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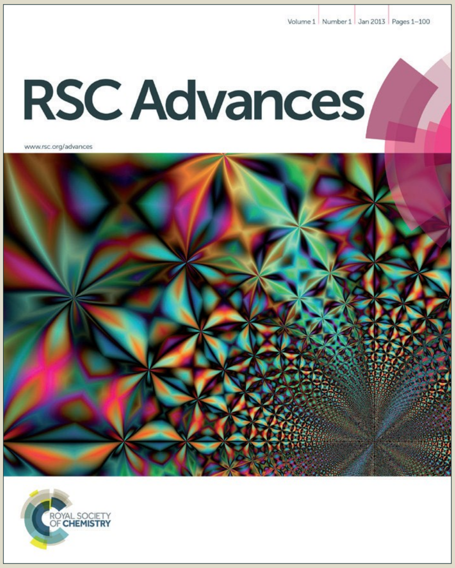

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PAPER

The assembly of polyethyleneimine-entrapped gold nanoparticles onto filter paper for catalytic applications†

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A facile approach to assembling polyethyleneimine (PEI)-entrapped gold nanoparticles (Au PENPs) onto filter paper is reported. In this work, Au PENPs with an Au core size of 3.2 ± 0.8 nm were formed using PEI as a template, followed by adsorption onto filter paper. The formed Au PENP-containing filter paper was characterized by various techniques. We show that the Au PENPs are able to be adsorbed onto filter paper likely due to the microfibrous structure of the paper and the electrostatic interaction between the positively charged Au PENPs and the negatively charged filter paper. Furthermore, we demonstrate that the Au PENP-assembled filter paper displays an excellent catalytic activity and reusability to converting 4-nitrophenol to 4-aminophenol. Such development of Au PENP-assembled filter paper may be applicable for the immobilization of other metal NPs onto filter paper for various applications in catalysis, sensing, and biomedical sciences.

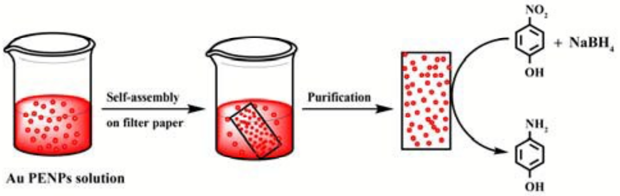
Introduction

Metal nanoparticles (NPs) have attracted tremendous interest due to their high surface to volume ratio, surface electronic properties and excellent chemical and physical characteristics.[1] The applications of metallic NPs include biomedicine,[2, 3] energy transfer,[4] molecular recognition,[5] sensors,[6-9] catalysts,[10] and environmental remediation.[11-13] Among the different types of metal NPs, gold NPs (AuNPs) have received more and more attention because of their unique physicochemical properties.[14, 15] Colloidal AuNPs with different morphologies have been investigated for catalytic applications;[16-19] however the use of them in solutions is usually limited due to their poor stability and recyclability. To overcome such shortcomings, AuNPs have been immobilized onto different supporting materials such as polymer fibers,[20-23] membranes,[24, 25] porous solids,[24, 26] and functionalized clays.[27]

Filter paper is a common material with good flexibility, easy accessibility, cost-effectiveness, robust mechanical durability, and chemical stability.[28] In addition, filter paper containing cellulose fibers that have a large number of ionizable moieties such as carboxyl and hydroxyl groups can be easily modified.[29, 30] Lastly, the porous structure and microfibrils of the filter paper can provide anchoring sites for the immobilization of metal NPs.[31] Therefore, filter paper has been employed as a reliable supporting material to immobilize Ni NPs,[32] Ag NPs,[33] Fe NPs,[34] Pd NPs,[35] and AuNPs.[36-40] For catalytic applications, Zheng *et al.* used filter paper to immobilize Pd NPs[41] or AuNPs[42] by a dip-coating process to render the particles with high catalytic efficiency and recyclability. However, the used approach to generate Pd NPs or AuNPs involved extreme conditions such as high temperature and toxic organic solvents, and may not be easily scaled up. In addition, most of the work regarding the fabrication of AuNP-loaded filter paper is concerned with the immobilization of AuNPs with a rather large size (20-58 nm).[36,38-40] This is obviously not advantageous for catalytic applications due to the fact that a decrease in particle sizes would significantly enhance their catalytic activities.

