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Enhanced Catalytic Reduction of 4-Nitrophenol Driven by Fe₃O₄-Au Magnetic Nanocomposite Interface Engineering: From Facile Preparation to Recyclable Application

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Abstract: In this work, we report the enhanced catalytic reduction of 4-nitrophenol driven by Fe₃O₄-Au magnetic nanocomposite interface engineering. A facile solvothermal method is employed for Fe₃O₄ hollow microspheres and Fe₃O₄-Au magnetic nanocomposite synthesis via a seed deposition process. Complementary structural, chemical composition and valence state studies validate that the as-obtained samples are formed in a pure magnetite phase. A series of characterizations including conventional scanning/transmission electron microscopy (SEM/TEM), Mössbauer spectroscopy, magnetic testing and elemental mapping is conducted to unveil the structural and physical characteristics of the developed Fe₃O₄-Au magnetic nanocomposites. By adjusting the quantity of Au seeds coating on the polyethyleneimine-dithiocarbamates (PEI-DTC)-modified surfaces of Fe₃O₄ hollow microspheres, the correlation between the amount of Au seeds and the catalytic ability of Fe₃O₄-Au magnetic nanocomposites for 4-nitrophenol (4-NP) is investigated systematically. Importantly, bearing remarkable recyclable features, our developed Fe₃O₄-Au magnetic nanocomposites can be readily separated with a magnet. Such Fe₃O₄-Au magnetic nanocomposites shine the light on highly efficient catalysts for 4-NP reduction at the mass production level.

Keywords: Fe₃O₄ hollow microspheres; Fe₃O₄-Au magnetic nanocomposites; catalytic reduction; 4-nitrophenol

1. Introduction

Nowadays, numerous nitroaromatic compounds have been discharged into rivers with the overuse of dyes, explosives and pesticides in industry, causing serious water pollution [1]. Regrettably, 4-nitrophenol (4-NP) is the most typical toxic and refractory organic pollutant, attacking the eco-systems of both humans, as well as animals and consequently promoting various diseases [2]. Therefore, the degradation of 4-NP into non-toxic small molecules and in turn preventing harm has become a research hotspot in recent years [3,4].

Although it is difficult to degrade 4-NP due to the high stability and low solubility of 4-NP in water, many semiconductor nanomaterials (such as, ZnO [5], Cu₂O [6] and TiO₂ [7]) and various methods (e.g., typical photocatalysis and chemical catalysis [8]) have been developed to solve the pollution problems of 4-NP. Generally, the catalytic conversion of 4-NP to 4-aminophenol (4-AP) is an imperative process, using excess sodium borohydride as the reducing agent, not only because 4-AP is less toxic than 4-NP, but also because 4-AP is in demand on the market in many industrial fields [9]. Unfortunately, the reduction process of 4-NP to 4-AP is very slow by NaBH₄ alone. Therefore, the use of catalysts is necessary to enable electron transfer from donor B⁻H₄⁻ to acceptor 4-NP [10].

Most recently, noble metal nanocrystals have received both fundamental and practical attention owing to their potential applications in many fields such as ultrasensitive biosensing [11], imaging agents [12], photothermal therapy [13], catalysts [14], etc. Especially, Au nanoparticles (NPs) have been intensely explored because of their unique and tunable optical properties and high catalytic activities [15–19]. Compared to the semiconductor photocatalysts, noble metal catalysts possess higher catalytic activity with respect to organic pollutants [20–24]. Typically, Au NPs have been intensely employed for the catalytic reduction of a variety of organic pollutants [25]. However, Au NPs tend to agglomerate to form clusters due to their high surface area, reducing their intrinsic high catalytic activities [26,27]. To restrain the aggregation of Au NPs, considerable research efforts have been devoted to immobilization of Au NPs onto various supporting materials [28]. Several excellent reviews discussed that the stability of Au NPs could be significantly improved through solid supporting materials, such as carbon, silica, magnetic materials, and so on [29–31]. Among the various above-mentioned supports, iron oxides have received much more attention because they can be readily separated with a magnet and thereby possess the advantage of being magnetically recoverable and recyclable [32–36].

Theoretically, the shape and the size of the Fe₃O₄ play a deterministic role in defining the chemical and physical properties of Fe₃O₄ owing to the shape anisotropy [37]. For instance, the nanomaterials with a hollow structure have potential application prospects as catalysis and in biotechnology due to their higher load efficiency compared to other solid structures [38]. Therefore, Fe₃O₄ hollow microspheres have become the focus of study owing to their large specific surface area, excellent magnetic properties and hollow structural characteristics, allowing multiple different molecules to be loaded [39]. Notably, it is hard to directly attach Au NPs to the surfaces of the Fe₃O₄ hollow microspheres owing to the dissimilar nature of the two species' surfaces. The use of the mediating "glue" layer of polymers supplying a certain kind of functional group is necessary, which not only can combine Au NPs with Fe₃O₄ hollow microspheres, but also enhance the stability, water solubility and the biocompatibility of nanomaterials [40]. For example, Wang et al. [41] reported that polyethyleneimine (PEI) could self-assemble on the surfaces of Fe₃O₄ to form a polymer shell, thus adhering to Au NPs via the abundant amine groups. However, the weak electrostatic interactions among positively-charged amino groups and negatively-charged Au NPs are unreliable, resulting in the partial separation of Au NPs from the polymers. Yan et al. [42] prepared bifunctional Fe₃O₄/Au nanocomposites by the direct reduction of HAuCl₄ in the presence of carboxylate-functionalized Fe₃O₄ particles. Liu and co-workers [43] recently discovered that the bidentate ligands with two chelating sulfur groups such as the dithiocarbamates (DTCs) featuring carbodithioate (CS₂) groups were more stable than other common ligands such as thiol and amino groups in adsorbing onto the surfaces of Au

NPs, indicating that the PEI-DTC polymers may boost the Au NPs' adhesive force onto Fe₃O₄ hollow microspheres' surfaces.

In this work, by adjusting the addition rounds of Au seeds, the amount of Au seeds coating the modified surfaces of Fe₃O₄ hollow microspheres can be well controlled, and the corresponding optical, magnetic and catalytic performances are investigated. Fe₃O₄-Au magnetic nanocomposites consisting of Fe₃O₄ hollow microspheres, PEI-DTC polymers and Au NPs are successfully utilized as effective nanocatalysts for the reduction of 4-NP to 4-AP by NaBH₄. The aim of this study is to provide a new generation of magnetic nanocomposites with high catalytic efficiency and recyclable application to organic pollutants. The preparation and catalytic process to 4-NP of the Fe₃O₄-Au magnetic nanocomposites are shown in Figure 1.

