Single-Step Preparation of Silver-Doped Magnetic Hybrid Nanoparticles for the Catalytic Reduction of Nitroarenes

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Supporting Information

ABSTRACT: This study adopts a simple but facile process for preparing silver-doped magnetic nanoparticles by the spontaneous oxidation—reduction/coprecipitation method. The preparation can be achieved in one pot with a single step, and the prepared silver-doped magnetic nanoparticles were utilized as nanocatalysts for the reduction of o-nitroaniline. Utilizing the magnetic characteristics of the prepared nanoparticles, the catalytic reactions can be carried out under quasi-homogeneous condition and the nanocatalysts can be easily collected after the conversion is achieved. It can be revealed from the results that the morphologies and the composition of the prepared silver-doped magnetic nanoparticles can be adjusted by changing the conditions during the production, which affects the efficacy of the catalysis. In addition, the catalysis efficiency is also controlled by the pH, temperature, and the amounts of nanocatalysts used during the catalytic reaction. Finally, the silver-doped magnetic nanocatalysts prepared in this study own the advantages of easy preparation, room-temperature catalysis, high conversion ability, and recyclability, which make them more applicable in real utilities.

INTRODUCTION

In contrast to bulk silver, nanometric silver materials exhibit many extraordinary properties such as a high surface-to-volume ratio, quantum tunneling effects, an abundance of free electrons, surface plasmon resonance, and antibacterial behaviors. Because of these unique properties, noble silver nanomaterials are widely applied in diverse areas, including thermotherapy, medicine, sensors, surface-enhanced spectroscopy, biology, catalysis, and electronics. Among these many applications, the catalysis of the reduction of nitroarenes to aromatic amines is one of the most favorable approaches for the catalytic reduction of nitroarenes. In this study, a simple but facile method was applied in a single step to prepare silver-doped magnetic nanoparticles (AgMNPs) for the catalytic reduction of nitroarenes through spontaneous oxidation—reduction and coprecipitation. When mixing Fe²⁺ with Ag⁺, a spontaneous reaction is caused by the difference in standard reduction potential between the ionic species. When Ag⁺ is reduced to Ag⁰, an equivalent number of moles of Fe²⁺ ions are simultaneously oxidized to Fe³⁺. After the addition of precipitation agents, AgNPs were coprecipitated with iron oxide magnetic nanoparticles, which led to the formation of AgMNPs. The proposed preparation can be achieved in a single step, and the prepared AgMNPs can subsequently be utilized as nanocatalysts for the reduction of o-nitroaniline (o-NA). The parameters (pH, temperature, and amount of nanocatalyst) that

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affect the morphology and composition of the prepared AgMNPs and efficiencies of the catalytic reduction were systematically studied to gain a greater understanding of the characteristics of the AgMNPs prepared using the method proposed in this study. Additionally, the catalytic activity of the AgMNPs prepared for the reduction of other nitroarenes and their recyclability were investigated to fully evaluate their potential for practical applications.

## RESULTS AND DISCUSSION

### Effect of Oxidation–Reduction Time on AgMNP Preparation

Figure S1 shows the typical measured hysteresis loops of the prepared AgMNPs, which confirmed that the prepared AgMNPs were paramagnetic and usable for further applications. Figure 1 depicts the transmission electron microscopy (TEM) images of AgMNPs obtained using various reaction times. From the images, dark-sphere-like Ag nanoparticles were mixed with light-colored Fe3O4 NPs because Ag has a higher electron density that allows fewer electrons to transmit.61,62 The AgNPs formed after a 10 min reaction time were larger than those formed after a 2 min reaction time. Notably, the size of the Fe3O4 NPs was mostly unaffected by the reaction time.

