Fe$_3$O$_4$@PANI Hybrid Shell as a Multifunctional Support for Au Nanocatalysts with a Remarkably Improved Catalytic Performance

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Supporting Information

ABSTRACT: Au@Fe$_3$O$_4$@PANI hybrid shells with controllable polyaniline (PANI) coatings as advanced supported catalysts have been fabricated. Specifically, Fe$_3$O$_4$ and Au nanoparticles were assembled on SiO$_2$ templates, followed by conducting polymer PANI coating, leading to the formation of Au@Fe$_3$O$_4$@PANI hybrid shells after the template removal. The resultant supported Au nanocatalysts not only maintain hollow structures but also possess high saturation magnetization (65.46 emu/g). Catalytic tests toward the reduction of 4-nitrophenol in the presence of NaBH$_4$ indicate that PANI and Fe$_3$O$_4$ not only endow high stability and recyclability but also can largely improve the catalytic activity of Au nanoparticles because of their synergistic effects. It is believed that Fe$_3$O$_4$@PANI hybrid shells can be regarded as multifunctional supports for noble metal nanocatalysts with a remarkably improved catalytic performance.

1. INTRODUCTION

Since the discovery of catalytic activity of Au nanoparticles toward CO oxidation, noble metal nanoparticles have been extensively studied as nanocatalysts involved in numerous catalytic reactions. As heterogeneous nanocatalysts, in addition to catalytic activity, recyclability and stability are also highly important from the economic and practical points of view. The most popular way is to introduce the typical superparamagnetic Fe$_3$O$_4$ microspheres as magnetic cores to improve the separation efficiency, followed by porous-structured materials coated with noble metal nanoparticles encapsulated in the channels or nanopores to avoid aggregation of neighboring nanocatalysts. However, the improvement in recyclability and stability is always accompanied by the loss of catalytic activity of noble metal nanoparticles. Undoubtedly, the introduction of Fe$_3$O$_4$ microspheres can bring in magnetism; however, the nanochannels of porous shells will be blocked inside, which is adverse to diffusion and concentration of reagents involved in catalytic reactions and therefore resulting in decreased catalytic activity. In addition, the synergistic effect toward improved catalytic activity of noble metal nanoparticles resulting from intact interfacial interaction between Fe$_3$O$_4$ and noble metal nanoparticles has rarely been used.

Recently, Fe$_3$O$_4$–noble metal Janus nanostructures have aroused considerable attention because of their intriguing nanostructures and novel properties. The interfacial interaction between Fe$_3$O$_4$ and noble metal nanoparticles has been established to contribute to the improved catalytic activity of noble metal nanoparticles. However, from the practical point of view as heterogeneous nanocatalysts, Fe$_3$O$_4$–noble metal Janus nanostructures still suffer from relatively low saturation magnetization. In addition, the dipole interactions between Fe$_3$O$_4$ nanoparticles will pull the adjacent Fe$_3$O$_4$ nanoparticles close to each other, resulting in aggregation. Although the construction of Fe$_3$O$_4$–noble metal Janus nanostructures can maintain the improved catalytic activity, the recyclability and stability remain unsolved.

Herein, we present a proof-of-concept demonstration that when Fe$_3$O$_4$ nanoparticles as the magnetic component are implanted in porous shells with compact interactions with noble metal nanoparticles, not only high saturation magnetization can be brought in but also the synergistic effect toward improved catalytic activity of noble metal nanoparticles can be exploited. Specifically, Fe$_3$O$_4$ and Au nanoparticles were assembled on SiO$_2$ templates, followed by conducting polymer polyaniline (PANI) coating, leading to the formation of Au@Fe$_3$O$_4$@PANI hybrid shells after the template removal. The choice of PANI as the porous shells is based on the facts that PANI can be synthesized in a facile and low-cost way with inherent porous structure because of its amorphous nature, together with its conducting nature that can contribute to the improved catalytic activity of Au nanoparticles. The magnetic component Fe$_3$O$_4$ with size down to 15 nm is chosen as it can form intact interactions with Au nanoparticles assembled in a single Au@Fe$_3$O$_4$@PANI hybrid shell will guarantee high saturation magnetization. Catalytic
the SiO2@Fe3O4 and SiO2@Fe3O4@Au nanoparticles. In these nanoparticles, leading to the formation of SiO2@Au@Fe3O4@PANI hybrids were shown in Figure 1d, where the PANI core−shell hybrids can be regarded as multifunctional supports for noble metal nanocatalysts with remarkably improved catalytic performance.