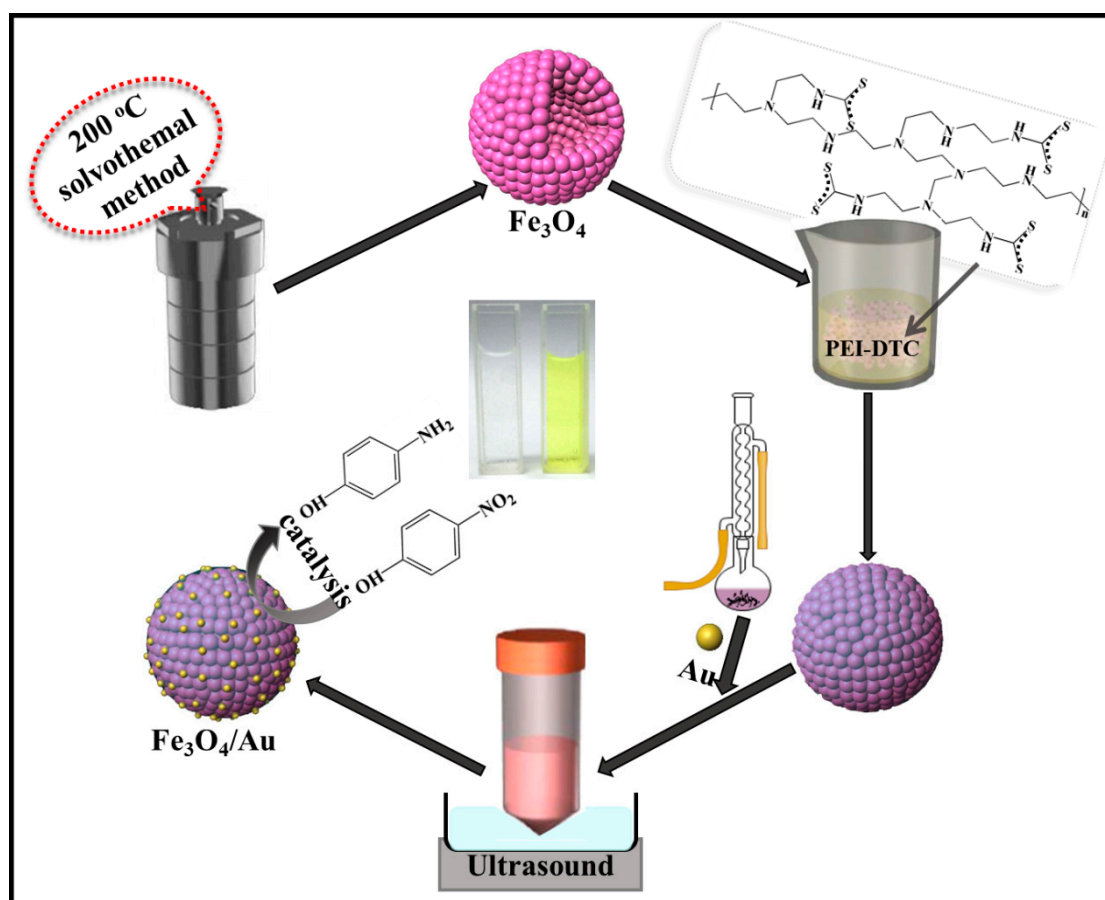


Figure 1. Schematic illustration of the fabrication process and catalytic application to 4-nitrophenol (4-NP) of Fe₃O₄-Au magnetic nanocomposites. PEI-DTC, polyethyleneimine-dithiocarbamate.

2. Experimental Section

2.1. Materials' Development

Chemicals, including methanol, polyethyleneimine (PEI, branched, MW \approx 25,000 g/mol) and carbon disulfide (CS₂), were purchased from Aladdin industrial Co., Ltd. (Shanghai, China). Iron chloride hydrate (FeCl₃·6H₂O) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Ethylene glycol (EG), sodium dodecyl sulfate (SDS), sodium acetate (NaAc·3H₂O), potassium hydroxide (KOH), sodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O), 4-nitrophenol (4-NP) and gold (III) chloride hydrate (HAuCl₄·3H₂O), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The aforementioned reagents were analytical grade and were utilized without further purification.

2.2. Synthesis of Fe₃O₄ Hollow Microspheres

In a typical synthesis process for the Fe₃O₄ hollow microspheres, 1.62 g FeCl₃·6H₂O were dispersed in 60 mL EG into a beaker with mechanical stirring at room temperature. After 30 min, 2.70 g NaAc·3H₂O and 0.1839 g SDS were added to the mixture. The mixture solution was vigorously stirred for 1 h until it became homogeneous. Then, the mixture was transferred to the Teflon-lined stainless steel autoclave, and it was kept at 200 °C for 12 h. After the samples were cooled to room temperature naturally, the products were obtained by centrifuging, sequentially rinsed with ethanol and deionized water for five times and subsequently dried under vacuum at 60 °C over night to obtain the Fe₃O₄ hollow microspheres.

2.3. Gold Seeds Synthesis

Approximately 80 mg Na₃C₆H₅O₇·2H₂O were dissolved in 8 mL deionized water. Two milliliters of 58 mM HAuCl₄·3H₂O were diluted into 198 mL of deionized water with vigorous stirring. The mixture was subsequently heated under reflux at 105 °C. The well-prepared sodium citrates were steadily added dropwise. The reaction mixtures were sustained for 15 min under stirring and reflux, leading to a buff to burgundy color change. The mixture was eventually cooled down to room temperature naturally.

2.4. PEI-DTC Synthesis

Five hundred milligrams of PEI (0.02 mmol) and 650 mg KOH (11.6 mmol) were dissolved in 50 mL methanol under magnetic stirring with completely dissolved KOH. The solution was then purged with N₂ for 15 s in order to exhaust the oxygen thoroughly, and 695 µL of CS₂ (11.6 mmol) was added by dripping slowly into the mixed solution. PEI-DTC was obtained with stirring for 10 min with a solution color change to light yellow.

2.5. Fe₃O₄@PEI-DTC-Au Seeds' Synthesis

In this step, the surfaces of Fe₃O₄ hollow microspheres were functionalized with PEI-DTC. Ten milligrams of Fe₃O₄ hollow microspheres were washed with methanol three times. PEI-DTC solution droplets were injected with a pipette under vortexing. The developed mixture was then kept for 1 h. The precipitate was gathered with a dedicated external magnet and rinsed with deionized water three times to remove the unnecessary PEI-DTC. Finally, Fe₃O₄@PEI-DTC NPs were re-dispersed in deionized water.

In comparison with counterpart bulk composites, equipped with a large surface area, the nanostructured materials demonstrate superior optical, magnetic and electrical characteristics [44–48]. The preparation of Fe₃O₄@PEI-DTC-Au seed nanocomposites is as follows. The as-obtained 10 mL of gold seed colloids were added dropwise into the 4 mL of Fe₃O₄@PEI-DTC NPs. Then, Fe₃O₄@PEI-DTC-Au nanocomposites were rinsed with deionized water and the same process repeated, and the sample was named as Fe₃O₄-Au 20 mL. Additional samples were prepared with the same conditions as Fe₃O₄-Au 20 mL, while the amount of gold seed colloids was changed to 40 and 60 mL, named as Fe₃O₄-Au 40 mL and Fe₃O₄-Au 60 mL, respectively.

