

Selective Reduction of Aromatic Nitro Compounds over Recyclable Hollow Fiber Membrane-Supported Au Nanoparticles

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ABSTRACT: Guanidylated poly(2,6-dimethyl-1,4-phenylene oxide) (GPPO) hollow fiber membrane (HFM) supported Au nanoparticles are prepared by a simple adsorption-reduction of Au^{3+} with sodium borohydride as a reducing agent and polyvinyl pyrrolidone as a dispersant. The novel heterogeneous catalyst shows high catalytic activity for the reduction of various aromatic nitro compounds in an aqueous medium at room temperature and can be easily reused for several runs, for example, for the reduction of nitrobenzene, the yield reaches up to 92% even after 10 cycles, indicating the potential application of GPPO HFM as a catalysts support material for sustainable chemistry. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41268.

KEYWORDS: aromatic nitro compounds; Au nanoparticles; hollow fiber membrane; poly(2,6-dimethyl-1,4-phenylene oxide); reduction

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INTRODUCTION

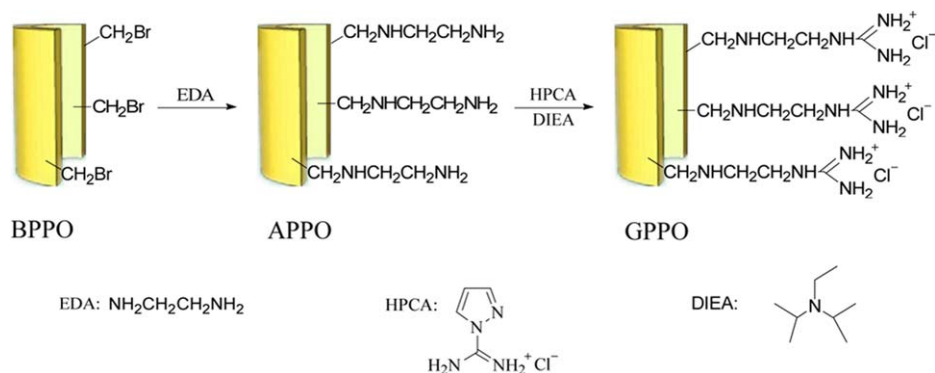
Great improvement has been made in Au nanocatalysts since the first study on the catalytic activity of Au nanoparticles (NPs) for the oxidation of CO.^{1,2} However, due to the high surface energy, Au NPs are prone to aggregate, resulting in a remarkable loss of catalytic activity. Immobilization of Au NPs onto supports, including inorganic and polymeric materials, is generally employed to minimize the aggregation. Considering the high cost and limited supply of noble metals, recycle of these catalysts should be concerned. However, it is very difficult to desorb Au NPs from inorganic supports such as zeolites,³ activated carbon,^{4,5} and metal oxides^{6,7} after catalysts getting deactivated due to their strong interaction. Aqua regia⁸ is usually used to destroy the strong interaction for catalysts recycling. However, the susceptibility of most inorganic supports toward acid makes difficulty in separation of Au NPs from the solution. Recently, polymeric supports including dendrimers,⁹ polyelectrolytes,¹⁰ polystyrene microspheres,^{11,12} and polyelectrolyte multilayers¹³ have attracted ever increasing attention due to their low cost and convenient fabrication.¹⁴ Most of the polymeric supports are directly produced from synthesized polymeric powders. They commonly have randomly distributed pores with varying sizes and uncontrollable shapes, which might make difficulty in mass diffusion and cleaning. Therefore, both the organic and inorganic supports face the challenge of recycle.

Polymeric hollow fiber membrane (HFM) is likely to solve the above problems owing to its unique geometry.^{15,16} HFM has three-dimensional hollow decent configurations¹⁴ consisting of regular spongy and finger-like pores. The catalysts can be easily separated from the reaction medium for the next cycle due to its macroscopical bar structure. In addition, its fully porous loose structure offers a larger effective membrane area per unit volume which is beneficial to effective catalysis.

The linear engineering poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which exhibits high glass transition temperature ($T_g = 210^\circ\text{C}$), high mechanical strength, and hydrolytic stability, has drawn increasing attention for membranes in recent years. Its specific but simple structure allows many analogous reactions in both aryl- and benzyl-positions. It has been well used as a starting material for ion exchange membranes in our group through bromomethylation due to the easy conversion of bromomethylated groups ($-\text{CH}_2\text{Br}$) into quaternary ammonium, guanidinium, and phosphonium groups.^{17–20} For example, we have performed the work concerning guanidylated poly(2,6-dimethyl-1,4-phenylene oxide) (GPPO) HFM as a potential chelating material for Au^{3+} .²¹ Inspired by this, the GPPO HFM supported Au NPs catalysts were prepared by a simple adsorption-reduction of Au^{3+} . The activity, chemoselectivity, versatility, recyclability and dynamics of the obtained GPPO supported Au NPs (Au/GPPO) catalyst were tested for the

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Scheme 1. Preparation of GPPO HFM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduction of aromatic nitro compounds^{22–24} which is getting more and more attention of researchers.²⁵ Overall, this job showcased the potential application of GPPO HFM as a catalyst support material for sustainable chemistry.

EXPERIMENTAL

Materials

The pristine membrane bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPO) HFM containing 80% benzyl bromide and 20% aryl bromide was kindly supplied by Shandong Tianwei Membrane Technology CO.; 1*H*-Pyrazole-1-carboxamide hydrochloride (HPCA), and *N,N*-Diisopropylethylamine (DIEA) were purchased from J&K Chemical reagent and used as received. The other reagents such as Ethylenediamine (EDA), triethylamine, Chloroauric acid (HAuCl_4), Polyvinyl pyrrolidone [PVP, (K-30, 40 kDa)], and sodium borohydride (NaBH_4) were purchased from Sinopharm Chemical Reagent and used as received. Deionized water was used throughout.

Preparation of GPPO HFM

GPPO was prepared according to our previous study²¹ as shown in Scheme 1. For instance, the pristine BPO HFM (1.15 g) was immersed in an EDA/ethanol (19/1 mL) solution, and then stirred at 60°C for 24 h. Subsequently, the aminated poly(2,6-dimethyl-1,4-phenylene oxide) (APPO) membrane was taken out and washed with deionized water and ethanol repeatedly to remove the remaining EDA. The obtained APPO was immersed into a HPCA (2.55 g) and DIEA (17 mL) aqueous solution. After being stirred at room temperature for 20 h, the product GPPO was obtained and washed with deionized water and ethanol repeatedly finally dried in an oven at 50°C for 6 h. It should be noted that the base membrane BPO HFM was cut into 1 cm length before use for convenience.

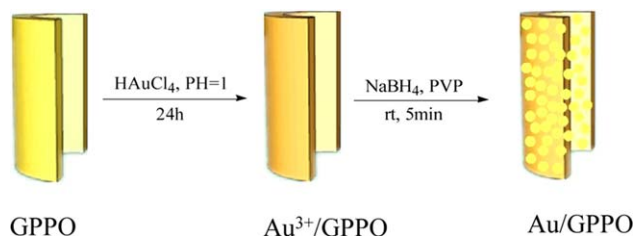
Preparation of Au/GPPO

The process for the preparation of the catalyst Au/GPPO is shown in Scheme 2. There are two main steps in the preparation of membrane containing Au NPs Au/GPPO: Au^{3+} adsorption²¹ and *in situ* reduction. (1) HAuCl_4 aqueous solution (400 mg/L) of 500 mL was prepared by adjusting the pH at 1 with concentrated hydrochloric acid, and then adding 50 mg GPPO HFM. Subsequently, the mixture was put on a shaker at room temperature for 24 h. The obtained Au^{3+} /GPPO HFM was washed with

deionized water repeatedly to remove excess AuCl_4^- . (2) The Au^{3+} /GPPO HFM was reduced according to the procedure in the literature.²⁶ The obtained Au^{3+} /GPPO HFM was immersed into a 10 mL aqueous solution of dispersant PVP (2.82 g) under constant stirring at room temperature for 10 min. Subsequently, 10 mL fresh NaBH_4 (0.01 M) aqueous solution was added into the mixture slowly. The color of the membrane immediately turned from yellow to dark red, indicating the formation of small Au NPs. After 2 min, the obtained red Au/GPPO HFM was taken out and washed with deionized water repeatedly, then dried at 30°C in a vacuum oven overnight.

Typical Procedure for the Reduction of Nitro Compounds to the Corresponding Amine

Au/GPPO of 25 mg (the corresponding molar ratio of Au to reactant nitro compound is 4.2%) was immersed into a suspension of nitro compound (0.9 mmol) and H_2O (3 mL), then 3 mL fresh NaBH_4 (18 mmol) aqueous solution was added under Ar atmosphere, then the reaction tube was sealed and stirred at room temperature for the lengths of time shown in Supporting Information Table S1. The reaction progress was monitored by gas chromatography (GC). After the completion of the reaction, the catalyst was taken out with tweezers and washed with deionized water. The reaction solution was extracted with ethyl acetate (3 mL), determined by GC, then extracted with ethyl acetate for additional two times (3 mL \times 2), and combined the organic layers. Subsequently, the product was dried using anhydrous Na_2SO_4 , filtered and finally separated by column chromatography (CC) for ^1H nuclear magnetic resonance (^1H NMR). When it refers to the recyclability and the dynamics, nitrobenzene was chosen as the model substrate for selective reduction.



Scheme 2. Preparation of Au/GPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

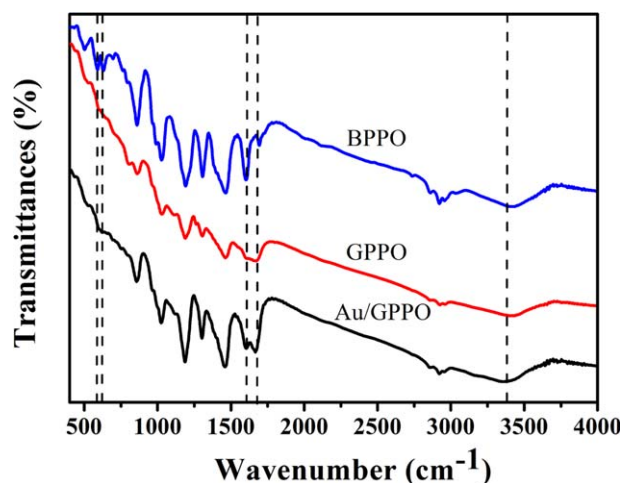


Figure 1. FTIR spectra of BPPO, GPPO and fresh Au/GPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Instrumental Characterizations

Fourier transform infrared spectroscopy (FTIR) of BPPO, GPPO, and Au/GPPO were recorded on KBr pellet using FTIR spectrometer (Vector22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of $4000\text{--}500\text{ cm}^{-1}$ under ambient conditions to confirm the formation of guanidium groups and to study the influence of Au NPs on functional groups. X-ray photoelectron spectroscopy (XPS) ESCALAB 250 was also used to further confirm the successful amination and guanidinylation reactions. The content of NPs was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (model: X series 2). To check the surface state of Au NPs, XPS was tested on Au. A Sirion200 scanning electron microscope (SEM) was performed to study the effect of modification and application procedures on pore structures of HFM. A Sirion200 SEM equipped with an X-ray energy dispersive spectroscope (EDS ESCALAB 250) was used to obtain information regarding the distribution of Au at nanoscale. The EDS specimens were frozen fractured in liquid nitrogen and coated with carbon before observation. The x-ray diffraction (XRD) measurements were performed on an X'Pert diffractometer (CuK α X-ray source, operated at 40 kV and 200 mA). Au particle sizes were calculated using Scherrer's equation. Transmission electron microscopy (TEM) measurements were carried out on a JEM-2010 electron microscope, operated at 200 Kv (point-to-point resolution, 0.194 nm). The size distribution of Au particles was calculated by measuring several hundred particles randomly. ^1H NMR test was conducted on a Bruker AVANCE AV400 400 MHz instrument. The ^1H NMR sample was obtained by CC. GC was performed on a 6890N with a FID detector equipped with a capillary column (Agilent 1909M-413, $30.0 \times 320 \times 0.25$). Parameters were as follows: initial oven temperature, 120°C ; ramp, $10^\circ\text{C}/\text{min}$; final temperature, 200°C ; injector temperature, 250°C ; detector temperature, 250°C ; injection volume, $2\ \mu\text{L}$.

RESULTS AND DISCUSSION

Catalyst Characterization

FTIR spectra of BPPO, GPPO, and Au/GPPO HFM are shown in Figure 1. Peaks at 588 and 630 cm^{-1} in the spectrum of BPPO

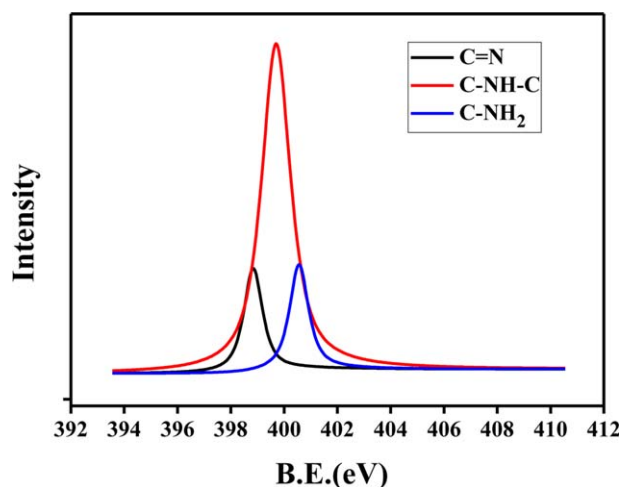


Figure 2. XPS spectrum of GPPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are attributed to the benzyl bromide ($-\text{CH}_2\text{Br}$) group (C—Br stretching). They disappear in the spectra of GPPO and Au/GPPO, suggesting that $-\text{CH}_2\text{Br}$ group is consumed during the amination reaction. Additionally, the wide broad peaks appear in both spectra of GPPO and Au/GPPO in the range of $1689\text{--}1630\text{ cm}^{-1}$, which are the characteristic peaks for guanidine compounds: approximately $1660\text{ C}=\text{N}$, approximately 1640 N-H , and approximately 1630 C-N ,²⁷ confirming that the guanidium groups have been effectively introduced. The result demonstrates that guanidium groups can be observed even though Au NPs was loaded on the support. Apparently, chelation between Au and guanidium group has no influence on the chemical structure of the support material. To further confirm the successful attachment of guanidium groups, XPS was performed on GPPO. Based on N1s peak of GPPO shown in Figure 2, the peaks at 398.85 , 400.00 , and 400.57 eV can be attributed to the neutral imine bonds $-\text{CH}=\text{NH}_2$, $-\text{NH}-$ groups, and free amine groups $-\text{NH}_2$, respectively.²⁸ This certified the successful proceeding of amination reaction and guanidinylation reaction. The actual content of Au in GPPO was about 500 mg/g (2.54 mmol/g), which was determined by ICP-AES by measuring the concentration difference of Au^{3+} in HAuCl_4 solution before and after the adsorption. The existence and distribution of Au NPs was observed by

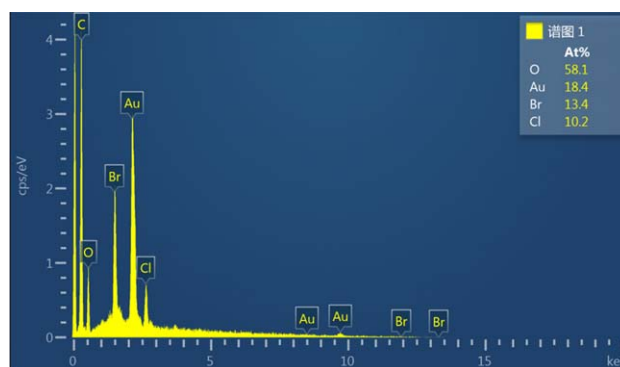


Figure 3. X-ray EDS analyses confirming that the NPs are constituted by pure Au. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

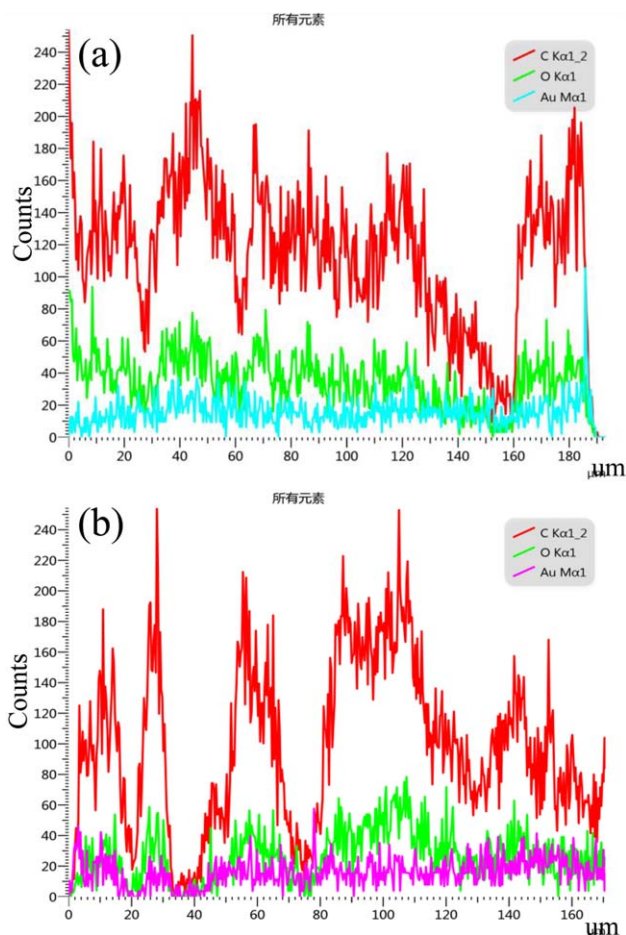


Figure 4. EDS spectrum of the cross section of (a) fresh Au/GPPO; (b) Au/GPPO-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EDS. Qualitative X-ray EDS spectrum in Figure 3 confirms that the NPs is pure gold. Figure 4(a) shows the uniform distribution of Au NPs through the cross-section of GPPO, demonstrating the completely proceeding of the amination reaction, guanidylation reaction, permeability of AuCl_4^- anions and the *in situ* reduction

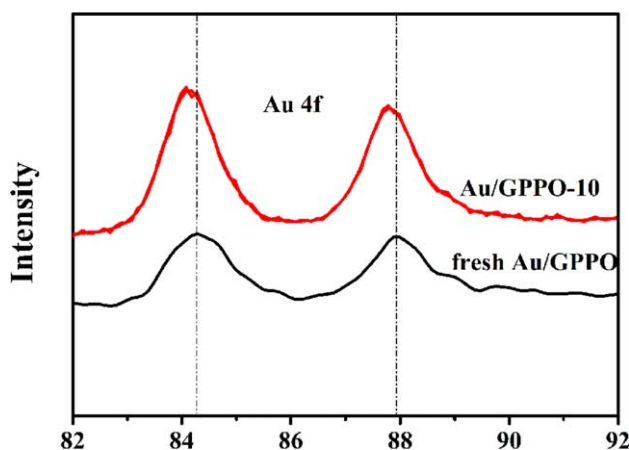


Figure 5. XPS spectra of fresh Au/GPPO and Au/GPPO-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

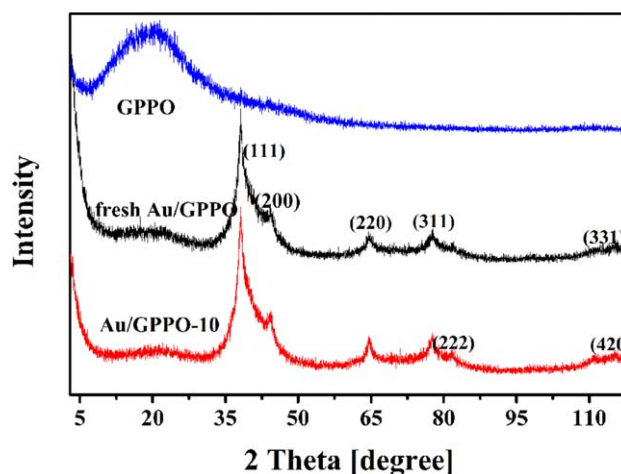


Figure 6. XRD patterns of GPPO, fresh Au/GPPO, and Au/GPPO-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of Au^{3+} through the HFM. The uneven distribution of some elements is attributed to the resulted uneven surface during the fracture in liquid N_2 and the intrinsic porous structure of HFM.

To check the surface state of Au NPs in GPPO HFM, XPS analysis was performed and shown in Figure 5. For the fresh catalyst Au/GPPO, the binding energy of Au_{4f} is about 84 eV. It can be concluded that Au is in the metallic state, because no peaks of oxidized gold species (located around 85.5 and 86.3 eV) are observed.^{29,30}

The XRD patterns of powder GPPO and Au/GPPO samples are shown in Figure 6. Compared with pristine GPPO, new peaks at 38.27° , 44.60° , 64.68° , 77.55° , 82.35° , 110.06° , and $115.66^\circ 2\theta$ appear for Au/GPPO, which are standard peak positions for Au,³¹ confirming the formation of Au/GPPO. The average crystalline size of Au was calculated using the Scherrer's equation. The approximate size of Au NPs of Au/GPPO is 4.0 nm, ensuring its high catalytic activity. To further investigate the structure of Au NPs, size and distribution of Au NPs in Au/GPPO HFM were studied by TEM. As shown in Figure 7(a), the average diameter of the as synthesized spherical particles is about 3.80 nm and nearly homogeneous dispersed, which is essentially consistent with the XRD result.

Catalytic Reduction of Aromatic Nitro Compounds in the Presence of Au/GPPO

Generally, aniline derivatives are prepared by catalytic reduction of nitroarenes. Although there are various catalysts for the reduction, organic solvent, relatively high temperature, and pressure are needed in most cases.³² In this study, the reduction of nitrobenzene catalyzed by Au/GPPO achieved excellent result even under mild conditions. Excitedly, we found that the nitrobenzene was totally transformed into phenylamine catalyzed by Au/GPPO at the original catalytic reaction. So it is necessary to further study the recyclability, reaction versatility, and reaction dynamics of Au/GPPO.

