Facile Synthesis of Fe₃O₄@Tannic Acid@Au Nanocomposites as a Catalyst for 4-Nitrophenol and Methylene Blue Removal

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ABSTRACT: A facile, cost-effective, and eco-friendly method was proposed to synthesize Fe₃O₄@tannic acid@Au nanocomposites (Fe₃O₄@TA@Au). First, Fe₃O₄ nanoparticles with diameters of 20 and 200 nm were synthesized by co-precipitation and solvothermal methods, respectively. Gold nanoparticles were deposited on magnetic Fe₃O₄ through tannic acid-metal-polymer intermediate-layer-mediated reductions. The catalytic activities of the as-prepared Fe₃O₄@TA@Au were investigated by spectroscopically monitoring the reduction of 4-nitrophenol (4-NP) and methylene blue (MB), which could be achieved within several minutes with an excess of NaBH₄. The impact of the Fe₃O₄ size on the overall catalytic ability of the Fe₃O₄@TA@Au was systematically studied. The reaction rate constants of the Fe₃O₄-20 nm@TA@Au for 4-NP and MB reduction were 0.432 and 0.543 min⁻¹, respectively. For the Fe₃O₄-200 nm@TA@Au nanocomposite, the optimized reaction rate constants for 4-NP and MB reduction were 3.09 and 0.441 min⁻¹, respectively. Due to magnetic separation, the Fe₃O₄@TA@Au could be easily harvested and recycled. After five recycling cycles, the catalytic ability remained over 90%, and the recycling process could be completed in several minutes, highlighting its potential as a catalyst for 4-NP and MB removal.

1. INTRODUCTION

Noble metal nanoparticles (NPs) have been intensively investigated for a wide variety of applications, especially in catalysis. They account for more than 70% of the global heterogeneous catalyst market owing to their large specific surface areas and increased number of active sites. Au NPs have attracted considerable attention because of their catalytic activities in a number of diverse types of reactions, such as the reduction of organic dyes, reduction of nitro-derivatives, direct electron transfer, and carbon monoxide oxidation. However, Au NPs in catalytic reactions suffer from aggregation because of their high surface energies, resulting in a significant decrease in their catalytic activities. Another challenge is determining how to improve recycling stability, which would increase the cost-effectiveness. Hence, the immobilization of Au nanoparticles on magnetic nanocomposites has attracted attention for targeting these challenges. The combination of magnetic separation abilities provided by magnetic particles and other superior characteristics of Au NPs has attracted broad interest. However, methods used for obtaining noble metal NPs mainly focus on reducing gold ions with reductants, such as citrate, borohydride, hydrazine, and borohydride, which are categorized as chemical hazards and have potential adverse environmental effects. Therefore, it is necessary to design and synthesize Au@magnetic composites using a green and cost-effective process.

Tannic acid (TA), as a plant polyphenol, is widely distributed in plant tissues. It is colorless and 100 times less costly than dopamine. TA coatings retain many of the advantages of polydopamine and deposit under similar conditions. To date, a number of researchers have reported that TA gives rise to broad chemical versatility, especially in metal ion complexation, due to the strong chelating interactions between the catechol groups and metal ions. Moreover, these reports showed the following excellent characteristics of TA: (1) the thickness of the TA layer can be readily controlled by repeating the coating process, and (2) the abundant catechol groups provide a high reduction ability to transform metal ions into metal NPs without an exogenous reducing agent. Inspired by the adhesion and reduction ability of TA, a facile synthesis method was proposed to prepare Fe₃O₄ magnetic particles with a TA coating through metal chelation polymerization of TA with Fe⁶⁺. The TA layer directly reduced gold ions into Au NPs, which were loaded onto TA-Fe₃O₄ to prepare Au@TA-Fe₃O₄ magnetic nanomaterials for the catalytic reduction of 4-NP and MB.
methylene blue (MB) and 4-nitrophenol (4-NP). Furthermore, we investigated the size effect of Fe3O4 as the core on gold ion reduction and the catalytic capacity of corresponding Au@TA-Fe3O4 for the reduction of methylene blue and 4-nitrophenol. The underlying mechanism is discussed, and the catalytic efficiency was characterized.

