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ARTICLE

Gold nanoparticles modified magnetic fibrous silica microsphere as a highly efficient and recyclable catalyst for the reduction of 4-nitrophenol

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Recently, catalysts with easily accessible active sites and high efficiency and recyclability have triggered various research interests. In this study, we prepared uniform fibrous silica microspheres with a γ -Fe₂O₃ magnetic core (γ -Fe₂O₃@SiO₂@KCC-1) as the catalyst support. The distance between two fibers was approximately 10–20 nm. Au nanoparticles (NPs) were highly dispersed on the silica fibers without aggregation to form the nanocatalyst Au/ γ -Fe₂O₃@SiO₂@KCC-1. The catalytic activity of Au/ γ -Fe₂O₃@SiO₂@KCC-1 for the reduction of 4-nitrophenol (4-NP) with NaBH₄ was measured by UV-vis spectroscopy. Au/ γ -Fe₂O₃@SiO₂@KCC-1 exhibited better catalytic activity toward the reduction of 4-NP compared with other reported Au NPs-based catalysts. The high catalytic activity was mainly attributed to the easy accessibility of the Au NPs of the prepared nanocatalyst. In addition, Au/ γ -Fe₂O₃@SiO₂@KCC-1 could be easily recycled by applying an external magnetic field while maintaining the catalytic activity without significant decrease even after six runs. The unique properties provided an ideal platform to study various noble metal/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalysts that can be potentially applied in a wide variety of fields such as catalysis and green chemistry.

1. Introduction

During the past few years, significant research progress has been made with noble metal nanoparticles (NMNPs) because of their excellent properties in many fields, especially in catalysis.^{1–3} In particular, NMNPs-based catalysts have been extensively studied in many organic catalytic reactions, including cross coupling, hydrogenation, and methanol oxidation.^{4–6} To date, various methods have been developed for preparing NMNPs-based catalysts, among which the chemical reduction of noble metal cations in a solution using a reducing reagent is the most common preparation procedure.^{7–9} However, in solution, NMNPs are unstable and tend to aggregate because of their high surface energy resulting from the high surface-to-volume ratio, which in turn leads to a remarkable reduction in the catalytic activity.^{10, 11} To solve this problem, NMNPs have been grafted onto various supporting matrices to generate hybrid catalysts to protect against the aggregation of NMNPs. Among most of the reported supporting materials, mesoporous silicas such as SBA-15, SBA-16, MCM-41, MCM-48, and other mesoporous silica microspheres have been widely used to fabricate NMNPs-based nanocatalysts.^{8, 12–16} Although these mesoporous silicas have regular mesopores and high specific surface areas that can support NMNPs with high dispersion, their mesopores can always be easily blocked because of the small pore size. For

example, by using cetyltrimethylammonium bromide as the surfactant, the prepared mesoporous silicas usually exhibit a pore size of 2–5 nm,^{17, 18} while the particle size of most of the NMNPs is 3–5 nm. Thus, designing silica supports with a large pore size and easily accessible high surface areas is required. Furthermore, the isolation and recovery of NMNPs-based catalysts from the catalytic reaction medium with high efficiency is also worthy of consideration due to the scarcity of noble metal resources. In this regard, magnetic-responsive nanomaterials have emerged as ideal catalyst supports since they can be isolated and recovered by magnetic separation, which is more efficient and rapid as compared with centrifugation or filtration, which prevents mass losses of catalyst or the use of additional solvents.^{19–23} Therefore, it is highly desirable to prepare magnetic silica materials with easy accessible high surface areas, high-efficiency mass transfer, as well as magnetic separation property, to further fabricate NMNPs-based catalysts for organic catalytic reactions.

On the other hand, 4-nitrophenol (4-NP) and related compounds are organic pollutants present in industrial and agricultural wastewaters as these compounds are primarily used to prepare dyes, pesticides, explosives, plasticizers, and herbicides.^{24–26} Hence, to meet increasingly stringent environmental quality standards, it is necessary to remove them from polluted waters.^{11, 27} Among all the processes to remove 4-NP, the catalytic reduction of 4-NP to 4-aminophenol (4-AP) is the most efficient because it is cost-effective and simple. In addition, 4-AP is formed as the reduction product, which is an industrially important raw material widely used as the intermediate for the manufacture of many analgesic and antipyretic drugs.^{28, 29} Thus far, various NMNPs-based catalysts such as Pd, Au,

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Ag, and Pt nanocatalysts have been widely used for the reduction of 4-NP to 4-AP due to their efficient catalytic activities.³⁰⁻³² However, cost-effective NMNPs based catalysts with easily accessible active sites, excellent catalytic activities, and efficient recoverable properties for the reduction of 4-NP to 4-AP are still needed.

