Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/apcata

Facile synthesis of silver-deposited silanized magnetite nanoparticles and their application for catalytic reduction of nitrophenols

Kuan Soo Shin^{a,*}, Young Kwan Cho^a, Jeong-Yong Choi^b, Kwan Kim^{b,**}

^a Department of Chemistry, Soongsil University, Seoul 156-743, Republic of Korea

^b Department of Chemistry, Seoul National University, Seoul 151-742, Republic of Korea

ARTICLE INFO

Article history: Received 18 August 2011 Received in revised form 18 October 2011 Accepted 3 November 2011 Available online 12 November 2011

Keywords: Fe₃O₄ particle Silanization Silver deposition Catalytic reduction Nitrophenol

ABSTRACT

We have demonstrated a facile fabrication of silver-deposited silanized magnetite (Fe₃O₄/SiO₂@Ag) beads, along with their catalytic performance in the reduction of nitrophenols. Initially, 283 ± 40 nm sized spherical magnetite (Fe₃O₄) particles composed of ~13 nm superparamagnetic nanoparticles were synthesized, and then they were silanized following the modified Stöber method. Silica-coated magnetic (Fe₃O₄/SiO₂) nanoparticles are then resistant to oxidation and coagulation. In order to deposit silver onto them, Fe₃O₄/SiO₂ nanoparticles were dispersed in a reaction mixture consisting of ethanolic AgNO₃ and butylamine. With this simple and surfactant-free fabrication method, we can avoid any contamination that might make the Fe₃O₄/SiO₂@Ag particles unsuitable for catalytic applications. The as-prepared Fe₃O₄/SiO₂@Ag particles were accordingly used as solid phase catalysts for the reduction of 4-nitrophenol (4-NP) in the presence of sodium borohydride. The reduction of other nitrophenols such as 2-nitrophenol (2-NP) and 3-nitrophenol (3-NP) were also tested using the Fe₃O₄/SiO₂@Ag nanoparticles as catalysts, and their rate of reduction has been found to follow the sequence, 4-NP>2-NP>3-NP. The Fe₃O₄/SiO₂@Ag particles could be separated from the product using an external magnet and be recycled a number of times after the quantitative reduction of nitrophenols.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Magnetic nanoparticles are a class of nanoparticle which can be manipulated using magnetic fields [1-3]. Such particles commonly consist of magnetic elements such as iron, nickel or cobalt and their chemical compounds [4-7]. These particles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis, biomedicine, magnetic resonance imaging, data storage, and environmental remediation [8-15]. Nonmagnetic metal nanoparticles have also attracted a great deal of interest today [16-20]. Among others, gold and silver nanoparticles are receiving great attention due to their unique optical properties associated with surface plasmon resonance [21–25]. Metallic nanoshells composed of a magnetic core and a concentric noble metal shell find many applications in trace analysis and in heterogeneous catalysis [26-28]. Unfortunately, these colloids are generally unstable, owing to aggregation of the metal nanoparticles. In order to improve the stability of metal

** Corresponding author. Tel.: +82 2 8806651; fax: +82 2 8891568.

E-mail addresses: kshin@ssu.ac.kr (K.S. Shin), kwankim@snu.ac.kr (K. Kim).

nanoparticles, various procedures have been employed to obtain silica-metal composites. This is because colloidal silica, which is thermostable and resistant to coagulation, avoids the aggregation of the metal particles. Guo et al. [29] reported a general route to construct multifunctional Fe_3O_4 /metal hybrid nanostructures using 3-aminopropyltrimethoxysilane (APTMS) as a linker.

Recently, we have shown that Ag can be deposited onto the silica beads, without using a linker like APTMS, by soaking them in ethanolic solutions of AgNO₃ and butylamine [30,31]. The extent of silvering could be adjusted by varying the relative concentrations of butylamine and AgNO₃. The Ag-deposited silica (SiO₂@Ag) beads were then used as efficient surface-enhanced Raman scattering (SERS) substrates that could be used as core materials of SERS-based biosensors [31]. We have also demonstrated the facile synthesis of Ag-deposited Fe₂O₃ (Fe₂O₃@Ag) particles and their application as solid phase catalysts for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of NaBH₄ [8]. The Fe₂O₃ (hematite) particles used earlier were commercial products with very irregular shape and size distribution. Accordingly, it was difficult to enjoy fully the properties of superparamagnetism, as would be expected from nanometer sized magnetite (Fe₃O₄) particles. Bare Fe₃O₄ nanoparticles are, however, likely to form a large

^{*} Corresponding author. Tel.: +82 2 8200436; fax: +82 2 8244383.