2. MATERIALS AND METHODS

2.1. Chemicals. All of the chemicals were of analytical grade and used as received. The aqueous solutions were prepared with ultrapure water (>18.25 MΩ·cm) obtained from a Q-Grad1 system (Millipore Corporation, USA). Tannic acid (TA), hydrogen tetrachloroaurate hydrate (HAuCl4·4H2O), ferric chloride hexahydrate (FeCl3·6H2O), ferrous chloride tetrahydrate (FeCl2·4H2O), ethylene glycol, polyethylene glycol, sodium acetate, methylene blue (MB), 4-nitrophenol (4-NP), and sodium borohydride (NaBH4) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ammonia solution (28% w/v) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of Fe3O4 Nanoparticles. Fe3O4 nanoparticles with different sizes were prepared with a coprecipitation method and a solvothermal method.

2.2.1. Coprecipitation Method. First, Fe3O4 NPs were prepared by a coprecipitation method according to a previous report with modifications.25 In brief, FeCl3·6H2O (3.244 g) and FeCl2·4H2O (1.988 g) were dissolved in water (80 mL), and 15 mL of ammonia solution (28% w/v) was added. The solution was left undisturbed. The mixture was then constantly mechanically stirred at 90 °C under nitrogen gas protection. After 30 min, the Fe3O4 NPs were isolated with a permanent magnet and washed several times with water. Finally, the Fe3O4 NPs were dried under a vacuum at 60 °C for 24 h. The obtained Fe3O4 NPs are named as Fe3O4 precipitation.

2.2.2. Solvothermal Method. Fe3O4 NPs were also synthesized using a solvothermal method.26 FeCl3·6H2O (2.7 g) was dissolved in 80 mL of ethylene glycol to form a clear yellow solution. After adding sodium acetate (7.2 g) and polyethylene glycol (1.0 g), the mixture was stirred for about 30 min and then transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated at 200 °C for 8 h and then cooled to room temperature. The black iron oxide magnetic Fe3O4 nanoparticles were washed several times with ethanol and dried at 60 °C for 24 h. The obtained Fe3O4 NPs are named Fe3O4-solvothermal.

2.3. Preparation of Fe3O4@Tannic Acid (TA) Nanocomposites. Next, to synthesize the TA–metal complex on the surfaces of Fe3O4 NPs, 2 mL of a tannic acid solution (4 mg/mL) was added to a suspension of the obtained Fe3O4 NPs (100 mL, 1 mg/mL) with vigorous stirring for 30 s followed by the introduction of a FeCl3·6H2O solution (2 mL, 1 mg/mL) into the above mixture with another 30 s of mixing. After mixing the reaction system with 100 mL of Tris-HCl buffer (10 mM, pH = 8.5) for 10 min, the sediment was recovered with a magnet and rinsed with water two times. The above process was repeated twice to obtain Fe3O4@TA. The products were isolated, washed, and vacuum-dried at 60 °C for 24 h.

2.4. Preparation of Fe3O4@TA@Au Nanocomposites. First, 40 mg of Fe3O4@TA was well dispersed in 400 mL of a chloroauric acid aqueous solution with different concentrations. The mixture was stirred at 90 °C for 0.5 h. After the reaction, the resulting Au NP-deposited Fe3O4@TA (Fe3O4@TA@Au) nanocomposites were magnetically separated from the suspension, after which they were washed with ultrapure water three times and dried under a vacuum overnight.

2.5. Characterization of Nanocomposites. Field emission-scanning electron microscopy (FESEM, JSM-7800F, Zeiss, Germany) and transmission electron microscopy (TEM, FEI Inc., USA) were used to examine the morphologies of the as-synthesized NPs. The hydrodynamic sizes and zeta potentials of the NPs were measured by dynamic light scattering (DLS). The optical absorbance spectra were analyzed using a UV-1800 spectrophotometer (Shimadzu, Japan). The crystalline forms of the products were characterized by X-ray diffraction (XRD, XRD-7000, Shimadzu, Japan) with Cu Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was also employed to analyze the elemental compositions of the intermediate and final products using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific, USA). Magnetic properties were examined on a magnetometer with an applied field between -20,000 and 20,000 Oe at room temperature (VSM, Quantum Design PPMS).

