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In-situ preparation of size-tunable gold nanoparticles in porous resorcinol–formaldehyde resin

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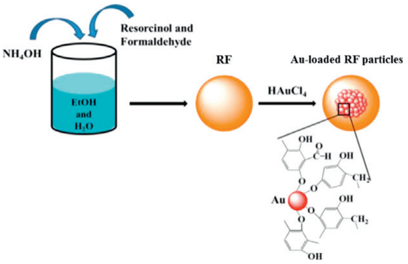
HIGHLIGHTS

- Au nanoparticles (NPs) with tunable size were prepared using porous resorcinol–formaldehyde resin (RF) as support.
- Au NPs can be deposited on the RF particle surface or inside the RF particles by adjusting pH of the solutions.
- Phenolic hydroxyl groups in RF support act as both ligand and reductant to promote formation of the Au NPs.
- Au NPs loaded in RF with optimal size show balanced activity and stability in catalytic reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, porous resorcinol–formaldehyde resin (RF) particles were used as support for in-situ preparation of Au nanoparticles (NPs) by directly immersing the RF into the solution of tetrachloroauric acid ($HAuCl_4$). The Au NPs can be deposited on the RF particle surface or inside the RF particles by simply mediating pH of the reaction solutions. It was revealed that the phenolic hydroxyl groups contained in the RF support can act as both ligand and reductant to promote the formation of the Au NPs. Size of the Au NPs deposited inside the RF particles was tunable in the range of 3.7–14.0 nm by changing the concentration of $HAuCl_4$. The Au NPs loaded in RF with optimal size were identified to show balanced activity and stability in catalyzing the reduction of 4-nitroaniline by $NaBH_4$.

1. Introduction

Catalytic performances of gold nanoparticles (Au NPs) loaded have been widely evaluated due to their size-dependent activity and excellent chemical stability [1–4]. It is known that Au NPs with smaller size usually exhibit better catalytic activity and poorer stability and those with larger size present better stability and poorer activity [5]. Loading Au NPs onto solid supports such as aluminum oxide [6], titania [7,8], silica [9–12] *etc.* is considered to be helpful to improve the performance and stability of the Au NPs and facilitate the separation of catalysts. When the supports used are nonporous in feature, Au NPs can only be loaded on outside surface of the supports [13–15]. The Au NPs located on the outside surface of the supports are susceptible to experience ripening and become larger in size. When the supports used are porous, Au NPs can be deposited inside the supports by in-situ reduction of the gold precursor absorbed into the pores of the supports [16]. The Au NPs embedded inside the porous supports showed improved stability compared to these located at outside surface of the nonporous supports [17–20]. However, it is difficult to tune the size of Au NPs and

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thus their activity and stability since size of the resulting Au NPs is usually dependent on the pore size of the supports [21,22].

In this work, we report the in-situ preparation of Au NPs with tunable size by using porous resorcinol–formaldehyde resin (RF) particles as support. Under optimal pH, the gold precursor (tetrachloroauric acid, $HAuCl_4$) could penetrate into the porous RF particles effectively and in-situ reduction of the precursor by the hydroxyl groups contained in RF resulted in the formation of Au NPs embedded in the RF support. Size of the Au NPs was tunable in the range of 3.7–14.0 nm by simply adjusting concentration of the precursor used. Size-dependent catalytic activity and stability of the loaded Au NPs were evaluated by a model reaction, the reduction of 4-nitroaniline into 4-aminoaniline.

2. Experimental

2.1. Materials and chemicals

Resorcinol was purchased from Aldrich (ACS reagent, 99%). Formaldehyde aqueous solution (37 wt%), 4-nitroaniline, sodium borohydride ($NaBH_4$), ammonia aqueous solution (NH_4OH, 25 wt%) and hydrogen tetrachloroaurate ($HAuCl_4$) were obtained from Shanghai Chemical Reagent Company. High-purity water (Pall Pure lab Plus) with a conductivity of 18 MΩ × cm was used for preparation of all the aqueous solutions.

2.2. Preparation of RF particles

RF particles were synthesized by using the extended Stöber method [23]. Typically, 0.1 mL of the ammonia solution (25 wt%) was mixed with a solution containing 20 mL ethanol and 8 mL pure water. After being heated to 30 °C, 0.14 mL of the formaldehyde solution (37 wt%) and 0.1 g resorcinol were added and stirred for 24 h. Then the reaction solution was transferred into a Teflon-lined autoclave and heated at 120 °C for 6 h. The resulting RF particles were separated by centrifugation (10,000 rpm/min, 15 min) and washed three times with pure water. Finally, the particles were redispersed in 30 mL pure water before use.