Our previous studies have shown that Au,[43] Pd,[44] Fe,[11-13] Fe/Pd,[45] and Fe/Ni[46] NPs can be *in situ* formed and immobilized onto or within electrospun polymer nanofibers. In addition, AuNPs preformed using dendrimers as a stabilizer can also be assembled onto electrospun polyacrylic acid (PAA)/polyvinyl alcohol (PVA) nanofibers through electrostatic interaction for catalytic applications.[47] In our recent work, we have shown that polyethyleneimine (PEI) that has abundant amine groups on the molecular periphery can be used as a template to entrap AuNPs.[48] The formed PEI-entrapped AuNPs (Au PENPs) are quite small (1.9-4.6 nm) and colloidally stable in different aqueous media. These prior studies related to the preparation of stable Au PENPs and the immobilization/assembly of metal NPs onto or within electrospun nanofibers lead us to speculate that positively charged Au PENPs may also be assembled onto negatively charged filter paper for catalytic applications.

In this paper, Au PENPs were synthesized using $NaBH_4$ as a reducing agent at ambient temperature. Then a filter paper was soaked into an aqueous suspension of the Au PENPs, followed by rinsing with water and drying under vacuum. This process led to the assembly of Au PENPs onto the filter paper. The formed Au PENPs and the Au PENP-containing filter paper were characterized *via* different technologies. Finally the catalytic activity and reusability of the formed Au PENP-containing filter paper were tested by transforming 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) (Scheme 1).[49] To our knowledge, this is the first report related to the use of Au PENP-immobilized filter paper for catalytic applications.



Scheme 1. Schematic illustration of the assembly of Au PENPs onto filter paper for catalytic applications.

Experimental

Materials

Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and filter paper were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 4-NP was obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). Branched PEI (Mw = 25 000) was acquired from Aldrich (St Louis, MO). The water used in all experiment was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) with a resistivity higher than 18.2 MΩ·cm.

Synthesis of Au PENPs

Au PENPs were synthesized according to protocols described in our previous studies.[48, 50] The molar ratio between Au salt/PEI was controlled to be 50:1. In brief, an aqueous $HAuCl_4$ solution (30 mg/mL, 0.686 mL) was dropped into a water solution of PEI (25 mg, 10 mL) under vigorous magnetic stirring for 30 min, then an icy aqueous $NaBH_4$ solution (10 mg, 5 mL, with 5 molar equivalents of the Au salt) was rapidly added into the $HAuCl_4$/PEI mixture solution. The reaction was continued under stirring for 3 h. Finally, the mixture was dialyzed against water (6 times, 2 L) for 2 days to remove the excess reactants, followed by lyophilization to get the powder of Au PENPs. The Au PENPs were stored at -20 °C before use.

Preparation of the Au PENP-assembled filer paper

The process to assemble Au PENPs onto filter paper is shown in Scheme 1. A filter paper (1×2 cm^2, 18 mg) was immersed into an aqueous solution of Au PENPs (2.4 mg/mL, 5 mL) for 48 h, followed by rinsing with water for 3 times to remove excess non-adsorbed Au PENPs. The formed Au PENP-containing paper was dried under vacuum at room temperature for 24 h, and stored in a desiccator before use.

Characterization techniques

The formed Au PENPs and the Au PENP-containing paper were characterized by transmission electron microscopy (TEM, JEM2100, JEOL Ltd., Tokyo, Japan) at an operating voltage of 200 kV. TEM samples of Au PENPs were prepared by dropping an aqueous solution of a sample (5 μL, 0.5 mg/mL) onto a carbon-coated copper grid and air dried before measurements. In order to confirm the distribution of the Au PENPs onto filter paper, the Au PENP-assembled paper was first embedded in epoxy resin and then cut into ultrathin sections with an ultramicrotome equipped with a diamond knife. The diameters of Au PENPs were measured using image analysis software ImageJ 1.40G (http://rsb.info.nih.gov/ij/download.html). More than 300 NPs in the representative TEM images were measured to obtain the diameter distribution histograms of the Au PENPs. The morphology of the filter paper before and after assembly of Au PENPs was observed using scanning electron microscopy (SEM, TM-100, Hitachi, Tokyo, Japan) with an operating voltage of 10 kV. Before the SEM measurements, the samples were sputter-coated with 10 nm thick carbon films. Energy dispersive spectroscopy (EDS, IE300X, Oxford, U.K.) attached to the SEM was used to analyze the elemental composition of the samples. UV-vis spectrometry (Lambda 950 UV-vis spectrometer) was also performed to characterize the Au PENPs on the filter paper *via* the measurement of the reflectance of the samples. The Au content of the Au PENP-assembled filter paper was determined with a Leeman Prodigy inductively coupled plasma-optical emission spectroscope (ICP-OES) system (Hudson, NH). The Au PENP-assembled paper (5 mg) was treated with *aqua regia* (5 mL) for 3 h and the extract solution of Au was diluted before analysis.