2. RESULTS AND DISCUSSION

2.1. Characterization of Au@Fe3O4@PANI Hybrid Shells. Scheme 1 outlines the general procedures for preparing Au@Fe3O4@PANI hybrid shells. First, the SiO2 nanoparticles were synthesized using a modified Stöber method,17 and the surfaces were modified with APTES. Monodisperse Fe3O4 (∼15 nm) nanoparticles stabilized with oleic acid were prepared,18 followed by replacing the oleic acid with DHCA.19 Then, Fe3O4 nanoparticles can assemble on the surfaces of SiO2 nanoparticles thanks to their electrostatic interactions. Au nanoparticles (∼5 nm) were subsequently assembled on the surfaces of SiO2@Fe3O4 nanoparticles, where almost all Fe3O4 nanoparticles were attached with Au nanoparticles. Aniline monomers were then added, followed by the chemical oxidation polymerization process after the addition of oxidants to yield PANI shells on the surface of SiO2@Fe3O4@Au nanoparticles, leading to the formation of SiO2@Au@Fe3O4@PANI core−shell hybrids. After the removal of SiO2 templates, Au@Fe3O4@PANI hybrid shells can be fabricated.

The TEM images of the products obtained after each synthesis step were shown in Figure 1. Figure 1a displays the TEM image of the SiO2 nanoparticles with a diameter of approximately 150 nm. Figure 1b,c shows the TEM images of the SiO2@Fe3O4 and SiO2@Fe3O4@Au nanoparticles. In these synthesis procedures, Fe3O4 and Au nanoparticles are assembled on amino-modified silica templates successively through electrostatic interactions. As shown in Figure 1b, tens of Fe3O4 nanoparticles can be found on the surfaces of a single SiO2 nanoparticle. The TEM image of the SiO2@Au@Fe3O4@PANI hybrids was shown in Figure 1d, where the PANI polymer coating can be clearly seen.

After the removal of SiO2 templates, Au@Fe3O4@PANI hybrid shells with good monodispersity were obtained (Figure 2a,b). Figure 2c displays the typical TEM image of a single Au@Fe3O4@PANI nanoparticle. It was interesting to find that Au nanoparticles tended to attach to the already existing Fe3O4 seeds on the SiO2 templates to form a unique Fe3O4−Au Janus structure, which gave the possibility of interfacial communication between Au and Fe3O4. The typical HRTEM image of a single Fe3O4−Au Janus nanoparticle in the PANI shell is shown in Figure 2d. The interfering distance was measured to be 0.24 nm for Au and 0.25 nm for Fe3O4, corresponding to the (111) plane of face-centered cubic (fcc)-structured Au and the (311) plane of inverse spinel-structured magnetite, respectively. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image was recorded to confirm the structure of Au@Fe3O4@PANI hybrid shells. As shown in Figure 2e, the Au and Fe3O4 nanoparticles show different brightness as the brightness is proportional to the atomic number (Z). Under this circumstance, the Au nanoparticles appear brighter than Fe3O4 nanoparticles because of their higher Z. The energy-dispersive X-ray spectroscopic (EDS) elemental maps (Figure 2f−i) further confirm the expected Au@Fe3O4@PANI hybrid shell structure.

The concentration of aniline monomer was found to affect the integrity and thickness of the PANI shell. For clarity, the products were denoted as Au@Fe3O4@PANI(x), where x is the added amount of aniline monomer (in μL). As for the Au@Fe3O4@PANI(6) hybrid shell, the PANI shells are approximately 10 nm in thickness, which is too thin to cover all Fe3O4 nanoparticles (Figure 2c). The PANI shells become complete with most Fe3O4 and Au nanoparticles buried inside when the thickness of PANI shells is increased to 20 nm (Au@Fe3O4@PANI(9) hybrid shells, Figure 3a,c). The thickness of PANI shells can be further increased to 35 nm for Au@Fe3O4@PANI(12) hybrid shells (Figure 3b,d).