2.3. Preparation of Au-loaded RF particles

Dispersion of the RF particles (1 mL, 8 mg/mL) was added into 9 mL solution (pH 2.3) of $HAuCl_4$ with different concentrations (0.1, 0.3, 0.5, 0.7, and 0.9 mM) at 30 °C. Color of the mixtures changed from orange to pink gradually and became red after 20 min, indicating the formation of Au NPs. The resulting Au-loaded RF particles were isolated by centrifugation (10,000 rpm/min, 10 min), and washed three times with pure water and redispersed in 10 mL pure water for the further characterizations.

2.4. Measurements of $AuCl_4^-$ concentration

A procedure reported previously was adopted to determine the consumption of $AuCl_4^-$ in the reaction solution. An aliquot of the reaction solution of the RF particles and $HAuCl_4$ was taken out at a given time interval and then quenched immediately by adding it into a pre-prepared solution of NaCl (0.9 M) and HCl (pH 1). After being isolated by centrifugation (10,000 rpm/min, 10 min), absorbance of the supernatant was measured by UV–Vis spectrophotometer to determine $AuCl_4^-$ concentration according the standard curve [24].

2.5. Evaluation of catalytic activity

The Au-loaded RF particles were mixed with 3 mL mixture solution of 4-nitroaniline (0.1 mM) and $NaBH_4$ (1.2 mg) in a quartz cuvette. The reaction solutions were monitored by UV–vis spectrophotometer until the peak of 4-nitroaniline at 380 nm disappeared.

2.6. Characterizations

Transmission electron microscopy (TEM) images were taken on a JEOL-2010 electron microscope operating at 200 kV. At least 100 particles were measured to calculate the average sizes of the Au nanoparticles (NPs) loaded in RF support. Fourier transform infrared (FT-IR) spectra were measured on a PerkinElmer Spectrum One FT-IR spectrophotometer by using KBr pellets. UV–vis spectra were recorded with a Shimadzu UV–vis-1800 spectrophotometer. Inductively coupled plasma (ICP) analyses were performed on PerkinElmer Optima 3300 DV spectrometry. To prepare the samples for ICP analyses, dispersion of the Au-loaded RF particles (10 mL) were centrifuged at 10,000 rpm/min for 10 min, washed three times with pure water and redispersed in aqua regia (1 mL) with centrifuge tube. The tube was then put on shaking table (20 rpm/min) for 6 h. After that, total volume of the solution was adjusted to 10 mL by the addition of pure water. The RF particles remained in the solutions were separated by centrifugation. The as-prepared samples were analyzed to determine the concentrations of Au(III) in the supernatants. Zeta-potential measurements were carried out on a Brookhaven ZetaPALS instrument to determine isoelecctric points of the RF particles. N_2 sorption isotherms of the RF particles were collected on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosimetry System.

3. Results and discussion

Scheme 1 illustrates the procedure to prepare the Au-loaded RF particles. First, porous RF particles were prepared by the extended Stöber method (the condensation of formaldehyde and resorcinol under ammonia). After being immersed into the solution of $HAuCl_4$, the gold precursor penetrates into pores of the RF particles. The abundant hydroxyl groups in RF may act as both ligands and reducing agents for Au(III) precursor [15] and thus facilitate the formation of Au NPs in RF support. TEM observations showed that average size of the as-prepared RF particles were 200 nm (Fig. 1a). The particles presented extensive absorbance in the longer wavelength region (500–800 nm) attributed to light scattering effect of the large RF particles (Fig. 1b). Isoelectric point (IEP) of the RF particles was determined to be 2.3 (Supplementary material, Fig. S1a). N_2 sorption isotherms illustrated that surface area and total pore volume of the RF particles were 18.13 m^2/g and 0.118 cm^3/g respectively (Supplementary material, Fig. S1b). When the aqueous dispersion of RF particles (1 mL, 8 mg/mL) was mixed with 9 mL solution of $HAuCl_4$ (0.5 mM) at the pH 2.3 (IEP of the RF particles), color of the mixture changed from orange to red gradually in 20 min, suggesting the formation of Au NPs. Au NPs with an average size of 4.2 nm were deposited mainly inside the RF particles as indicated by TEM observations (Fig. 1c). Dispersion of the Au-loaded RF particles presented an absorbance at 540 nm (Fig. 1d), corresponding to the characteristic surface plasmon resonance (SPR) of the Au NPs. In addition, IR spectra (Supplementary material, Fig. S2) of the RF indicate that after being immersed into the solution of $HAuCl_4$ (0.5 mM, pH 2.3) for 20 min, stretching vibration of CH_2OH of RF particles at 1343 cm^{-1} became weaker, accompanied by the appearance of a new peak of COOH at 1714 cm^{-1} [25–27], indicating the hydroxymethyl groups act as the reducing agent for the formation of Au NPs.

Preparations of the Au-loaded RF particles were carried out at pH higher or lower than the IEP. As shown in Fig. 2, the resulting particles prepared under pH 1.0, 1.5, 2.0, 2.3 and 3.0 presented char-