2.6. Fe3O4@TA@Au Catalyzed 4-NP and MB Reduction. 2.6.1. Catalyzing the Reduction of 4-NP by NaBH4. First, 2 mg of the Fe3O4@TA@Au nanocomposite was added to 2 mL of deionized water. Next, 1 mL of fresh NaBH4 (0.1 M) and 1 mL of 4-NP (0.5 mM) were added in sequence. The yellow color of the 4-NP gradually vanished due to catalytic reduction in the presence of reducing agents. The catalytic process was monitored by measuring the changes in absorbance at 400 nm with a UV–Vis spectrophotometer (Shimadzu UV-2550, Shimadzu, Japan).

2.6.2. Catalyzing the Reduction of MB by NaBH4. A total of 2 mg of the Fe3O4@TA@Au nanocomposite was added to 4 mL of MB (0.06 mM) in a centrifuge tube, after which 0.5 mL of NaBH4 (0.1 M) was added. The blue color of the MB gradually vanished by catalytic reduction in the presence of the reducing agents. The catalytic process was monitored by measuring the changes in absorbance at 663 nm with the UV-Vis spectrophotometer.

The catalytic effect is expressed by the reaction kinetics in the following equation:

\[ \ln(c_t/c_0) = \ln(A_t/A_0) = -kt \]

where k is the apparent first-order rate constant (min⁻¹) and t is the reaction time (min). The ratio of \( C_t \) (the concentration at reaction time t) to \( C_0 \) (the initial concentration) was directly obtained from the relative intensity ratio corresponding to the absorbance values \( (A_t/A_0) \).

3. RESULTS AND DISCUSSION

3.1. Synthesis of Fe3O4@TA@Au Composites with Different Sizes of Fe3O4 NPs. Previous studies indicated that the Fe3O4 synthesis method determined the overall sizes of the nanoparticles. In this study, Fe3O4 nanoparticles were synthesized through a co-precipitation method using FeCl3 and FeCl2 as iron sources (Scheme 1A) and a solvothermal method using FeCl3 as an iron source (Scheme 1B). The morphologies of the nanoparticles were characterized by SEM and TEM measurements. As shown in Figure 1, the Fe3O4 NPs were well-defined spheres. The NPs obtained from the co-precipitation method had diameters of ~20 nm (Figure 1A), while the sizes of the NPs synthesized using the solvothermal method were ~200 nm (Figure 1D). The DLS characterization further proved that the sizes of the Fe3O4 particles obtained from co-precipitation and solvothermal methods were ~20 and ~200 nm, respectively.
NPs with different diameters were used to fabricate Fe₃O₄@TA@Au nanocomposites (Scheme 1). Specifically, the strong chelation of catechol-Fe(III) ensured the rapid fabrication of the TA layer, and the greater number of phenolic hydroxyl groups on the TA-Fe(III) complex yielded a sufficient reduction ability for the reduction of Au³⁺ without extra reagent. Consequently, the synthesis procedure was green and greatly simplified. When the Fe₃O₄ NPs were mixed with the TA and FeCl₃·6H₂O solutions (in 10 mM Tris, pH 8.5), a thin Fe³⁺-TA supra-molecular layer with TA as the organic ligand and Fe³⁺ as the cross-linker was coated on the surface of the Fe₃O₄ nanoparticles. The free TA or small Fe³⁺-TA complexes initially adsorbed onto the Fe₃O₄ NP surfaces and were subsequently cross-linked by further Fe³⁺ complexation. Finally, chloroauric acid was added to the mixture and was reduced by the TA layer, leading to the deposition of Au NPs on the Fe₃O₄ core. In this step, the TA played an important role for Au NP immobilization and formation. Coating of TA was repeated two times to ensure the formation of a TA layer on Fe₃O₄ NPs. The anchoring patterns of the gold nanoparticles on the Fe₃O₄ cores with different sizes were not the same. As shown in Figure 1B, Au NPs were sporadically deposited around the Fe₃O₄-20 nm, while Au NPs were inlaid into the surfaces of the Fe₃O₄-200 nm (Figure 1E and Figure S1 in the Supporting Information). As shown in Scheme 1A, the Fe₃O₄ nanocomposites obtained by the co-precipitation method (Fe₃O₄-20 nm) had relatively small diameters, and those of Au NPs were nearly the same as that of the core. For the Fe₃O₄ nanocomposites obtained through the solvothermal method (Fe₃O₄-200 nm), the average diameter was around 200 nm, which was much larger than that of the Au NPs, and the TA-reduced Au NPs were attached on the surfaces of the Fe₃O₄-200 nm. Because the catalytic activities of the obtained materials depended mainly on the quantity of Au NPs immobilized on the Fe₃O₄@TA NPs, the Fe₃O₄ diameter affected the growth of the Au NPs, which may affect the catalytic abilities of the Fe₃O₄@TA@Au NPs.