2.6. Application of Fe₃O₄-Au Magnetic Nanocomposites for Catalytic Reduction of 4-NP

The catalytic ability of Fe₃O₄-Au magnetic nanocomposites was performed in a cuvette with 1 mg of Fe₃O₄-Au for the reduction of 4-NP (0.005 mol/L, 1 mL) in the presence of NaBH₄ (0.2 mol/L, 1 mL). The UV-Vis spectrophotometer was used to record the catalytic reduction rate at different time intervals in the scanning range of 200–500 nm.

In order to study the recyclability of the prepared Fe₃O₄-Au magnetic nanocomposites, the samples were collected with a magnet from the reaction solution when the reduction process was completed. The obtained magnetic nanocomposites were rinsed with deionized water and ethanol

three times and then repeated in the next reaction. The same catalytic reduction process to 4-NP was repeated six times.

2.7. Characterizations

The structure and morphology of the samples were characterized by X-ray diffractometer (XRD) (Rigaku D/Max-2500, Rigaku Corporation, Tokyo, Japan), Mössbauer spectrum (FAST Comtec Mössbauer system, FAST Comtec, Oberhaching, Germany), X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA), field-emission scanning electron microscopy (FESEM) (JEOL JSM-7800F, JEOL Ltd., Tokyo, Japan) and transmission electron microscope (TEM) (JEOL 2100, JEOL Ltd., Tokyo, Japan). Ultraviolet-visible spectroscopy (UV-Vis) spectra and magnetic properties were measured with a Shimadzu UV 3600 spectrophotometer (Shimadzu Corporation, Tokyo, Japan) and a quantum design MPMS3 superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc., San Diego, CA, USA), respectively.

3. Results and Discussion

3.1. X-ray Diffraction of the Fe_3O_4 -Au Magnetic Nanocomposites

Figure 2a shows XRD patterns of the as-obtained pure Fe_3O_4 hollow microspheres and Fe_3O_4 -Au magnetic nanocomposites with the various amounts of gold seed colloids added (Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL). As for the pure Fe_3O_4 hollow microspheres, the diffraction peaks located at 30.4° , 35.5° , 43.4° , 53.4° , 57.3° and 62.8° were indexed to (220), (311), (400), (422), (511) and (440) of Fe_3O_4 (Joint Committee on Powder Diffraction Standards, JCPDS 19-0629), respectively [21,49]. The average crystallite size of the pure Fe_3O_4 hollow microspheres was about 576.5 nm calculated by the Debye–Scherrer equation [50]. Four additional peaks of Fe_3O_4 -Au magnetic nanocomposites at about 38.4° , 44.5° , 64.7° and 77.5° could be assigned into the (111), (200), (220) and (311) of Au (JCPDS 04-0784), respectively, suggesting the coexistence of Fe_3O_4 and Au [51,52]. Figure S1 presents the Pawley refinement of the XRD pattern of the pure Fe_3O_4 hollow microspheres. The residual weighted profile R-factor (Rwp) of the sample is 15.74%, which indicates that the sample is in agreement with the standard magnetite Fe_3O_4 . In addition, it is well established that the area of the diffraction peak of XRD patterns is proportional to the contents of that phase in the mixture. Increasing addition times of gold seed colloids enhanced the diffraction peaks of Au, implying that the number of the gold seeds coating the surfaces of Fe_3O_4 hollow microspheres increases.

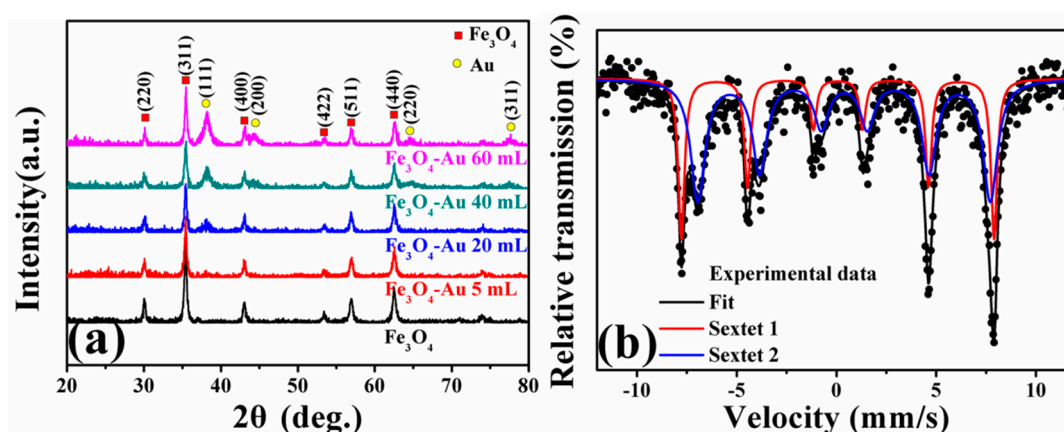


Figure 2. XRD patterns of the as-prepared pure Fe_3O_4 hollow microspheres and Fe_3O_4 -Au magnetic nanocomposites with the different addition quantities of the gold seed colloids (Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL) (a); Mössbauer spectra of pure Fe_3O_4 hollow microsphere (b).

Because magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$ have nearly the same crystal structure of an inverse spinel type, it is difficult to differentiate them only based on the XRD results. The Mössbauer spectrum is an available characterization technique to distinguish magnetite from maghemite [53,54]. Mössbauer spectra of Fe_3O_4 hollow microspheres fitted with two sextets (Zeeman splitting patterns) are shown in Figure 2b. The acute and strong lines of the magnetic sextets show a characteristic double six-peak structure of magnetite Fe_3O_4 [55]. The hyperfine field is 48.5 and 45.5 Tesla, and the isomer shift is 0.603 and 0.287 mm/s, corresponding to Fe^{2+} and Fe^{3+} ions at octahedral interstitial sites and Fe^{3+} ions at tetrahedral interstitial sites, respectively. Table 1 lists the fitted Mössbauer parameters. All these results testify that the as-obtained sample is a pure magnetite Fe_3O_4 instead of maghemite $\gamma\text{-Fe}_2\text{O}_3$ and consistent with the results reported by Ghosh et al. [56]. In fact, the oxidation product of the magnetite Fe_3O_4 is either maghemite $\gamma\text{-Fe}_2\text{O}_3$ or hematite $\alpha\text{-Fe}_2\text{O}_3$, which strongly depends on the oxidation temperature. Generally, a high temperature heat treatment is necessary to realize the phase transition of magnetite Fe_3O_4 , which indirectly suggests that the structure of magnetite Fe_3O_4 is stable at room temperature [57,58].

Table 1. Mössbauer spectrum parameters of pure Fe_3O_4 hollow microspheres: IS is the isomer shift, QS the quadrupole splitting, HIN the hyperfine field, HWHM the half width at half maximum and AREA the relative absorption area.