Recycling Test. The catalytic reduction of nitrobenzene [eq. (1)] to the corresponding derivative phenyl amine, in the

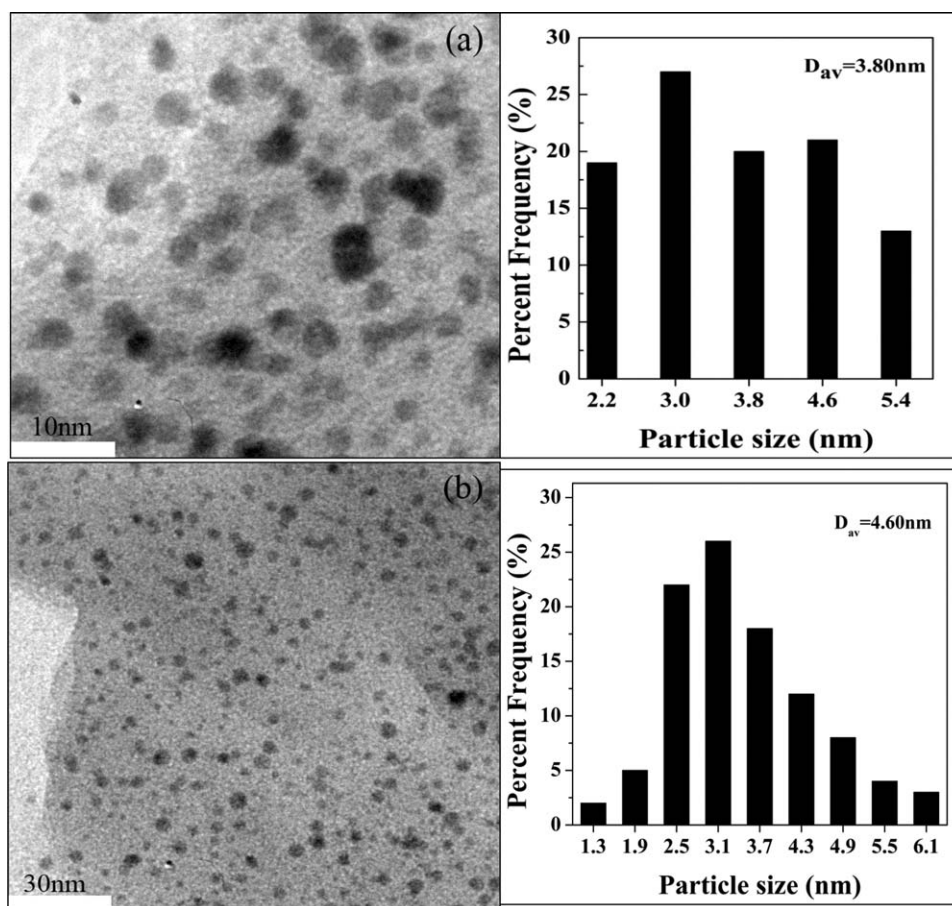


Figure 7. TEM micrograph and size distributions of (a) fresh Au/GPPO; (b) Au/GPPO-10.

presence of NaBH_4 aqueous solution, was chosen as a model reaction to investigate the recyclability of Au/GPPO. Such reaction catalyzed by Au catalyst has been previously reported because it can be rapidly and easily characterized.^{13,33} To regenerate the catalyst, Au/GPPO was taken out from the reaction medium and washed several times with deionized water after

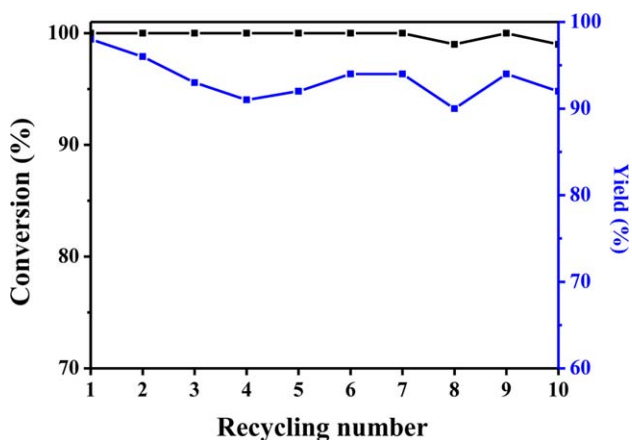
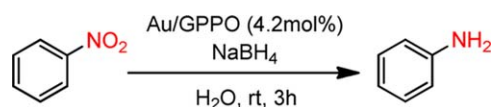


Figure 8. The conversion and yield determined by GC using biphenyl as an internal standard for nitrobenzene reduction by Au/GPPO as a function of recycling number. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

each cycle. It is worth noting that the catalyst gives an almost 100% conversion of nitrobenzene at the original reaction and 92% yield after 10 cycles without a significant loss of activity (Figure 8). ^1H NMR data (Supporting Information Table S2) of the isolated product proves the formation of phenylamine. On the contrary, the reaction was sluggish in the absence of Au/GPPO.



