Magnetic separable PSA@Fe₃O₄/Ag composites — Fabrication and catalytic properties

Cuifeng Jiang, Mingwei Chen, Shouhu Xuan, Wanquan Jiang, Xinglong Gong, and Zhong Zhang

Abstract: A novel PSA@Fe$_3$O$_4$/Ag composite, with high efficiency in the degradation of Rhodamine B, was synthesized through a simple wet-chemistry method. The results showed that the rate of the catalytic reaction was significantly concentration-dependent. Furthermore, there was no significant loss in the catalytic activity of the recycled catalysts, even after being recycled nine times (average 83%), from which one can deduce that almost all the nanosilver were regathered due to the super-paramagnetic Fe$_3$O$_4$ nanoparticles.

Key words: recyclable catalysts, magnetite, silver, rhodamine B.

Résumé : Faisant appel à une méthode simple de chimie humide, on a synthétisé un nouveau composite PDA@Fe$_3$O$_4$/Ag très efficace pour la dégradation de la Rhodamine B. Les résultats montrent que la vitesse de la réaction catalytique dépend fortement de la concentration. De plus, il n'y a pas de perte significative de l'activité des catalyseurs recyclés, même après neuf recyclages (moyenne de 83%); ces résultats permettent de déduire que pratiquement tout le nanoargent est récupéré en raison des nanoparticules de Fe$_3$O$_4$ superparamagnétiques.

Mots-clés : catalyseurs recyclables, magnétite, argent, rhodamine B.

[Traduit par la Rédaction]

Introduction

Recently, metal nanoparticles have become a hotspot in various fields,[1–3] not only because of their particular properties,[4,5] which are obviously different from their bulk materials, but also for their widespread applications in the practical world.[6] It has been extensively demonstrated that metal nanoparticles have high catalytic activities for NO reduction, CO oxidation, and degradation of organic dyes[7–9] because of their very large surface-to-volume ratio.

However, metal-nanoparticle catalysts have proved to be of somewhat limited use owing to the difficulties in separating the products and residual catalysts using traditional methods such as filtration or centrifugation.[10] The immobilization of metal-nanoparticle catalysts has therefore attracted a lot of attention. Among various support materials, magnetic-nanoparticle supports are now frequently used just because they allow the catalysts to be recovered conveniently through applying an external magnetic field.[11] Many efforts

have been made to develop this kind of recyclable catalyst. For example, T.J. Yoon and co-workers considered magnetic nanoparticles as a catalyst vehicle for simple and easy recycling.[12] Unfortunately, since magnetic nanoparticles themselves have strong magnetic properties and could easily aggregate together, the preparation of magnetic recyclable catalysts with better dispersion is rather challenging.

Generally, to obtain better dispersion, the magnetic components are modified with layers of rigid materials (SiO$_2$, carbon, and so forth) and (or) functional organic agents (amines, oleate, and so forth) in advance.[4,11,13,14] PSA (poly(styrene-*o*-acrylic acid)), an important and versatile polymer, is the expected template for composites, especially for those needed to be modified. Though various modified metal nanoparticles catalysts have been obtained,[15–17] to the best of our knowledge no PSA-based recyclable metal catalysts have been reported so far. In this report, a novel magnetically recycled PSA@Fe$_3$O$_4$/Ag composite catalysts have been successfully synthesized by a simple wet-chemistry method. Consequently, the catalysts cannot only be recovered easily, but also be dispersed homogeneously without an excess amount of surface active agent.

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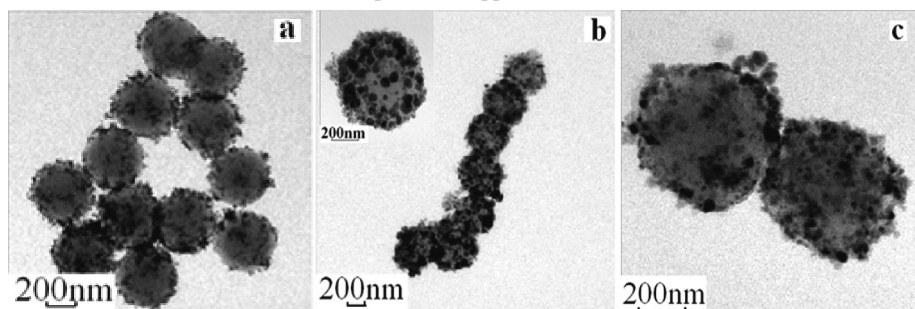
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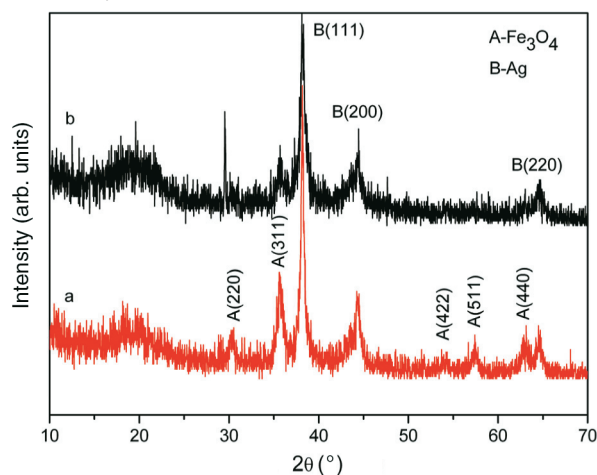
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Experimental

