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# Magnetic recyclable Ag catalysts with a hierarchical nanostructure

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## Abstract

This study reports the fabrication of a novel hierarchically structured nanocatalyst system possessing a well-defined nickel silicate (NS) protected Fe<sub>3</sub>O<sub>4</sub> core and a layer of uniform Ag nanoparticles on the NS shell by using a multi-step approach. The multifunctional microparticles show high performance in the reduction of 4-nitrophenol and the rate of the catalytic reaction can be controlled by changing the concentration of nanocatalysts. In particular, there was no visible decrease in the catalytic activity of the reused catalysts even after being recycled five times. Thus the hierarchically structured Fe<sub>3</sub>O<sub>4</sub>@NS particles are very suitable as a catalyst support for catalyst separation and redispersion.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Metal nanoparticles have unique properties that are significantly distinct from their bulk materials. Aside from high surface-to-volume ratio, nanoscale-metal particles are also attractive for their remarkable catalytic activity [1–6]. However, metal nanocatalysts encounter difficulty in separation from the reaction solution and recycling, which limits their practical application for environmentally friendly process. To overcome this problem, the immobilization of metal nanoparticles on a suitable magnetic support matrix, which can be reversibly recovered and redispersed by applying an external magnetic field, has gained much attention [7–10]. For instance, Jiang *et al* reported nanocomposites containing Pd catalysts immobilized on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PAMAM and their catalysis for the hydrogenation of allyl alcohol [8].

Among various magnetic support materials, hollow nano-materials, especially hierarchically structured spheres, have attracted more and more attention because of their unique properties, such as large surface area, multifunctionality, excellent loading capacity [11–18] and great potential applications in catalysis [19], drug carriers [20] and building blocks of photonic crystals [21]. Li *et al* synthesized mesoporous titania spheres with a tunable chamber structure

and the as-prepared porous materials exhibited enhanced photocatalytic activity toward phenol degradation [22]. Zhao *et al* reported the fabrication of uniform magnetic composite spheres with a magnetic core/mesoporous silica shell structure for the storage and release of ibuprofen [23]. To the best of our knowledge, rare work in designing magnetic particles with hierarchical nanostructure has been reported. Based on this strategy, hierarchically structured particles containing superparamagnetic Fe<sub>3</sub>O<sub>4</sub> core and nickel silicate shells (Fe<sub>3</sub>O<sub>4</sub>@NS) were synthesized as a support matrix to attach the noble metal. The advantages of this catalyst system are as follows: (1) as a catalyst support, Fe<sub>3</sub>O<sub>4</sub>@NS magnetic particles facilitate its separation from the reaction medium with the help of a magnetic field; (2) high catalyst loading capacity can be realized in such a catalyst system.

In this paper, we report a novel kind of nanoscale composite consisting of nanosized Ag catalysts and nickel silicate (NS)-coated Fe<sub>3</sub>O<sub>4</sub> microspheres by a multi-step approach. The Fe<sub>3</sub>O<sub>4</sub>@NS microspheres were synthesized through a hydrothermal route based on a Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sacrificial templating process [24]. Subsequent reduction of Ag(I) by hexamethylene tetramine yields catalytic Ag nanoparticles embedded in a hierarchical Fe<sub>3</sub>O<sub>4</sub>@NS nanostructure, designated as Fe<sub>3</sub>O<sub>4</sub>@NS/Ag. The obtained

microspheres were successfully applied to the degradation of 4-nitrophenol (4-NP). As a consequence, the unique multicomponent nanostructured Fe<sub>3</sub>O<sub>4</sub>@NS/Ag microspheres have high catalytic activity toward the 4-nitrophenol and good reusability for recycling. Therefore, the unique Fe<sub>3</sub>O<sub>4</sub>@NS nanostructure makes the microspheres a promising carrier for metal catalyst loading.

## 2. Experimental section

### 2.1. Chemicals

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, AR), trisodium citrate (AR), sodium acetate (NaAc), ethylene glycol, ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, 25%–28%), tetraethylorthosilicate (TEOS), ethanol, sodium borohydride (NaBH<sub>4</sub>), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), urea, silver nitrate (AgNO<sub>3</sub>), hexamethylene tetramine, polyvinylpyrrolidone (PVP), and 4-NP are of analytical grade and purchased from Sinopharm Chemical Reagent Co, Ltd. All reagents were used as received without further purification. Deionized water was used for all experiments.

