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ARTICLE

One pot synthesis of gold hollow nanospheres with efficient and reusable catalysis

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In this paper, gold hollow nanospheres (GHNSs) have been prepared by one step method using 2-mercaptothiazoline as both reductant and stabilizer. The gold hollow nanospheres were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). The gold hollow nanospheres exhibit excellent catalytic activity toward the reduction of 4-nitrophenol and potassium hexacyanoferrate (III) by sodium borohydride in water. The kinetic investigations were carried out for the GHNSs-catalyzed reactions at different turns. Importantly, the catalyst, GHNSs, can be recycled and exhibits good reusability.

Introduction

Noble metal nanomaterials have attracted much attention in recent years due to their promising potential in heterogeneous catalysis, biological or chemical sensing,^{1,4} optoelectronic devices and disease therapy.^{5,7} Since their performances in these fields strongly depend on the shape, structure and composition, a myriad of metallic nanostructures including nanorods, nanoplates, nanoboxes and nanocages have been synthesized. Catalytic activity is strongly affected by particle size and shape, and consequently, the synthesis of colloidal nanoparticles with well-controlled size and shape has become very important.⁸⁻⁹ Compared with the solid metal nanostructures, the hollow ones are quite distinguishable, because of their large specific surface area, unique optical properties, high reactivity and atom economy.^{5,7,10} A specific feature of hollow shells is their relatively low density, which generally makes them more attractive than the corresponding core-shell particles.¹¹ For example, the advantages of the hollow nanostructures of noble metals in catalysis are also in evidence.^{6,12} In past years, many hollow nanostructures of noble metals have been reported by all kinds of method. Most of them were synthesized by the assistance of templates. A common strategy for synthesis is based on solid templates, for instance, colloidal polymer lattices, silica, or gold particles. Caruso's group has prepared gold nanoparticle-based core shell and hollow spheres by polystyrene cores and polyelectrolyte template.¹³ Ji and co-workers have synthesized an Au NP-loaded flake-shell silica spheres and investigated the catalysis activity.¹⁴ Li's group has demonstrated a liposome induced self-assembly of gold nanoparticles into hollow spheres, which was

used the 3,4-ethylenedioxythiophene as reduction.¹⁵ Jiang's group has synthesized polydiacetylene vesicles terminated with $-NH_2$ and used as templates for forming gold hollow spheres with application in DNA immobilization.¹⁶ Xu *et al.* developed the super-hydrophobic yolk-shell nanostructure with Au NPs in the shell, which showed excellent performance as catalyst in the reduction of 4-nitrophenol.⁸ Although some template-free approaches can be found in the literature for the fabrication of shells,^{4,7,10-13} to date, template-mediated methods have been most popular and still provide better control of the final morphology.¹¹ Feldmann and co-workers synthesized nanoscale gold hollow spheres through a microemulsion approach which was without any solid template. However, the process of synthesis was complex and time wasted.¹⁷ Though the fabrication of nano/micro hollow spheres is still a challenge, due to their advantage of low density and high specific surface, the gold hollow nanospheres were pursued by researchers. Considering the nanoscale gold hollow sphere directly synthesized by one step without any template, they are relatively few reported, to our knowledge. Thus, development of synthesis strategies is of high importance. Herein, we present the construction of gold hollow nanospheres through one step method by the reduction of chloroauric acid in presence of 2-mercaptothiazoline (2-MT). The electron catalytic behavior of the GHNSs as catalysts has also been investigated in reduction of 4-nitrophenol (4-NP) and potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) reduction in aqueous solutions. One of the most important applications of noble metal nanostructures is to catalyze or activate some reactions that will otherwise be unlikely to occur.