Reagents

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, AR), sodium sulfite anhydrous (Na$_2$SO$_3$, AR), sodium borohydride (NaBH$_4$), hexamethylene tetramine (AR), and rhodamine B (RhB, AR) were obtained from Sinopharm Chemical Reagent Co. Ltd. Silver nitrate (AgNO$_3$) and ammonium hydroxide (NH$_3$·H$_2$O, 25%–28%) were obtained from Lingfeng Chemical Reagent Co. Ltd. of Shanghai. All reagents were used as received without further purification.
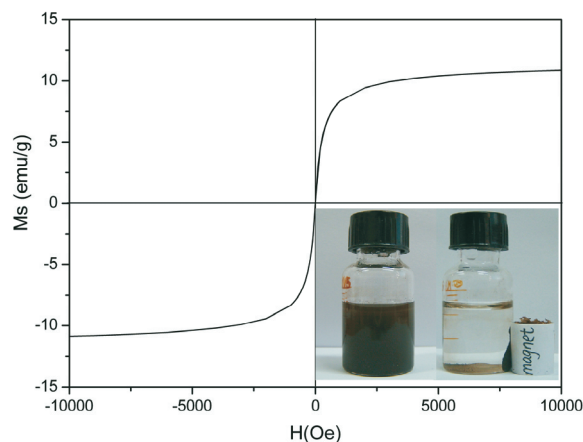
Fig. 1. TEM micrographs of (*a*) PSA@ Fe₃O₄ and silver nanoparticles supported on PSA@ Fe₃O₄ before (*b*) and after (*c*) the catalytic reaction.

Fig. 2. X-ray diffraction patterns of PSA@Fe₃O₄/Ag before (*a*) and after (*b*) catalytic reaction.

Fig. 3. Magnetization curve of PSA@Fe₃O₄/Ag.

Preparation of PSA@Fe₃O₄/Ag

Uniform PSA microspheres with an average diameter of 400 nm were synthesized by a method reported previously.[18] In a typical synthesis, PSA was dispersed in a blend solution with volume ratio of 2:1 ($v_{ethanol}/v_{water}$ = 2:1), and 50 mL of FeCl₃·6H₂O (0.006 mol/L), which has been purged with nitrogen for 20 min to remove all traces of oxygen, was added. After stirring for 20 min, Na₂SO₃ (0.001 mol/L) aqueous solution was gradually added under stirring, followed by a dropwise addition of NH₃·H₂O to adjust the pH value to 8. The mixture was stirred for 3 h at 65 °C under nitrogen atmosphere and then placed in a magnetic field (B = 300 mT) for separation. After that, the PSA@Fe₃O₄ precipitate was obtained.

The magnetic catalysts were prepared as follows: First, 0.05 g of AgNO₃ was added to an ethanol solution containing 0.1 g of PVP and 0.05 g of PSA@Fe₃O₄ as described above, and the mixture solution was sonicated for dispersion. Then, 20 mL of ethanol solution containing 0.2 g of hexamethylene tetramine was gradually dropped into the above-mentioned mixture suspension under stirring, and the resulting solution was vigorously stirred for 1 h. Then, the reaction system was allowed to stand for 10 h under circumfluence at 85 °C. After being separated by magnetic field, the resulting samples were washed with water and ethanol, then dried at 50 °C under vacuum. Finally, the PSA@Fe₃O₄/Ag composites were obtained.