Composition	IS (mm/s)	QS (mm/s)	HIN (T)	HWHM (mm/s)	AREA (%)
A	0.287	0.015	48.5	0.186	34.3
B	0.603	0.012	45.5	0.433	65.7

3.2. Morphology of the Fe_3O_4 -Au Magnetic Nanocomposites

The specific structure and morphology of the developed Fe_3O_4 -Au magnetic nanocomposites were studied by TEM and SEM. In particular, TEM measurement is an effective methodology for structure research in materials science and materials engineering [59–71]. Figure 3 displays SEM and TEM images of pure Fe_3O_4 hollow microspheres. It can be observed that the pure Fe_3O_4 hollow microspheres are spherical shape. The average crystallite size is about 576 nm, and the samples show the narrow size distribution, as shown in Figure S2. TEM and SEM images of Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL are presented in Figure 4 and Figure S3. The as-prepared Fe_3O_4 -Au magnetic nanocomposites consist of the Fe_3O_4 hollow microspheres and the gold seeds of about 16 nm in diameter. Clearly, the gold seeds are randomly and homogeneously attached to the surfaces of the Fe_3O_4 hollow microspheres. Gold seeds are seen black, and Fe_3O_4 hollow microspheres present a light color in the TEM images, attributed to the higher electron density of Au compared to that of Fe_3O_4 [72]. It can be easily observed from the high-resolution TEM (HRTEM) image in the inset of Figure 4b that the interplanar distance values are 0.204 and 0.217 nm, matching the (220) lattice plane of Fe_3O_4 and the (111) lattice plane of Au, respectively [73]. The selected area electron diffraction (SAED) pattern of Fe_3O_4 -Au 40 mL is presented in the inset of Figure 4c, consisting of both the (220), (311), (400) and (511) diffraction rings of Fe_3O_4 and the (111), (200), (220) and (311) diffraction rings of Au [43]. The HRTEM and SAED results further verify the coexistence of Fe_3O_4 and Au. An interesting finding is that when increasing Au seed colloids' addition times, the gold seed contents on Fe_3O_4 surfaces are further boosted, which is consistent with the aforementioned XRD data. This is supported by the following elemental mapping images.

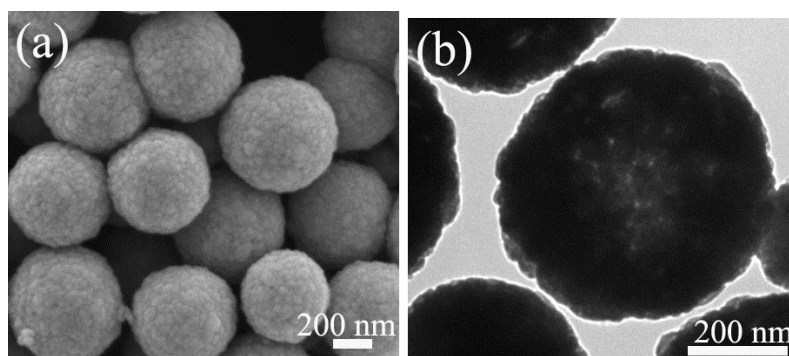


Figure 3. SEM images (a) and TEM images (b) of pure Fe_3O_4 hollow microspheres.

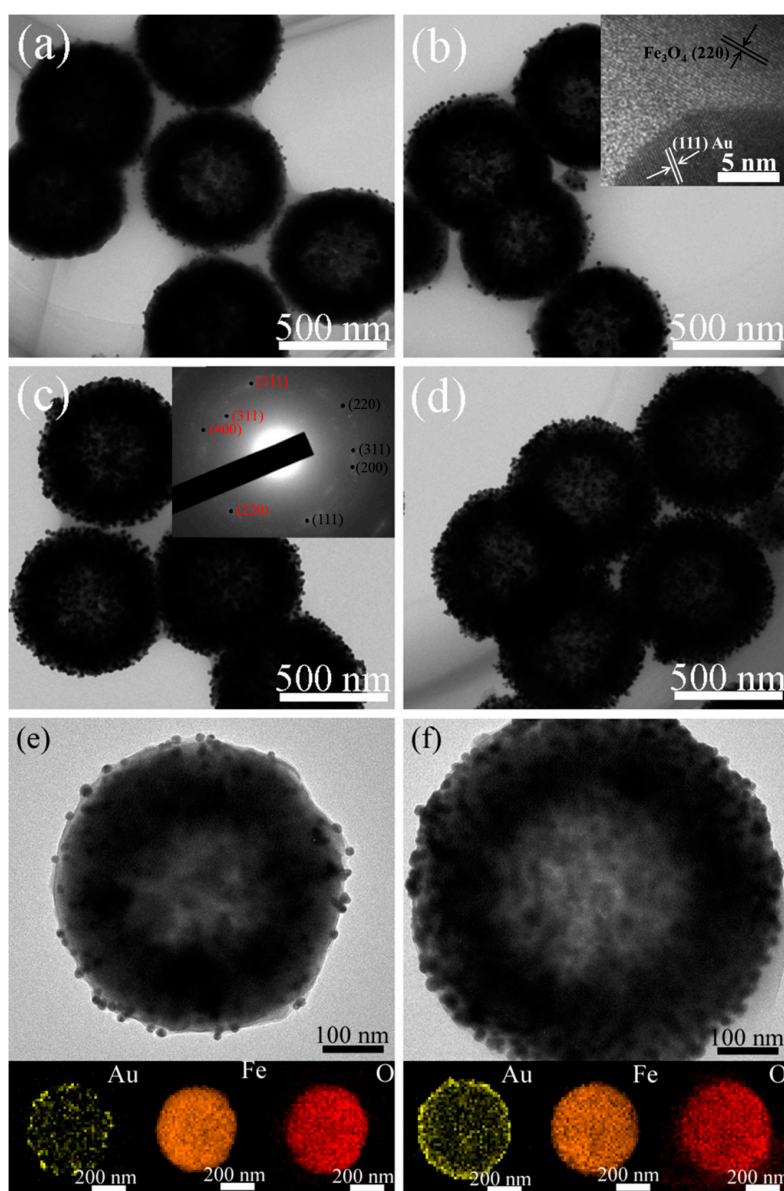


Figure 4. TEM images of Fe_3O_4 -Au 5 mL (a) and Fe_3O_4 -Au 20 mL with the HRTEM image (inset) (b); Fe_3O_4 -Au 40 mL with the SAED pattern (inset) (c) and Fe_3O_4 -Au 60 mL (d); TEM images of single Fe_3O_4 -Au 5 mL (e) and Fe_3O_4 -Au 60 mL (f) microspheres and corresponding EDS elemental mapping images (Au, Fe and O).

Figure 4e,f shows the TEM images of single Fe_3O_4 -Au 5 mL and Fe_3O_4 -Au 60 mL microspheres and corresponding energy-dispersive X-ray (EDS) mapping images of Au, Fe and O elements [74,75]. It could be clearly found that the Fe_3O_4 hollow microspheres have hollow internal structures, and Au seeds are homogeneously attached to the surfaces of the Fe_3O_4 hollow microspheres. In addition, compared with Fe_3O_4 -Au 5 mL, the amount of gold seeds on the surfaces of Fe_3O_4 for Fe_3O_4 -Au 60 mL increases significantly.