Figure 2a shows the evolution of the UV–vis spectra for the reduction of o-NA catalyzed by AgMNPs over time. The absorbance peak at 412 nm, which corresponds to the characteristic o-NA peak,63 decreased as the reaction proceeded. The variations of the spectra indicated that o-NA was reduced to 1,2-phenylenediamine (1,2-PPD).61,64 The relative concentration (\(C_o/C_0\)) of o-NA was obtained by dividing the absorbance recorded at 412 nm at the specified time (\(C_o\)) by the absorbance at 412 nm before the addition of AgMNPs (\(C_0\)). The results in Figure 2b were plotted using various AgMNPs prepared using various reduction durations. In Figure 2b, the catalytic efficiency of the AgMNPs shows no significant difference between when the reaction time was 4–10 min and when more than 95% of o-NA was reduced within 240 s. This finding suggests remarkable catalytic activity. By contrast, achieving the same conversion percentage required more than 500 s when the reaction time to prepare the AgMNPs was 2 or 12 min. Because the catalytic efficiency of nanocatalysts depends on their size and the amount of catalyst loaded,26 we concluded that the reaction time to achieve the optimal morphology and catalyst loading was 10 min. For comparison, the results of an experiment conducted in parallel, where AgMNPs were replaced with Fe3O4 NPs, are also plotted in Figure 2b, showing that the reduction of o-NA can proceed only when AgNPs are doped. In the absence of AgNPs, the reduction of o-NA is suspended.

### Effect of Fe2+/Ag+ on AgMNP Preparation

As described in the previous section, catalytic efficiency is related to the size and amount of doped AgNPs. In addition, we expected the morphology and amount of doped AgNPs to be affected by the ratio of initial concentration of Fe2+ to Ag+ because AgNO3 acts as the oxidation agent in the formation of AgMNPs. Figure 1 shows the TEM images of the AgMNPs with different ratios of \([\text{Fe}^{2+}]_0\) to \([\text{Ag}^+]_0\). The images reveal that the morphologies of the AgNPs are similar. Figure S2 shows the typical X-ray diffraction (XRD) spectra of the prepared AgMNPs and illustrates that the locations and intensity of the diffraction peaks were consistent with the standard patterns for JCPDS card no. (79-0417) magnetite and JPCPDS card no. (4-0783) standard Ag crystal. The size of AgNPs can be estimated using the Scherrer equation, and all AgNPs are approximately 20 nm.10 To further explore the effect of the initial Fe2+ to Ag+ concentration ratio, energy-dispersive X-ray spectroscopy (EDS) analysis was performed and the typical spectra for the AgMNPs are shown in Figure S3A. The atomic percentages of Ag, Fe, and O for various initial concentration ratios of Fe2+ to...
Ag⁺ obtained through EDS are plotted in Figure S3B, which shows that the atomic percentage of Ag increased as the initial concentration ratio of Fe²⁺ to Ag⁺ decreased. When the initial concentration ratio of Fe²⁺ to Ag⁺ was 2.0, the atomic percentage of Ag in the AgMNPs was 8.23%. The atomic percentage decreased to 0.76% when the initial concentration ratio of Fe²⁺ to Ag⁺ was 6.0. Therefore, we can conclude that the initial concentration ratio of Fe²⁺ to Ag⁺ should be between 2 and 3 to ensure that a sufficient amount of Fe²⁺ is oxidized so that the ratio of Fe²⁺ to Fe³⁺ is close to 2 before the coprecipitation agent is added to form magnetic Fe₃O₄ NPs.

Effects of pH and Temperature on the Catalytic Reaction. The acceleration of the reduction reaction by AgMNPs originates in a relay between the nucleophile and electrophile. Therefore, the catalyzed reduction rate is affected by the abundance of electrons in the reaction system. To observe the relationship between the electron abundance and reaction rate, the catalysis reaction was performed at various pH values. The relative o-NA concentration (C/C₀) was recorded as a function of reaction time at various pH values, and the results are plotted in Figure 4a. The pH played a key role in the catalysis reaction; when the pH was 9.8, the reduction of o-NA was completed within 4 min. The reduction rate significantly decreased when the pH was set to 8.8 and less than 85% of o-NA was reduced after approximately 5 min of reaction. When the pH was lower than 8, almost no conversion of o-NA could be observed. Because the acceleration of the reduction reaction by AgMNPs originates in a relay between the nucleophile and electrophile, alkaline conditions enriched the electron densities on the AgNP surfaces by adsorbing more OH⁻, which promoted the reduction of o-NA. When the pH was set to 10.8, the reduction of o-NA decelerated, possibly because of the formation of yellow-colored 2,3-diaminophenazine under extremely alkaline conditions.