Catalysis experiments

The catalytic efficiency and reusability of the Au PENP-assembled paper were tested by transforming 4-NP to 4-AP according to our previous study.[47] In brief, 4-NP (0.6 mL, 10 mM), $NaBH_4$ aqueous solution (0.6 mL, 10 M) and water (16.8 mL) were mixed in a 50-mL flask under magnetic stirring; the Au PENP-assembled paper was then immersed into the above flask at room temperature. At a given time interval, 0.5 mL solution was withdrawn and diluted to 1.5 mL with water before UV-vis spectroscopic measurements using a Lambda-25 UV-vis spectrophotometer (Perkin-Elmer, Waltham, MA). To test the reusability of the Au PENP-assembled paper, the paper was pulled out from the reaction mixture after one cycle of catalytic reaction and rinsed with water, and then the paper was dried for the next cycle of catalytic reaction. For comparison, the filter paper without Au PENPs was also investigated. The catalytic efficiency was calculated according to the following equation:

$$\text{Remaining fraction of 4-NP} = C_t/C_0 \times 100\% \quad (1)$$

Where C_0 is the initial concentration of 4-NP and C_t is the concentration of 4-NP at time *t*.

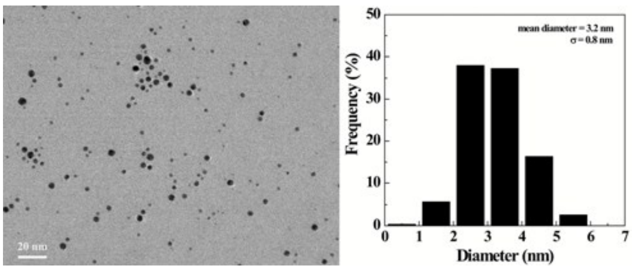


Fig. 1 TEM image and size distribution histogram of the Au PENPs.

Results and discussion

Preparation and characterization of the Au PENP-assembled paper

Au PENPs were first formed using PEI as a template. The formed Au PENPs were characterized via TEM (Figure 1). It can be seen that the Au core particles have a spherical shape and are pretty uniform with a mean diameter of 3.2 ± 0.8 nm. It seems that with the PEI templating approach, uniform AuNPs can be formed, in agreement with our previous work.[48]

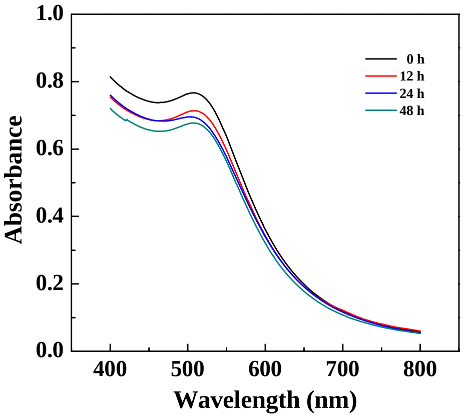


Fig. 2 UV-vis spectra of the Au PENP solution after immersed with the filter paper at different time points.

Au PENPs were then assembled onto the surface of the filter paper *via* electrostatic interaction since Au PENPs are known to be quite positive,[48] and the filter paper in aqueous solution has a negatively charged surface.[38, 51] The filter paper became quite brown after the assembly of the Au PENPs (Figure S1, Electronic Supplementary Information, ESI†), confirming the success of the assembly of Au PENPs. Meanwhile, the adsorption of the Au PENPs onto the filter paper was investigated by UV-vis spectroscopy. The characteristic surface plasmon resonance (SPR) peak of the Au PENPs at 518 nm decreases with the time and at 48 h the adsorption of the Au PENPs reaches the lowest (Figure 2). Therefore, the assembly time was set at 48 h for the preparation of the Au PENP-containing filter paper.

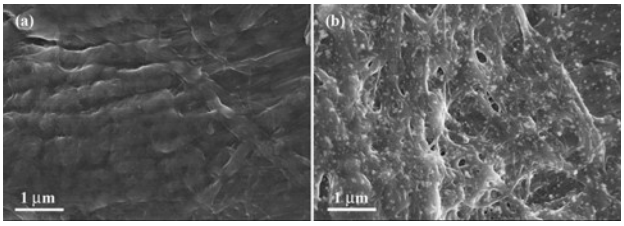


Fig. 3 SEM images of the filter paper without (a) and with (b) the assembled Au PENPs.