3.3. Optical Properties of the Fe_3O_4 -Au Magnetic Nanocomposites

UV-Vis spectroscopy studies are carried out to investigate the optical properties of pure Fe_3O_4 hollow microspheres and Fe_3O_4 -Au magnetic nanocomposites. Figure 5 presents the UV-Vis spectra of pure Fe_3O_4 hollow microspheres, Au seed colloids, Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL magnetic nanocomposites. No absorption peak is observed for the pure Fe_3O_4 hollow microspheres in the visible wavelength span [34,76]. The Au gold seed colloids display a characteristic surface plasmon resonance (SPR) peak at ~ 520 nm on account of the coherent excitation of the free electrons within the conduction band [77]. In addition, all the Fe_3O_4 -Au magnetic nanocomposites show a clear characteristic SPR band of gold nanostructures. Interestingly, the absorption peak of Fe_3O_4 -Au magnetic nanocomposites is broadened and shows a slight red shift compared with that of pure Au seed colloids. The more Au seeds are deposited on Fe_3O_4 hollow microspheres' surfaces, the more evident the red shift of the absorption peak is. The absorption band shows a red-shift from 526 nm for Fe_3O_4 -Au 5 mL to 540 nm for Fe_3O_4 -Au 60 mL. This red shift of the SPR absorption band can be ascribed to plasmon hybridization and the surface plasmon coupling of neighboring Au seeds deposited on Fe_3O_4 hollow microspheres [52,78].

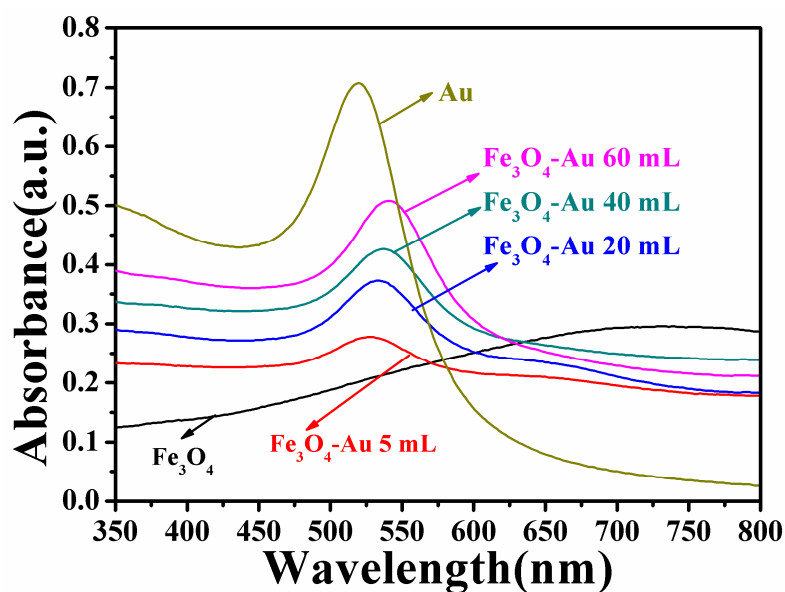


Figure 5. UV-Vis absorption spectra of pure Fe_3O_4 hollow microspheres, Au seed colloids, Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL magnetic nanocomposites.

3.4. XPS of the Fe_3O_4 -Au Magnetic Nanocomposites

XPS was applied to characterize the elemental chemical states and chemical compositions of the pure Fe_3O_4 hollow microspheres and Fe_3O_4 -Au magnetic nanocomposites. The C 1s peak at 284.8 eV is applied as the reference for charge correction [79]. The XPS results of Fe_3O_4 , Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL are shown in Figure 6. Figure 6a is the high-resolution scans of the XPS spectra for Fe 2p. The binding energy of pure Fe_3O_4 hollow microspheres is assessed at 711.2 and 724.5 eV by using Gaussian-Lorentzian fitting and assigned to

the Fe 2p_{3/2} and Fe 2p_{1/2} of magnetite Fe₃O₄, respectively [80]. As for Fe₃O₄-Au 20 mL (Figure 6b), the peak doublet appearing at 83.9 and 87.9 eV with a spin orbit splitting of ~4 eV is assigned to Au 4f_{7/2} and Au 4f_{5/2}, respectively [81]. It is important to highlight that with the increase of the quantity of the Au seeds on the Fe₃O₄ surfaces, the intensity of Fe 2p decreases and the intensity of Au 4f increases, because the intensity of XPS spectra is proportional to the atomic concentration and the atomic sensitivity factor [82]. Meanwhile, Fe 2p-associated peaks shift toward lower binding energy, while Au 4f peaks shift toward the opposite binding energy side. The shift in binding energy provides evidence of an interaction between Au and Fe₃O₄. The chemical shifts in the Fe 2p peaks and Au 4f peaks are probably caused by the transfer of charge carriers at the metal-oxide interfaces [83–85]. As shown in Figure 6c, the O 1s spectrum of pure Fe₃O₄ exhibits only a single peak at 532.8 eV, and no obvious shift of peak position is observed [86]. The survey scan results demonstrate that all the indexed peaks correspond to those of Fe, Au, O and C (Figure 6d).