The properties of the Fe₃O₄@TA@Au NPs were further studied. First, the crystallinities of the samples were characterized by XRD. Figure 2A shows the XRD pattern of the Fe₃O₄-20 nm@TA@Au. The six characteristic 2θ peaks at 30.56°, 35.52°, 43.52°, 53.80°, 57.24°, and 62.56° corresponded to the (220), (311), (400), (422), (511), and (440) lattice planes of Fe₃O₄ with a spinel structure, respectively. Furthermore, the presence of Au NPs was proven by the four characteristic 2θ peaks at 38.16°, 44.26°, 64.50°, and 77.56°, which corresponded to the (111), (200), (220), and (311) lattice planes, respectively. These revealed that Au NPs and Fe₃O₄ were present in the obtained Fe₃O₄-20 nm@TA@Au composite. As for the Fe₃O₄-200 nm core, six characteristic peaks at 2θ of 30.10°, 35.56°, 43.24°, 53.46°, 57.24°, and 62.24° corresponded to the (220), (311), (400), (422), (511), and (440) lattice planes of Fe₃O₄ with a spinel structure. Four other peaks at 37.84°, 44.18°, 64.52°, and 77.18° were also observed, which may have corresponded to the (111), (200), (220), and (311) crystal planes of the cubic phase of the Au nanoparticles (Figure 2B).

XPS analysis was conducted to examine the surface elements present in the magnetic composites more deeply. The XPS of the Fe₃O₄-20 nm@TA@Au showed characteristic peaks at 710.98 and 724.88 eV, which were assigned to Fe 2p (Figure 3A−C). Moreover, the peaks at 84.28 and 87.98 eV were assigned to Au 4f and Au 4f, respectively, which were close to the typical
binding energy of metallic Au, confirming the formation of Au NPs on the surfaces of the Fe₃O₄-20 nm@TA@Au particles. As for the Fe₃O₄-200 nm@TA@Au particles, the presence of ferric species was confirmed by the Fe 2p core-level spectrum ranging from 711.58 to 725.08 eV. The Au 4f peaks at 85.08 and 88.78 eV were attributed to the Au 4f⁷/₂ and Au 4f⁵/₂ of Au⁰, respectively (Figure 3D–F), suggesting the presence of Au NPs.

Figure S2 in the Supporting Information shows the magnetic hysteresis loops of the Fe₃O₄-20 nm and Fe₃O₄-200 nm@TA@Au nanocomposites at room temperature. The saturation magnetization (Ms) values of the Fe₃O₄-20 nm and Fe₃O₄-200 nm@TA@Au were measured to be 71.78 and 51.62 emu/g, respectively. The saturation magnetization values of the Fe₃O₄-200 nm and Fe₃O₄-200 nm@TA@Au magnetic composite could reach 72.54 and 41.96 emu/g, respectively. Such a decrease in saturation magnetization could be attributed to the decrease in the effective masses of the Fe₃O₄ cores in these cases. Almost no hysteresis loops were found in the magnetization curves, suggesting that the microspheres possessed superparamagnetism. Owing to the high magnetization values and superparamagnetic characteristics, the Fe₃O₄-20 nm@TA@Au and Fe₃O₄-200 nm@TA@Au nanocomposites could be magnetically separated from an aqueous solution within a few seconds and re-dispersed well once the magnet was removed, rendering them economical and reusable for various applications.