Inspired by the abovementioned perspective, herein, we prepared uniform fibrous silica microspheres (KCC-1) with a γ -Fe₂O₃ magnetic core as the catalyst support (γ -Fe₂O₃@SiO₂@KCC-1) for the immobilization of NMNPs. The silica fibers were functionalized with mercaptopropyl groups followed by the immobilization of Au NPs onto the fibers without aggregation. Besides, the large space between fibers can significantly increase the accessibility of the active sites of the prepared nanocatalyst. In addition, the catalytic performance of Au/ γ -Fe₂O₃@SiO₂@KCC-1 with respect to efficiency and recyclability was also evaluated for the reduction of 4-NP in the presence of NaBH₄.

2. Experimental

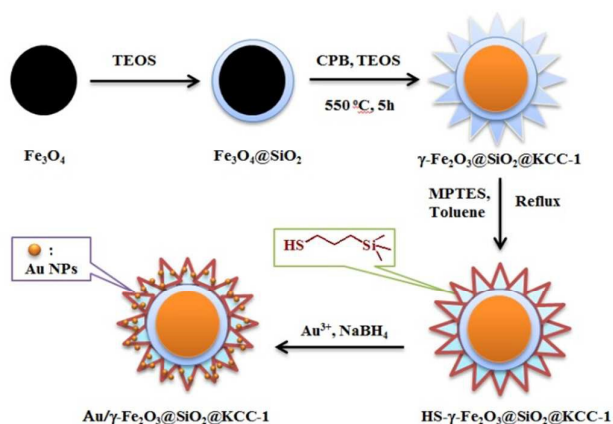
2.1 Materials

In this study, the starting reagents tetraethoxysilane (TEOS), 3-mercaptopropyltrimethoxysilane (MPTES), cetylpyridinium bromide (CPB), sodium dodecyl sulfate (SDS), glycol, urea, ferric trichloride (FeCl₃·6H₂O), chloroauric acid (HAuCl₄), and anhydrous sodium acetate (NaAc) were commercially obtained from Shanghai Chemical Company (Shanghai, China) and used as received. Reagent-grade 4-NP, cyclohexane, pentanol, and NaBH₄ were purchased from Tianjing Guangfu Chemical Company (Tianjin, China). All reagents and solvents used for synthesis and measurements were used as supplied.

2.2 Preparation of Fe₃O₄ NPs

Fe₃O₄ magnetic NPs were synthesized according to the reported literature.^{18,33} Typically, FeCl₃·6H₂O (2.7 g), SDS (1.0 g), and NaAc (7.2 g) were mixed in 100 mL of glycol and stirred at room temperature for 30 min. Then, the solution was poured into a Teflon flask and aged at 200 °C for 8 h. After being cooled, the solid product was filtered and thoroughly washed with deionized water to obtain Fe₃O₄ NPs.

2.3 Fabrication of γ -Fe₂O₃@SiO₂@KCC-1



Scheme 1. Preparation of Au/ γ -Fe₂O₃@SiO₂@KCC-1

First, the Fe₃O₄ NPs were covered by amorphous silica (Fe₃O₄@SiO₂) to allow further growth of fibrous nano-silica. Typically, 0.5 g of fresh Fe₃O₄ NPs was dispersed in 200 mL of ethanol, 50 mL of deionized water, and 2.5 mL of concentrated ammonia and ultrasonicated for 30 min. Second, 0.5 g of TEOS was added dropwise. The mixture was stirred at room temperature for 5 h. Then, the resulting solid product was separated by magnetic suction and thoroughly washed with deionized water and ethanol.