The reaction rate was affected by the temperature of the reaction system because the reactants had more kinetic energy at higher temperatures and were able to cross the activation state more easily. Figure 4b depicts the relationship between C/C₀ and reaction times at various reaction temperatures. As shown in Figure 4b, the higher the temperature of the reaction system, the faster was the observed reduction of o-NA. Furthermore, when the temperature was 0 °C, the reduction rate of o-NA was similar to that at 25 °C in the first minute and...
Ct/C0 was almost unchanged after the first minute, suggesting that the reduction was almost interrupted after 1 min at 0 °C.

**Effect of the Catalyst Amount on the Catalytic Reaction.** As described in the previous sections, the conversion efficiency is related to the amount of AgNP loading. Accordingly, the conversion efficiency can also be related to the amount of AgMNPs used per experiment. Figure 5 plots the relationship between the Ct/C0 of o-NA and reduction time when various amounts of AgMNPs were used. As shown in Figure 5, when 1 mg of AgMNPs was used per experiment, approximately 20% of o-NA was reduced after 5 min of conversion and the conversion efficiency increased with the amount of AgMNPs used. When 20 mg of AgMNPs was used per experiment, the conversion of o-NA was almost 100% within 250 s at room temperature, which is promising for further applications.

**Activity of AgMNPs for the Catalytic Reduction of Other Nitroarenes.** After studying the characteristics and catalytic properties of the prepared AgMNPs, we investigated the catalytic reduction of other nitroarenes, including m-NA, p-NA, and p-NP, through the same procedures to investigate the ability of the AgMNPs to accelerate the reduction of other nitroarenes. Figure S4 plots the evolution of the UV−vis spectra for reducing m-NA, p-NA, and p-NP in the presence of AgMNPs over time. The absorption maxima, which were located at 360 nm for m-NA, 380 nm for p-NA, and 400 nm for p-NP, decreased as the catalytic reduction proceeded. The relationship between Ct/C0, where Ct is the absorbance at the specific reaction and C0 is the absorbance at the initial time, for the nitroarenes tested and the reaction time under optimal conditions is plotted in Figure 6. As indicated in the figure, the reductions of the four nitroarenes examined in this study were all completed within 4 min, which suggested that the AgMNPs prepared in this study were capable of catalytically reducing various nitroarenes.

Furthermore, as reported in other works, the catalytic reduction of nitroarenes follows the pseudo-first-order reaction.
The linear relations between $\ln(C_0/C_t)$ of nitroarenes examined in this study against reaction time were obtained and the rate constant ($k$) can be estimated by calculating the slopes of the obtained lines. The calculated $k$ values at room temperature are 0.0192, 0.0145, 0.0185, and 0.0196 s$^{-1}$ for the catalytic reduction of o-NA, m-NA, p-NA, and p-NP, respectively. To compare the results obtained in this study to those reported recently, Table 1 tabulates the catalytic activities of various AgNP-based catalytic systems. As can be observed in the table, the rate constants of AgMNPs prepared in this study for the reduction of nitroarenes are as good as or better than those reported recently.