### 2.2. Materials for synthesis of multicomponent Fe<sub>3</sub>O<sub>4</sub>@NS/Ag microspheres

The water dispersible Fe<sub>3</sub>O<sub>4</sub> microspheres were prepared according to the method previously reported by Liu with tiny modification [25]. Typically, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.3 g, 8 mmol), trisodium citrate (0.5 g, 1.7 mmol) and sodium acetate (NaAc) (2.0 g, 24.4 mmol) were dissolved in ethylene glycol (40 ml) successively, then magnetically stirred for 30 min. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (50 ml in capacity) and treated at 200 °C for 12 h. The black products were first washed five times with deionized water. For the sixth washing, the Fe<sub>3</sub>O<sub>4</sub> suspension was first rested for 1 h, then the upper of the iron oxide suspension was decanted and magnetically separated. Finally, the obtained Fe<sub>3</sub>O<sub>4</sub> microspheres were dried under vacuum at 50 °C.

In order to obtain well-dispersed Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres, a modified sol–gel method [26–28], conducted in a sonochemical reaction system, was employed. The details are summarized as the follows. Firstly, Fe<sub>3</sub>O<sub>4</sub> microspheres (10 mg) were added to a mixture of deionized water (3 ml), NH<sub>3</sub>·H<sub>2</sub>O (1 ml) and ethanol (30 ml), and sonicated for 4 h at room temperature. Secondly, TEOS (0.15 ml) was dissolved in ethanol (5 ml). Thirdly, TEOS/ethanol mixture (1 ml) was injected into Fe<sub>3</sub>O<sub>4</sub> suspension at every 10 min interval under sonication, and the same procedures repeated for five times. After that, the mixture was further sonicated for 70 min. The obtained products were separated by a magnet and washed several times with ethanol. Then, deionized water (5 ml) was added into the above collected Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres. Afterward, 5 ml of 10 g l<sup>-1</sup> NiCl<sub>2</sub> solution and 0.675 g urea were added. The total mixture was sonicated for 5 min, and then 5 ml of ethanol were introduced. Finally, the reaction solution was transferred into a Teflon-lined stainless-steel autoclave (30 ml in capacity) and heated at 180 °C for

6 h. After the collection and rising of the microspheres, the as-prepared microspheres were dried under vacuum at 50 °C.

A simple *in situ* wet chemistry method was employed for the immobilization of Ag nanoparticles onto the hierarchically structured Fe<sub>3</sub>O<sub>4</sub>@NS microspheres to form the Fe<sub>3</sub>O<sub>4</sub>@NS/Ag microspheres. First, 0.05 g of AgNO<sub>3</sub> was added to an ethanol solution containing 0.1 g of PVP and 0.05 g of Fe<sub>3</sub>O<sub>4</sub>@NS as described above, and the mixture was subjected to sonication for well dispersion. Then, 20 ml of ethanol solution containing 0.2 g of hexamethylene tetramine was added dropwise and the reaction solution was further stirred for 1 h. After that, the reaction system was allowed to proceed for 10 h at 85 °C with continuous mechanism stirring. Finally, the resulting products were magnetically separated, washed several times with ethanol and dried at 50 °C under vacuum.

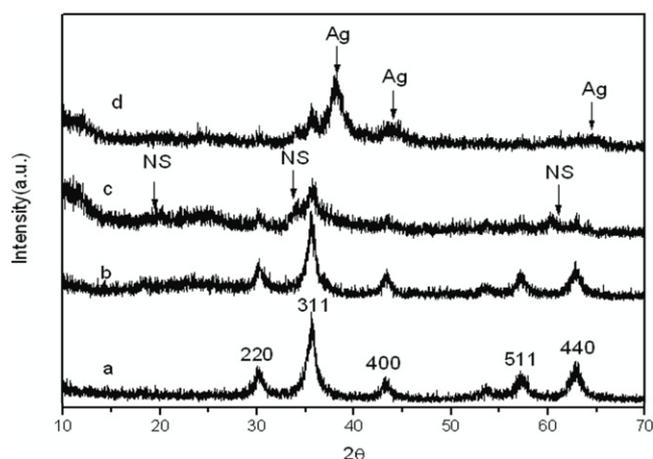
### 2.3. Catalytic reduction of 4-NP

1.7 ml, 2.3 ml, 2.8 ml of aqueous dispersion of the Fe<sub>3</sub>O<sub>4</sub>@NS/Ag multicomponent microspheres were added in an aqueous solution containing 4-NP ( $2 \times 10^{-4}$  M), respectively. Then, the volume of the mixture was diluted to 30 ml with distilled water. Subsequently, 10 ml of fresh NaBH<sub>4</sub> solution was rapidly injected at room temperature under magnetic stirring. The concentration of 4-NP solution was monitored by UV–vis measurement to obtain the successive information about the changes of 4-NP. The color of the reaction mixture gradually vanished, indicating the reduction of the 4-NP dye.

