



Polymer shell as a protective layer for the sandwiched gold nanoparticles and their recyclable catalytic property

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ARTICLE INFO

Article history:

Received 29 October 2012

Accepted 5 December 2012

Available online 26 December 2012

Keywords:

Silica/polymer core-shell microspheres

Sandwiched gold nanoparticles

Recoverable catalyst

ABSTRACT

Poly(ethyleneglycol methacrylate) (PEGDMA) shell was used as a protective layer for the sandwiched gold nanoparticles, which were prepared through the *in situ* reduction in the H₂AuCl₄ precursor in the presence of (aminopropyl)trimethoxysilane (APS) modified silica/PEGDMA core-shell microspheres. In this process, the silica/PEGDMA core-shell microspheres were afforded by the distillation-precipitation polymerization of the EGDMA monomer on the APS-modified silica particles with the aid of hydrogen-bonding interaction. The gold nanoparticles were formed at the interface between the silica core and the PEGDMA outer layer through the strong coordinate interaction between the gold nanoparticles and the amino groups on the surface of the silica during the reduction in H₂AuCl₄. The sandwiched gold nanoparticles exhibited highly catalytic efficiency and facile recovery with good stability.

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1. Introduction

In recent years, gold nanoparticles have attracted much attention due to their wide application in chemical or bio-sensor [1], surface enhanced Raman spectroscopy [2], biomedicine [3], and especially extraordinary properties for heterogeneous catalytic reaction such as reduction, oxidation, and hydrogenation of unsaturated substrates [4,5]. However, the neat gold nanoparticles are prone to aggregation and loss of their catalytic activity. Further, the separation of the catalyst in the reaction system was very difficult due to their relatively small size. In order to solve this problem, a series of catalytic supports were developed for the stabilization and facile separation of the gold material from the reaction system after the catalysis [6–9]. In the past few years, various inorganic and organic supports were applied for loading of the gold nanoparticles [6–9]. Although the gold nanoparticles loaded on the supports can be efficiently separated from the reaction system, the aggregation and loss of the gold nanoparticles from the support occurred, which remarkably reduced the catalytic efficiency after several cycles of catalysis.

The efficient method for prevention of the gold nanoparticles from aggregation to retain their catalytic efficiency together with the facile separation of the catalyst was to coat a protective shell for encapsulation of the gold nanoparticles. Thus, a series of core-shell particles with the gold nanoparticles as the core material were prepared for the protection of the gold nanoparticles. Me-

tal oxide, especially the silica, as the most common shell material for preparation of the core-shell particles, was used to protect the gold nanoparticles through the construction of Au@SiO₂ core-shell particles [10]. However, the catalytic efficiency of the gold nanoparticles was remarkably reduced due to the low permeable property of the silica shell. Although the resultant mesoporous silica improved the permeability for the substrate, the preparation procedure and the further removal of the pore-directing agent were relatively complex. Further, the calcination of the organic component (surfactant or polymer) in the silica matrix may result in the sintering of the gold particles or reduce the catalytic activity of the gold particles and the dispersion of the catalyst in water. As the polymer has a loose structure with the intrinsic pores in the matrix, especially under the catalytic conditions, the polymer shell was highly permeable for the reactant. Further, the functional group on the polymer shell can adjust the surface property from hydrophilicity to hydrophobicity. Thus, the gold/polymer core-shell particles may exhibit some advantages comparing to the gold/metal oxide core-shell particles. For example, Liz-Marzán et al. [11–13] used a two-successive emulsion polymerization technique to afford a polymer shell on the gold nanoparticles. The shell thickness and crosslinking degree were easily controlled for tuning the catalytic efficiency due to the intrinsic porous structure of the polymer shell [11]. In another way, the gold nanorattle, in which gold nanoparticles were encapsulated in a hollow protective shell, was developed as efficient recyclable catalyst for a wide range of reactions [14–18]. For instance, Lu et al. [16] synthesized gold/PNIPAM rattle-type microspheres via the removal of the middle silica layer from the corresponding Au@SiO₂@PNIPAM tri-layer

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microspheres, which were prepared through the successive sol–gel process and emulsion reaction on the gold nanoparticles. Song et al. [15,18] prepared a gold nanoparticle in a silica rattle-type particle through the etching of the inner gold content from the gold@silica core–shell particles. The catalytic efficiency of the gold/silica rattle-type microspheres can be efficiently tuned by the porosity of the silica shell, the size of the inner gold particles, and the functionality on the surface of the gold cores [15]. In the above two routes, the particle with one gold core was favored for preventing them from the aggregation, which resulted in the low loading of the gold nanoparticles in the support. Moreover, the direct coating of the gold nanoparticles was crucial and difficult, during which the process should be well controlled to avoid the aggregation of the gold nanoparticles. However, the synthesis involved the post-preparation of the gold nanoparticles, in which the procedure was relatively complex due to the indispensable multi-step operation.