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2011.11.006

aggregation and be easily oxidized or dissolved in an acid conditions during the treatment procedure. Therefore, a protective layer on top of the Fe₃O₄ nanoparticles is required. In that sense, silica has been reported to be not only one of the ideal protective layers for Fe₃O₄ nanoparticles due to its high chemical and thermal stability but also a suitable supporting matrix to immobilize Ag nanoparticles [32].

Aminophenol is an important intermediate in the preparation of several analgesic and antipyretic drugs such as acetaminophen. acetanilide, phenacetin, and so forth [33]. It is a strong reducing agent and is used as a photographic developer. It is also used as a corrosion inhibitor in paints and anticorrosion-lubricating agent in fuels. In the dye industry, aminophenol is used as a wood stain and as a dyeing agent for fur and feathers [34]. Due to the significance of aminophenols, there is a demand for direct catalytic reduction of nitrophenols [35]. Indeed, several research groups have investigated the catalytic reduction of nitrophenols with NaBH₄ to aminophenols, using a number of noble metal nanoparticles [36-39]. In these studies, catalytic metal nanoparticles were mostly deposited onto dendrimer/polymers or resin beads before conducting the catalytic reduction of nitrophenol with sodium borohydride. Recently, Mandal et al. [38,39] reported the preparation of spongy type gold or dendritic Ag nanostructures for such catalytic reactions. Although these nanostructures may possess high catalytic activity, it is still difficult to avoid their contamination caused by the formation of undesired byproduct in the reaction medium

In this work, we have firstly synthesized spherical Fe₃O₄ (magnetite) particles with a mean diameter of 283 ± 40 nm, but are actually composed of \sim 13 nm superparamagnetic particles, and then the as-prepared Fe_3O_4 particles are coated with SiO₂ onto which Ag nanoaggregates are finally assembled to endow them with both the superparamagnetism and catalytic activity. With this simple and surfactant-free fabrication method, we can avoid any contamination that might make the Ag-deposited SiO₂-coated Fe₃O₄ particles (hereafter, denoted by Fe₃O₄/SiO₂@Ag) unsuitable for catalytic applications. The Fe₃O₄/SiO₂@Ag nanoparticles are seldom used as catalysts for the reduction of nitrophenols by NaBH₄. We demonstrate the usefulness of those Fe₃O₄/SiO₂@Ag nanoparticles especially in the catalytic reduction of 4-NP to 4-AP by sodium borohydride in aqueous solution. Other nitrophenols like 2-nitrophenol (2-NP) and 3-nitrophenol (3-NP) were also tested with NaBH₄ using Fe₃O₄/SiO₂@Ag nanoparticles as catalyst. The hybrid magnetic nanoparticles prepared in this work can be separated from the product using a neodium magnet and can be recycled a number of times after the quantitative reduction of nitrophenols. Fig. 1 depicted the performance of Fe₃O₄/SiO₂@Ag nanoparticles as catalysts in the reduction of nitrophenols to aminophenols by NaBH₄.

4-Nitrophenol NBH, Remetion 4-Aminophenol

Fig. 1. Schematic representation of the performance of $Fe_3O_4/SiO_2@Ag$ nanoparticles as catalysts in the reduction of nitrophenols to aminophenols by NaBH₄.

2. Experimental

2.1. Materials

Ferric chloride six hydrate (FeCl₃·6H₂O), tetraethyl orthosilicate (TEOS, 98%), silver nitrate (AgNO₃, 99.8%), n-butylamine ($C_4H_{11}N$, 99%), 2-NP (99%), 3-NP (99%), 4-NP (99%) and sodium borohydride (NaBH₄, 99%) were purchased from Aldrich and used as received. Ammonia solution (28–30 wt%) was obtained from Samchun Pure Chemical Company. Other chemicals, unless specified, were of reagent grade, and highly purified water, of resistivity greater than 18.0 M Ω cm, was used throughout the experiments.