According to the preparation method of fibrous nano-silica KCC-1,³⁴⁻³⁶ the core-shell magnetic fibrous silica microspheres were prepared as follows: the above obtained Fe₃O₄@SiO₂ (0.25 g) was ultrasonically dispersed in an aqueous solution (30 mL) containing urea (0.3 g) to form solution A. CPB (0.5 g) was added to 0.75 mL of n-pentanol and 30 mL cyclohexane to form solution B. Solution A was added to solution B under stirring at room temperature. Then, 1.25 g TEOS was added dropwise to the above mixed solution. The resulting mixture was continuously stirred for 1 h at room temperature and then aged at 120 °C for 5 h. Then, the mixture was allowed to cool to room temperature and isolated by strong magnetic suction, washed with deionized water and acetone, and dried overnight in a drying oven at 40 °C overnight. The obtained material was then calcined at 550 °C for 5 h in air to obtain γ -Fe₂O₃@SiO₂@KCC-1.

2.4 Preparation of Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst

γ -Fe₂O₃@SiO₂@KCC-1 was functionalized with MPTES prior to the immobilization of Au NPs onto the fibrous nano-silica. First, γ -Fe₂O₃@SiO₂@KCC-1 (0.3 g) was added to 30 mL of anhydrous toluene under ultrasonication for 10 min to disperse it homogeneously. Second, 30 mg of MPTES was added dropwise, and the mixture was refluxed for 5 h in a N₂ atmosphere. Next, the mixture was cooled to room temperature, and the resulting mercaptopropyl-functionalized material (HS- γ -Fe₂O₃@SiO₂@KCC-1) was magnetically isolated, washed repeatedly with chloroform, dichloromethane, and ethanol, and dried under vacuum.

HS- γ -Fe₂O₃@SiO₂@KCC-1 (0.1 g) was ultrasonically dispersed in 10 mL H₂O, and 5 mL of an HAuCl₄ solution containing 5 mg Au was added. After being stirred and ultrasonically dispersed for 1 h, an excess of a NaBH₄ solution was added dropwise. Then, the Au NPs were formed and anchored on the mercaptopropyl-functionalized fibrous silica. Thus, the Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst was obtained.

2.5 Procedure for the reduction of 4-NP

For the catalytic reduction of 4-NP, a 4-NP aqueous solution (0.01 M, 30 μ L) was first mixed with H₂O (2.7 mL) and then a freshly prepared aqueous NaBH₄ solution (0.1 M, 0.25 mL) was added, which resulted in the formation of a bright yellow solution. Then, the prepared Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst (10 μ L, 20 mg mL⁻¹) was added to the bright yellow solution, and the reaction was continued until the solution became colorless. The progress of the reduction process was monitored by measuring the ultraviolet-visible (UV-vis) absorption spectra from 250 nm to 500 nm. To investigate the reusability of the nanocatalyst, the reduction reaction was amplified 20 times, and a magnet was used to recover the nanocatalyst for the next catalytic run.

2.6 Characterization

Transmission electron microscopy (TEM, Tecnai G2F30) was used to investigate the size and morphology of the prepared samples. X-ray diffraction measurements were performed on a diffractometer (XRD, Rigaku D/max-2400) using Cu-K α radiation as the X-ray source in the 2θ range of 10–80°. X-ray photoelectron spectroscopy (XPS, PHI-5702) was employed, and the C 1S line at 284.6 eV was used as the binding energy reference. Magnetic measurements of γ -Fe₂O₃@SiO₂@KCC-1 and Au/ γ -Fe₂O₃@SiO₂@KCC-1 were performed using a vibrating sample magnetometer (VSM, Quantum Design) at room temperature in an applied magnetic field sweeping from –10 to 10 kOe. A Fourier transform infrared spectrometer (FTIR, Bruker IFS66/S) was used to obtain the FTIR spectra of γ -Fe₂O₃@SiO₂@KCC-1 and HS- γ -Fe₂O₃@SiO₂@KCC-1. Elemental analysis (Gmbh Vario El Elementar) and inductively coupled plasma (ICP-AES, IRIS Advantage analyzer) were employed to measure the S, C, H, and Au content of the samples. A UV–Vis spectrophotometer (Shimadzu UV 2100 PC) was used to collect the absorption data.