The weight percentages of Fe and Au in the Fe₃O₄@TA@Au composite were quantified by the EDS elemental mappings. The
Fe and Au weight percentages in the Fe₃O₄-20 nm@TA@Au synthesized from 0.2 mM chloroauric acid are 4.19 and 0.59 wt %, respectively. For Fe₃O₄-200 nm@TA@Au (0.05 mM chloroauric acid), the EDS-measured Fe and Au weight percentages are 1.59 and 0.19 wt %, respectively.

3.2. Fe₃O₄@TA@Au Effectively Catalyzed the Reduction of 4-NP and MB by NaBH₄. The catalytic reduction of 4-NP and MB by NaBH₄ was used as the typical model reaction to investigate the catalytic performances of the Fe₃O₄@TA@Au composites. This reaction was monitored by the color bleaching of 4-NP and MB and quantitatively analyzed by UV−Vis absorption spectroscopy.

3.2.1. Catalyzing Reduction of 4-NP by NaBH₄. As shown in Figure 4A, the yellow color of the 4-NP solution vanished gradually when Fe₃O₄@TA@Au was added. The colorimetric changes were characterized by a decrease in absorbance at 400 nm, and a new peak centered at 298 nm appeared. These changes indicated that the reduction of 4-NP to 4-AP occurred (Figure S3A in the Supporting Information).

To investigate the size effect of the Fe₃O₄ on the Au NP synthesis and the catalytic performance of the final Fe₃O₄@TA@Au composite, Fe₃O₄-20 nm and Fe₃O₄-200 nm were reacted with different concentrations of chloroauric acid. First, the catalytic abilities of the Fe₃O₄-20 nm@TA@Au synthesized from chloroauric acid solutions with concentrations of 0.05, 0.1, 0.2, 0.3, and 0.4 mM were compared. The relationship between Fe₃O₄-20 nm@TA@Au and chloroauric acid concentration is displayed in Figure 5. As shown in Figure 5A−E, as the chloroauric acid concentration increased from 0.05 to 0.4 mM, the catalytic rate varied. The reaction kinetics were further calculated. The ratio of Ct (the concentration of 4-NP at reaction time t) to C₀ (the initial concentration of 4-NP) was directly obtained from the relative intensity ratio of the respective absorbance (A_t/A₀). The linear relationship between ln(C_t/C₀) and the reaction time is displayed in Figure 5F, which was calculated from the slope of the straight line. The reaction rate constants were 0.177, 0.277, 0.377, 0.432, and 0.296 min⁻¹ at 25 °C for chloroauric acid concentrations of 0.05, 0.1, 0.2, 0.3, and 0.4 mM (k₅).

Figure 5. UV−Vis spectral changes in 4-NP catalyzed by Fe₃O₄-20 nm@TA@Au synthesized from chloroauric acid concentrations of (A) 0.05 mM, (B) 0.1 mM, (C) 0.2 mM, (D) 0.3 mM, and (E) 0.4 mM. (F) First-order kinetics plot of the catalytic reduction of 4-NP in the presence of the Fe₃O₄-20 nm@TA@Au synthesized from chloroauric acid concentrations of 0.05 mM (k₁), 0.1 mM (k₂), 0.2 mM (k₃), 0.3 mM (k₄), and 0.4 mM (k₅).

Figure 6. UV−Vis spectral changes in 4-NP catalyzed by Fe₃O₄-200 nm@TA@Au synthesized from chloroauric acid concentrations of (A) 0.01 mM, (B) 0.02 mM, (C) 0.05 mM, (D) 0.1 mM, and (E) 0.2 mM. (F) First-order kinetics plot of the catalytic reduction of 4-NP in the presence of the Fe₃O₄-200 nm@TA@Au synthesized from chloroauric acid concentrations of 0.01 mM (k₁), 0.02 mM (k₂), 0.05 mM (k₃), 0.1 mM (k₄), and 0.2 mM (k₅).
0.4 mM, respectively. The best constant rate was obtained from the Fe₃O₄-20 nm@TA@Au synthesized from 0.3 mM chloroauric acid.