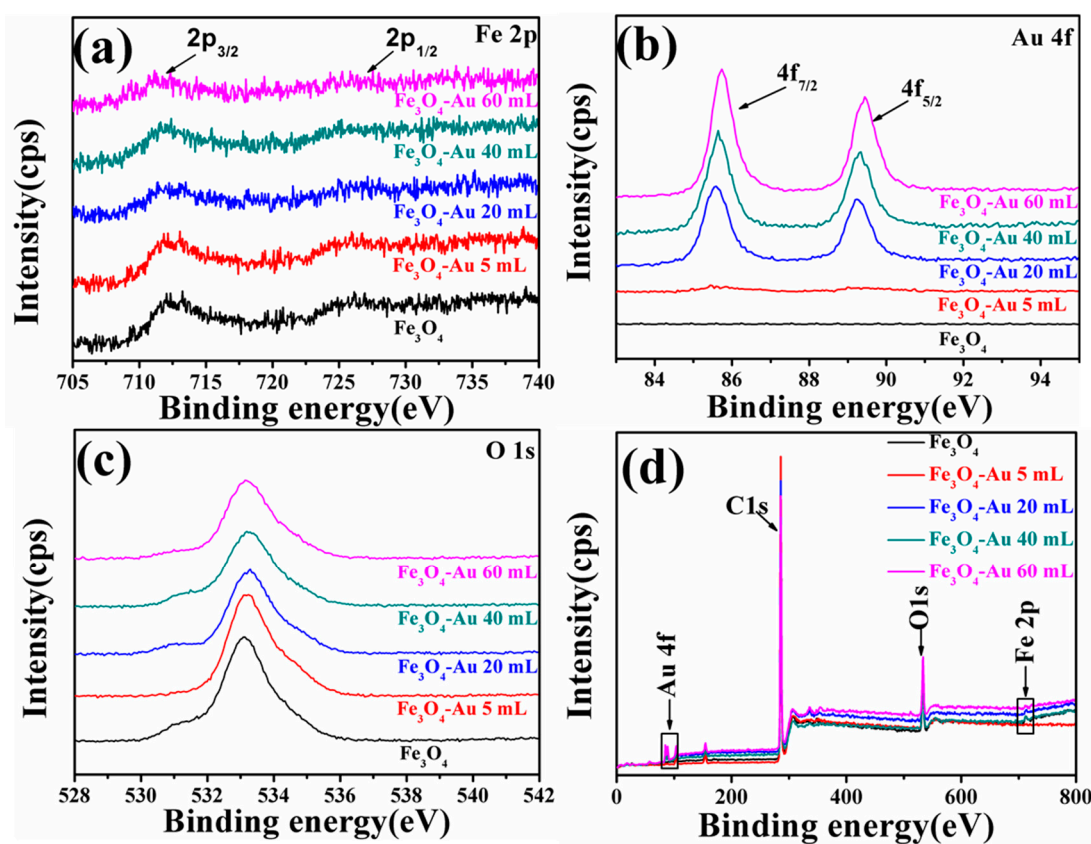


Figure 6. XPS spectra of the as-obtained Fe₃O₄, Fe₃O₄-Au 5 mL, Fe₃O₄-Au 20 mL, Fe₃O₄-Au 40 mL and Fe₃O₄-Au 60 mL: the Fe 2p binding energies (a); the Au 4f binding energies (b); the O1s binding energies (c) and XPS survey spectra (d).

3.5. Magnetic Properties of the Fe₃O₄-Au Magnetic Nanocomposites

The magnetic properties of the obtained samples were measured using SQUID. The magnetization versus magnetic field (M-H) loops of pure Fe₃O₄ hollow microspheres and Fe₃O₄-Au magnetic nanocomposites are presented in Figure 7. The M-H loops of all the samples are S-shaped curves and exhibit negligible coercivity and remanence, which is the typical characteristic of superparamagnetic nanomaterials [87]. Moreover, in order to confirm the superparamagnetism of the as-obtained sample, the temperature-dependent magnetization (M-T) on pure Fe₃O₄ hollow microspheres was measured under zero-field-cooled (ZFC) and 1000 Oe field-cooled (FC) conditions (Figure S4). With the increase of temperature, the magnetization increases to a maximum at the blocking temperature and then

decreases, consistent with the superparamagnetic behavior [88]. The saturation magnetization (M_s) of pure Fe_3O_4 hollow microspheres reaches up to 93.2 emu/g, but the M_s value of Fe_3O_4 -Au 5 mL reduces to 88.1 emu/g. Further coating with the gold seeds results in a continuous decrease of the M_s value. As for Fe_3O_4 -Au 60 mL, the M_s value is only 68.6 emu/g. The gradual decrease in the M_s value can be ascribed to the increase in the weight ratio of Au seeds to Fe_3O_4 hollow microspheres or the diamagnetic contribution of the Au seeds deposited onto the surfaces of the Fe_3O_4 hollow microspheres [89–91]. It must also be mentioned that although M_s values decrease owing to the introduction of Au seeds, the Fe_3O_4 -Au magnetic nanocomposites retain the strong magnetic responsiveness and can be easily magnetically collected from aqueous solution by the magnet (as shown in the inset of Figure 7), which is beneficial to their economic and reusable applications.

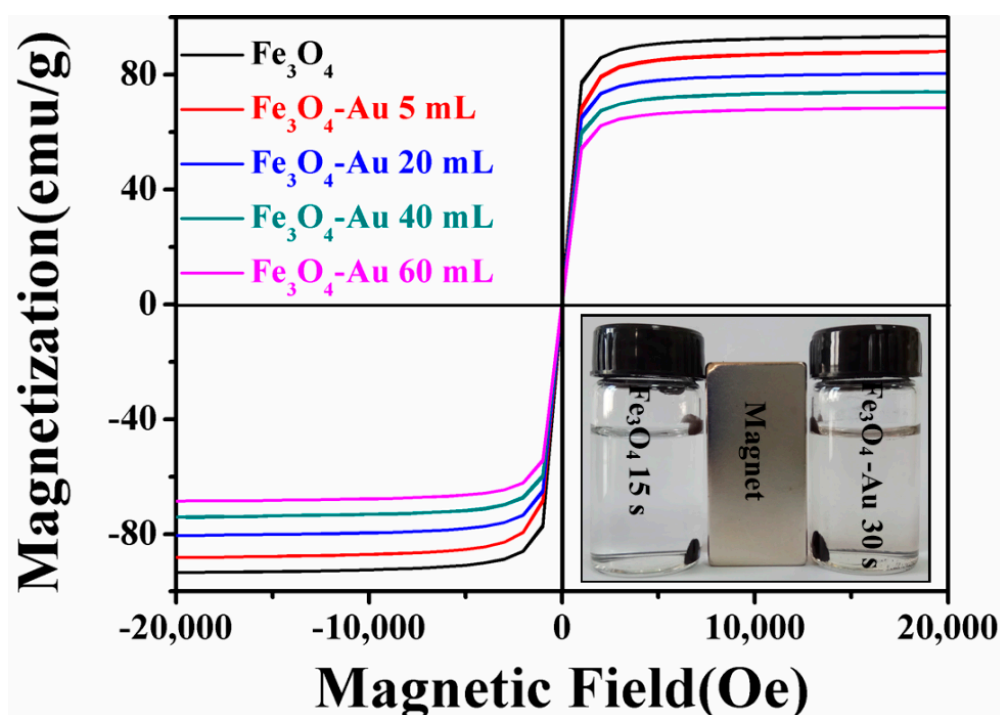


Figure 7. Magnetic hysteresis (M-H) loops of Fe_3O_4 , Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL. The inset is the photograph of pure Fe_3O_4 hollow microspheres and Fe_3O_4 -Au 60 mL magnetic nanocomposites in deionized water after using a magnet.

3.6. Catalytic Activity of Fe_3O_4 -Au Magnetic Nanocomposites to 4-NP

To study the catalytic performance of Fe_3O_4 -Au magnetic nanocomposites to organic pollutants, the catalytic reduction of 4-NP in the presence of excess NaBH_4 was selected as a model reaction. As shown in Figure S5, the original aqueous 4-NP solution has a maximum absorption peak at 317 nm. If the catalysts are absent, the absorption peak at 317 nm is unchanged even after a couple of days [20]. Once freshly obtained NaBH_4 solution is added, the absorption peak at 317 nm shifts to 400 nm due to the formation of 4-nitrophenolate ions, and meanwhile, the color of the mixture changes from light yellow to dark yellow [92]. However, the reduction reaction cannot be produced without gold seeds even in the presence of excess NaBH_4 , as can be testified in Figure S6. There is almost no change in the intensity at 400 nm after 480 min, indicating that the addition of pure Fe_3O_4 hollow microspheres has little influence on the reduction of 4-NP. Figure 8 exhibits UV-Vis absorption spectra of 4-NP catalyzed by the different Fe_3O_4 -Au magnetic nanocomposites (Fe_3O_4 -Au 5 mL, Fe_3O_4 -Au 20 mL, Fe_3O_4 -Au 40 mL and Fe_3O_4 -Au 60 mL) in the presence of NaBH_4 at a certain time interval. When Fe_3O_4 -Au magnetic nanocomposites are introduced into the reaction system, the absorption peak of all the samples at 400 nm decreases in intensity. At the same time, a new peak located at 300 nm