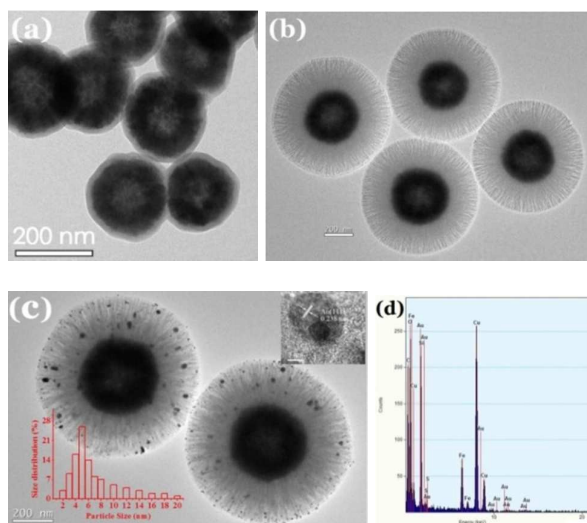


Fig. 1. (a) TEM of Fe₃O₄@SiO₂, (b) TEM of γ -Fe₂O₃@SiO₂@KCC-1, (c) TEM of Au/ γ -Fe₂O₃@SiO₂@KCC-1 and (d) EDX spectra of Au/ γ -Fe₂O₃@SiO₂@KCC-1.

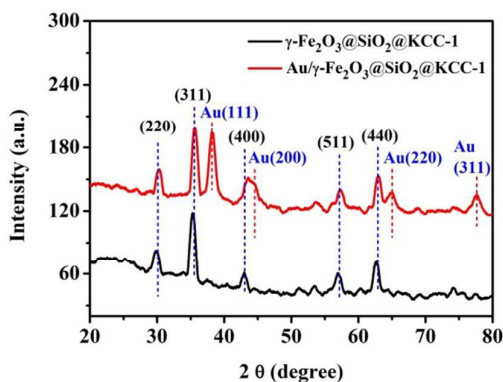


Fig. 2. XRD patterns of γ -Fe₂O₃@SiO₂@KCC-1 and Au/ γ -Fe₂O₃@SiO₂@KCC-1.

3. Results and discussion

Scheme 1 shows the schematic of preparing the Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst. First, γ -Fe₂O₃@SiO₂@KCC-1 was functionalized with MPTES to form mercaptopropyl-functionalized material (HS- γ -Fe₂O₃@SiO₂@KCC-1). The mercaptopropyl groups on the fibrous silica acted as adsorption centers for Au³⁺. When NaBH₄ was introduced, the Au³⁺ ions were reduced and immobilized onto the fibers of γ -Fe₂O₃@SiO₂@KCC-1.

3.1 Catalyst characterization

In the preparation of γ -Fe₂O₃@SiO₂@KCC-1, Fe₃O₄ NPs were covered by amorphous silica to form Fe₃O₄@SiO₂ (black powder, Fig. S1a) to allow for the further growth of fibrous nano-silica. When the as-synthesized material was calcined at 550 °C for 5 h in air, the Fe₃O₄ NPs in the core were converted into magnetic γ -Fe₂O₃ as previously reported,^{37, 38} resulting in the formation of γ -Fe₂O₃@SiO₂@KCC-1 (brown powder, Fig. S1b). Fe₃O₄@SiO₂ has a near spherical morphology with a Fe₃O₄ core of approximately 160 nm and a SiO₂ shell of approximately 20 nm (Fig. 1a). When covered with fibrous nano-silica, the diameter of the NPs increased to 600 nm, and the morphology was uniform microspheres with fibrous nano-silica on the surface (Fig. 1b). To easily load the Au NPs on the fibrous nano-silica, γ -Fe₂O₃@SiO₂@KCC-1 was then functionalized with MPTES. As displayed in the FTIR spectra (Fig. S2), the absorption peak at 2920 cm⁻¹ corresponded to –CH stretching, indicating the successful grafting of mercaptopropyl groups on the γ -Fe₂O₃@SiO₂@KCC-1 surface. As measured by elemental analysis, the mercaptopropyl group content was approximately 4.5% (Table S1). The distance between two fibers was approximately 10–20 nm. This large distance permits the easy loading of the Au NPs onto fibrous nano-silica. Fig. 1c shows the TEM image of Au/ γ -Fe₂O₃@SiO₂@KCC-1. The Au NPs with an average diameter of approximately 5 nm (Fig. 1c, inset) were remarkably grafted on the fibers of the γ -Fe₂O₃@SiO₂@KCC-1 microspheres, and no obvious aggregation was observed. The lattice fringe with a spacing of 0.238 nm corresponded to the Au(111) planes (Fig. 1c, inset). Energy-dispersive spectroscopy (EDX) analysis clearly shows the chemical composition of Au/ γ -Fe₂O₃@SiO₂@KCC-1 (Fig. 1d). Furthermore, ICP-AES analysis revealed that the content of Au NPs loaded on the surface of γ -Fe₂O₃@SiO₂@KCC-1 was approximately 4.63% (Table S1).