Equation 1 The recycling test of the reduction of nitrobenzene using H_2O as solvent. General conditions: nitrobenzene (0.90 mmol), Au/GPPO (4.20 mol %), H_2O (6.0 mL), and NaBH_4 (18 mmol) at room temperature, under Ar.

After 10 cycles, various characterizations were carried out to examine the recycled catalyst Au/GPPO-10 (10 represents that Au/GPPO is recycled by 10 times). EDS result [Figure 4(b)] shows a similar uniform distribution of Au NPs on the cross-section of Au/GPPO-10 to that of the fresh one [Figure 4(a)], indicating that no obvious aggregation or loss of Au NPs occurs during reaction. Compared with the binding energy of Au_{4f} on fresh Au/GPPO shown in Figure 5, the binding energy of Au_{4f} in Au/GPPO-10 is slightly lower, this may in turn provide the

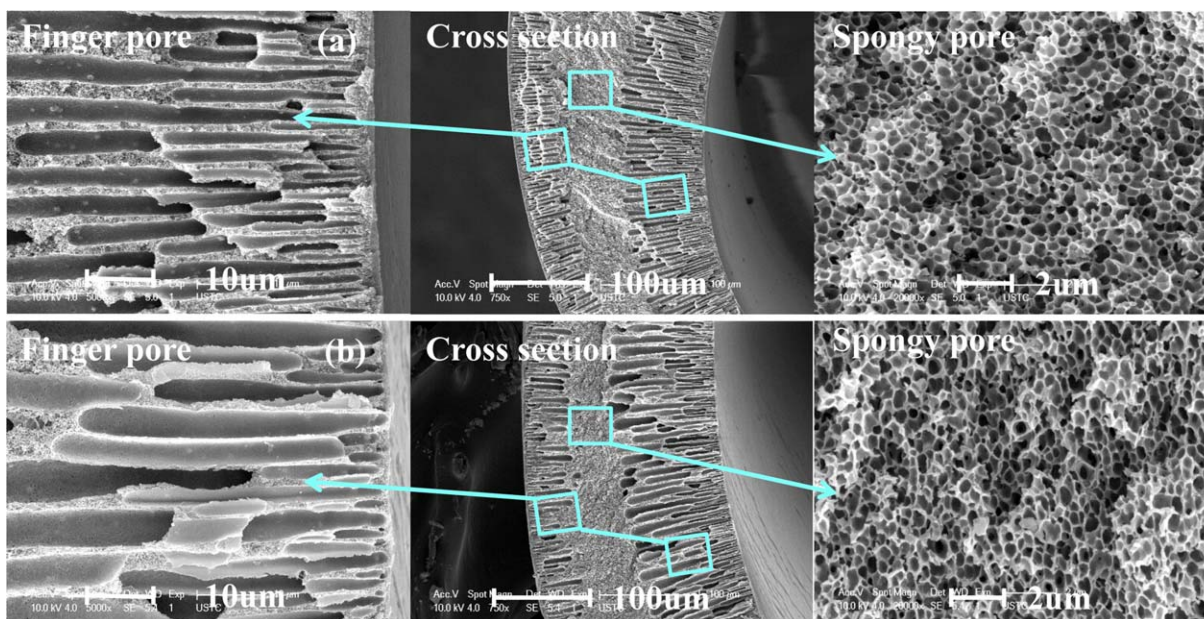
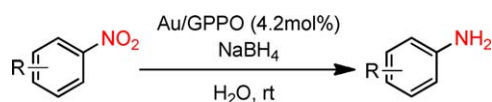


Figure 9. SEM micrograph of (a) BPPO and (b) Au/GPPO-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Au/GPPO with higher stability for catalysis.² The TEM image [Figure 7(b)] shows that Au NPs change slightly in shape and size relative to the fresh catalyst [Figure 7 (a)]. According to XRD shown in Figure 6, the Au particle size in Au/GPPO-10 is about 5 nm, slightly larger than the initial size, leading to a little decrease in catalytic activity. Apparently, Au/GPPO is stable for reduction of nitrobenzene, which is superior to many supported Au catalysts.^{24,34,35} This may arise from the chelation between Au and guanidium group²¹ and the steric constraint from the special pore structure of HFM. Compared with BPPO HFM shown in Figure 9, the thicknesses and pore diameters of Au/GPPO-10 HFM are not changed. This means the modification and catalytic processes did not destroy the pore structures of HFM, which is beneficial for the further catalysis reaction. All the above results confirmed the stability of Au/GPPO.