appears and increases concomitantly in intensity with the reaction time, which is attributed to the formation of 4-AP, the corresponding product in the reduction of 4-NP. The whole peak at 400 nm disappears after 40, 12, 4 and 2 min catalyzed by Fe₃O₄-Au 5 mL, Fe₃O₄-Au 20 mL, Fe₃O₄-Au 40 mL and Fe₃O₄-Au 60 mL, respectively. The color of the solution transforms from yellow to colorless, demonstrating that the 4-NP is completely changed into 4-AP and no other byproducts are generated. The corresponding pseudo-first-order plots of $\ln(C/C_0)$ versus reaction time over different Fe₃O₄-Au magnetic nanocomposites are portrayed in Figure 9. The concentration of NaBH₄ is identified as a constant because it is much more excessive compared to that of 4-NP. The ratio of C (the concentration of 4-NP at reaction time t) to C₀ (the initial concentration of 4-NP) is obtained from the relative intensity of respective absorbance (A_t/A_0) at 400 nm. The linear relationship of $\ln(C/C_0)$ against reaction time represents that the reduction of 4-NP by the Fe₃O₄-Au magnetic nanocomposites follows the pseudo first order kinetics. The rate constant (k) can be calculated by a liner plot of $\ln(C/C_0)$ vs. reduction time. The rate constants of 4-NP are 0.0738, 0.228, 0.857 and 3.031/min using Fe₃O₄-Au 5 mL, Fe₃O₄-Au 20 mL, Fe₃O₄-Au 40 mL and Fe₃O₄-Au 60 mL as nanocatalysts, respectively. Obviously, the rate constants for 4-NP reduction increase when increasing Au seed addition rounds. It is reasonable that if the noble metal nanomaterials' loading is increased, the mass fraction of the noble metal nanomaterials is higher in the final samples, and thus, a better catalytic performance should be accomplished [93]. We thus propose that the catalytic capability of Fe₃O₄-Au magnetic nanocomposites could be greatly improved when more gold seeds cover the surfaces of the Fe₃O₄ hollow microspheres.

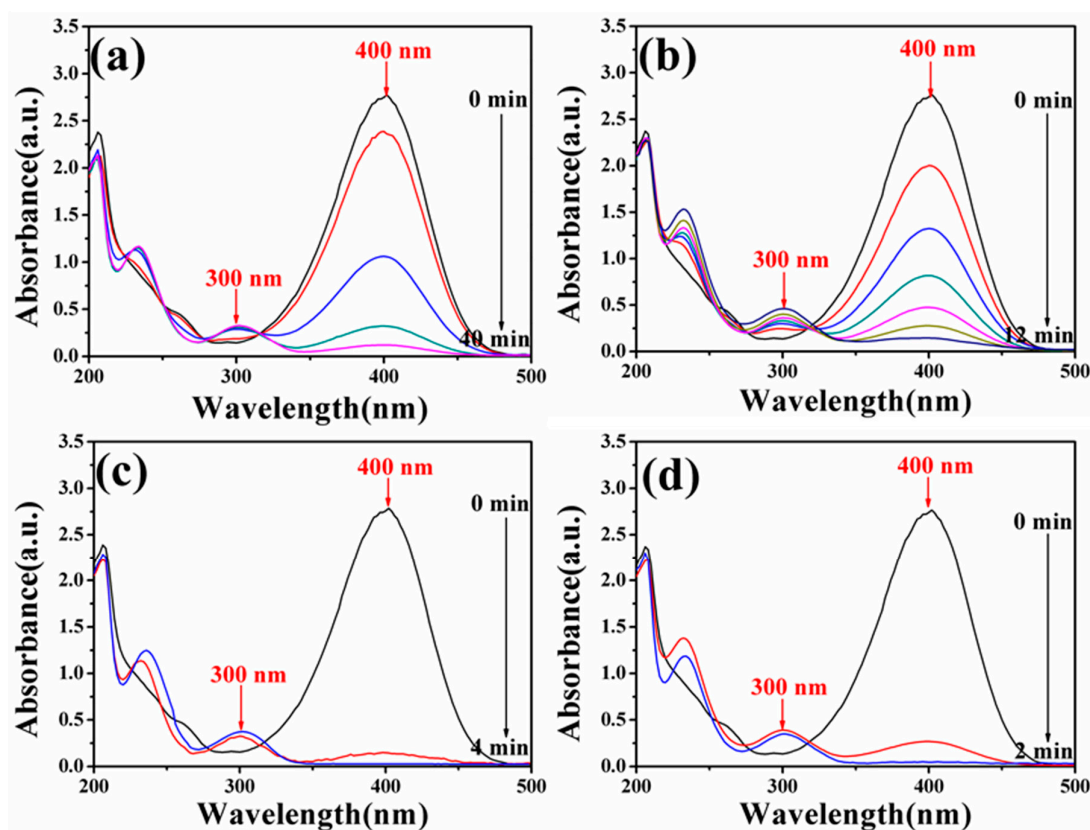


Figure 8. UV-Vis absorption spectra of 4-NP after reduction catalyzed by Fe₃O₄-Au 5 mL (a); Fe₃O₄-Au 20 mL (b); Fe₃O₄-Au 40 mL (c) and Fe₃O₄-Au 60 mL (d).

To implement the practical application of Fe₃O₄-Au magnetic nanocomposites, their stability and the recyclability are essential. All the Fe₃O₄-Au magnetic nanocomposites were separated magnetically and reused after catalytic reduction of 4-NP. As shown in Figure 10, all the samples can be successfully reused for at least six reaction runs for the catalytic reduction of 4-NP, elaborating that the Fe₃O₄-Au

magnetic nanocomposites possess the excellent stability and can serve as recoverable and efficient nanocatalysts of the organic pollutants.