Next, Fe₃O₄-200 nm@TA@Au was synthesized from chloroauric acid with concentrations of 0.01, 0.02, 0.05, 0.1, and 0.2 mM. The performance of Fe₃O₄-200 nm@TA@Au for catalyzing 4-NP was also studied (Figure 6A–E). Figure 6F reveals the linear relationship between ln(Ct/C₀) and the reaction time t. The values of the rate constant k of the 4-NP reduction were calculated to be 0.314, 0.623, 3.094, 0.885, and 0.542 min⁻¹ with the Fe₃O₄-200 nm@TA@Au synthesized from chloroauric acid with concentrations of 0.01, 0.02, 0.05, 0.1, and 0.2 mM, respectively. It was found that with the increase in chloroauric acid concentration from 0.01 to 0.05 mM, the catalytic performance of Fe₃O₄-200 nm@TA@Au also increased. However, keeping the increase in chloroauric acid concentration (0.1 and 0.2 mM) did not improve the catalytic effect.

As shown in Figure 4A, the reduction reaction does not proceed in the absence of Au NPs, suggesting that the reduction of 4-NP by NaBH₄ is solely catalyzed by Au NPs in the Fe₃O₄@TA@Au NP composites. Au NPs serve as an electron relay system, facilitating the electron transfer from BH₄⁻ to the 4-NP, thus accelerating the reduction reaction rate. In the Fe₃O₄@TA@Au NP composites, the quantity of the Au NPs is determined by the amount of TA coating on Fe₃O₄ NPs. Since the TA on the Fe₃O₄ NPs is constant, with the increase in chloroauric acid concentration, the reduction of Au NPs gradually increases, leading to an improved catalytic effect. When the capacity of the TA-reduced Au NPs reaches the plateau, further increase in the chloroauric acid concentration will not boost the overall catalytic effect of Fe₃O₄@TA@Au.

Figure 7. UV–Vis spectral changes in MB catalyzed by Fe₃O₄-20 nm@TA@Au synthesized from chloroauric acid concentrations of (A) 0.05 mM, (B) 0.1 mM, (C) 0.2 mM, (D) 0.3 mM, and (E) 0.4 mM. (F) First-order kinetics plot of the catalytic reduction of 4-NP in the presence of the Fe₃O₄-20 nm@TA@Au synthesized from chloroauric acid concentrations of 0.05 mM (k₁), 0.1 mM (k₂), 0.2 mM (k₃), 0.3 mM (k₄), and 0.4 mM (k₅).

Figure 8. UV–Vis spectral changes in MB catalyzed by Fe₃O₄-200 nm@TA@Au synthesized from chloroauric acid concentration of (A) 0.01 mM, (B) 0.02 mM, (C) 0.05 mM, (D) 0.1 mM, and (E) 0.2 mM. (F) First-order kinetics plot of the catalytic reduction of 4-NP in the presence of the Fe₃O₄-200 nm@TA@Au synthesized from a chloroauric acid concentration of 0.01 mM (k₁), 0.02 mM (k₂), 0.05 mM (k₃), 0.1 mM (k₄), and 0.2 mM (k₅).
The optimized chloroauric acid concentrations of Fe₃O₄-20 nm@TA@Au and Fe₃O₄-200 nm@TA@Au were 0.3 and 0.05 mM, respectively. With the optimized chloroauric acid concentration, the constant rates of Fe₃O₄-20 nm@TA@Au and Fe₃O₄-200 nm@TA@Au in 4-NP reduction are 0.432 and 3.094 min⁻¹, respectively.