The morphology of the Au PENP-assembled filter paper was then observed *via* SEM (Figure 3). In contrast to the filter paper without the adsorption of the Au PENPs, the Au PENP-assembled paper shows some white particles, indicating that the Au PENPs have been successfully assembled onto the surface of the cellulose fibers of the filter paper. Moreover, it seems that the Au PENPs are uniformly distributed onto the cellulose fiber surface and do not aggregate. The adsorption of the Au PENPs onto the surface of cellulose fibers of the filter paper was also confirmed by EDS (Figure S2, ESI), where elemental Au can be clearly seen. The elemental oxygen observed in the EDS spectrum could be mostly attributed to the hydroxyl group of the cellulose fibers in the filter paper.

The distribution of the Au PENPs onto the filter paper was also characterized *via* TEM. A typical cross sectional TEM image of the Au PENP-assembled paper is shown in Figure 4a. It is obvious that the Au PENPs are well distributed along the cellulose fiber surface of the filter paper. High-resolution TEM (Figure 4b) shows that the Au PENPs possess a uniform spherical shape with a mean diameter of 3.5 ± 0.9 nm (Figure 4c), more or less similar to the ones before assembly. This means that the size and morphology of the Au PENPs do not have a significant change before and after the assembly process.

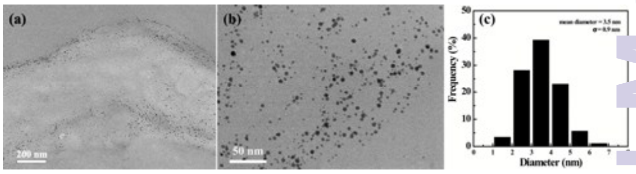


Fig. 4 Cross-sectional TEM image (a) and high-resolution TEM image (b) of the Au PENP-assembled filter paper. (c) shows the diameter distribution histogram of the assembled Au PENPs.

To further confirm the adsorption of Au PENPs onto the filter paper, reflectance UV-vis spectroscopy[47, 52] was also performed (Figure 5). Compared with the filter paper without Au PENPs which does not display apparent absorption features, the Au PENP-assembled paper shows the typical SPR peak of AuNPs at 525 nm. This also demonstrates the successful adsorption of the Au PENPs onto the surface of cellulose fibers of the filter paper. ICP-OES was used to quantify the percentage of AuNPs loaded onto the filter paper. We show that the Au loading percentage . 1.4%.

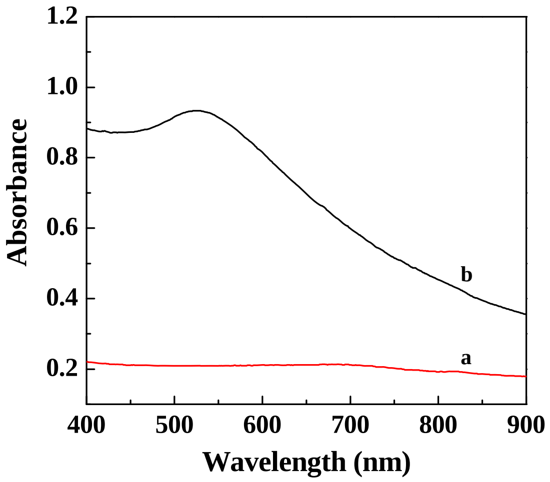


Fig. 5 Reflectance UV-vis spectra of filter paper without (Curve a) and with (Curve b) the assembled Au PENPs.

Catalytic transformation of 4-NP to 4-AP

The catalytic activity of the Au PENP-assembled filter paper was tested by a model reaction to transform 4-NP to 4-AP in the presence of $NaBH_4$.[43, 47] By exposing the filter paper without Au PENPs to the reaction mixture, the yellow color of 4-NP solution does not change with the reaction time (Figure S3, ESI†). UV-vis spectra data further show that the absorption peak of 4-NP at 400 nm slightly decreases within 36 min (Figure 6a), which is probably due to the physical adsorption of the 4-NP by the filter paper. This means that the filter paper without Au PENPs does not have any catalytic activity to transform 4-NP to 4-AP. In contrast, when the Au PENP-assembled filter paper was immersed into the reaction mixture solution, the color of 4-NP solution gradually fades with the reaction time (Figure S4, ESI†), and the intensity of the absorption peak of 4-NP at 400 nm also gradually decreases and disappears at 8 min. With the decrease of the characteristic absorption peak of 4-NP, the absorption peak of 4-AP at 300 nm gradually increases (Figure 6b), indicating that the Au PENP-assembled filter paper is able to effectively catalyze the transformation of 4-NP to 4-AP. Our results clearly support that the superior catalytic activity of the Au PENP-assembled paper is solely related to the assembled Au PENPs.