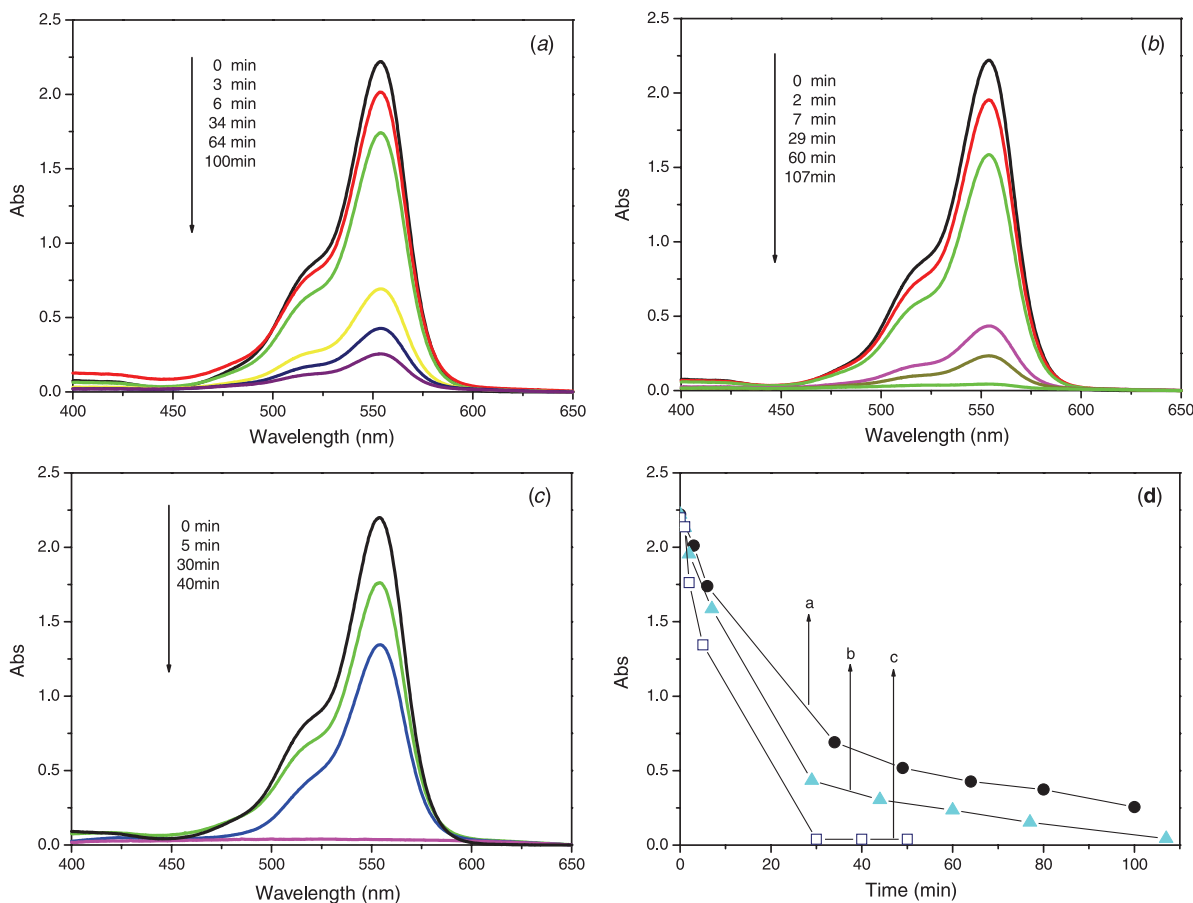## The catalytic properties of the obtained PSA@Fe₃O₄/Ag composites

A given amount of PSA@Fe₃O₄/Ag composite was well-dispersed in an aqueous solution containing RhB, and the volume of the mixture was adjusted to 30 mL with distilled water. After that, 10 mL of NaBH₄ solution were rapidly injected under stirring. The colour of the mixture gradually vanished, indicating the reduction of the dye. Changes in the concentration of RhB were monitored by examining the variations in maximal absorption in UV–vis spectra at 553 nm.

Catalyst-recycling experiments were examined to find the recycle efficiency. 1.5 mL of PSA@Fe₃O₄/Ag solution were used to catalyze RhB ([RhB] = 2 × 10⁻⁵ mol/L, [NaBH₄] = 1 × 10⁻² mol/L). After the reaction was completed, the catalysts were separated by a magnetic field, then followed by another "repeat". The recycle catalytic efficiency was determined by measuring the absorption value of RhB at the end of the catalytic reaction.