4-NP has attracted great public concern because it can cause water pollution, while its derivative, 4-aminophenol (4-AP), is a potent industrial intermediate for analgesic and antipyretic drugs, photographic developers, anticorrosion lubricants, and so on.¹⁸⁻¹⁹ However, the 4-AP used to be produced by the selective catalytic hydrogenation of the corresponding nitro-precursors (4-NP) by using tri-*n*-butylamine or pyridine as solvents at high pressure and temperature, which is costly and less benign.²⁰ The reduction of 4-NP over noble metal NPs in the presence of NaBH₄ has been rigorously investigated for the efficient production of 4-AP. The reduction of nitrophenols in water using the GHNSs illustrates its high catalytic efficiency. The recycling and reuse of this composite system was also achieved without a visible decrease in the performance for at least 20 catalytic cycles.²¹⁻²⁵ Otherwise, since the reduction of K₃Fe(CN)₆ has received considerable interest for academic research as a model electron-transfer inorganic reaction,^{11,26} the model system for redox catalysis was employed to evaluate the catalytic activity of the GHNSs towards an inorganic reaction. The GHNSs were applicable for the reduction of K₃Fe(CN)₆ catalytic processes.

Experimental section

Materials

All chemicals used were of analytical grade or of the highest purity available. 2-mercaptothiazoline (2-MT, 98%) was obtained from Alfa Aesar. Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, 99.9%) and sodium borohydride (NaBH₄, 98%) were obtained from Aladin and used as received. Potassium hexacyanoferrate (III) (K₃Fe(CN)₆, 99%) and 4-nitrophenol (4-NP) were supplied by Shanghai Chemical Corp. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO₃ (aqua regia) and rinsed thoroughly with Mill-Q (18.2 MΩ cm⁻¹ resistance) water prior to use. Mill-Q water was used to prepare all the solutions in this study.

Characterization

The morphology and size of the GHNSs were characterized by transmission electron microscopy (TEM) using a Hitachi H-7650 electron at an acceleration voltage of 120 KV with a CCD camera. The high-resolution TEM was performed using a JEOLFETEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) was recorded on an Axis Ultra DLD (SHIMADZU, Japan), and the C1s line at 284.6 eV was used as the binding energy reference. Scanning electron microscopy (SEM) image was obtained by using a Hitachi Su-70 electron at a celeration voltage of 20 KV. X-ray powder diffraction (XRD) pattern was carried out by using a Rigaku DMax-2600 PC diffraction meter using monochromatic Cu Kα radiation. Absorption spectra were recorded on a UV-vis spectroscopy was performed with a UV-2550 spectrophotometer (SHIMADZU, Japan) at room temperature.

Synthesis of gold hollow nanospheres (GHNSs)

In this paper, 2-MT was used as both reducing and capping agents to prepare the GHNSs through a facile one-pot aqueous approach. Briefly, a 5 mL of (3.0 mM, 3.8 mM, 4.5 mM) 2-MT aqueous solution was dropwise added to 5 mL of HAuCl₄ aqueous solution under vigorous magnetic stirring at room temperature. The corresponding molar ratio of HAuCl₄ versus 2-MT was 1:1, 1:1.2, 1:1.5, respectively. After addition of 2-MT, the deep brown precipitate appeared immediately. Within several minutes, the color of the solution changed from light yellow to brown. The precipitates were then centrifuged for 15 min (at 6000g) to remove the redundant 2-MT. After washed several times with deionized water and ethanol and dried at 50 °C, the 2-MT protected GHNSs were obtained.

Catalytic reduction of 4-nitrophenol (4-NP)

The catalytic properties of GHNSs were systematically examined by two experiments the reduction of 4-NP and K₃Fe(CN)₆.²⁷⁻²⁸ For catalytic reduction of 4-NP, aqueous solutions of 4-NP (0.01 M, 0.03 mL) and freshly prepared aqueous NaBH₄ solution (0.5 M, 0.2 mL) were mixed with water (2.5 mL) in a quartz cuvette without stirring. Then the GHNSs aqueous suspension (25 μL, 2.8 mg·mL⁻¹) was injected without any stirring. The reaction was monitored by taking absorption spectra.

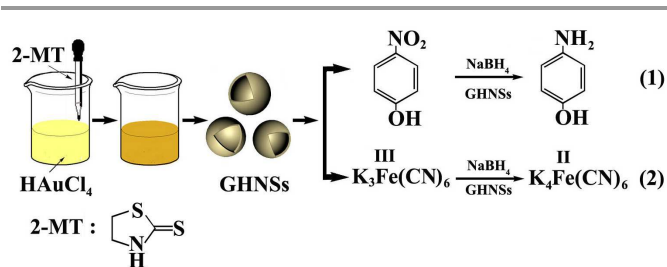
To further test the reusability of the GHNSs as catalysts, the used GHNSs were separated from the solution by pipetting the solution and adding the equal amount fresh reactant solution in next cycles. Similar to the above mentioned procedure was repeated 20 times. In order to ensure the quantity of catalyst was enough in the process of recycle, the 2 mg of GHNSs was added in reaction solution.