Recycle catalysis experiments were conducted in order to study the reusability of the magnetic catalysts. Similar to the above reduction process, a given amount of the as-prepared Fe<sub>3</sub>O<sub>4</sub>@NS/Ag microspheres (1.8 mg) were used to catalyze 4-NP ( $c(4\text{-NP}) = 1 \times 10^{-4}$  mol l<sup>-1</sup>,  $c(\text{NaBH}_4) = 1 \times 10^{-2}$  mol l<sup>-1</sup>). After reaction for 15 min, the catalysts were separated by a magnet, and the supernatant was measured using UV–vis spectroscopy. The same procedures were repeated five times. No significant loss in the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@NS/Ag nanocatalysts was detected.

### 2.4. Characterization methods

The crystalline structure of the obtained products was investigated by a Japan Rigaku D<sub>Max</sub>-γA rotation anode x-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ( $\lambda = 0.154178$  nm). Transmission electron microscopy (TEM) images were taken on a JEM-2100F FETEM and JEM-2100 TEM microscope at an accelerating voltage of 200 kV, respectively. The infrared spectra of the samples were obtained on an EQUINOX 55 Fourier transform spectrometer (Bruker, Germany). The magnetic properties of the prepared products were measured on a Lakeshore 9300 Vibrating Sample Magnetometer (VSM) with an applied field between –10000 and 10000 Oe at room temperature. The UV–vis spectra were recorded on a UV-365 spectrophotometer.



**Figure 1.** The XRD patterns of (a)  $\text{Fe}_3\text{O}_4$  microspheres, (b)  $\text{Fe}_3\text{O}_4@SiO_2$  microspheres, (c)  $\text{Fe}_3\text{O}_4@NS$  microspheres, and (d)  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres.