XRD measurements were conducted to confirm the surface composition of the prepared samples (Fig. 2). Characteristic peaks of (220), (311), (400), (511), and (440) were observed for γ -Fe₂O₃@SiO₂@KCC-1, which are typical of a spinel magnetite structure of γ -Fe₂O₃.^{39, 40} After modifying by Au NPs, the characteristic peaks of γ -Fe₂O₃ were still preserved. However, compared with the XRD pattern of γ -Fe₂O₃@SiO₂@KCC-1, that of Au/ γ -Fe₂O₃@SiO₂@KCC-1 exhibited four characteristic peaks at $2\theta = 38, 44, 65,$ and 78° , corresponding to the (111), (200), (220), and (311) lattice planes of Au, respectively (JCPDS, No. 4-0784). These results indicated that the Au NPs are successfully immobilized onto the fibers of the γ -Fe₂O₃@SiO₂@KCC-1 microspheres.

To examine the valence states of Au NPs, XPS analysis was conducted; the results are shown in Fig. 3. As shown in Fig. 3a, the XPS elemental survey scan of Au/ γ -Fe₂O₃@SiO₂@KCC-1 clearly revealed the presence of Si, O, C as well as Au elements in the

sample. A very weak peak was observed for the Fe element because γ -Fe₂O₃ was in the core of the microsphere. Using the C 1s line at 284.6 eV as the binding energy reference (Fig. 3b), the peaks at 710.6 and 724.3 eV were assigned to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Fig. 3c). Two obvious Au 4f peaks were observed in Fig. 3d, which are indicative of metallic Au at binding energies of 83.8 and 87.4 eV in Au 4f_{7/2} and Au 4f_{5/2} levels, respectively.

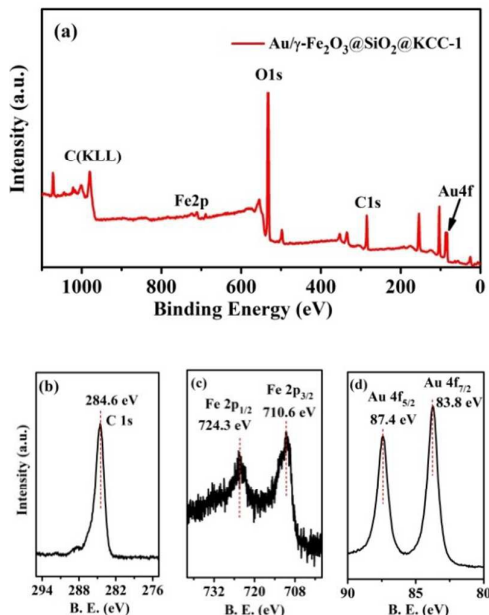


Fig. 3. XPS wide-scan spectra of Au/γ-Fe₂O₃@SiO₂@KCC-1 (a), C 1s (b), Fe 2p (c) and Au 4f (d).

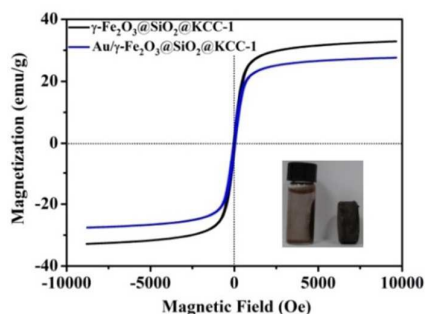
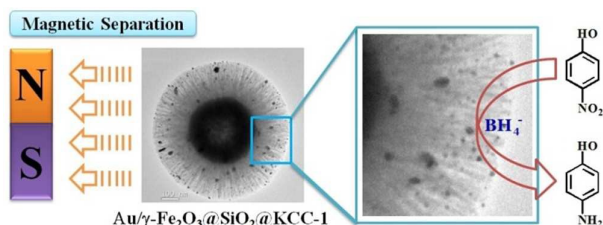


Fig. 4. Room temperature magnetization curves of γ-Fe₂O₃@SiO₂@KCC-1 and Au/γ-Fe₂O₃@SiO₂@KCC-1.