Catalytic reduction of K₃Fe(CN)₆

The reduction of K₃Fe(CN)₆ was carried out according to a typical reaction,²⁸⁻²⁹ 0.1 mL of 8×10⁻³ M K₃Fe(CN)₆ was added into 1 mg of GHNSs, followed by the rapid addition of 0.2 mL of 0.040 M ice-cold fresh NaBH₄ solution. In the experiments of reusability, the obtained GHNSs were redispersed in 1.2 mL deionized water, then 0.4 mL of 8×10⁻³ M K₃Fe(CN)₆ and 0.8 mL of 0.04 M ice-cold fresh NaBH₄ solution. The solution was measured using UV-vis spectroscopy quickly. The above process was repeated 10 times.

Results and Discussion

The synthetic procedure in Scheme 1 demonstrates the synthesis of the GHNSs. In the process of synthesis of GHNSs, when 2-MT added, the Au³⁺ can be reduced immediately, with the thiol group tethering to the surface of Au⁰ due to the strong Au-S bond. The products were GHNSs which were assembled by small gold nanoparticles. The obtained GHNSs can be used as catalyst in the reduction of 4-NP [Eq. (1)] and K₃Fe(CN)₆ [Eq. (2)] by NaBH₄ in water. With regard to this, the catalytic property of the GHNSs was investigated in this study, where the overall reaction is presented in Scheme 1.



Scheme 1 View of the preparation process and the evaluation of catalysis activity of GHNSs.

The XRD pattern was carried out to characterize the phase and purity of the as-synthesized final product (Fig. 1). As can be seen, the GHNSs exhibited relatively strong diffraction peaks at 37.82, 44.12, 64.40, and 77.34°, which was corresponded to four typical face-centered cubic (fcc) diffraction peaks (111), (200), (220), and (311) planes of the fcc lattice of Au, respectively (Fig. 1, JCPDS No. 04-0784).³⁰ The peak corresponding to the (111) plane is much sharper and stronger compared with other planes. The ratio between the intensities of the (200) and (111) peaks is 0.31, which is much lower than the conventional value of 0.52,³¹ revealing the predominant orientation of the (111) planes. This has been proved by the formation of metal multipods, which is associated with the competitive growth between the (111) and (200) planes.³² Characteristic diffraction patterns of the fcc lattice planes of metallic Au (0) were observed for GHNSs.³³

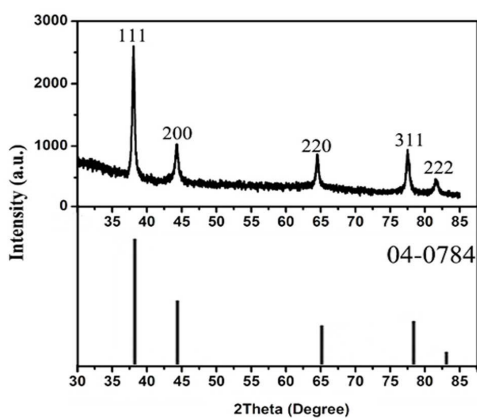


Fig. 1 XRD pattern of GHNSs and compared with the standard card.

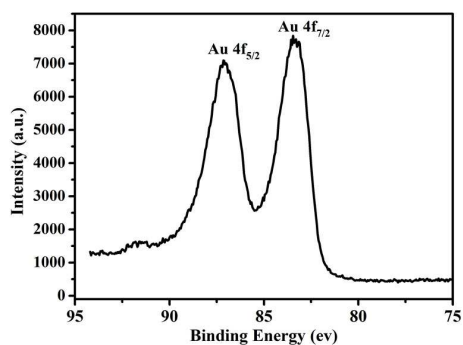


Fig. 2 High-resolution XPS of Au4f spectrum of GHNSs.