Characterization

Transmission electron microscopy (TEM) photographs were taken on a Hitachi model H-800 transmission electron microscope at an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) patterns of the products were obtained on a Japan Rigaku D/Max-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.154 178 nm). The magnetization curves

Fig. 4. UV–vis spectra of RhB during the degradation catalyzed by PSA@Fe₃O₄/Ag, [RhB] = 4 × 10⁻⁵mol/L.The arrows mark the increase of the reaction time. (*a*) 1 mL PSA@ Fe₃O₄/Ag; (*b*) 1.4 mL PSA@ Fe₃O₄/Ag; (*c*) 2 mL PSA@ Fe₃O₄/Ag, (*d*) curves of absorption vs. time at different concentrations of the catalyst (a: 1 mL, b: 1.4 mL, c:2 mL PSA@ Fe₃O₄/Ag solution).

(M–H curve) of the samples were recorded on a MPMS XL-7 magnetometer made by Quantum Design Corp. The optical absorption was recorded on an ultraviolet–visible (UV)-2401(PC)S made by Shimadzu Corporation.

Results and discussion

The characterization of PSA@Fe₃O₄/Ag composites

As mentioned above, the PSA@Fe₃O₄/Ag composites were prepared by a simple and rapid method. The formation of the composites was confirmed by TEM as presented in Fig. 1, from which monodisperse composites can be seen. TEM analysis on both PSA@Fe₃O₄ and PSA@Fe₃O₄/Ag reveal that silver and magnetite nanoparticles decorated the PSA substrate with a diameter of 400 nm. It is evident that the darker dots represent the silver nanoparticls while the others are Fe₃O₄ nanoparticles. The absorption function is strong enough so that the silver nanoparticles remain attached to the PSA@Fe₃O₄ during the catalytic reaction, which was verified by the TEM images of the silver particles supported on PSA@Fe₃O₄ before and after catalytic reactions (Fig. 1*b* and 1*c*).

To study the stability of the composite catalysts, the sample was subjected to XRD. As shown in Fig. 2, all of the diffraction peaks match well with Ag crystal and Fe₃O₄ crystal.[19,20] As one can see, peaks of both Ag and Fe₃O₄ be-

come a little weaker in Fig. 2*b* compared with Fig. 2*a*, which means that a portion of the crystal has been lost during the catalytic reaction. That is why in the recycle experiments, the composite catalysts deactivated more or less during the degradation reaction.

The magnetic properties of the composites have been elucidated in Fig. 3. The saturation magnetization of the composites is 11 emu/g at an external field of 10 kOe at room temperature. Obviously, it is much lower than the reported saturation magnetization of Fe₃O₄ (68.7 emu/g).[21] The emerging of this phenomenon is because of the existence of silver in very small size. On one hand, this feature allows catalysts separation under relatively low external magnetic field. On the other hand, the negligible coercivity indicates the superparamagnetic property of the sample, which is available for redispersion of the catalysts in solution without the occurrence of severe assembly or aggregation usually appearing in ferromagnetic nanoparticles.[22–25] That is why Fe₃O₄ rather than Fe serves as the magnetic support.

The inset of Fig. 3 illuminates the effective model of catalysts separation and redispersion under an external magnetic field. Before applying an external field, the catalysts were homogeneously dispersed to show their high catalytic activity.[26] After applying an external field, the intact catalysts were separated from the mixture suspension for reusage. Thus, the PSA@Fe₃O₄ composites are very appropriate

Fig. 5. The change of RhB's colour under the catalysis of PSA@Fe₃O₄/Ag.

Table 1. Catalytic efficiency at different concentrations of the catalyst.

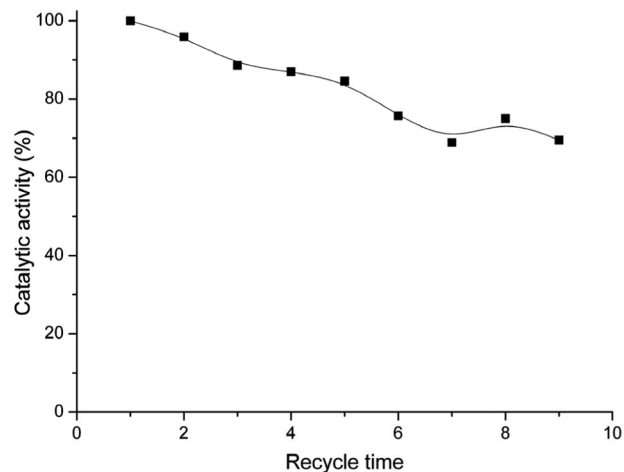| (mL)	Catalytic efficiency (%)									
	0	1	2	6	30	45	50	60	80	100 (min)
1.0	0	2.54	9.4	21.7	68.8	75.5	76.8	80.6	83.2	88.5
1.4	0	3.96	12.0	28.6	80.5	86.3	87.6	89.5	93.1	98.0
2.0	0	2.74	19.8	38.8	98.2	98.2	98.2	98.2	98.2	98.2

as catalyst supports for separation and redispersion[4] because of superparamagnetic Fe₃O₄ nanocrystals.