2.2. Synthesis of Fe₃O₄ particles

Spherically shaped Fe₃O₄ particles were synthesized following the protocols of Deng et al. [40]. Initially, FeCl₃·6H₂O (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL) to form a clear solution, followed by the addition of sodium acetate (3.6 g) and polyethylene glycol (1.0 g). The mixture was stirred vigorously for 30 min and then refluxed at 200 °C for 24 h. After cooling to room temperature, the black products were washed several times with ethanol and then dried at 60 °C for 6 h. The formation of Fe₃O₄ was confirmed by X-ray diffraction (XRD). According to Transmission electron microscopy (TEM) images, the size of Fe₃O₄ particles was approximated to be 283 ± 40 nm in diameter.

2.3. Preparation of Fe₃O₄/SiO₂@Ag beads

Silver can be deposited directly onto Fe₃O₄ (magnetite) particles. However, a more homogeneous deposition of Ag and the increased dispersion stability are accomplished once Fe₃O₄ is coated with SiO₂ beforehand [41]. Accordingly, Fe₃O₄ particles (10 mg) were dispersed in 30 mL ethanol into which water (8 mL), NH₃ (30%, 0.5 mL) and TEOS (0.5 mL) were added with sonication. After 1h, the black precipitate was collected with a permanent magnet, and rinsed with ethanol three times. Subsequently, 2 mg of silica-coated Fe₃O₄ (Fe₃O₄/SiO₂) particle was placed in a polypropylene container into which 10 mL of a silvering solution was added, and then incubated for 40 min at 50 °C with vigorous shaking. The 4 mM of AgNO₃ and 4 mM of butylamine in absolute ethanol were used as a silvering mixture. The polypropylene container was used to avoid nonspecific silvering of the reaction vessel. The Fe₃O₄/SiO₂@Ag particles were separated from the reaction mixture by using a neodium magnet, rinsed with ethanol, and redispersed in purified water (2 mg/10 mL).

2.4. Catalytic reduction of nitrophenols

In a typical reaction, 2.5 mL of $2.0 \times 10^{-7} \text{ M}$ nitrophenols (2-NP, 3-NP, and 4-NP) were mixed with 0.02 mg of Fe₃O₄/SiO₂@Ag nanoparticles at room temperature in a glass vial. A fresh prepared aqueous solution of 0.1 mL NaBH₄ (1.0 M) was then added with constant stirring. In order to avoid magnetic condensation, the stirring was performed with a mechanical stirrer. Then, UV-visible (UV-vis) absorption spectra were recorded with time to monitor the change in the reaction mixture.

2.5. Instruments

UV–vis absorption spectra were obtained using SCINCO S-4100 and Avantes 3648 spectrometers. The magnetic properties were measured using a Quantum Design SQUID Magnetometer. TEM images were obtained on a LIBRA-120 transmission electron microscope at 120 kV. XRD patterns were obtained on a MAC Science Co M18XHF-SRA powder diffractometer for a 2θ range of 30–80° (d)

(e)

200 n

Fig. 2. XRD spectra of (a) Fe_3O_4 , (b) Fe_3O_4/SiO_2 , and (c) $Fe_3O_4/SiO_2@Ag$ particles: TEM images of (d) Fe_3O_4 , (e) Fe_3O_4/SiO_2 , and (f) $Fe_3O_4/SiO_2@Ag$ particles.

60

20 (Degree)

(511) (440)

(a)

(b)

(220) (C) (311)

70

80

at an angular resolution of 0.05° using Cu K α (1.5406 Å) radiation. Infrared spectra were obtained using a Bruker IFS 113v FT-IR spectrometer equipped with a Globar light source and a liquid N₂-cooled wide-band mercury cadmium telluride detector.