The XPS was performed to investigate the electronic state of Au on the surface of the GHNSs. As shown in Fig. 2, the high-resolution XPS Au 4f spectrum displays a doublet indicative of metallic Au, with binding energies of 83.45 and 87.14 eV for the Au4f_{7/2} and Au4f_{5/2} levels,³⁴ demonstrating that most of the Au³⁺ ions were reduced by 2-MT.

The TEM measurements were carried out to characterize the morphology and size distribution of the GHNSs. As shown in the TEM images (Fig. 3), the as-synthesized GHNSs with different reactant molar ratio were observed exactly hollow spherical structure. The strong contrast between the edge and centre parts provides convincing evidence for its hollow nature (Fig. 3b). The TEM images show that the as-obtained hollow spheres with different sizes from 90 to 120 nm. The inner diameter can be deduced to be about 65–95 nm, which can be observed from the images. The presence of hollow nanospheres exhibiting a wall thickness of 20–25 nm (Fig. 3). An enlarged view of the hollow sphere (inset of Fig. 3a and 3b) showed that the hollow spheres were composed of small gold nanoparticles. These gold nanoparticles were about 5 nm in diameter, and the formation of small-sized nanoparticles could be ascribed to the weak reductant of 2-MT. To investigate the influence of concentration of 2-MT on the hollow spherical structures, the molar ratio of HAuCl₄ versus 2-MT was varied as described in Fig. 3. In all the three cases, hollow spherical structures composed of tiny gold nanoparticles were observed. Except the byproducts around the hollow spheres were increased accompany the addition of the 2-MT, the results indicate that the concentration of the 2-MT reductant has little influence on the self-assembled hollow spheres.

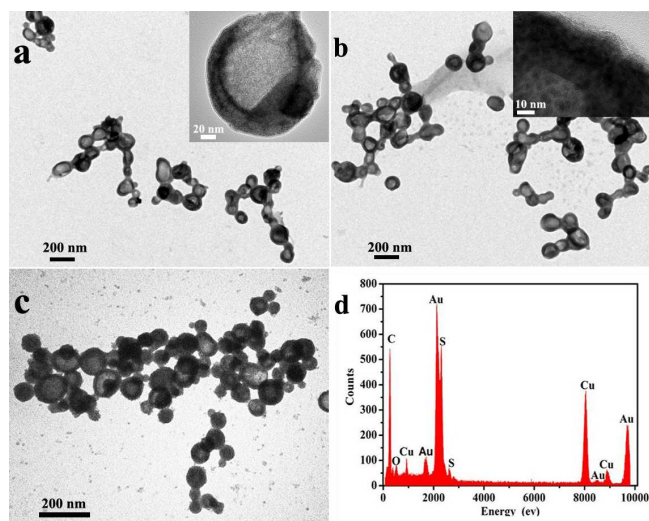


Fig. 3 TEM images of GHNSs, the corresponding molar ratio of HAuCl₄ versus 2-MT was 1:1 (a), 1:1.2 (b), 1:1.5 (c), respectively, (inset: enlarged view of GHNSs), and (d) EDX spectrum analysis of GHNSs.

The EDX microanalysis of the GHNSs confirmed the presence of characteristic peaks of pure Au (Fig. 3d). The presence of small amounts of oxygen and sulfur can be ascribed to the carboxylate and thiol groups of 2-MT, which is

unavoidable. C and Cu peaks are due to the grid used to perform the measurement.

The SEM analysis was performed to characterize the morphology of GHNSs. From Fig. 4(a), the large range of hollow nanosphere shell structures can be observed with diameter in 90-120 nm. The magnified images (Fig. 4b) showed the hollow shell structure of nanospheres clearly. Especially some hemispheres can be detected, which proved the hollow structure of the GHNSs distinctly. The thickness of the shell of GHNSs was about 20-25 nm, which was consistent with the results of TEM. These spherical nanostructures composed of such tiny particles were expected to have potential applications in material science.