3.2.2. Catalyzing Reduction of MB by NaBH₄. In addition, the reduction of MB was also studied. As shown in Figure 4B, the blue color of the MB solution vanished gradually until it became colorless when Fe₃O₄@TA@Au was added. From the UV–Vis changes in Figure 4B, it was found that both Au NPs and Fe₃O₄ NPs can catalyze the reduction of MB. As shown in Figure S3B in the Supporting Information, the n–π* transitions of the MB molecule could cause the oxidized form of MB, which normally exhibits the decreasing absorption intensity at 663 nm. Fe₃O₄@TA@Au has a lower Zeta potential in neutral solution (Figure S4, Supporting Information) and thus favors the electrostatic interaction between the Fe₃O₄@TA@Au and an anionic dye.29 Figure 7A–E shows the successive UV–Vis spectra of the MB reduction solution in the presence of Fe₃O₄-20 nm@TA@Au. The MB reduction also followed pseudo-first-order kinetics with respect to the MB concentration. Figure 7F shows the linear relationship between ln(Ct/C₀) and the reduction time. The catalyzed reaction rates of MB reduction were determined to be 0.260, 0.348, 0.543, 0.374, and 0.281 min⁻¹ at 25 °C for chloroauric acid concentrations of 0.05, 0.1, 0.2, 0.3, and 0.4 mM, respectively. Similar to the reduction of 4-NP, as the chloroauric acid concentration increased, the catalytic rate gradually increased. Because of the fixed quantity of the TA layer on Fe₃O₄, the TA-assisted Au NPs synthesis reached a plateau at a chloroauric acid concentration of 0.2 mM.

For the case of Fe₃O₄-200 nm@TA@Au, as shown in Figure 8A–E, the chloroauric acid concentration increase impeded the catalytic activity. Figure 8F shows the values of the rate constant k for MB catalytic reduction, which were calculated to be 0.129, 0.357, 0.441, 0.257, and 0.138 min⁻¹ at 25 °C for chloroauric acid concentrations of 0.01, 0.02, 0.05, 0.1, and 0.2 mM, respectively. A similar plateau was observed. The best rate constant was obtained from the Fe₃O₄-200 nm@TA@Au synthesized from 0.05 mM chloroauric acid. The rate constants were higher than those reported in the recent literature with other catalysts, as compared in Table S1.

3.3. Fe₃O₄ Magnetic Particle Enabled Cycling. The most significant advantage of the Fe₃O₄@TA@Au composite catalyst prepared in this work was that recovery could be easily achieved by magnetic separation. As shown in Scheme 1, the Fe₃O₄@TA@Au catalysts could be easily separated from the reaction media for both of the two model reactions using an external magnet. To examine the cost and environmental protection capabilities, the recyclability of the sorbents was also evaluated. Figure 9 shows that the Fe₃O₄-20 nm@TA@Au and Fe₃O₄-200 nm@TA@Au composites could be recycled and reused at least five times with a stable adsorption of more than 90%. Moreover, the recycling process of the novel Fe₃O₄@TA@Au materials could be completed in several minutes, which facilitated fast recycling.

4. CONCLUSIONS

We developed a facile method to prepare Fe₃O₄@TA@Au nanoparticles for the reduction of 4-NP and MB with NaBH₄. These Au NP-decorated Fe₃O₄ magnetic nanoparticles exhibited excellent magnetic separation and catalytic properties. The Fe₃O₄-20 nm@TA@Au synthesized from 0.3 and 0.2 mM chloroauric acid shows constant rates of 0.432 and 0.543 min⁻¹ in the reduction of 4-NP and MB, respectively. While for Fe₃O₄-200 nm@TA@Au synthesized from 0.05 mM chloroauric acid, the constant rates of 4-NP and MB reduction are 3.094 and 0.441 min⁻¹, respectively. The remarkable catalytic reduction...
performance was attributed to the TA-assisted synthesis of Au NPs on the magnetic spheres. More importantly, the as-prepared Fe3O4@TA@Au microspheres exhibited excellent reusability for at least five cycles via the magnetic separation technique. Such composite catalysts are expected to have many potential applications in catalysis and industries.

ASSOCIATED CONTENT

Supporting Information
FESEM images of Fe3O4@20 nm@TA@Au microspheres, magnetic hysteresis loops of Fe3O4@TA@Au microspheres, structures of 4-NP and MB, zeta potential of Fe3O4@TA@Au microspheres, comparison of kinetic constant (k) of NaBH4 reducing 4-NP and MB reported in recent literatures using different catalysts (PDF)

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Notes
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