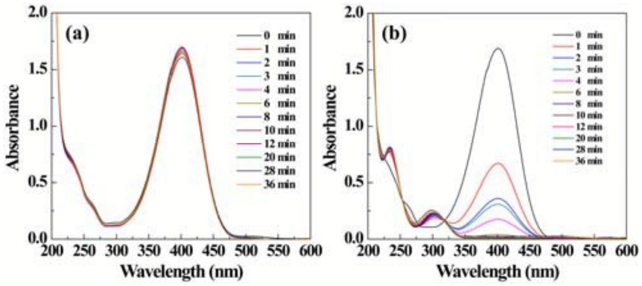


Fig. 6 UV-vis spectra of the 4-NP solution treated with the filter paper without (a) and with (b) Au PENPs assembled at different time points.

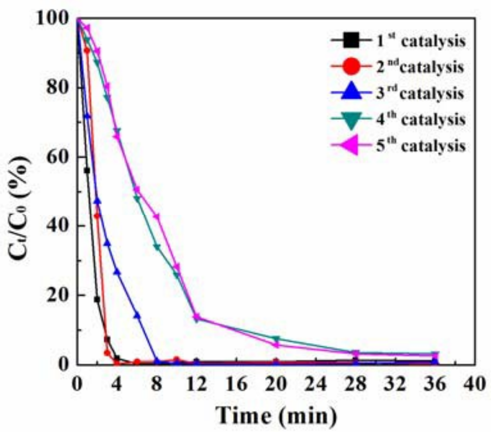


Fig. 7 Remaining fraction of 4-NP as a function of time in the presence of Au PENP-assembled filter paper for the first, second, third, fourth, and fifth cycle of catalytic reaction.

Although colloidal AuNPs are able to catalyze the conversion of 4-NP to 4-AP with a high catalytic activity,[53] the colloidal AuNPs are difficult to be recycled for further use. Therefore, the reusability of the Au PENP-assembled paper is rather essential as a catalyst. After one cycle of catalysis reaction, the Au PENP-assembled filter paper was washed with water and dried for the next cycle of catalytic reaction. It can be seen that more than 97% of 4-NP can be transformed to 4-AP in 4, 4, 8, 36, and 36 min for the 1st, 2nd, 3rd, 4th, and 5th reaction cycle, indicating that the Au PENP-assembled filter paper has excellent reusability (Figure 7). The slightly decreased catalytic activity of the Au PENP-assembled filter paper may be due to the swelling of the cellulose fibers during the catalytic reactions. In addition, the Au PENPs assembled onto the filter paper did not seem to have any appreciable release into the reaction solution. ICP-OES analysis shows that no Au content is detected in the reaction mixture solution even after 5 cycles' catalytic reactions. It should be noted that the catalytic activity of the Au PENP-assembled filter paper is superior to that of the electrospun PAA/PVA nanofibrous mats physically assembled with dendrimer-stabilized AuNPs.[47] By using nanofibrous mats physically assembled with dendrimer-stabilized AuNPs, more than 97% of 4-NP is able to be transformed to 4-AP after 8, 12, and 20 min for the 1st, 2nd, and 3rd reaction cycle, respectively. Apparently, the reaction time for the PAA/PVA nanofibrous material is longer. Furthermore, the employed materials of filter paper and the PEI polymer are quite cost-effective and sustainable. Hence the developed Au PENP-assembled filter paper is quite advantageous in terms of future mass production.

Conclusion

In conclusion, we report a facile approach to assembling Au PENPs onto filter paper *via* electrostatic interaction for catalytic applications. We show that with the porous fibrous microstructure and the negatively charged surface, filter paper can be assembled with the positively charged Au PENPs with an Au core size of 3.2 nm. The Au PENP-loaded filter paper can be used to catalyze the transformation of 4-NP to 4-AP with a conversion rate of 97% within 36 min and with a nice reusability. The developed approach to assembling Au PENPs onto filter paper may be extended to prepare other types of NP-immobilized filter paper for applications in catalysis, sensing, and biomedical sciences.

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Notes and references

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Table of Contents (TOC) Image

The assembly of polyethyleneimine-entrapped gold nanoparticles onto filter paper for catalytic applications†

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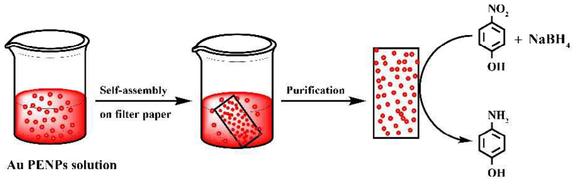

Polyethyleneimine-entrapped gold nanoparticles can be assembled onto filter paper *via* electrostatic interaction for high-performance catalytic applications.