Reaction Versatility. To investigate the versatility of the catalyst, various substituted nitrobenzenes were subjected to the reduction with NaBH₄ in the presence of Au/GPPO [eq. (2)]. Satisfyingly, desired products were obtained in high yields and selectivity in all cases. (Supporting Information Table S1). Furthermore, several reducible groups including aryl-chloride (Entry 3) and aryl-aldehyde (Entry 6) are compatible with the catalyst. For the reduction of 4-nitrobenzaldehyde, 100% transition of blank reaction is achieved within 3 h, but interestingly, the single product is *p*-nitrobenzyl alcohol, which was confirmed by ¹HNMR (Supporting Information Table S2). While the 4-nitrobenzaldehyde is almost totally transformed into 4-amino benzene formaldehyde (Supporting Information Table S2) in the presence of Au/GPPO [eq. (3)]. This is a valid proof of selective reduction of aromatic nitro compounds. These results indicate that the Au/GPPO has both high activity and high selectivity in the reduction of aromatic nitrobenzenes.

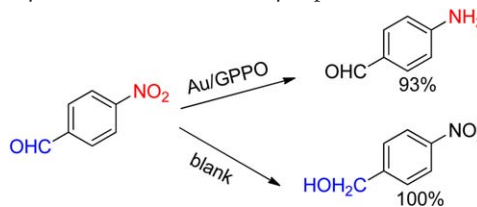
TLC, NMR, and GC data of products are listed in Supporting Information Table S2.



Equation 2 Selective reduction of various aromatic nitro compounds with Au/GPPO

General conditions: substrate (0.90 mmol), Au/GPPO (4.20 mol %), H₂O (6.0 mL), and NaBH₄ (18 mmol) at room temperature under Ar.

Compared with most reaction catalyzed by inorganic materials supported Au catalyst, Au/GPPO catalyzed reaction can be performed in more environmental-friendly medium (i.e., H₂O), and under milder condition (i.e. room temperature). Most importantly, Au/GPPO can be easily separated and reused.



Equation 3 Selective reduction of 4-nitrobenzaldehyde with Au/GPPO

General conditions: substrate (0.90 mmol), Au/GPPO (4.20 mol %), H₂O (6.0 mL), and NaBH₄ (18 mmol) at room temperature under Ar.

Dynamic Test. To get knowledge about the catalytic property of Au/GPPO quantitatively, kinetic measurement was performed

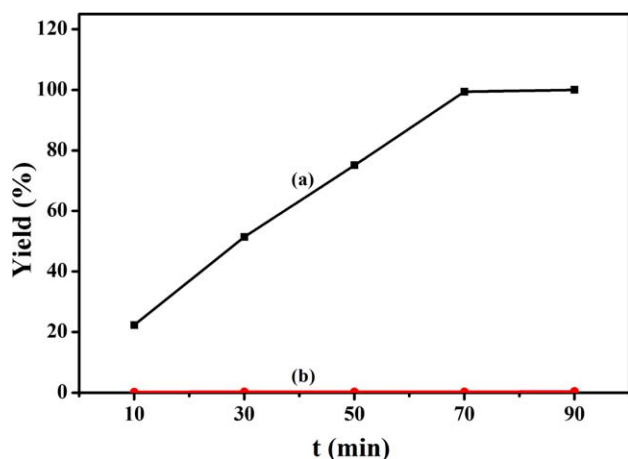


Figure 10. Reaction time dependence of phenylamine yield (a) with Au/GPPO; (b) blank reaction. General conditions: nitrobenzene (0.50 mmol), Au/GPPO (4.20 mol %), H₂O (3.0 mL), and NaBH₄ (10 mmol) at room temperature under Ar. The Yield was determined by GC using biphenyl as an internal standard. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using the reduction of nitrobenzene as a probe reaction. Figure 10 shows the change of concentration of phenylamine with respect to time. It only takes 70 min to reach 100% conversion (yield: 98%). Additionally, there is a linear relationship between the yield and the reaction time from 10 to 70 min, indicating that the reaction is zero order in the presence of Au/GPPO. The rate constant, k , is, therefore, obtained from the slope, being equal to 0.12 M/h. However, the blank reaction can only achieve a yield of 0.4% even after 90 min. This result clearly indicates that Au/GPPO HFM is a highly active catalyst.

CONCLUSIONS

In conclusion, we report the preparation and characterization of Au/GPPO HFM catalyst for the first time. The catalytic activity of Au/GPPO was tested through the reduction of some aromatic nitro compounds. The reaction can be performed smoothly in an environment-friendly medium (H₂O) at room temperature. In addition, the chelation force between guanidium group and Au prevents aggregation and leaching of Au NPs and the yield can reach to 92% even after 10 cycles for the reduction of nitrobenzene. Most importantly, the catalyst can be removed from the medium and reused for several runs easily. Hence, Au/GPPO HEM catalyst is an economical as well as potential material for applications in large scale production.

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