Figure 4a shows the FTIR spectra of SiO2@Fe3O4@Au core−shell nanoparticles and Au@Fe3O4@PANI hybrid shells. In comparison with SiO2@Fe3O4@Au core−shell nanoparticles, the characteristic absorption bands for PANI polymer in Au@Fe3O4@PANI hybrid shells can be indexed. The peaks at 1602 and 1500 cm−1 can be assigned to the quinonoid ring and the benzenoid ring, respectively,22,23 and the peaks at 1172
and 787 cm$^{-1}$ can be assigned to the aromatic C–H in-plane bending modes and out-of-plane deformations of C–H bonds on 1,4-disubstituted rings, respectively. XRD measurements were used to characterize the crystalline and phase structure of Au@Fe$_3$O$_4$@PANI hybrids. As observed in Figure 4b, the peaks at 38.18°, 44.40°, 64.68°, and 77.77° can be indexed to the (111), (200), (220) and (311) planes of fcc Au (JCPDS 04-0784), respectively, indicating the attachment of Au nanoparticles to silica templates. After the introduction of PANI, the SiO$_2$@Au@PANI core–shell nanoparticles show a broad band between 20° and 30°, which corresponded to amorphous PANI. After the addition of Fe$_3$O$_4$ and the removal of SiO$_2$ templates, the broad band of PANI becomes clearer and the peaks at 2θ = 30.18°, 35.54°, 43.10°, 57.16°, and 62.78° can be ascribed to the (220), (311), (400), (501), and (440) planes of fcc Fe$_3$O$_4$ (JCPDS 19-0629), respectively. Figure 4c shows the UV–vis spectra of SiO$_2$@Au, SiO$_2$@Fe$_3$O$_4$@Au, and Au@Fe$_3$O$_4$@PANI hybrids. SiO$_2$@Au nanoparticles display a surface plasmon resonance peak of Au at 540 nm. After the addition of Fe$_3$O$_4$, the surface plasmon resonance peak shows a 13 nm blue shift to 527 nm. The change in the surface plasmon resonance confirms the interface communication between Au and Fe$_3$O$_4$ which will contribute to the improvement in the catalytic activity. When PANI was further introduced, the surface plasmon resonance peak of Au was covered by the strong adsorption of PANI. The chemical compositions and chemical states were then detected using XPS. As shown in Figure 4d, the Au 4f doublet peaks of SiO$_2$@Au particles can be located at the binding energies of 83.6 and 87.3 eV with the splitting of the 4f doublet of 3.7 eV, indicating that Au exists only in its metallic state. The Au 4f doublet peaks of SiO$_2$@Au@Fe$_3$O$_4$ core–shell nanoparticles shifted to 83.9 and 87.6 eV, and the peaks of Au@Fe$_3$O$_4$@PANI hybrid shells further shifted to 84.1 and 87.8 eV, indicating the existence of not only the interface communication between Au and Fe$_3$O$_4$ but also the communication between Au and PANI. The VSM was used to investigate the magnetic properties of the as-prepared Au@Fe$_3$O$_4$@PANI hybrids. As shown in Figure 4e, no remanence or coercivity was detected at room temperature, indicating their superparamagnetic character. The saturation magnetization of Au@Fe$_3$O$_4$@PANI hybrids is 65.46 emu/g, which means the easy separation of the as-prepared Au@Fe$_3$O$_4$@PANI hybrid shells from reaction mixtures with a low magnetic field gradient (insets in Figure 4e). N$_2$ adsorption–desorption measurements were used to reveal the surface properties (Figure 4f). The surface area of the Au@Fe$_3$O$_4$@PANI hybrid shells is 61.08 m$^2$/g, and the average pore diameter calculated from the desorption curve is 4 nm (inset in Figure 4f).

2.2. Catalytic Performances of Au@Fe$_3$O$_4$@PANI Hybrid Shells. A model reaction, the reduction of 4-NP to 4-AP in the presence of NaBH$_4$, was chosen to monitor the catalytic performance of the as-formed Au@Fe$_3$O$_4$@PANI hybrid shells. The mixtures of 4-NP and NaBH$_4$ show an adsorption band at 400 nm corresponding to the 4-NP ions under alkaline conditions. After the addition of catalysts to the above reaction mixture, the peak at 400 nm successively decreases and another peak at 300 nm appears because of the formation of 4-AP (Figure 5a−c). It is commonly accepted that when Au nanoparticles are used for catalytic reduction, BH$_4^-$

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**Figure 2.** (a–c) TEM images of Au@Fe$_3$O$_4$@PANI(6) hybrid shells. (d) HRTEM image of a single Fe$_3$O$_4$–Au Janus nanoparticle in the PANI shell. (e) HAADF-STEM image of a single Au@Fe$_3$O$_4$@PANI(6) hybrid shell. (f–i) EDS maps of a single Au@Fe$_3$O$_4$@PANI(6) hybrid shell for (f) C, (g) Fe, (h) O, and (i) Au.

**Figure 3.** TEM images of (a,c) Au@Fe$_3$O$_4$@PANI(9) and (b,d) Au@Fe$_3$O$_4$@PANI(12).
and 4-NP are first diffused from the aqueous solution to the Au surfaces, and then, Au nanoparticles serve as catalysts to transfer electrons from BH$_4^-$ to 4-NP, leading to the formation of 4-AP.28,29

Figure 5a−c shows the time-dependent adsorption spectra of the reaction solution in the presence of SiO$_2$@Au, SiO$_2$@Fe$_3$O$_4$@Au, and Au@Fe$_3$O$_4$@PANI hybrids as catalysts. The peak at 400 nm successively decreases, and another peak at 300 nm appears because of the formation of 4-AP. It is worth noting that the adsorption effect of PANI toward 4-NP should be taken into consideration. As shown in Figure 5a−c, the adsorption equilibrium can be reached within 2 min. The reduction of 4-NP to 4-AP was totally finished within 10, 7, and 5 min (after deducting the absorption time) using SiO$_2$@Au, SiO$_2$@Fe$_3$O$_4$@Au, and Au@Fe$_3$O$_4$@PANI hybrids as catalysts, respectively. Because the reduction of 4-NP by NaBH$_4$ does not occur without catalysts and the NaBH$_4$ concentration in the reaction is much more excess, the reaction can be considered to fit the first-order rate law with respect to the concentration of 4-NP.30 The linear relation of ln($C_t$/C$_0$) versus time was observed for different catalysts (Figure 5d), where the concentration of 4-NP at time $t$ and time 0 was recorded as C$_t$ and C$_0$, respectively. The rate constant ($k$) of SiO$_2$@Au, SiO$_2$@Fe$_3$O$_4$@Au, and Au@Fe$_3$O$_4$@PANI(9) as catalysts was estimated to be 0.261, 0.353, and 0.433 min$^{-1}$, respectively. In addition, the turnover frequency (TOF) also follows the same sequence. The results indicate that both Fe$_3$O$_4$ and PANI contribute to the enhanced catalytic activity of Au (Figure 5e). The catalytic activity of Au@Fe$_3$O$_4$@PANI hybrid shells is superior to those of the reported PANI- and/or Fe$_3$O$_4$-supported noble metal nanocatalysts (Table S1). It is believed that the improvement in the catalytic activity of Au@Fe$_3$O$_4$@
PANI is due to the synergetic effect caused by electron transfer across the interface between both Au−PANI and Au−Fe3O4, which was confirmed using UV−vis and XPS analyses.

The catalytic activity of Au@Fe3O4@PANI hybrid shells with different thicknesses of PANI shells was also investigated. As shown in Figures 6a, 5c, and 6b, the reaction time first increases and then decreases as the thickness of the PANI shell increases, and the rate constant also follows the same sequence (Figure 6c). It is believed that when the PANI shell is too thin to cover all Au nanoparticles (Figure 2c), Au nanoparticles cannot make full contact with PANI. As a result, the synergetic effect between Au and PANI cannot be fully used. If the PANI shell is very thick (Figure 3d), it will take more time for the reaction molecules to establish contact with Au nanoparticles, which decrease the catalytic activity.

Magnetic property of the catalysts plays a vital role in catalytic reactions because it makes the separation and reuse of catalysts easier. As the as-formed Au@Fe3O4@PANI hybrid shells show excellent magnetic properties, they can be collected easily after the catalytic reduction. When unsupported Au nanoparticles are used as catalysts, they cannot be effectively collected after the catalytic reduction (Figure 6d). When Au nanoparticles are attached to SiO2 nanoparticles, complete loss in the catalytic activity after the fourth run can be found because of the aggregation of Au nanoparticles. After the introduction of the PANI shell, the catalysts can be recycled for six runs. As for the Au@Fe3O4@PANI hybrid shells, they can be simply recycled using a magnet and reused for at least nine successive cycles with a stable conversion efficiency of approximately 100%. Besides, the original nanostructures remained after nine cycles. These results indicate their high recyclability and stability.

3. CONCLUSIONS

In conclusion, Au@Fe3O4@PANI hybrid shells as advanced supported catalysts have been fabricated. The catalytic results indicated that the introduction of PANI and Fe3O4 could largely improve the catalytic activity because of the synergetic

Figure 5. UV−vis spectra showing gradual reduction of 4-NP using (a) SiO2@Au, (b) SiO2@Au@PANI, and (c) Au@Fe3O4@PANI(9) in the first run. (d) Plots of ln(Ct/C0) of 4-NP against time using different catalysts and (e) k and TOF of different catalysts.
effects between both Au−PANI and Au−Fe3O4. In addition, PANI and Fe3O4 could also improve the stability and recyclability of Au nanoparticles by preventing them from aggregation. The superior catalytic performance of Au@Fe3O4@PANI hybrid shells clearly indicates their potential applications as efficient heterogeneous catalysts in liquid-phase catalysis. It should be noted that there are still Au nanoparticles not well-attached to Fe3O4 nanoparticles in this case, and further improvement in the catalytic activity of Au@Fe3O4@PANI hybrid shells is still possible by maximizing the synergetic effect between Au and Fe3O4, which will be our continuing interest.

4. EXPERIMENTAL METHODS

4.1. Materials. 1-Octadecene (ODE, 90%), n-tetracosane (TCA), 3,4-dihydroxyhydrocinnamic acid (DHCA), tetraethyl orthosilicate (TEOS), and (3-aminopropyl)triethoxysilane (APTES) were purchased from Sigma-Aldrich. Oleic acid, auric acid, and all other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). The water used in this study was deionized and purified through a Millipore system.

4.2. Synthesis of Hydrophobic Fe3O4 Nanoparticles. The hydrophobic Fe3O4 nanoparticles were synthesized according to the literature.18 First, iron oleate was prepared. Iron chloride (10.8 g) and oleate sodium (36.5 g) were dissolved in a mixture solvent involving 60 mL of distilled water, 80 mL of ethanol, and 140 mL of hexane. After the reaction, the solution was stirred until the sodium oleate was dissolved completely; the mixed reaction solution was heated to 60 °C and kept refluxing for 4 h. When the reaction was finished, the upper organic layer was washed three times with 90 mL of distilled water. After the removal of hexane using a rotary evaporator, the final product is a reddish-brown viscous oil. After that, 1.8 g of iron oleate and 0.285 g of oleic acid were dissolved in 10 g of ODE at room temperature under an N2 atmosphere. After 20 min, the reaction solution was heated to 320 °C (~18 °C/min) and then kept at this temperature for 60 min. After, the resultant reaction solution containing the nanoparticles cooled to room temperature. The nanoparticles were washed three times with a mixture of hexane and acetone. The magnetic nanoparticles were dispersed into 36 mL of tetrahydrofuran (THF).

4.3. Ligand Exchange of Hydrophobic Fe3O4 Nanoparticles with DHCA. The hydrophobic magnetic nanoparticles were transferred into aqueous solution according to the literature with a reasonable modification.19 DHCA (50 mg) was dissolved in 6 mL of THF followed by heating the resultant solution to 50 °C. Then, 6 mL of hydrophobic magnetic nanoparticles in THF were added dropwise. After stirring at this temperature for 3 h, the reaction solution was cooled to room temperature. To precipitate the Fe3O4 nanoparticles, 500 μL of NaOH (0.5 M) was then added to the solution. The precipitate was collected by centrifugation (4000 rpm) and redispersed into water for further use (1 mg/mL, pH = 4).

4.4. Synthesis of Au Nanoparticles. In a typical synthesis, 555.5 mg of polyvinylpyrrolidone (PVP-K30) was added to the HAuCl4 aqueous solution (1 mM, 50 mL). The mixture was further stirred for 30 min in an ice bath. Then, NaBH4 aqueous solution (0.1 M, 5 mL) was added into the mixture rapidly under vigorous stirring and kept under stirring for 10 min.

4.5. Synthesis of Surface-Modified SiO2 Nanoparticles. Typically, ethanol (92 mL) was mixed with water (17.2 mL), ammonium aqueous solution (4 mL), and TEOS (3.44 mL). After stirring for 4 h at room temperature, the solids were separated by centrifugation and dispersed in water for further use (1 mg/mL, pH = 4).