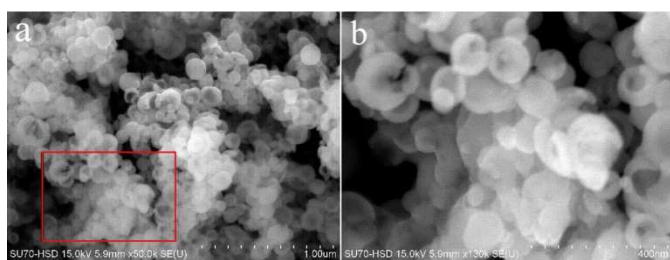


Fig. 4 SEM images (a, b) of GHNSs, A magnification image taken from the selected red rectangular area of (a) was show in the (b).

In order to investigate the process of growth and mechanism of the GHNSs, the reaction of preparation of GHNSs were carried out at different reaction time. The GHNSs were prepared in different reaction time which accounted on the grown for 1 min, 5 min, 30 min, 1 h and 2 h, respectively. The TEM images and the particle size distribution of GHNSs were displayed in Fig. S1. The mechanism of the growth of the GHNSs can be deduced formation by three steps in short reaction time. First, the synthesis of Au NPs in 2-MT was carried out by direct reduction of AuCl_4^- . The little gold nanoparticles with diameter at about 5 nm were produced in the process of the reduction of HAuCl_4 by 2-MT, and the little nanoparticles coalesced and assembled to nucleation, which resulted in the formation of big gold nanospheres with diameter of about 100-120 nm in the second step. Accompanied the growth of the big nanospheres, the Ostwald mode occurred in the third step, the further growth requires more little nanoparticles which emptied the core of the spheres induced the formation of hollow structure.¹⁷ Though the reaction time was too short within 1 minute, the formation of GHNSs was complex due to it occurred without any templates. Although a great number of papers described the outstanding work on gold nanoshells with a template,¹⁷ very few papers reported an easy and reproducible method to preparing hollow capsules.

Catalytic Properties of GHNSs

Catalytic applications have been envisaged, because noble metal NPs have emerged as active and efficient catalysts for a broad field of inorganic and organic reactions. The reduction of 4-NP by NaBH_4 was chosen as a model reaction for studying the catalytic performances of GHNSs. The advantage of this

system is that the whole reaction can be monitored spectroscopically.

As usual, the light yellow aqueous 4-NP solution shows absorption at 317 nm. The addition of NaBH_4 deprotonates the OH group of 4-NP, the absorption peak shifts to 400 nm immediately (Fig. S2), which is due to the formation of 4-nitrophenolate ion. No change in the absorption was determined even after standing for 10 h, indicating that there reduction does not proceed without catalyst. After addition of a small amount (25 μL of GHNSs solution with 2.8 mg dispersed in 1mL) of the GHNSs, the color of the 4-nitrophenolate ions diminished after 225 s without stirring or ultrasonic treatment. The catalytic activity of GHNSs prepared with different concentrations of 2-MT were investigated respectively. In Fig. 5 (a, b, c), the characteristic absorption peak of 4-nitrophenolate ion at 400 nm significantly decreased, while a new peak appears at about 309 nm and gradually increases, revealing there reduction of 4-NP to form 4-AP. The catalytic performance of the GHNSs was quantitatively evaluated in the liquid-phase reduction of 4-NP by NaBH_4 . In order to estimate the efficiency of the catalyst, the predetermined calibration curve has been confirmed in Fig. S3. The reduction kinetics was monitored by UV-vis absorption spectroscopy of the reaction mixture after the addition of the catalyst. Considering the reductant concentration was much higher than that of 4-NP, there action should be of first order with regard to the reactant. Fig. 5(d, e, f) showed the linear relationships between $\ln(C_{(t)}/C_{(0)})$ and reaction time, where $C_{(t)}$ and $C_{(0)}$ were the concentrations of 4-NP at time t and 0, respectively. They were converted from the peak absorbances at 400 nm according to the predetermined calibration curve (Fig. S3). The rate constant (k) of the catalytic reaction was determined from the slope of the linear plot. According to the linear plot (Fig. 5d, 5e and 5f), the reaction rate constant k was determined to be $16.84 \times 10^{-3} \text{ s}^{-1}$, $17.66 \times 10^{-3} \text{ s}^{-1}$ and $16.93 \times 10^{-3} \text{ s}^{-1}$, respectively. The highest catalytic sample was the GHNSs prepared by 2-MT ratio of 1.2. Compared with the similar catalysis condition (molar of Au and the substrates), the GHNSs showed a higher activity than other Au nanocatalysts.³⁵⁻³⁶