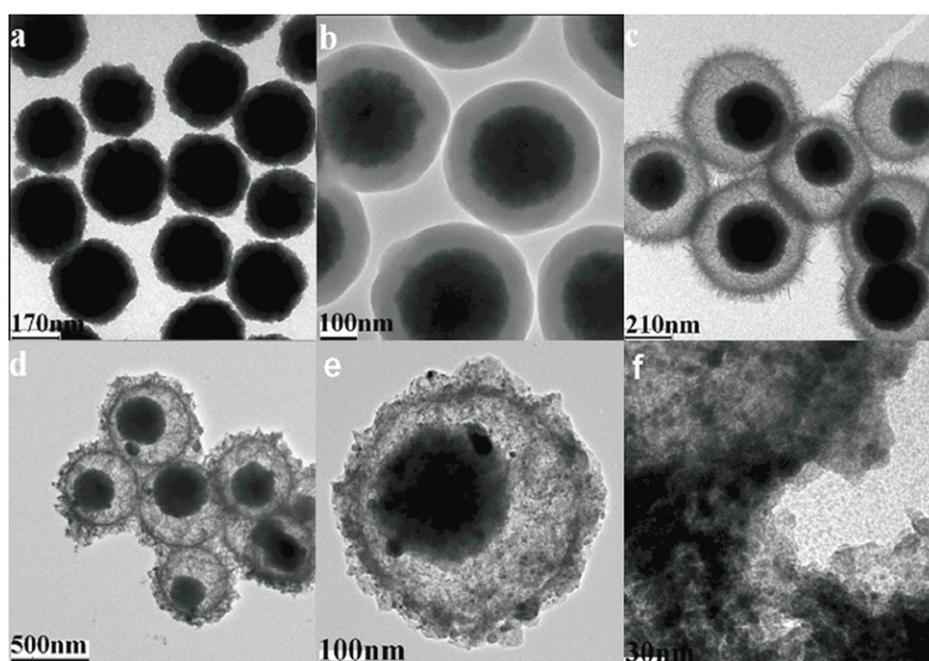
### 3. Results and discussion

#### 3.1. The characterization of $\text{Fe}_3\text{O}_4@NS/Ag$ composite microspheres

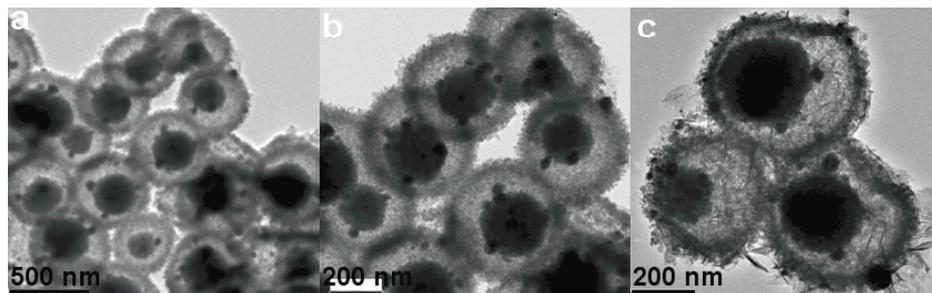
In order to determine the crystallographic structure of the iron oxide nanoparticles before and after coating, the as-prepared samples were subjected to XRD measurement. As shown in figure 1(a), the characteristic diffraction peaks for the iron oxide nanoparticles have been indexed to be face-centered cubic magnetite (JCPDS No. 19-0629). A broad diffraction band between  $20^\circ$  and  $24^\circ$  was observed (figure 1(b)) when the iron oxide nanoparticles were coated with a layer of silica, confirming the existence of amorphous silica shell on iron

oxide. In figure 1(c), the representative Bragg reflections indicated that both  $\text{Fe}_3\text{O}_4$  and NS co-existed in the samples. However, due to the low concentration of the NS, only three low intensity peaks were observed. The diffraction peaks located at  $20^\circ$ ,  $34^\circ$ ,  $61^\circ$  are the characteristic peaks of nickel silicate hydroxide hydrate hexagonal phase (JCPDS No. 43-0064). The apparent broadening of NS peaks indicated low crystallinity property of the nickel silicate shell. To verify the formation of the silver nanoparticles, the specific XRD pattern of  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres was measured (figure 1(d)), showing three characteristic peaks positioned at  $2\theta$  values of  $38^\circ$ ,  $44^\circ$ ,  $64^\circ$ , which correspond to the (111), (200) and (220) lattice planes of the face-centered cubic phase Ag, respectively (JCPDS No. 03-0931). This reveals that silver nanoparticles are successfully fixed on or within the  $\text{Fe}_3\text{O}_4@NS$  microspheres. It is notable that all diffraction peaks of  $\text{Fe}_3\text{O}_4$  were maintained after the coating process, further proving the well-retained magnetite phase in the multifunctional composite microspheres.

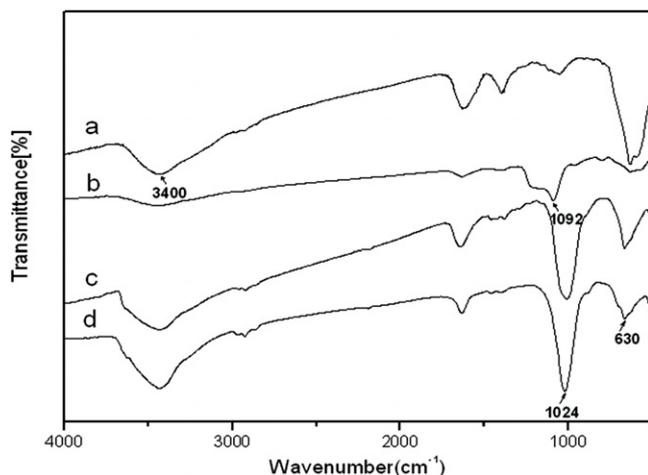
The citrate group functionalized magnetite particles were synthesized through a robust solvothermal reaction based on a high temperature reduction of Fe(III) salts with ethylene glycol [27–29]. Trisodium citrate was not only serving as a base but also a surface modification agent in the hydrothermal system. The representative TEM image of magnetite is displayed in figure 2(a). It is apparent that the obtained magnetite particles are uniform with a mean diameter of  $\sim 200$  nm. Through a modified Stöber's process, uniform silica coating ( $\sim 60$  nm in thickness) can be formed on individual magnetite particle seed, resulting in clear core-shell  $\text{Fe}_3\text{O}_4@SiO_2$  structures (figure 2(b)), which was subsequent used as the template and starting materials for the fabrication of hierarchical  $\text{Fe}_3\text{O}_4@NS$  nanostructures. In



**Figure 2.** TEM images of (a)  $\text{Fe}_3\text{O}_4$  microspheres, (b)  $\text{Fe}_3\text{O}_4@SiO_2$  microspheres, (c)  $\text{Fe}_3\text{O}_4@NS$  microspheres, ((d)–(f))  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres.



**Figure 3.** TEM images of  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres after recyclable experiment ((a)–(c)).



**Figure 4.** The FT-IR spectra of (a)  $\text{Fe}_3\text{O}_4$  microspheres, (b)  $\text{Fe}_3\text{O}_4@SiO_2$  microspheres, (c)  $\text{Fe}_3\text{O}_4@NS$  microspheres, and (d)  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres.

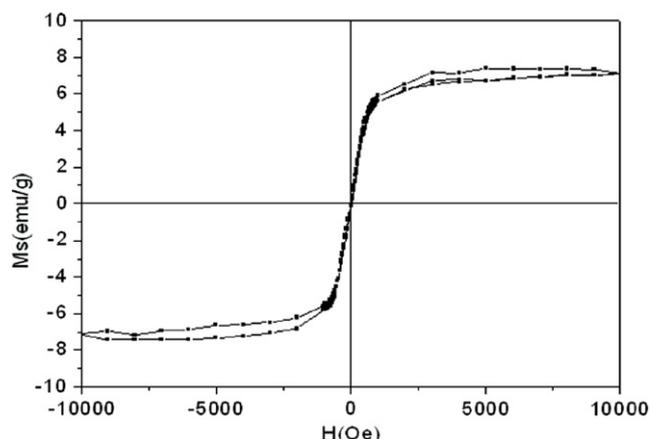
comparison to the uncoated  $\text{Fe}_3\text{O}_4$  microspheres,  $\text{Fe}_3\text{O}_4@SiO_2$  microspheres exhibit a perfectly spherical with smooth surface due to the deposition of silica. Then the resulting well-dispersed  $\text{Fe}_3\text{O}_4@SiO_2$  particles were reacted with the  $Ni^{2+}$  cations under alkaline conditions to give the hierarchical NS nanostructures, and the TEM images of the  $\text{Fe}_3\text{O}_4@NS$  microspheres are shown in figure 2(c). It can be observed that the typical outer shell is rather rough and composed of a large number of nanosheets. The hierarchically structured  $\text{Fe}_3\text{O}_4@NS$  microspheres are uniform with a diameter of  $\sim 300$  nm and the NS layer is  $\sim 100$  nm in thickness.

To deposit silver nanoparticles efficiently, a simple wet chemistry method was employed. Reduction of  $AgNO_3$  was accomplished by a mild hexamethylene tetramine. After incubation with  $\text{Fe}_3\text{O}_4@NS$  microspheres for 10 h in solution, the silver nanoparticles can deposit on the surface of hierarchically structured microspheres. As revealed by transmission electron microscopy (TEM), uniform  $\text{Fe}_3\text{O}_4@NS/Ag$  magnetic particles with a diameter of  $\sim 500$  nm were obtained (figures 2(d)–(f)). It is very clear that the  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres are well-dispersed without occurrence of severe aggregation after the deposition of silver nanoparticles, indicating the uniform property of our nanocatalyst products. To clearly examine the condition of silver coating, the outer surface area of an enlarged

single  $\text{Fe}_3\text{O}_4@NS/Ag$  particle was investigated, and the TEM photograph is shown in figure 2(f). It can be seen that a large number of dark dots are observed on the surface of the  $\text{Fe}_3\text{O}_4@NS$  microspheres, which clearly indicate the silver nanoparticles are evenly dispersed on or within the hierarchical NS shell. Furthermore, after the recyclable experiment, the silver nanoparticles were well maintained on the surface of the  $\text{Fe}_3\text{O}_4@NS$  microspheres (in figure 3), indicating the well-binding between the silver nanoparticles and the hierarchically structured  $\text{Fe}_3\text{O}_4@NS$  support.

To investigate the surface coating conditions of the as-prepared samples, the FT-IR spectra were also recorded. In the FT-IR spectrum of  $\text{Fe}_3\text{O}_4$  microspheres,  $630\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  are related to the stretching vibration of Fe–O and the stretching vibration of O–H, respectively. Figure 4(b) shows the FT-IR spectrum of  $\text{Fe}_3\text{O}_4@SiO_2$  sample. The obvious band appeared at  $1092\text{ cm}^{-1}$  originates from the absorption of a rocking motion of oxygen perpendicular to the Si–O–Si plane, demonstrating the successful surface modification on  $\text{Fe}_3\text{O}_4$  microspheres. The band located at  $1024\text{ cm}^{-1}$  is derived from the Si–O vibration of hierarchical NS shell (figure 4(c)). Figure 4(d) shows the FT-IR spectrum of  $\text{Fe}_3\text{O}_4@NS/Ag$  sample, which is almost the same as that of the  $\text{Fe}_3\text{O}_4@NS$  sample but a weak intensity. This is mainly because silver nanoparticles do not have absorption in the infrared region [30].

The magnetic properties of the composite catalysts were investigated by using a vibrating sample magnetometer (VSM) with an applied field between  $-1$  and  $1$  T at room temperature (Lakeshore 9300). A representative hysteresis loop of the as-used  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres is shown in figure 5. The saturation magnetization ( $M_s$ ) of the product is about  $7\text{ emu g}^{-1}$  and the relatively low value can be attributed to the loading of the NS component and the Ag nanoparticles in the nanocatalyst system. The coercivity of the magnetic composites is close to zero, indicating the superparamagnetic nature of our products. The superparamagnetic behavior of the prepared  $\text{Fe}_3\text{O}_4@NS/Ag$  enables the catalysts to be separated easily by an external magnetic field. Meanwhile, the negligible remanent magnetization can largely reduce severe assembly and/or aggregation of nanocatalysts usually appearing for ferromagnetic nanoparticles. Therefore, the composite nanocatalysts can be easily redispersed in a solution for recycling.

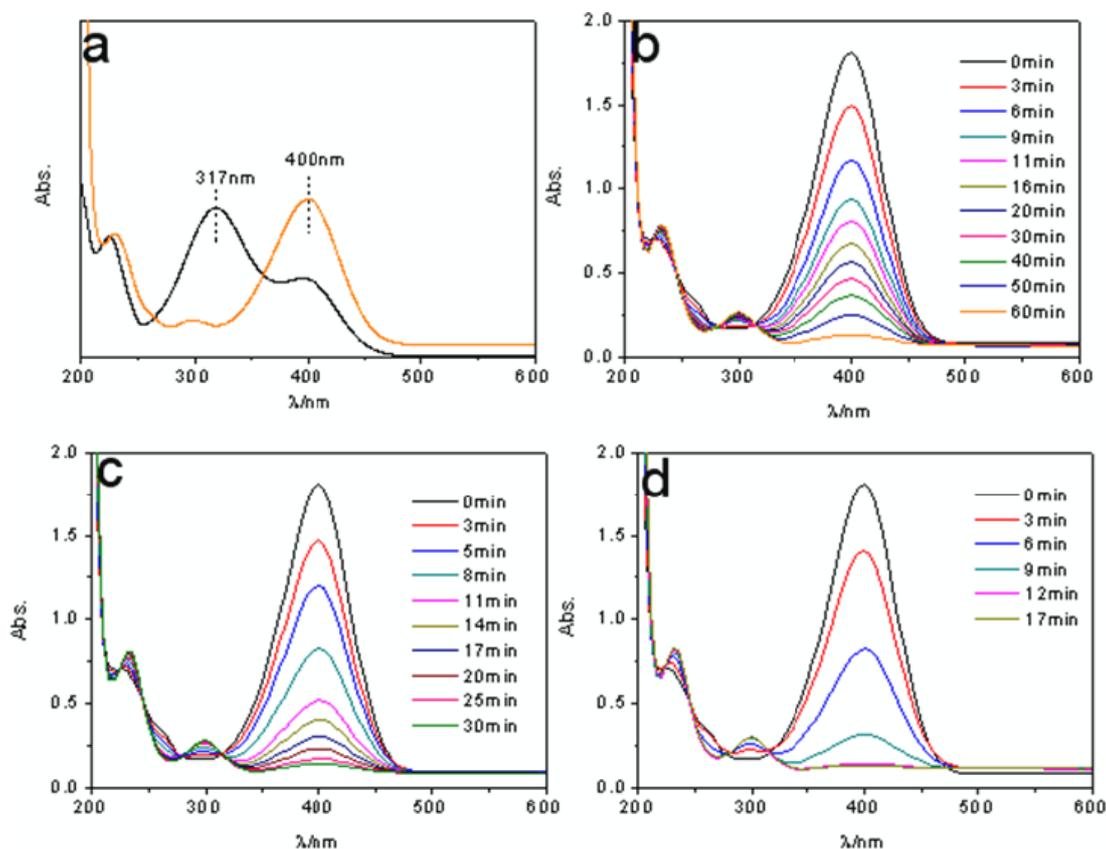


**Figure 5.** Magnetic hysteresis loop of hierarchically structured  $\text{Fe}_3\text{O}_4@NS/Ag$  composite microspheres at room temperature.

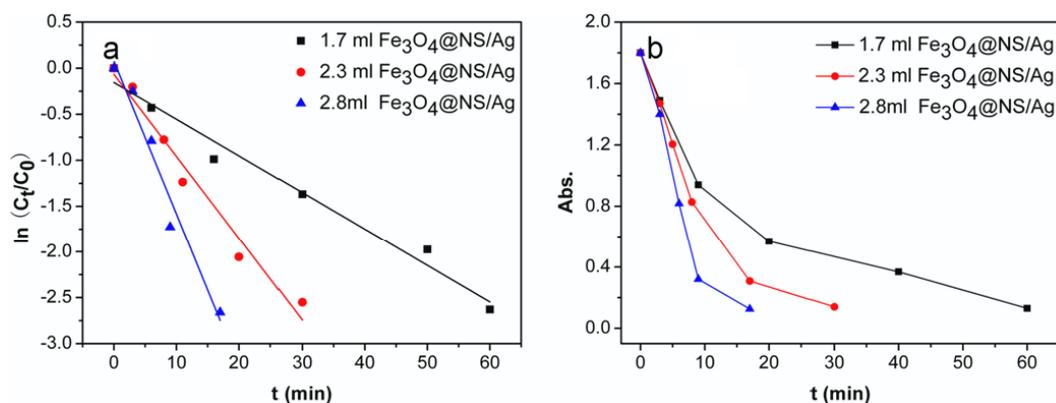
### 3.2. Application of $\text{Fe}_3\text{O}_4@NS/Ag$ microspheres for catalytic reduction of 4-NP

The catalytic reduction of aromatic nitro compounds to their corresponding amino derivatives is environmentally significant. However, aromatic nitro compounds are not reduced by  $\text{NaBH}_4$  in aqueous or alcoholic solution. Up to now, there have been a number of reports on the reduction of organic dyes with sodium borohydride by catalyzed noble

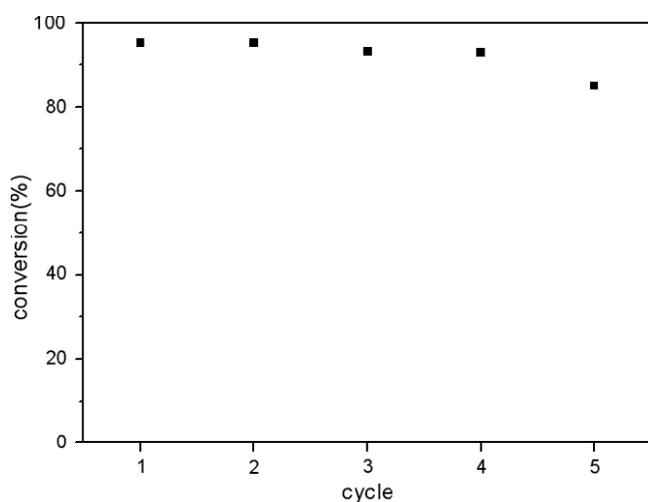
metal [31–33]. In this work, 4-NP dye was chosen as the representative model system to explore the catalytic performance of  $\text{Fe}_3\text{O}_4@NS/Ag$  nanocatalysts in the presence of  $\text{NaBH}_4$ . This is possible because the 4-NP and its product can be easily monitored by UV–vis absorption spectroscopy without the formation of byproduct. As figure 6(a) shows, the maximal absorption of the pure 4-NP is at 317 nm. However, after the introduction of  $\text{NaBH}_4$  solution, the absorption maximum red shifts to 400 nm which corresponds to the formation of 4-nitrophenolate [34]. Without catalyst, no changes of the 4-NP solution were observed even after 10 h. When a small amount (2.0 mg) of the  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres are added into the 4-NP solution, the absorption peak at  $\sim 400$  nm decreases gradually with time. Meanwhile, a new peak appears at  $\sim 300$  nm and gradually increases, revealing the reduction of 4-NP and the formation 4-AP. The evolution of the UV–vis spectra of 4-NP during catalytic reduction at the  $\text{Fe}_3\text{O}_4@NS/Ag$  solution is shown in figure 6. The catalytic reduction of the dyes proceeds successfully, wherein no deactivation or poisoning of the catalysts is detected. The reduction of 4-NP catalyzed with various concentrations of catalysts was investigated. Considering  $\text{NaBH}_4$  concentration is highly excessive, the reduction reaction can be assumed to be pseudo-first-order with respect to the reactant. The relationship between  $\ln(C_t/C_0)$  and reaction time is linear, which could be directly reflected by the reduction curves (figure 7(a)). In this work, the ratios of 4-NP concentrations ( $C_t$  at time  $t$ ) to its initial value  $C_0$



**Figure 6.** UV–vis spectra of (a) 4-nitrophenol before and after adding  $\text{NaBH}_4$  solution, ((b)–(d)) the catalytic reduction of 4-NP by different concentrations of  $\text{Fe}_3\text{O}_4@NS/Ag$  suspension ((b) 1.7 ml, (c) 2.3 ml, (d) 2.8 ml), the mass concentration of catalysts is 0.01 g/20 ml.



**Figure 7.** (a) The relationship between  $\ln(C_t/C_0)$  and reaction time, (b) curves of absorption versus time at different concentrations of the catalysts.



**Figure 8.** The reusability of the  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres as a catalyst for the reduction of 4-NP with  $\text{NaBH}_4$ .

( $t = 0$ ) can be obtained by evaluating the relative intensity of the corresponding absorbance  $A_t/A_0$ . The rate constant  $k$  was calculated to be 0.04, 0.09, and  $0.16 \text{ min}^{-1}$  for the reactions using three volumes of  $\text{Fe}_3\text{O}_4@NS/Ag$  solution 1.7 ml, 2.3 ml, 2.8 ml. These results indicate that increasing the concentration of the catalyst solution can help to increase the reduction rate of 4-NP. The complete reduction time of 4-NP for three volumes of  $\text{Fe}_3\text{O}_4@NS/Ag$  solution 1.7 ml, 2.3 ml, 2.8 ml was 60 min, 30 min and 12 min, respectively (figure 7(b)). It can be concluded that the reduction rate of 4-NP can be controlled by changing the concentration of catalysts.

The reusability of the catalysts was examined to evaluate the recyclable ability of multifunctional  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres. The hybrid composite catalysts, consisting of magnetic hierarchically structured  $\text{Fe}_3\text{O}_4@NS$  microspheres and immobilized silver nanoparticles, can be separated by a magnet and reused for consecutive reactions. As shown in figure 8, it can be concluded that the catalysts exhibit good catalytic performance without visible reduction in the conversion for the same reaction time (15 min) even after running for five cycles. All these results demonstrated

that the hierarchically structured  $\text{Fe}_3\text{O}_4@NS$  support matrix played an important role in the catalytic process. On the one hand, aggregation and dissolution of the nanocatalysts were eliminated during the reduction process. On the other hand, such unique microstructures of the multifunctional microspheres ensured Ag nanoparticles were well retained after plenty of repeating of the catalytic processes. Therefore, this magnetic catalyst is a novel stable catalyst system for various industry catalytic processes.

#### 4. Conclusion

In conclusion, we have prepared novel multifunctional magnetic microspheres composed of nanosized Ag catalysts immobilized on hierarchically structured  $\text{Fe}_3\text{O}_4@NS$ . The results showed that the obtained nanocatalysts exhibited excellent catalytic activity for the degradation of 4-NP. Furthermore, these characteristic hierarchically structured  $\text{Fe}_3\text{O}_4@NS/Ag$  microspheres could be recycled several times by magnetic separation without obvious loss of activity. The unique structure of  $\text{Fe}_3\text{O}_4@NS$  particles played a significant role in the multicomponent nanocatalyst system for avoiding the aggregation and dissolution of silver nanoparticles during the catalytic process and offered a convenient separation approach after catalysis. Therefore, these magnetically separable hierarchically structured  $\text{Fe}_3\text{O}_4@NS$  particles are very appropriate for the immobilization of metal nanocatalysts for various industry catalytic processes.

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