3. Results and discussion

3.1. Characterization of Fe₃O₄/SiO₂@Ag beads

All the XRD peaks of iron oxides synthesized in this work can be indexed to the magnetite structure of Fe₃O₄ (JCPDS 75-1609), as in Fig. 2a. The average size of the Fe₃O₄ nanoparticles deduced from Sherrer's formula is about 13 nm [42]. The TEM image (see Fig. 2d) shows that Fe₃O₄ particles are spherical with a mean diameter of 283 ± 40 nm. The discrepancy between the XRD and TEM data can be understood by assuming that the 283-nm sized particles were actually composed of 13-nm sized Fe₃O₄ nanoparticles [26]. This suggests that Fe₃O₄ nanoparticles have self-assembled into spherical aggregates. In fact, a close look at the TEM image indicated that large particles consisted of agglomeration of small particles. Disordered pores existed among the primary nanoparticles but within spherical aggregates. As explained in Section 2, a more homogeneous deposition of Ag and the increased dispersion stability are accomplished once Fe₃O₄ is coated with SiO₂ beforehand.



Fig. 3. Diffuse reflectance infrared spectra of (a) before and (b) after silanization onto the ${\rm Fe}_3O_4$ nanoparticles.



Fig. 4. (a) Magnetization curve of the as-prepared Fe_3O_4 particles measured at room temperature: Inset shows a magnified view at low applied fields. (b) A similar magnetization curve measured for $Fe_3O_4/SiO_2@Ag$ particles.

The existence of polyethylene glycol used during the synthesis of Fe₃O₄ particles can be verified from the IR spectrum (shown in Fig. 3a). The peaks around 2930, 2844, and 1444 cm^{-1} can be assigned, respectively, to the asymmetric and the symmetric C-H stretching vibration and to the deformation of the -CH₂ - groups. On the other hand, the peaks at 1386 and 888 cm⁻¹ can be attributed, respectively, to the deforming and the out-of-plane bending vibration for both the isolated and bridged surface hydroxyls. In addition, the peak centered at \sim 595 cm⁻¹ would be indicative of the presence of a strong interaction between polyethylene glycols and Fe₃O₄ particles [43]. The successful silanization can also be confirmed from the IR spectrum (shown in Fig. 3b). The two strong bands appearing at ${\sim}1230\,and\,{\sim}1120\,cm^{-1}$, as well as a somewhat weaker band at ~801 cm⁻¹, can be attributed to the vibrational modes involving the bridging oxygen atoms in Si-O-Si moieties, while the peak at \sim 948 cm⁻¹ is due to the Si–O stretching vibration of the Si–OH bonds [44,45]. According to the TEM image (see Fig. 2e), the silica shell thickness is estimated to be about 50 nm. The deposition of Ag onto silica-coated Fe₃O₄ (Fe₃O₄/SiO₂) using a 1:1 molar ratio of Ag⁴ and butylamine can be confirmed from the corresponding XRD data shown in Fig. 2c as well as from the TEM image shown in Fig. 2f. The four XRD peaks of Fe₃O₄/SiO₂@Ag particles appearing at 2θ values of 38.1° , 44.3° , 64.4° , and 77.3° can be attributed to the reflections of the (111), (200), (220), and (311) crystalline planes of cubic Ag, respectively [46]. According to the Sherrer's equation, the size of the Ag nanoparticles is estimated to be 30 nm. Therefore, the average size of Fe₃O₄/SiO₂@Ag particles is estimated to be about 363 nm. The XRD peaks of (311) planes of Fe₃O₄, marked with asterisks (*) in Fig. 2b and c, are barely seen in the patterns of Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂@Ag particles. This means that once the Fe₃O₄ particles

Intensity

30

(311)

(111)

40

(440)

(200)

50

(422)



Fig. 5. UV-vis absorption spectra of 4-nitrophenol (4-NP) taken (a) before and (b) after immediate addition of NaBH₄ and (c) that of 4-aminophenol (4-AP) shown for comparison. (d) UV-vis absorption spectra of 4-NP taken up to 20 min with the addition of NaBH₄ and Fe₃O₄/SiO₂ particles.

are completely covered by thick layers of SiO_2 , the reflection peaks that corresponding to Fe_3O_4 must almost disappear.

Fig. 4a shows the magnetization curve of the as-prepared Fe₃O₄ particles measured at room temperature. The curve presents a small hysteresis loop, and the magnetic saturation value is \sim 70 emu/g. From a magnified view of the magnetization curve at low applied fields, the remnant M_r defined as the magnetization at H=0 is about 1.3 emu/g, while the coercity H_c defined as the field magnitude necessary to obtain M=0 is about 9.5 Oe. It has been reported that the magnetic Fe₃O₄ particles exhibit superparamagnetic behavior when the particle size decreases to below a critical value, generally around 20 nm. The relatively high $M_{\rm S}$ value with relatively low H_c and M_r values in this work can then be attributed to the small primary particle size of about 13 nm in dimension. as well as to the oriented attachment of primary particles in large spherical aggregates. Fig. 4b then shows the magnetization curve measured for the Fe₃O₄/SiO₂@Ag particles. The magnetic saturation value has decreased nearly to one third of the initial value after coating with silica and silver, i.e. ~25 emu/g. A part of the decrease is due to mass effect of silica and silver, and the remaining part is due to their diamagnetic shielding. Anyhow, the Fe₃O₄/SiO₂@Ag particles could be magnetically concentrated and readily picked up using a small magnet.

3.2. Catalytic activity of Fe₃O₄/SiO₂@Ag beads

In order to study the catalytic activity of the $Fe_3O_4/SiO_2@Ag$, we have chosen the reduction of 2-NP, 3-NP, 4-NP, and 4-NA by NaBH₄ as model reactions. UV–vis absorption spectra were recorded with time to monitor the change in the reaction mixture. It has been



Fig. 6. (a) Successive UV–vis absorption spectra of the reduction of 4-nitrophenol by NaBH₄ in the presence of Fe₃O₄/SiO₂@Ag particles. (b) Plot of $ln(A_t/A_0)$ against reaction time for Fe₃O₄/SiO₂@Ag nanoparticles in the catalytic reduction of 4-nitrophenol.

observed that, after immediate addition of freshly prepared aqueous solution of NaBH₄, the peak due to 4-nitrophenol was red shifted from 317 to 400 nm (see Fig. 5a and b). This peak was due to the formation of 4-nitrophenolate ions in alkaline condition caused by the addition of NaBH₄. In the absence of proper catalyst, the thermodynamically favorable reduction of 4-nitrophenol (the standard reduction potentials for 4-nitrophenol/4-aminophenol and H₃BO₃/BH₄⁻ are -0.76 and -1.33 V, respectively) was not observed and the peak due to 4-nitrophenol ions at 400 nm remains unaltered even a couple of days as reported in the literatures. The UV-vis absorption spectrum after the addition of Fe₃O₄/SiO₂ beads in the mixture of 4-nitrophenol and NaBH₄ also remains unaltered with time, as shown in Fig. 5d, which means that pure Fe₃O₄/SiO₂ beads do not work as catalyst for this reaction.

Fig. 6a shows the UV–vis absorption spectra, representing the reduction of 4-NP to 4-AP by NaBH₄ in the presence of Fe₃O₄/SiO₂@Ag beads. In the absence of Fe₃O₄/SiO₂@Ag beads, the aqueous mixture of 4-NP and NaBH₄ shows a maximum absorption at 400 nm, which, as mentioned above, corresponds to 4-nitrophenolate ion in alkaline conditions, and the peak remains unaltered with time. However, the addition of small amount of purified Fe₃O₄/SiO₂@Ag beads (0.02 mg) with stirring causes fading and ultimate bleaching of the yellow color of the reaction mixture. As shown in Fig. 6a, time-dependent UV–vis spectra of this catalytic reaction mixture shows the disappearance of 400 nm peak and the gradual development of the new peak



Fig. 7. Successive UV–vis absorption spectra of the reduction of (a) 3-nitrophenol and (b) 2-nitrophenol by NaBH₄ in the presence of Fe₃O₄/SiO₂@Ag particles. (c) Plot of $ln(A_t/A_0)$ against reaction time for Fe₃O₄/SiO₂@Ag nanoparticles in the catalytic reduction of 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol.