Scheme 2. Reduction of 4-NP to 4-AP over Au/γ-Fe₂O₃@SiO₂@KCC-1 and the catalyst recycle procedure.

The magnetic behavior of Au/γ-Fe₂O₃@SiO₂@KCC-1 that was essential for magnetic applications was evaluated through magnetic measurements conducted at room temperature (Fig. 4). The measured saturation magnetization (M_s) value of γ-Fe₂O₃@SiO₂@KCC-1 was 32.8 emu g⁻¹. When loaded with Au NPs, the magnetic saturation values reduced to 27.6 emu g⁻¹. Thus, Au/γ-Fe₂O₃@SiO₂@KCC-1 could be efficiently separated from the reaction mixture by an external magnetic force and reused (Fig. 4, inset).

3.2 Catalytic reduction of 4-NP

The catalytic performance of Au/γ-Fe₂O₃@SiO₂@KCC-1 was evaluated by the catalytic reduction of 4-NP with an excess of NaBH₄ (Scheme 2). Here, reaction conditions of room temperature and distilled water were chosen to ensure an energy saving and environmentally friendly reaction.⁴¹

As shown in Fig. 5a, the 4-NP aqueous solution with light yellow color exhibited a typical absorption peak at 317 nm. When a NaBH₄ solution was added, the 4-NP aqueous solution changed to bright yellow, and the absorption peak red-shifted to 400 nm, corresponding to the formation of 4-nitrophenolate in alkaline conditions.⁴² The peak at 400 nm remained unaltered with time, suggesting that reduction does not occur in the absence of a catalyst as previously reported.⁴³ The addition of Au/γ-Fe₂O₃@SiO₂@KCC-1 (Fig. 5b) to 4-NP led to the decrease in the peak intensity of the 4-nitrophenolate ion at 400 nm with a concomitant increase in the peaks corresponding to 4-AP at 300 nm, reflecting the conversion of 4-NP to 4-AP.

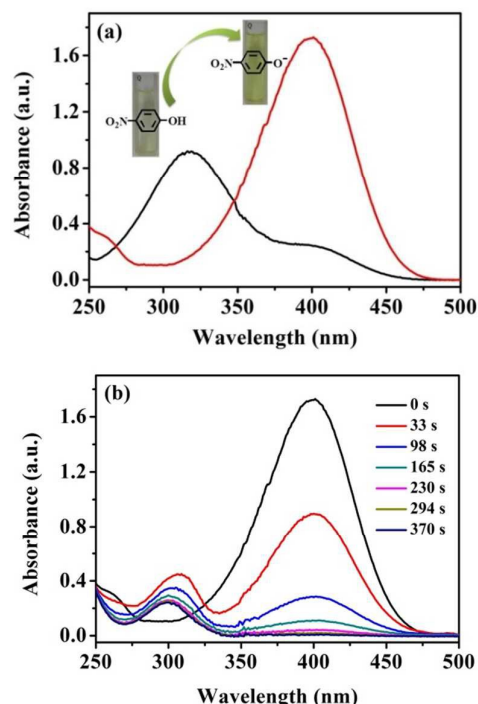


Fig. 5. (a) UV-Vis spectra of 4-NP before and after adding NaBH₄ solution and (b) successive UV-vis spectra for the reduction of 4-NP by NaBH₄ with Au/γ-Fe₂O₃@SiO₂@KCC-1.

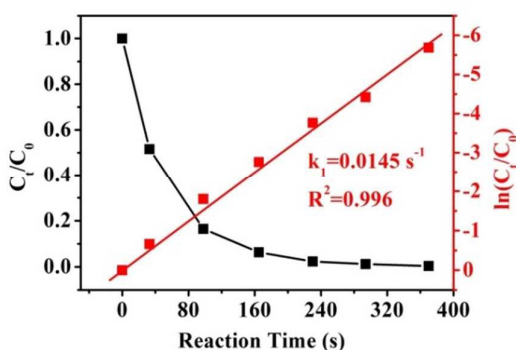


Fig. 6. Kinetic curve for the reduction of 4-NP catalyzed by Au/ γ -Fe₂O₃@SiO₂@KCC-1 (C_t and C_0 are 4-NP concentrations at time t and 0, respectively).