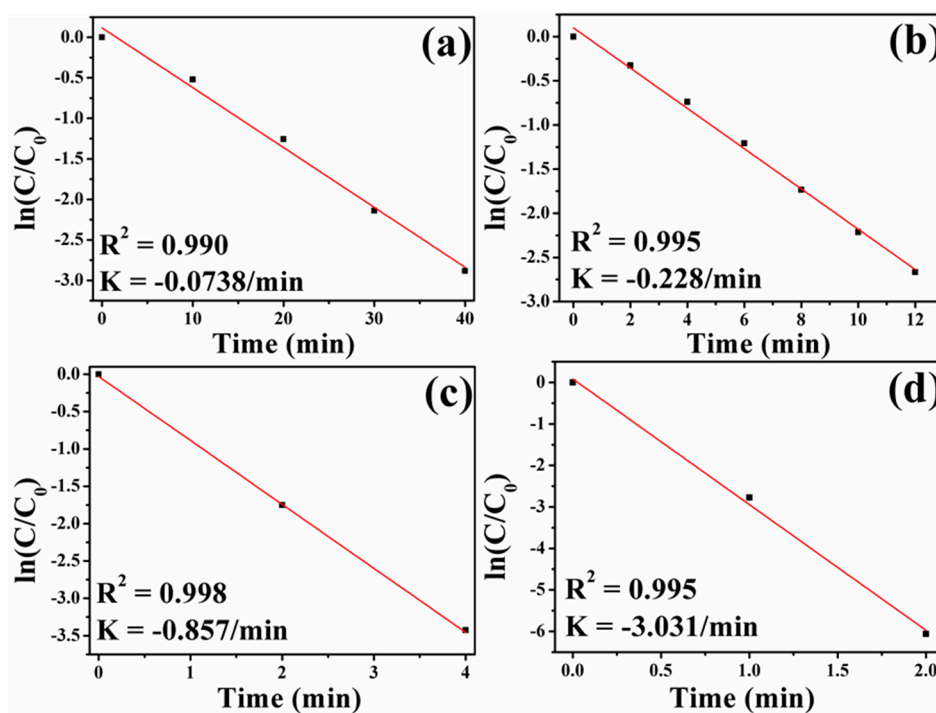


Figure 9. Plots of $\ln(C/C_0)$ against reaction time: $\text{Fe}_3\text{O}_4\text{-Au}$ 5 mL (a); $\text{Fe}_3\text{O}_4\text{-Au}$ 20 mL (b); $\text{Fe}_3\text{O}_4\text{-Au}$ 40 mL (c) and $\text{Fe}_3\text{O}_4\text{-Au}$ 60 mL (d).

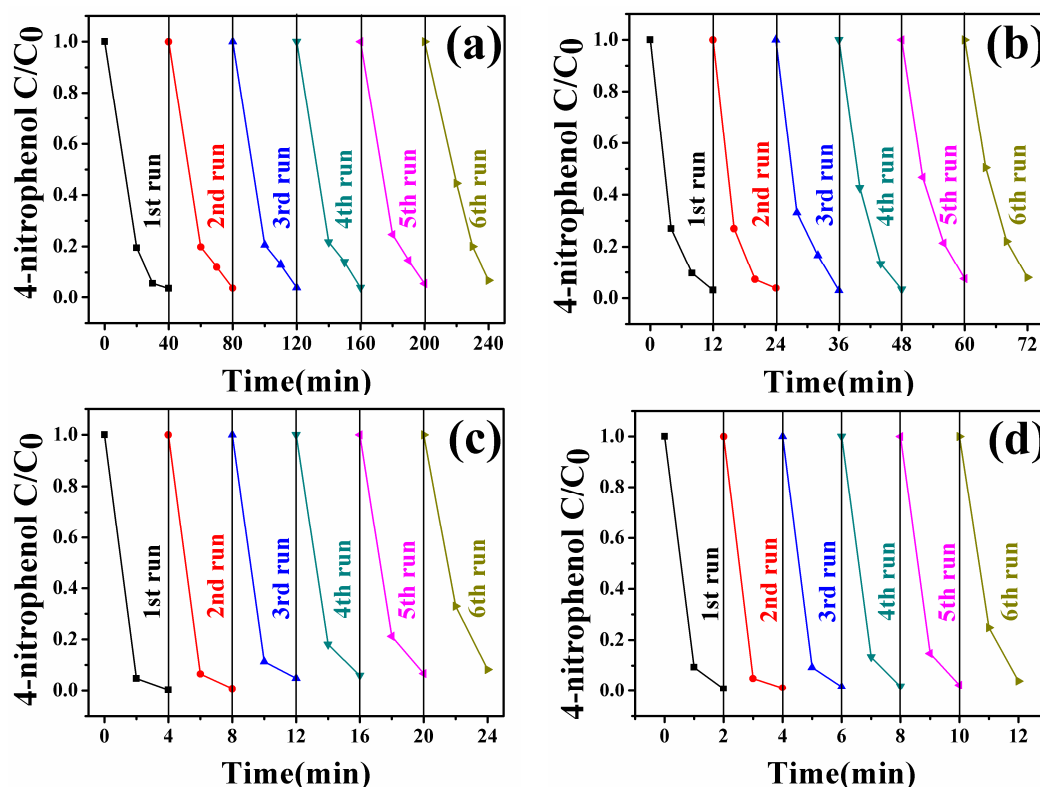


Figure 10. Reusability of $\text{Fe}_3\text{O}_4\text{-Au}$ 5 mL (a); $\text{Fe}_3\text{O}_4\text{-Au}$ 20 mL (b); $\text{Fe}_3\text{O}_4\text{-Au}$ 40 mL (c) and $\text{Fe}_3\text{O}_4\text{-Au}$ 60 mL (d) for catalytic reduction of 4-NP.

4. Conclusions

In summary, Fe₃O₄-Au magnetic nanocomposites were prepared by a well-developed seed deposition method. Structural analyses confirmed that the as-prepared Fe₃O₄-Au magnetic nanocomposites possessed a high surface area and that the gold seeds were homogeneously deposited onto the Fe₃O₄ hollow microspheres' surfaces. The increase of the quantity of the gold seeds attached to the surfaces of the Fe₃O₄ hollow microspheres results in Fe 2p peaks shifting toward a lower binding energy and Au 4f peaks shifting towards a higher binding energy. Although the Ms value decreases with the increase of the gold seed amount deposited on the Fe₃O₄ surfaces, the samples retain the strong magnetic responsivity and can be easily collected by a magnet. The pseudo-first-order kinetics are used to calculate the rate constant of 4-NP, and the rate constants for the 4-NP reduction increase when increasing the added amount of gold seeds. Furthermore, Fe₃O₄-Au magnetic nanocomposites can serve as recyclable nanocatalysts for 4-NP. Therefore, Fe₃O₄-Au magnetic nanocomposites can be excellent nanocatalysts for the catalytic reduction of organic pollutants in the treatment of waste water.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/8/5/353/s1>. Figure S1: Pawley refinement of the XRD pattern of the pure Fe₃O₄ hollow microspheres. Red dots, blue lines and olive bars represent the experimental data, the calculated date and the peak position of the sample, respectively. The bottom line in black shows the different experimental-calculated data, Figure S2: Particle size distribution obtained from the analysis of the TEM images for pure Fe₃O₄ hollow microspheres, Figure S3: SEM and corresponding EDS images of the as-prepared Fe₃O₄-Au nanocomposites with the different addition quantities of the gold seed colloids (Fe₃O₄ (a, b and c), Fe₃O₄-Au 5 mL (d, e and f), Fe₃O₄-Au 20 mL (g, h and i), Fe₃O₄-Au 40 mL (j, k and l) and Fe₃O₄-Au 60 mL (m, n and o), Figure S4: ZFC and FC curves of pure Fe₃O₄ hollow microspheres under an applied field of 1000 Oe, Figure S5: UV-Vis absorption spectra of 4-NP before (red line) and after adding NaBH₄ solution (black line), Figure S6: UV-Vis absorption spectra of 4-NP catalyzed by pure Fe₃O₄ hollow microspheres in presence of NaBH₄ before and after 480 min.

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