at 300 nm which substantiates the formation of the 4-AP (see Fig. 5c). These results indicate that $Fe_3O_4/SiO_2@Ag$ catalyze the reduction process. In this experiment, the concentration of the borohydride ion, used as reductant, largely exceeds (~100 times) that of 4-NP. As soon as we added the NaBH₄, the Fe₃O₄/SiO₂@Ag beads started the catalytic reduction by relaying electrons from the donor BH₄⁻ to the acceptor 4-NP right after the adsorption of both onto the particle surfaces. As the initial concentration of sodium borohydride was very high, it remained essentially constant throughout the reaction. Therefore, for evaluation of the catalytic rate pseudo-first-order kinetics with respect to 4-NP was used.



Fig. 8. The variation of the rate constant of the reduction of 4-nitrophenol by $NaBH_4$ in the presence of $Fe_3O_4/SiO_2@Ag$ nanoparticles up to 20 cycles.

The rate constant of this catalytic reaction in the presence of the Fe₃O₄/SiO₂@Ag beads is $2.5 \times 10^{-2} \text{ s}^{-1}$, as measured from the plot of lnA (A = absorbance at 400 nm) versus time (shown in Fig. 6b).

3.3. Reduction of other nitrophenols

Reduction of different nitro compounds was also studied using NaBH₄ in presence of Fe₃O₄/SiO₂@Ag beads. The yellow color of 2-NP and 3-NP was discharged during the course of reduction under identical condition. As shown in Fig. 7a, the peak at 390 nm corresponding to the absorbance peak of 3-NP $(1.0 \times 10^{-5} \text{ M})$ decreases gradually on NaBH₄ (1.0 M) reduction in presence of Fe₃O₄/SiO₂@Ag beads (0.02 mg). Again similar situation occurred in case of 2-NP whose peak in alkaline aqueous solution appeared at 416 nm but disappeared in the course of Ag catalyzed NaBH₄ reduction (Fig. 7b). In all cases, the silver plasmon band remained masked with the absorption band of the nitro compounds until complete conversion of the corresponding amino derivatives. The rate constants of the catalytic reduction of 2-NP and 3-NP in the presence of the Fe₃O₄/SiO₂@Ag beads are determined to be 5.5×10^{-3} and 2.4×10^{-3} s⁻¹, respectively. A comparative study revealed that the rate of reduction follows the order, 4-NP>2-NP>3-NP (Fig. 7c).

3.4. Catalytic recyclability of Fe₃O₄/SiO₂@Ag beads

The Fe₃O₄/SiO₂@Ag nanoparticles are very effective for the catalytic reduction of 4-NP. At the end of the reaction, the catalyst particles remained active and were easily separated from the product, 4-AP, using a neodium magnet. After one cycle of reaction, the particles were washed thoroughly with distilled water and could be recycled a number of times for the reduction reaction. To demonstrate magnetic recovery of the Fe₃O₄/SiO₂@Ag nanoparticles, we increased the volume of reagents and catalysts by 30 times so that the Fe₃O₄/SiO₂@Ag nanoparticles can be recovered more efficiently using a neodium magnet. The catalytic recyclable usage of the Fe₃O₄/SiO₂@Ag (0.02 mg) nanoparticles for the reduction of 4-NP (0.06 mL, 1.0×10^{-5} M) in the presence of NaBH₄ (0.2 mL, 1.0 M) and purified water (2.5 mL) was studied. Fig. 8 shows the catalytic efficiency of the $Fe_3O_4/SiO_2@Ag$ nanoparticles after 20 cycles. The result shows that the catalytic activity of the Fe₃O₄/SiO₂@Ag nanoparticles decreased slightly after 20 cycles of the catalysis experiments. The reason for slight decrease of the catalytic activity may be that some of Fe₃O₄/SiO₂@Ag nanoparticles are not fully recovered using an external magnet or the Ag nanoparticles are detached away from the Fe₃O₄/SiO₂@Ag nanoparticles when they

are stirred, as a result, the catalytic efficiency of the $\rm Fe_3O_4/SiO_2@Ag$ nanoparticles decreases.