The catalytic properties of as-prepared PSA@Fe₃O₄/Ag catalysts

Previous results[6,27,28] demonstrated that silver nanoparticles exhibit catalysis on organic dyes, such as rhodamine B (RhB), methylene blue (MB), and eosin (EO). In this paper, catalysis experiments were conducted to study the catalytic properties of the nanosilver. Figure 4 shows the evolution of the UV–vis spectra of RhB during catalytic reductions at the PSA@Fe₃O₄/Ag solution. Evidently, the absorbance at λ_{max} = 553 nm of the RhB gradually decreased with reaction time, which is indicative of the reduction of RhB. As expected, the catalytic reduction of RhB proceeded successfully, and no deactivation or poisoning of the catalysts was observed. Changing of RhB's colour in the process of catalysis reaction (Fig. 5) further affirms the degradation. With time, the colour of RhB became lighter and lighter. As one can see, the pure RhB was carmine; after 20 min reaction, the solution became peachblow; and then at the end of the reaction (50 min), the colour almost disappeared. It was observed that the reduction of RhB by PSA or PSA@Fe₃O₄ did not occur to an appreciable extent in the absence of the Ag nanoparticles. This indicates that silver nanoparticles play the key role of the catalysts for the reduction of RhB, while PSA supports the catalyst, and Fe₃O₄ makes it possible to be reused. According to earlier work,[7] the catalytic process can be explained by an electrochemical mechanism, where PSA@Fe₃O₄/Ag serve as an electron relay for an oxidant and a reductant, and electron transfer occurs via the supported silver particles. Dyes are electrophilic, while BH_4^- ions are nucleophilic in nature with respect to silver nanoparicles.

Reactions with various concentrations of catalysts were examined to find the optimal conditions for the reaction. The rate of the catalytic reaction proved to be significantly concentration-dependent.

It is apparent that the rate of the catalyzed reduction of RhB increased with the increase of the concentration of the PSA@Fe₃O₄/Ag as displayed in Table 1. It is obviously ob-

Fig. 6. Recycle experiments of the degradation reaction of RhB catalyzed by PSA@Fe₃O₄/Ag.

served that after 30 min reaction, the degradation of RhB for three volumes of PSA@Fe₃O₄/Ag solution (1 mL, 1.4 mL, and 2 mL) was 60%, 83%, and almost 100%, respectively. Therefore, to improve catalytic efficiency, increasing the mass of catalysts is effective.

Recycleability of the catalysts was examined to evaluate the role of PSA@Fe₃O₄. The hybrid composite catalysts, doped with magnetic particles, can be isolated by a magnetic device and reused for consecutive reactions. When the external magnetic field was applied after the reaction was accomplished, the magnetic composites were regathered (B = 300 mT), and the rest of the solution became clean within 5 min. Under these reaction conditions, the degradation of RhB was carried out nine times with the recycled catalysts. As shown in Fig. 6, there was no significant change in the catalytic activity of the recycled magnetic composite even after being recycled nine times (average 83%). Consequently, the small decrease of the catalytic activity can result from incomplete separation of catalysts or the loss of catalysts during the degradation reduction. All these results showed that the PSA@Fe₃O₄ substrate played an important role in the catalytic process. One is to avoid the aggregation

of the metal nanoparticles during the catalytic process, which ensures the catalyzed reduction of RhB.[6] The other is to facilitate separation of catalysts from the solution system. This fascinating property of magnetic catalysts is expected to be applied in many other important industrial processes.

Conclusion

With the assistance of PSA, a novel magnetically recyclable Ag-based catalyst was synthesized. Results showed the obtained magnetic catalysts exhibited good catalytic activity and could be recycled for several times by magnetic separation without major loss of activity. The significance of PSA@Fe_3O_4 lies in avoiding the aggregation of the silver nanoparticles during the catalytic process and offering an easy separation approach after catalysis. Furthermore, the overall synthetic process for the composites is simple and rapid, and it is anticipated that this synthetic approach may be readily extended to recyclable catalysts that contain catalytically active metals instead of Ag.

Acknowledgements

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