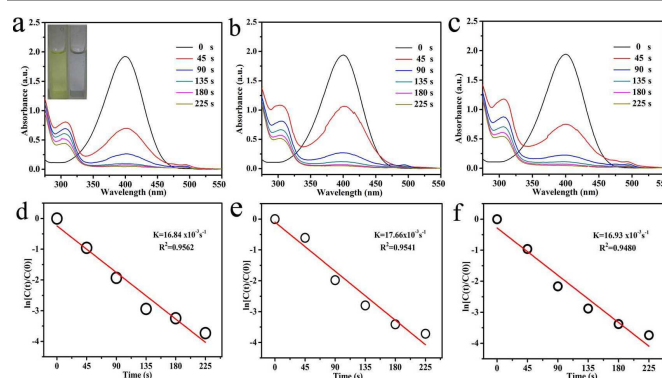


Fig. 5 UV-vis absorption spectra of reduction of 4-NP by NaBH_4 under the catalysis of GHNSs, molar ratio of HAuCl_4 versus 2-MT was (a) 1: 1, (b) 1: 1.2, (c) 1: 1.5, (d, e, f) were corresponding the $\ln(C_{(t)}/C_{(0)})$ versus reaction time for the reduction of 4-NP over GHNSs, respectively ($C_{(0)}$ and $C_{(t)}$ was the absorption peak at 400 nm initially and at time t).

The results indicated that GHNSs is a good catalyst with high efficiency, which is mainly due to the hollow shells were composed of the small gold nanoparticles, so as to improve the catalysis efficiency. The GHNSs were well-dispersed and exposed inside and outside surface of gold nanoparticle, allowing effective contact between the reactants with catalyst of the reaction. Thus, the GHNSs exhibited a good catalytic activity.

Recyclability of catalysts is an important parameter for their practical application. To check the recyclability of the GHNSs, 20 successive cycles of catalytic reduction were carried out (Fig. 6 and Fig. S4). From the absorbance spectra monitored using UV-vis spectroscopy (Fig. 6), the first 5 successive cycles of the reaction were completed by the same GHNSs as catalyst. The corresponding reduction kinetics (inset of Fig. 6a-6e) was monitored, and the reaction rate constant k was determined respectively. In the first three cycles, reduction of more than 99% 4-NP was complete within 12 min (Fig. 6a-6c, Fig. 6f). From the fourth to the fifth turns, more than 90 % 4-NP reacted within 15 min (Fig. 6d and 6e). The main reason for the reduced catalytic performance was deduced the loss of the catalyst.

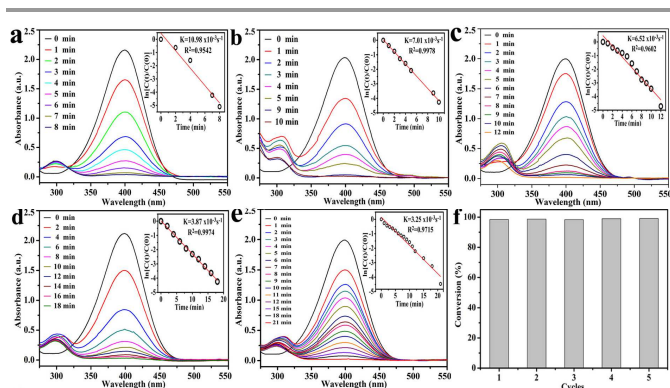


Fig. 6 UV-vis spectra of the reduction of 4-NP by NaBH_4 in the presence of GHNSs recorded for the 1st (a), 2nd (b), 3rd (c), 4th (d), 5th (e), insets: the corresponding $\ln(C_t/C_0)$ versus reaction time for reduction of 4-NP. (f) The reusability of GHNSs as a catalyst for the reduction of 4-NP with NaBH_4 .