4. Conclusions

In the present study, Fe₃O₄/SiO₂@Ag beads are prepared and their application for the catalytic reduction of nitrophenols in the presence of sodium borohydride is examined. In order to avoid the aggregation of the metal particles, silica was coated on Fe_3O_4 nanoparticles using the modified Stöber method. Then silver was deposited onto Fe₃O₄/SiO₂ nanoparticles simply by soaking them in ethanolic solutions of AgNO3 and butylamine and their characteristics are examined by TEM, XRD, UV-vis, and magnetometer analyses. With this simple and surfactant-free fabrication of Fe₃O₄/SiO₂@Ag nanoparticles, we can avoid contamination in the final product, which makes them suitable for further catalytic applications. The catalytic activity of Fe₃O₄/SiO₂@Ag nanoparticles thus prepared was investigated in the reduction reaction of nitrophenols (2-NP, 3-NP and 4-NP) to aminophenols by NaBH₄. A comparative study revealed that the rate of reduction follows the order, 4-NP>2-NP>3-NP. Since the magnetic particles are readily recovered from the solution phase mixture without centrifugation and/or filtering, $Fe_3O_4/SiO_2@Ag$ nanoparticles, separated from the product using a neodium magnet, could be recycled a number of times.

Acknowledgement

This work was supported by National Research Foundation (NRF) of Korea Grant funded by the Korean Government (MEST) (Nos. 2011-0001218, 2011-0006737, 2010-0019204, 0409-20100172, and 2009-0072467).

References

- W. Gao, S. Sattayasamitsathit, K.M. Manesh, D. Weihs, J. Wang, J. Am. Chem. Soc. 132 (2010) 14403–14405.
- [2] C. Xu, S. Sun, Polym. Int. 56 (2007) 821-826.
- [3] G. Leem, S. Sarangi, S. Zhang, I. Rusakova, A. Brazdeikis, D. Litvinov, T.R. Lee, Cryst. Growth Des. 9 (2009) 32–34.
- [4] J. Park, J. Joo, S.G. Kwon, Y. Jang, T. Hyeon, Angew. Chem. Int. Ed. 46 (2007) 4630–4660.
- [5] J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, Nat. Mater. 3 (2004) 891–895.
- [6] J.R. Davis, Nickel, Cobalt, and there Alloys, ASM International, Materials Park, 2000.
- [7] D.-H. Chen, C.-H. Hsieh, J. Mater. Chem. 12 (2002) 2412-2415.
- [8] K.S. Shin, J.-Y. Choi, C.S. Park, H.J. Jang, K. Kim, Catal. Lett. 133 (2009) 1-7.
- [9] X. Wang, H. Ji, X. Zhang, H. Zhang, X. Yang, J. Mater. Sci. 45 (2010) 3981-3989.