4.6. Synthesis of SiO2@Au@Fe3O4 Core−Shell Nanoparticles. Typically, ethanol (92 mL) was mixed with water (17.2 mL), ammonium aqueous solution (4 mL), and TEOS (3.44 mL). After stirring for 4 h at room temperature, the solids were separated by centrifugation and dispersed in water for further use (1 mg/mL, pH = 4).

Figure 6. UV−vis spectra showing gradual reduction of 4-NP using (a) Au@Fe3O4@PANI(6) and (b) Au@Fe3O4@PANI(12) in the first run. (c) Plots of ln(Ct/C0) of 4-NP against time using Au@Fe3O4@PANI hybrid shells with different PANI thicknesses and (d) synthesis yield of 4-AP in the successive reactions with different catalysts.
collected by centrifugation, redispersed into 12 mL of water (pH = 4), and mixed with 4 mL of as-prepared Au aqueous solution. After stirring at room temperature for 4 h, the solid material was obtained by centrifugation.

4.7. Synthesis of Au@Fe3O4@PANI Hybrid Shells. The as-formed SiO2@Au@Fe3O4 hybrid shells were dispersed into 5 mL of deionized water. Subsequently, a certain amount of aniline was added to the above solution (pH = 1), and the solution was stirred in an ice bath for 2 h. Then, ammonium persulfate (APS) dissolved in 1 mL of deionized water (molar ratio of APS to aniline was set at 1:1) was added into the reaction solution, and the solution was stirred for 4 h. After that, the precipitate was collected by centrifugation and washed three times with deionized water and ethanol. The as-prepared SiO2@Au@Fe3O4@PANI core-shell nanoparticles were dispersed into 5 mL of water, followed by adding 0.4 g of NaOH and stirring at 70 °C for 4 h. After the solution was cooled to room temperature, the Au@Fe3O4@PANI hybrid shells were obtained by centrifugation, washed three times with water and ethanol, and then dispersed into 4 mL of water for further use.

4.8. Catalytic Reaction. Typically, an aqueous solution of NaBH4 (1.0 mL, 1.5 × 10−2 M) and 4-NP (1.7 mL, 2.0 × 10−4 M) was added into a quartz cell (1 cm path length), followed by adding 25 μL of as-prepared catalysts. Then, the progression of the conversion of 4-NP to 4-aminophenol (4-AP) was monitored using the UV–vis spectroscopy, which could record the time-dependent adsorption spectra of the reaction mixture with a time interval of certain minutes in a scanning range of 200–600 nm at ambient temperature. After each run, the catalysts were collected using a magnet, purified twice with water, and then redispersed into water for further use in the next cycle.

4.9. Characterization. Morphologies were characterized using transmission electron microscopy (TEM, JEM-2100 F) and high-resolution TEM (HRTEM, Tecnai G2 F30 S-Twin TEM, FEI) instruments. The crystal phase was analyzed using X-ray diffraction (XRD) using a Bruker AXS D8 ADVANCE X-ray diffractometer. The samples were recorded in the 2θ range from 10° to 80.0° in steps of 0.04° with a count time of 1 s each time. Fourier transform infrared (FTIR) spectra of the products were recorded in the range of 400–4000 cm−1 using FTIR spectroscopy (Tensor 27, Bruker, Germany). The samples were prepared in a pellet form with spectroscopic-grade KBr. UV–vis diffuse reflectance spectra (Cary 5000, Varian) was used to test the optical properties. The Axis Ultra X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., UK) equipped with a standard monochromator Al Kα source (hν = 1486.6 eV) was used to measure the phase composition. The binding energy of the photoelectrons was recorded under the assumption that Au has a binding energy of 84.0 eV. Magnetic measurements were recorded using a vibrating sample magnetometer (VSM, EV7, ADE, USA) with a maximum applied continuous field of 10 000 Oe at room temperature. The specific surface and the pore size were measured using a Beishide 3H-2000PS2 analysis instrument. The surface area was determined from the adsorption isotherm using the multipoint method, and the average pore size and distribution using the Barrett–Joyner–Halenda method.

■ ASSOCIATED CONTENT

* Supporting Information
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Comparison of catalytic activity of different catalysts (Table S1) (PDF)

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The authors declare no competing financial interest.

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