The reaction proceeded rapidly and was almost completed in 6 min catalyzed by Au/ γ -Fe₂O₃@SiO₂@KCC-1. The conversion of 4-NP was calculated from the C_t/C_0 ratio, where C_0 and C_t represent the concentration of 4-NP at time 0 and t , respectively, and it was measured from the relative intensity of the absorbance (A_t/A_0) at 400 nm. After the completion of the reaction, the reaction mixture became colorless. According to the traditional theory about the catalytic reduction of 4-NP by metal NPs, the catalytic mechanism was described as follows: when BH_4^- ions and 4-NP molecules are adsorbed onto the catalytic centers, electron transfer occurs from BH_4^- to 4-NP, resulting in the reduction of 4-NP.⁴³

The reduction rate can be assumed to be independent of NaBH_4 because when the initial concentration of the NaBH_4 solution is very high, it can be considered constant throughout the whole reduction process. Thus, the reaction can be considered as a pseudo-first-order reaction with regard to 4-NP only to evaluate the catalytic rate.²⁴ The apparent rate constant k_{app} can be defined as [Eq. (1)]:

$$\ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = -K_{\text{app}}t \quad (1)$$

Using the above equation [Eq. (1)], a linear relationship between $\ln(C_t/C_0)$ and reaction time was obtained for the reduction catalyzed by Au/ γ -Fe₂O₃@SiO₂@KCC-1 (Fig. 6), which matches well with the first-order reaction kinetics. The reaction rate constant K_{app} was calculated to be $1.45 \times 10^{-2} \text{ s}^{-1}$ for the reduction reaction catalyzed by Au/ γ -Fe₂O₃@SiO₂@KCC-1 (Fig. 6).

However, it is not entirely reasonable to compare k_{app} of different supported catalysts because the metal loadings were different. To further compare the catalytic activity of Au/ γ -Fe₂O₃@SiO₂@KCC-1 with other reported catalysts, the rate constant per gram active sites was then calculated [Eq. (2)]:

$$K_M = \frac{K_{\text{app}}}{M} \quad (2)$$

where M is the weight of active sites used.^{48, 49} Based on the amount of catalyst used and the ICP-AES data (Table S1), the activity parameter K_M was calculated to be $1565.9 \text{ s}^{-1} \text{ g}^{-1}$ for the reduction reaction catalyzed by Au/ γ -Fe₂O₃@SiO₂@KCC-1 (Fig. 6).

The catalytic activities of Au/ γ -Fe₂O₃@SiO₂@KCC-1 and other NMNPs loaded on different supports were compared for the reduction of 4-NP; these results are listed in Table 1. Our group

previously reported that a Au/magnetic porous carbon (Au/MPC) nanocatalyst exhibited an activity parameter of $848.2 \text{ s}^{-1} \text{ g}^{-1}$ for the reduction of 4-NP,⁴⁴ while the K_M values for the reported Au/graphene catalyst and carbon@Au core-shell nanofiber catalyst were 132.08 and $238.98 \text{ s}^{-1} \text{ g}^{-1}$, respectively.^{45, 46} For the reported Pd NPs-based catalyst Pd/PPy, the activity parameter K_M was approximately $1400 \text{ s}^{-1} \text{ g}^{-1}$.⁴⁷ Thus, Au/ γ -Fe₂O₃@SiO₂@KCC-1 with the activity parameter K_M of $1565.9 \text{ s}^{-1} \text{ g}^{-1}$ exhibits excellent catalytic activity, which is mainly attributed to the ease of access of active sites and the low aggregation of the Au NPs on the γ -Fe₂O₃@SiO₂@KCC-1 support. In this situation, mass transfer has been dramatically enhanced, and both 4-NP and BH_4^- can be easily adsorbed on the Au NPs surface, which allows the reduction to start and end rapidly.