- [10] Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, J. Phys. D: Appl. Phys. 36 (2003) R167–R181.
- [11] P.N.L. Lens, M.A. Hemminga, Biodegradation 9 (1998) 393-409.
- [12] J. Giri, A. Ray, S. Dasgupta, D. Datta, D. Bahadur, Bio-Med. Mater. Eng. 13 (2003) 387-399.
- [13] T.-J. Yoon, J.S. Kim, B.G. Kim, K.N. Yu, M.-H. Cho, J.-K. Lee, Angew. Chem. Int. Ed. 44 (2005) 1068–1071.
- [14] Z. Liao, H. Wang, R. Lv, P. Zhao, X. Sun, S. Wang, W. Su, R. Niu, J. Chang, Langmuir 27 (2011) 3100–3105.
- [15] J.R. Weertman, in: C.C. Koch (Ed.), Nanostructured Materials: Processing, Properties and Applications, William Andrews Publishing, Norwich, NY, 2002.
- [16] W.L. Barnes, A. Dereux, T.W. Ebbesen, Nature 424 (2003) 824-830.
- [17] C.F. Bohren, D.R. Huffman, Absorption and Scattering of Light by Small Particles,
- John Wiley & Sons, New York, 1998.
- [18] S.K. Gray, T. Kupka, Phys. Rev. B 68 (2003) 0454151-04541511.
- [19] J.M. Oliva, S.K. Gray, Chem. Phys. Lett. 379 (2003) 325–331.
 [20] S.A. Maier, P.G. Kik, H.A. Atwater, S. Meltzer, E. Harel, B.E. Kowel, A.A.G.
- [20] S.A. Maler, P.G. Kik, H.A. Alwaler, S. Meitzer, E. Harel, B.E. Kower, A.A.G Requicha, Nat. Mater. 2 (2003) 229–232.
- [21] A.J. Haes, R.P. Van Duyne, J. Am. Chem. Soc. 124 (2002) 10596-10604.
- [22] S. Eustis, M.A. El-Sayed, Chem. Soc. Rev. 35 (2006) 209-217.
- [23] T.R. Jensen, M.D. Malinsky, C.L. Haynes, R.P. Van Duyne, J. Phys. Chem. B 104 (2000) 10549–10556.
- [24] A.J. Haes, S. Zou, G.C. Schatz, R.P. Van Duyne, J. Phys. Chem. B 108 (2004) 6961–6968.
- [25] M.D. Malinsky, K.L. Kelly, G.C. Schatz, R.P. Van Duyne, J. Am. Chem. Soc. 123 (2001) 1471–1482.
- [26] K. Kim, J.-Y. Choi, H.B. Lee, K.S. Shin, ACS Appl. Mater. Interfaces 2 (2010) 1872–1878.
- [27] L. Wang, J. Bai, Y. Li, Y. Huang, Angew. Chem. Int. Ed. 47 (2008) 2439-2442.
- [28] Z. Xu, Y. Hou, S. Sun, J. Am. Chem. Soc. 129 (2007) 8698-8699.
- [29] S. Guo, S. Dong, E. Wang, Chem. Eur. J. 15 (2009) 2416-2424.
- [30] K. Kim, H.B. Lee, Y.M. Lee, K.S. Shin, Biosens. Bioelectron. 24 (2009) 1864–1869.
- [31] K. Kim, H.B. Lee, J.-Y. Choi, K.S. Shin, ACS Appl. Mater. Interfaces 3 (2011) 324-330.
- [32] L. Li, E.S.G. Choo, X. Tang, J. Ding, J. Xue, Acta Mater. 58 (2010) 3825-3831.
- [33] S. Mitchell, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Wiley-Interscience, NY, 1992.
- [34] M.J. Vaidya, S.M. Kulkarni, R.V. Chaudhari, Org. Process Res. Dev. 7 (2003) 202-208.
- [35] T. Swathi, G. Buvaneswari, Mater. Lett. 62 (2008) 3900-3902.
- [36] K. Hayakawa, T. Yoshimura, K. Esumi, Langmuir 19 (2003) 5517-5521.
- [37] J. Ge, T. Huynh, Y. Hu, Y. Yin, Nano Lett. 8 (2008) 931-934.
- [38] M.H. Rashid, T.K. Mandal, J. Phys. Chem. C 111 (2007) 16750-16760.
- [39] M.H. Rashid, R.R. Bhattacharjee, A. Kotal, T.K. Mandal, Langmuir 22 (2006) 7141-7143.
- [40] H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, Angew. Chem. Int. Ed. 44 (2005) 2782–2785.
- [41] L. Xia, N.H. Kim, K. Kim, J. Colloid Interface Sci. 306 (2007) 50-55.
- [42] L.S. Birks, H. Friedman, J. Appl. Phys. 17 (1946) 687-692.
- [43] W. Zhang, L. Gai, Z. Li, H. Jiang, W. Ma, J. Phys. D: Appl. Phys. 41 (2008) 225001–225006.
- [44] M. Tomozawa, J.-W. Hong, S.-R. Ryu, J. Non-Cryst. Solids 351 (2005) 1054–1060.
- [45] A. Balamurugan, G. Sockalingum, J. Michel, J. Fauré, V. Banchet, L. Wortham, S. Bouthors, D. Laurent-Maquin, G. Balossier, Mater. Lett. 60 (2006) 3752–3757.
- [46] R. He, X. Qian, J. Yin, Z. Zhu, J. Mater. Chem. 12 (2007) 3783-3786.