In order to test the stability of the GHNSs in the reaction of catalysis, the SEM and EDX of the catalyst after reused 5 and 10 times were recorded and showed in the Fig. S5 and S6. After recycled five times, as catalyst, the GHNSs kept the high catalytic activity. As can be seen in the SEM of Fig. S5a, the GHNSs were still remained hollow spheres structure. Though the small gold nanoparticles have been exposed due to the loss of stabilizer, they remained the group of orbicular nanospheres. The average diameter of gold nanoparticles was about 5 nm, which was consistent with the results of the TEM image of Figure 3b. After 10 recycles (Fig. S6a), the hollow shell structure has been destroyed seriously, just few of the original spherical shells morphology of GHNSs can be observed. The gold nanoparticles became the main structure of the catalyst. The EDX of the two samples (Fig. S5b and Fig. S6b) were proved that the main component of Au was still remained, despite the stabilizer has been lost and the morphology was also

changed. Due to the poor dispersion of the gold nanoparticles, the catalytic activity reduced gradually at the last ten recycles (Fig S4). So, the above results indicated that the GHNSs show good reusability for at least 5 successive cycles.

As a model electron-transfer inorganic reaction, the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ by GHNSs was also performed in a quartz cuvette and monitored using UV-vis spectroscopy at room temperature.³⁷ The light yellow aqueous $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution shows absorption at 420 nm. After the addition of NaBH_4 , the intensity of absorption can decrease gradually due to the formation of $\text{K}_4[\text{Fe}(\text{CN})_6]$ within 12 h (Fig. S7). However, after the addition of a small amount of GHNSs as catalyst, the absorption peak at 420 nm significant decreased and the reaction process totally completed within 50 seconds in the first run, indicating the high catalytic activity of GHNSs (Fig. 7a). From Fig. 7a, it can be observed clearly, during the period required for complete reduction of $\text{K}_3\text{Fe}(\text{CN})_6$, as the reaction proceeds, the color of the solution changed from yellow to colorless.

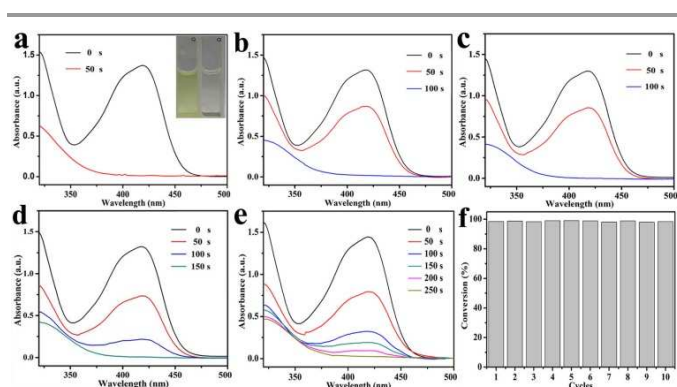


Fig. 7 UV-vis spectra of the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ by NaBH_4 in the presence of GHNSs (1.0 mg) recorded at different times: (a) for the first run, the reduction was finished 50 s and change the color of the solution before and after reaction; (b)-(e) for the second, third, fourth and fifth, and (f) the reusability of GHNSs as a catalyst for the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ with NaBH_4 .

To test the reusability of GHNSs as a catalyst, the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ was repeated ten times, using the same GHNSs, through sequential addition of $\text{K}_3\text{Fe}(\text{CN})_6$ to an aqueous solution containing excess borohydride and a constant concentration of GHNSs.³⁷⁻³⁸ As shown in Fig. 7, the catalyst can be successfully recycled and still kept their high activity after reusing in 10 successive reactions with a conversion rate close to 100%. These results indicated that GHNSs exhibited good catalytic efficiency and reproducibility in the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ reaction.

Conclusion

In summary, gold hollow nanospheres are successfully realized on the nanoscale by one step without the application of a solid template at facile condition. TEM, SEM and XPS analysis clearly evidences the presence and chemical composition of the GHNSs. In addition, the use of GHNSs as a novel catalyst for the reduction of 4-NP and $\text{K}_3\text{Fe}(\text{CN})_6$ in the presence of NaBH_4 were also investigated. The results indicated that as-prepared

GHNSs exhibit good performance as a catalyst. We anticipated that the GHNSs may provide a platform broad potential in catalysis due to the well hollow nanostructures.

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Notes and references

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Graphical Abstract:

