that of the SiO_2 shell (Fig. 1(c)). This observation is consistent with the TEM results.

The morphology of the recycled $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ particles after several runs of catalytic reduction of RhB was also analyzed. Figure 1(d) and (e) show two representative TEM images of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanocatalysts after 5 cycles of catalytic reaction. The surface of individual $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanospheres is still decorated with Ag NPs, revealing the strong binding between the Ag NPs and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ support. However, large Ag NPs with a diameter of 48 ± 2 nm are also observed alongside the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ catalysts. These Ag NPs are approximately ten times larger than those in the freshly prepared

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ catalysts in Fig. 1(b). Figure 1(e) shows lattice-resolution HRTEM images of Fe_3O_4 (top) and Ag (bottom), which reveal that the sample is highly crystallized, as evidenced by the well-defined lattice fringes. Fringes of $d = 0.2045$ nm match the (200) plane of Ag nanocrystals, while those of $d = 0.4607$ nm match the (111) plane of Fe_3O_4 nanocrystals. The HRTEM results further demonstrate that Fe_3O_4 and Ag nanocrystals coexist in the hybrid materials.

The deposition of Ag NPs on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was further confirmed by XRD, as illustrated in Fig. 1(f). Compared to the XRD patterns of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs, four additional peaks are observed for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ particles at 2θ values of 38.1° , 44.3° , 64.4° , and 77.3° , which correspond to the (111), (200), (220), and (311) lattice planes of face-centered cubic phase Ag (labeled with the symbol *), respectively. Meanwhile, all diffraction peaks of Fe_3O_4 are preserved after the coating process, confirming the retention of the magnetic phase in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids.

XPS analysis (Fig. 2) was conducted to further elucidate the surface composition of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids. Peaks with binding energy of 285, 532, 103, 711, and 368 eV are attributed to C 1s, O 1s, Si 2p, Fe 2p, and Ag 3d, respectively, revealing the presence of C, O, Si, Fe, and Ag in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ hybrids (Fig. 2(a)). To investigate the electronic states of the elements, higher-resolution spectra were also measured. In the spectrum of Ag 3d in Fig. 2(b), two peaks at 368 and 374 eV with a spin-orbit separation of 6 eV that are attributed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, are observed. For the Fe 2p spectrum presented in Fig. 2(c), the binding energy of 725 and 711 eV for Fe $2p_{1/2}$ and Fe $2p_{3/2}$, respectively, is very weak. This demonstrates that most of the Fe_3O_4 cores in the hybrids are confined within a shell of $\text{SiO}_2\text{-Ag}$.

Fig. 1. TEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs (a) and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs (b), STEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs (c), lower (d) and higher (e) magnification images of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs after five runs of catalytic reaction, and XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs (f). Insets in (a) and (c) are the structure models for $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs, respectively, inset in (b) is a high-magnification TEM image, and insets in (e) are HRTEM images of Fe_3O_4 NPs (top) and Ag NPs (bottom).

Fig. 2. Survey XPS spectra (a) of the prepared $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ nanohybrids and enlarged areas corresponding to the Ag 3d (b) and Fe 2p (c) peaks of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs.

Figure 3 shows magnetic hysteresis loops of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@/\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs measured at room temperature. The measured saturation magnetization values (M_s) were 79, 32, and 24 emu/g for Fe_3O_4 , $\text{Fe}_3\text{O}_4@/\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$, respectively. The remnant magnetization (M_r) is about 2.8 emu/g, while the coercivity (H_c) is about 8.8 Oe for $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs. The relatively low H_c and M_r indicate that the $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs exhibit superparamagnetic behavior, revealing their potential for magnetic actuation and

Fig. 3. Magnetic hysteresis loops of Fe_3O_4 MNPs (1), $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ MNPs (2), and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs (3).

manipulation. M_s of Fe_3O_4 particles is higher than those of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs. The lower M_s of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs may be caused by a mass effect from nonmagnetic SiO_2 and Ag. The $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs could be rapidly separated from aqueous dispersions using a magnet (inset of Fig. 3). Such magnetic separation of the nanohybrids should be an advantage for their reuse as catalysts.

3.2. Catalytic performance

The catalytic reduction of RhB and EY was chosen as model reactions to evaluate the catalytic performance of the $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ nanohybrids in the presence of NaBH_4 . Figure 4 shows a typical evolution of the UV-Vis spectra of these dyes

Fig. 4. Time-dependent UV-Vis spectral changes of RhB (a), EY (b), and a mixture of RhB and EY (c) during reduction catalyzed by $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-Ag}$ MNPs. The inset of each UV-Vis spectra shows the color of each dye solution before (right) and after (left) reduction.

during catalytic reduction after addition of NaBH_4 . The adsorption efficiency for RhB and EY is 4.2% and 0.7%, respectively. The catalytic reduction reaction is completed within 8.5 min for RhB (Fig. 4(a)) and 13.5 min for EY (Fig. 4(b)). On the basis of pseudo-first-order kinetics, $\ln(C_t/C_0) = kt$, where C_t is the concentration of dye at time t , C_0 is the initial concentration of dye solution, and the slope k is the apparent reaction rate. The calculated rate constants for reduction of RhB and EY with the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ nanohybrids in the presence of NaBH_4 are 0.522 and 0.237 min^{-1} , respectively. These rates are much faster than those reported for other catalysts [33–35]. The insets show that each dye solution becomes almost colorless on the right side where the nanohybrids accumulate, while there is no obvious change in color on the left side. This result clearly confirms that the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ MNPs possess magnetic-catalytic dual functionalities, as well as enhanced catalytic activity compared with that of traditional catalysts.

The catalytic reduction of a dye mixture of cationic dye RhB and anionic dye EY was also carried out (Fig. 4(c)). RhB is reduced first followed by EY. The nature of a dye (i.e., charge, hydrophobicity, presence of S/N donor atoms) may influence its reduction rate [36]. In general, positively-charged dyes such as RhB have a higher catalytic reaction rate than negatively-charged ones such as EY because of electrostatic interactions. Ag NPs would be cathodically polarized by BH_4^- ions through the following reaction [37]:

Therefore, Ag NPs are more effective at reducing RhB than EY. In addition, the higher hydrophobicity of EY than RhB caused by the presence of Br in its skeleton may be a plausible reason for its lower reaction rate. Figure 5 depicts the performance of the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ nanohybrids as catalysts in the reduction of RhB and EY to their leuco form by NaBH_4 .

3.2.1. Effect of temperature on reaction

Chemical reactions are usually sensitive to changes of temperature, so the effect of temperature can provide some insight

Fig. 5. Reduction reactions of dyes to their leuco forms.

Table 1

Reduction rates of EY by $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ MNPs at different temperatures.

Temperature ($^{\circ}\text{C}$)	Rate of reduction (min^{-1})
15	0.1825
25	0.2367
45	0.4417
60	0.6207

into the mechanism of a reaction [38]. The catalytic reduction of EY was performed at four different temperatures (15, 25, 45, and 60 $^{\circ}\text{C}$); the dependence of the rate of the reaction on temperature is presented in Table 1. An increase in temperature caused the rate of the reaction to increase, as expected. Based on the kinetic constants determined at different temperatures, the activation energy (E_a) of the reduction of EY by $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ can be obtained according to Arrhenius equation: $\ln k = -E_a/RT + \ln A$.

We calculated that $E_a = 22$ kJ/mol, which is lower than 36 and 32.84 kJ/mol reported for other catalysts [34,39]. The lower E_a of the reaction catalyzed by $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ indicates that the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ nanohybrids possess strong activity.

3.2.2. Influence of catalyst dosage

The effect of the amount of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ on catalytic efficiency was also studied. As expected, the catalytic efficiency is improved by increasing the amount of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$ present (Fig. 6(a)). Moreover, in a control experiment lacking catalyst, there was no obvious decrease in λ_{max} even after 47 min. In addition, there is a significant induction period in the reaction when the concentration of catalyst is low, which decreases as the catalyst concentration increases. The induction period that decreases with increased catalyst concentration may be caused by the activation of the catalyst in the reaction media. This is consistent with other reports of catalytic reduction by Ag NPs [10,40].

An important parameter indicating the efficiency of a catalyst is the turnover frequency (TOF) [41]. TOF is defined as $\text{TOF} = M/(N_s \times t)$, where M is the number of molecules (EY here) reacting in the presence of a catalyst in time t to produce a product, and N_s is the number of surface atoms of the catalyst that are involved in the reaction. In our case, the average particle size of Ag NPs supported on $\text{Fe}_3\text{O}_4/\text{SiO}_2$ is 5 nm according to TEM analysis. The number of reactant molecules (EY) was fixed at 4.82×10^{16} . TOF was calculated for each of the reactions performed using different amounts of catalyst. Table 2 lists the amount of Ag NPs used, total time, and TOF for each reaction. TOF decreases as the concentration of Ag NPs increases. This is possibly because an increased catalyst dosage decreases adsorbate mobility, which eventually increases the residence time of the adsorbate on the surface of the catalyst.

3.2.3. Influence of surfactants on catalysis

The effects of surfactants on the catalyzed reduction of dyes were measured in the presence of CTAB (a cationic surfactant), SDS (an anionic surfactant), and TX-100 (a nonionic surfactant). Detailed kinetic studies of the influence of these surfac-

Fig. 6. Plots of C_t/C_0 at $\lambda_{\max}$ of EY versus time. (a) Using different amounts of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$; (b) In the absence and presence of different surfactants; (c) In the absence and presence of different concentrations of Na_2SO_4 .

tants on reduction of EY were performed. As shown in Fig. 6(b), the reduction rates of dyes are apparently decreased after the addition of surfactants. In most cases, surfactants would move to the surface of Ag NPs and pack around them, thus affecting the accessibility of the dye molecules to the Ag NPs and reducing catalytic activity. The ultimate reduction rate of a dye is related to the charge of the surfactant used [42]. Figure 6(b) shows that the reduction rate of EY is slower in the presence of SDS or TX-100 than CTAB. This is mainly because SDS and EY have similar charges, which hinders access of dye molecules to the Ag NPs because of electrostatic repulsion. In many cases, the reduction rate of dye is decreased to a considerable extent, which indicates that surfactants can deactivate or hamper the catalyst by interacting with its surface and aggregating around it.

3.2.4. Effect of sodium sulfate

Dye wastewater includes numerous inorganic salts such as Na_2SO_4 , which is a widely used as a promoter and buffering agent in the dye industry. The effect of Na_2SO_4 on the catalytic activity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ is presented in Fig. 6(c). The rate of reduction increases with Na_2SO_4 concentration. The addition of Na_2SO_4 might significantly promote the electron transfer mobility of the solution, causing an increase of catalytic rate. However, SO_4^{2-} with a lone pair of electrons could adsorb onto the surface of particles by a coordinate bond, resulting in a reduction of the reaction rate. Figure 6(c) shows that the effect promoting the migration of charges predominates for Na_2SO_4 , which causes reduction rate to increase when the Na_2SO_4 concentration is increased.

Table 2

Number of surface atoms, reaction time including induction period, and TOF for different concentrations of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$.

Amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ (mg)	Number of Ag NPs ($N_{\text{NPs}}, 10^{13}$)	Number of surface atoms ($N_s, 10^{17}$)	Time including induction period (s)	TOF (10^3 s^{-1})
0.5	1.4	0.545	960	0.92
1.0	2.8	1.09	840	0.53
2.0	5.6	2.18	600	0.37
3.0	8.4	3.27	480	0.31

3.2.5. Mechanism of catalysis

As to the catalytic mechanism of reduction, Ag NPs supported on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surfaces serve as an electron relay system and play an important role during electron transfer (ET) [36,40,42,43]. Figure 7 schematically illustrates the possible catalytic mechanism for the reduction of dyes by Ag NPs in the presence of BH_4^- ions. With respect to Ag NPs, dyes are electrophilic and BH_4^- is nucleophilic. In the reaction mixture, both dyes and BH_4^- are adsorbed onto the surface of Ag NPs. Therefore, ET from BH_4^- to the dye via Ag NPs seems reasonable. When NaBH_4 is added to the reaction solution, the hydride from NaBH_4 may be trapped by Ag NPs and adsorbed on their surface. It then transfers its electron to the Ag NPs. The hydrogen atom formed from BH_4^- after ET to the Ag NPs subsequently attacks a nearby dye molecule, and then ET-induced hydrogenation of the dye occurs spontaneously. A negatively-charged Ag NP may be regarded as a nanoelectrode at a negative potential. The electrons on the Ag NPs are finally released to an electron acceptor (dye molecule), producing their reduced form (leuco RhB or leuco EY). This mechanism is similar to reported models including the Langmuir-Hinshelwood and Eley-Rideal mechanisms [44].

Fig. 7. Mechanism of dye reduction on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs.

Fig. 8. Reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ MNPs as a catalyst for the reduction of RhB in the presence of NaBH_4 .

3.3. Catalytic recyclability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ NPs

The magnetic recyclability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids following reduction of RhB in the presence of NaBH_4 was also investigated. Unlike other reported catalysts [14,44], magnetic catalysts can be recycled using an external magnet without recourse to centrifugation, filtration, or an ionic liquid. As shown in Fig. 8, the reduction efficiency on RhB was 85% after five cycles. The decrease of catalytic activity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ NPs may be caused by incomplete recovery of catalytic power or the aggregation of Ag NPs after repeated catalytic reactions. TEM images (Fig. 1(e)) show that many large Ag NPs are present alongside the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ composite after 5 runs, implying that catalytic activity is reduced after multiple recycling steps. Moreover, NaBH_4 in a relatively high concentration slowly etched the silica surfaces, leading to the gradual detachment of Ag NPs from $\text{Fe}_3\text{O}_4@\text{SiO}_2$, resulting in the observed reduction in the catalytic activity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$.

4. Conclusions

We demonstrated a facile, effective route to fabricate $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanospheres. The as-prepared nanohybrids can be used as a high-performance catalyst for the reduction of RhB and EY. Furthermore, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ catalysts can be recycled several times simply by magnetic separation. Their catalytic activity decreases slightly after each cycle, and the reduction efficiency on RhB was 85% after 5 cycles, which indicates that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids can be used as a convenient recyclable catalyst. The presence of surfactants and Na_2SO_4 in the reaction media influences the catalytic activity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanohybrids. These magnetic particles are rapid, efficient, and recyclable catalysts for dye pollutants and can be extended to catalytic reduction of other reducible contaminants.

References

- [1] Hai F I, Yamamoto K, Fukushi K. *Crit Rev Environ Sci Technol*, 2007, 37: 315
- [2] Park H, Choi W. *J Photochem Photobiol A*, 2003, 159: 241
- [3] Hassan S S, Sirajuddin, Solangi A R, Agheem M H, Junejo Y, Kalwar N H, Tagar Z A. *J Hazard Mater*, 2011, 190: 1030
- [4] Burda C, Chen X B, Narayanan R, El-Sayed M A. *Chem Rev*, 2005, 105: 1025
- [5] Asadullah M, Asaduzzaman M, Kabir M S, Mostofa M G, Miyazawa T. *J Hazard Mater*, 2010, 174: 437
- [6] Ramakrishna K R, Viraraghavan T. *Water Sci Technol*, 1997, 36(2-3): 189
- [7] Pandit P, Basu S. *Environ Sci Technol*, 2004, 38: 2435
- [8] Chen W X, Lu W Y, Yao Y Y, Xu M H. *Environ Sci Technol*, 2007, 41: 6240
- [9] Zhao X M, Zhang B H, Ai K L, Zhang G, Cao L Y, Liu X J, Sun H M, Wang H S, Lu L H. *J Mater Chem*, 2009, 19: 5547
- [10] Jana N R, Sau T K, Pal T. *J Phys Chem B*, 1999, 103: 115
- [11] Snehalatha T, Rajanna K C, Saiprakash P K. *J Chem Educ*, 1997, 74: 228
- [12] Kim M R, Lee D K, Jang D J. *Appl Catal B*, 2011, 103: 253
- [13] Wen C Y, Shao M W, Zhuo S J, Lin Z Q, Kang Z H. *Mater Chem Phys*, 2012, 135: 780
- [14] Shokouhimehr M, Piao Y Z, Kim J Y, Jang Y J, Hyeon T. *Angew Chem, Int Ed*, 2007, 46: 7039
- [15] Nie L H, Huang Z Q, Xu H T, Zhang W X, Yang B R, Fang L, Li S H. *Chin J Catal* (聂龙辉, 黄征青, 徐洪涛, 张旺喜, 杨柏蕊, 方磊, 李帅华. 催化学报), 2012, 33: 1209
- [16] Dang G F, Shi Y, Fu Z F, Yang W T. *Chin J Catal* (党高飞, 石艳, 付志峰, 杨万泰. 催化学报), 2012, 33: 651
- [17] He H, Yu Y B, Li Y, Wu Q, Zhang X L, Zhang C B, Shi X Y, Song X P. *Chin J Catal* (贺泓, 余运波, 李毅, 吴强, 张秀丽, 张长斌, 石晓燕, 宋小萍. 催化学报), 2010, 31: 491
- [18] Pal T, Sau T K, Jana N R. *J Colloid Interf Sci*, 1998, 202: 30
- [19] Pal T, Sau T K, Jana N R. *Langmuir*, 1997, 13: 1481
- [20] Fendler J H. *Chem Rev*, 1987, 87: 877
- [21] Kundu S, Mandal M, Ghosh S K, Pal T. *J Colloid Interf Sci*, 2004, 272: 134
- [22] Jiang J, Gu H W, Shao H L, Devlin E, Papaefthymiou G C, Ying J Y. *Adv Mater*, 2008, 20: 4403
- [23] Zhang X P, Jiang W Q, Gong X L, Zhang Z. *J Alloy Compd*, 2010, 508: 400
- [24] Guo S J, Dong S J, Wang E. *Chem Eur J*, 2009, 15: 2416
- [25] Zhang X L, Niu H Y, Yan J P, Cai Y Q. *Colloids Surf A*, 2011, 375: 186
- [26] Hu H B, Wang Z H, Pan L, Zhao S P, Zhu S Y. *J Phys Chem C*, 2010, 114: 7738
- [27] Du J J, Jing C Y. *J Colloid Interf Sci*, 2011, 358: 54
- [28] Deng Y H, Qi D W, Deng C H, Zhang X M, Zhao D Y. *J Am Chem Soc*, 2008, 130: 28
- [29] Stöber W, Fink A, Bohn E. *J Colloid Interf Sci*, 1968, 26: 62
- [30] Du X Y, He J, Zhu J, Sun L J, An S S. *Appl Surf Sci*, 2012, 258: 2717
- [31] Kim K, Lee H B, Choi J Y, Shin K S. *ACS Appl Mater Interf*, 2011, 3: 324
- [32] Ai L H, Zeng C M, Wang Q M. *Catal Commun*, 2011, 14: 68
- [33] Guo J F, Ma B W, Yin A Y, Fan K N, Dai W L. *Appl Catal B*, 2011, 101: 580
- [34] Feral-Martin C, Birot M, Deleuze H, Desforages A, Backov R. *React Funct Polym*, 2007, 67: 1072
- [35] Ghosh S K, Mandal M, Kundu S, Nath S, Pal T. *Appl Catal A*, 2004, 268: 61
- [36] Jana N R, Pal T. *Langmuir*, 1999, 15: 3458
- [37] Lu Y, Mei Y, Ballauff M. *J Phys Chem B*, 2006, 110: 3930
- [38] Fan J, Guo Y H, Wang J J, Fan M H. *J Hazard Mater*, 2009, 166: 904
- [39] Srivastava S, Sharma S K, Sharma R K. *Colloids Surf A*, 2011, 373: 61
- [40] Panigrahi S, Basu S, Praharaj S, Pande S, Jana S, Pal A, Ghosh S K,

Graphical Abstract

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Recyclable $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ magnetic nanospheres for the rapid decolorizing of dye pollutantsSUN Lijuan, HE Jiang*, AN Songsong, ZHANG Junwei, ZHENG Jinmin, REN Dong
Lanzhou University

Show STEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ nanospheres and their catalytic mechanism for reduction of rhodamine B and eosin Y in the presence of NaBH_4 . The catalytic activity depends on the Ag nanoparticles on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles.

Pal T. *J Phys Chem C*, 2007, 111: 4596[41] Murugadoss A, Chattopadhyay A. *Nanotechnology*, 2008, 19: 015603[42] Jiang Z J, Liu C Y, Sun L W. *J Phys Chem B*, 2005, 109: 1730[43] Hu H, Shao M W, Zhang W, Lu L, Wang H, Wang S. *J Phys Chem C*, 2007, 111: 3467[44] Cazaux S, Caselli P, Tielens A G G M, Le Bourlot J, Walmsley M. *J Phys Conf Ser*, 2005, 6: 155可回收 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 磁性纳米微球对染料污染物的快速脱色处理孙丽娟^a, 何 疆^{a,*}, 安松松^a, 张军伟^b, 郑金敏^a, 任 栋^a^a兰州大学功能有机分子化学国家重点实验室, 甘肃兰州730000^b兰州大学磁学与磁性材料教育部重点实验室, 甘肃兰州730000

摘要: 介绍了一种采用无毒廉价的前驱物制备 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 磁性纳米微球的快捷方法, 制备的 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 纳米微球在 NaBH_4 存在下可以催化还原染料污染物. 实验结果表明, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 磁性纳米粒子保持了Ag纳米粒子和 Fe_3O_4 纳米粒子的双重优点, 不仅对染料罗丹明B和曙红Y具有良好的催化还原效率, 而且可以在外加磁场作用下从溶液中快速有效的分离. 催化还原反应速率与反应温度及 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 催化剂用量有关, 反应体系中表面活性剂和无机盐(Na_2SO_4)的存在也会影响催化剂的催化活性. 该 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ 磁性纳米粒子在工业染料污染物处理方面具有应用前景.

关键词: 四氧化三铁纳米颗粒; 催化还原; 染料; 可回收催化剂

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*通讯联系人. 电话: (0931)8912591; 传真: (0931)8912582; 电子邮箱: hejiang@lzu.edu.cn

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