### Table 1. Comparison of Catalytic Activities of Several AgNP-Based Systems

| catalysts                        | nitroarene (final concentration; mM) | concentration of NaBH$_4$ (mM) | temperature °C | apparent rate constant ($k$) | ref  |
|----------------------------------|--------------------------------------|--------------------------------|----------------|-------------------------------|------|
| AgNPs/polypyrrole/porous graphene oxide | o-NA (1.13)                          | 400                            | RT$^a$         | 0.0013                        | 40   |
| biogenic AgNPs                   | p-NP (0.20)                           | 10                             | b$^b$          | 0.00406                       | 41   |
| AgNPs/partially reduced graphene oxide | p-NP (0.10)                          | 13                             | RT$^a$         | 0.0374                        | 43   |
| AgNPs on porous glass filters    | o-NA (1.00)                           | 30                             | 50             | 0.0094                        | 26   |
|                                 | p-NA (1.00)                           | 30                             | 50             | 0.0071                        | 26   |
| AgNPs in microgels               | p-NP (0.08)                           | 24                             | 22             | 0.0153                        | 50   |
| AgNPs in microgels               | o-NA (0.09)                           | 18                             | 22             | 0.0067                        | 51   |
|                                 | p-NA (0.09)                           | 18                             | 22             | 0.0101                        | 51   |
|                                 | p-NP (0.09)                           | 18                             | 22             | 0.0052                        | 51   |
| AgNPs on fibrous nanosilica      | o-NA (0.17)                           | 22                             | RT$^a$         | 0.0043                        | 52   |
|                                 | p-NP (0.099)                          | 83                             | RT$^a$         | 0.01                           | 52   |
| Fe$_3$O$_4$@SiO$_2$/Ag nanocomposite | p-NP (0.06)                          | 6                              | 25             | 0.00767                       | 59   |
| AgNPs/HLaNb$_2$O$_7$             | p-NP (0.091)                          | 18                             | b$^b$          | 0.00301                       | 53   |
| this study                       | o-NA (1)                              | 30                             | RT$^a$         | 0.0192                        |      |
|                                 | p-NA (1.00)                           | 30                             | RT$^a$         | 0.0185                        |      |
|                                 | p-NP (1.00)                           | 30                             | RT$^a$         | 0.0196                        |      |

$a$Room temperature. $b$Not mentioned.

**Figure 7.** $C_t/C_0$ time profile of 1 mM o-NA (■: first run; ●: second run without regeneration; ▲: third run after regeneration; ▼: fourth run after regeneration) in the presence of 30 mM NaBH$_4$ and 20 mg of AgMNPs, where the other conditions are the same as described in Figure 2a.

**CONCLUSIONS**

In this study, a simple but facile approach to prepare silver-doped magnetic hybrid nanoparticles was proposed based on a chemical reduction and coprecipitation method. The nanoparticles prepared through this method were used as nanocatalysts for the reduction of o-NA. Using the AgMNPs prepared in this study as nanocatalysts exploits the advantages of reactant transferability. To reactivate the silver nanocatalysts, we soaked the used AgMNPs in an aqueous solution at pH 3 for 20 min and rinsed them with neutral water before the next use. As shown in Figure 7, more than 90% of the o-NA was reduced within 5 min and more than 95% was reduced within 8 min. Furthermore, after treating the reused AgMNPs with an aqueous acidic solution, the AgMNPs could be recycled and their performance was similar to that in the previous run. Therefore, the AgMNPs prepared in this study can be recycled after treatment with an acidic solution, which significantly extends the practical applicability of these silver nanocatalysts.

**Recyclability of the Ag Nanocatalysts.** The recyclability of the AgMNPs prepared in this study was evaluated by consecutively reusing the nanocatalysts for the catalytic reduction of o-NA. As shown in Figure 7, only approximately 40% of o-NA was reduced to 1,2-PPD after 10 min of reaction in the second consecutive test. This is possibly related to the adsorption of o-NA or 1,2-PPD on the surface of the silver nanocatalysts, which consequently reduced the electron transferability. To reactivate the silver nanocatalysts, we soaked the used AgMNPs in an aqueous solution at pH 3 for 20 min and rinsed them with neutral water before the next use. As shown in Figure 7, more than 90% of the o-NA was reduced within 5 min and more than 95% was reduced within 8 min. Furthermore, after treating the reused AgMNPs with an aqueous acidic solution, the AgMNPs could be recycled and their performance was similar to that in the previous run. Therefore, the AgMNPs prepared in this study can be recycled after treatment with an acidic solution, which significantly extends the practical applicability of these silver nanocatalysts.