Furthermore, the stability and recyclability of the catalyst is an important issue. After each catalytic cycle, Au/ γ -Fe₂O₃@SiO₂@KCC-1 was quantitatively separated from the reaction mixture using an external magnet as described in Fig. 4. The spent catalyst was then thoroughly washed in turn with water and ethanol and reused in subsequent runs under identical reaction conditions. As displayed in Fig. 7, Au/ γ -Fe₂O₃@SiO₂@KCC-1 could be successfully recycled and reused for at least six times with stable conversion above 96% within 6 min in the reduction of 4-NP.

Table 1. Comparison of the catalytic activity for the reduction of 4-NP between Au/ γ -Fe₂O₃@SiO₂@KCC-1 and some catalysts reported in the literature.

Samples	Catalyst used (mg)	NMNPs loading (wt%)	K_{app} (s^{-1})	K_M ($\text{s}^{-1} \text{ g}^{-1}$)
Au/MPC ⁴⁴	0.3	3.93	1×10^{-2}	848.2
Au/graphene ⁴⁵	0.1	24	3.17×10^{-3}	132.08
carbon@Au ⁴⁶	0.1	22.68	5.42×10^{-3}	238.98
Pd/PPy ⁴⁷	0.0125	50.2	8.87×10^{-3}	1413
This work	0.2	4.63	1.45×10^{-2}	1565.9

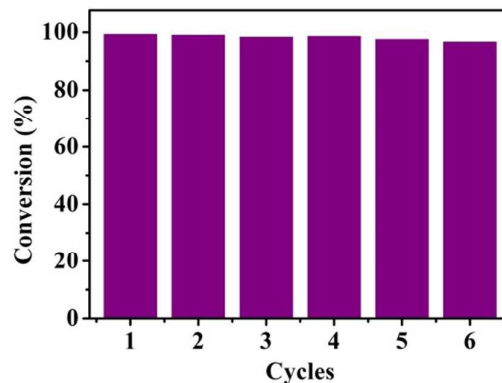


Fig. 7. The reusability of Au/ γ -Fe₂O₃@SiO₂@KCC-1 for the reduction of 4-NP with NaBH_4 .

4. Conclusions

In conclusion, the Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst was prepared by modifying uniform magnetic fibrous silica microspheres γ -Fe₂O₃@SiO₂@KCC-1 with Au NPs. The as-prepared Au/ γ -Fe₂O₃@SiO₂@KCC-1 nanocatalyst exhibited higher catalytic activity for the reduction of 4-NP to 4-AP as compared with other reported Au NPs-based catalysts, probably caused by the easy accessibility of the Au active sites. Au/ γ -Fe₂O₃@SiO₂@KCC-1 can also be easily recycled and reused, which is attributed to its superparamagnetic property. We believe that these results will be beneficial for improving catalytic activity and recyclability to develop advanced noble-metal-based catalysts.

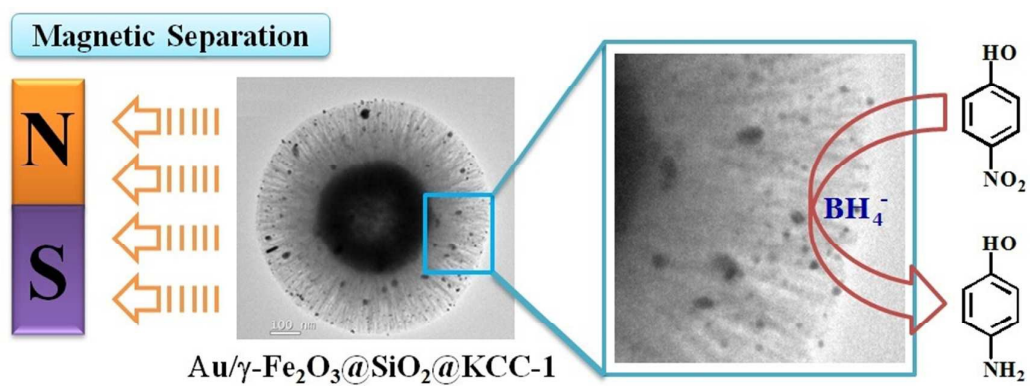
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Graphical Abstract



Au nanoparticles were immobilized on magnetic fibrous silica microspheres as highly activity and recyclable nanocatalyst for the catalytic reduction of 4-nitrophenol to 4-aminophenol.