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of quasi-homogeneous reaction conditions and enables the easy removal of nanocatalysts from the solution with a magnet. The results indicated that the composition of the AgMNPs prepared can be tuned by adjusting the ratio of [Fe^{2+}]_0 to [Ag^{+}]_0 and the chemical reduction time during the production of AgMNPs. During the catalytic reduction of o-NA, the pH and temperature of the system affect the reduction rate, which is also affected by the amount of nanocatalyst used in the reaction. Furthermore, the prepared AgMNPs were applicable to the catalytic reduction of other nitroarenes. Finally, the silver-doped magnetic nanocatalysts proposed in this study have several advantages, namely, easy preparation, significant catalytic activity at room temperature, high conversion ability, and recyclability, all of which enhance their usefulness for real applications.

### EXPERIMENTAL SECTION

**Materials.** Ferrous sulfate and ferric chloride were obtained from Showa Chemical (Tokyo, Japan). Silver nitrate, o-NA, m-nitroaniline (m-NA), p-nitroaniline (p-NA), and p-nitrophenol (p-NP) were purchased from Alfa Aesar (Ward Hill, MA). Sodium borohydride was obtained from Acros Organics (Geel, Belgium). Ammonium hydroxide (28–30%, v/v) and nitric acid were purchased from Fisher Scientific (Hampton, NH). All chemicals were of reagent grade and used as received without further purification. Deionized Milli-Q water (Simplicity, Millipore, Burlington, MA) was used throughout this study.

**Preparation of AgMNPs.** The preparation of AgMNPs was based on a chemical reduction and coprecipitation method. Briefly, 100 mL of 12 mM ferrous aqueous solution was mixed with various volumes of 200 mM silver nitrate aqueous solution under vigorous stirring for a specified amount of time. During stirring, a spontaneous oxidation–reduction reaction occurred between Ag^{+} and Fe^{2+}. Ag^{+} was reduced to Ag^0 and an equivalent number of moles of Fe^{2+} ions were oxidized to Fe^{3+}. After the specified reaction time, 50 mL of 1.44 M ammonia solution, which acted as the precipitating agent, was rapidly added to the solution under vigorous stirring for 10 min to complete the coprecipitation process. After 3 h in storage, the formed nanoparticles were collected with a magnet and washed three times with distilled water and ethanol. Finally, the washed AgMNPs were dried in an oven at 140 °C for 8 h before further use. As an alternative for comparison, magnetite nanoparticles (Fe_{3}O_{4} NPs) without silver doping were prepared following previous reports.\(^{22}\) We conducted transmission electron microscopy (TEM) with a Hitachi HT-7700 microscope operated at 100 kV, energy-dispersive X-ray spectroscopy (EDS) analysis with a Hitachi SU-8010 microscope at an accelerating voltage of 15.0 kV, and powder X-ray diffraction (PXRD) with a Siemens D5000 XRD system to characterize the morphologies and compositions of the prepared AgMNPs. Hysteresis loops of the prepared AgMNPs were recorded at room temperature with a Quantum Design MPMS 3 SQUID vibrating sample magnetometer system.

**Reduction of Nitroaniline Catalyzed by AgMNPs.** The catalytic efficiency of the AgMNPs was evaluated using the nanoparticles as prepared for the catalytic reduction of o-NA. A specific amount of AgMNPs was mixed with 15 mL of an aqueous solution consisting of 1 mM o-NA and 30 mM NaBH\(_4\) at room temperature. Ultraviolet–visible (UV–vis) spectra of the solution were recorded at chosen intervals. All UV–vis spectra in this study were measured using a Thermo Fisher Scientific Genesys 10S Bio UV–Vis spectrometer with a 1 nm resolution. The spectra were recorded within a wavelength range of 250–550 nm. The optical path of the UV–vis cell was 3 mm.

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