In order to increase the gold content in the microspheres together with the stabilization of the gold nanoparticles by a protective shell, the recent developed method using core–shell microspheres for loading of the gold nanoparticles was feasible. Yin et al. used a sol–gel process with the subsequently protective etching process to coat a porous silica layer onto the magnetic gold composite [19]. Zhao et al. prepared a multifunctional microsphere with a silica coated Fe_3O_4 core with the sandwiched gold nanoparticles and the external ordered mesoporous silica with perpendicularly aligned pore channels [20]. However, the preparation process was tedious. The gold nanoparticles were relatively large which reduced the utility ratio of the gold components. Thus, it is urgent to develop a facile method for preparation of gold nanoparticles with a tiny size and a protective shell to prevent the coagulation.

In this paper, a core–shell silica/poly(ethyleneglycol dimethacrylate) ($\text{SiO}_2/\text{PEGDMA}$) composite microsphere was prepared by distillation-precipitation polymerization of EGDMA in presence of the (3-aminopropyl)trimethoxysilane (APS)-modified silica core as a template. Subsequently, the gold nanoparticles were sandwiched between the PEGDMA shell and inorganic silica core by a facile *in situ* reduction in HAuCl_4 with NaBH_4 as reductant, during which the amino groups on the silica surface played an essential role for the formation of well-dispersed gold nanoparticles via the coordination effect as well as the electrostatic interaction to gold species. The catalytic property of the sandwiched gold nanoparticles was primarily investigated by the reduction 4-nitrophenol to 4-aminophenol as a model reaction.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) was purchased from Acros. (3-Aminopropyl)trimethoxysilane (APS) was purchased from Aldrich. Ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25% in aqueous solution), ethyleneglycol dimethacrylate (EGDMA), and acetonitrile (dried over calcium hydride and purified by distillation) were obtained from Tianjin Chemical Reagent II Co. Tetrachloroauric acid trihydrate ($\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$) was purchased from Shenyang Research Institute of Nonferrous Metals, China. Sodium borohydride (NaBH_4) was purchased from Tianjin Chemical Reagents III Co. in analytical grade. 4-Nitrophenol (4-NP) was purchased from Tianjin Chemical Reagent Factory. 2,2'-Azobisisobutyronitrile (AIBN) was provided by Chemical Factory of Nankai University and recrystallized from methanol. All the other reagents were of analytical grade and used without any further treatment.

2.2. Synthesis of APS-modified silica particles

APS-modified SiO_2 particles were prepared through a sol–gel process. About 9.0 mL of TEOS was added to a mixture of 150 mL of ethanol, 15 mL of de-ionized water, and 3 mL of ammonium hydroxide aqueous solution (25 wt%). The mixture was vigorously stirred at room temperature for 24 h. Then, 1.0 mL of APS was added for stirring another 48 h. The product was collected by centrifugation and purified through extraction with ethanol for five times and finally dried at vacuum oven till constant weight. The nitrogen of the APS-modified silica microspheres was 1.58% by elemental analysis (EA), which meant that the amino group on the surface was 1.13 mmol/g.

2.3. Preparation of the $\text{SiO}_2/\text{PEGDMA}$ core–shell microspheres

$\text{SiO}_2/\text{PEGDMA}$ core–shell microspheres were prepared through distillation-precipitation polymerization of EGDMA in the presence of APS-modified silica particles as seeds. The details were as follows: 0.10 g APS-modified silica particles, 0.45 mL of EGDMA monomer, and 0.0090 g AIBN initiator were dissolved in 80 mL of acetonitrile in a 100 mL flask. The flask attaching with a fractionating condenser and receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 15 min, and the reaction system was kept under refluxing state for further 15 min. The polymerization was further carried out with distilling the solvent out of the reaction system, and the reaction was ended after 40 mL of acetonitrile was distilled off the reaction mixture within 100 min. After the polymerization, the resultant $\text{SiO}_2/\text{PEGDMA}$ microspheres were purified by repeating centrifugation, decantation, and resuspension in ethanol for three times. The products were dried in a vacuum oven at room temperature till constant weight. The $\text{SiO}_2/\text{PEGDMA}$ microspheres with other shell thicknesses were prepared via altering the EGDMA feed to 0.40, 0.50, and 0.60 mL while retaining the other reaction condition the same as the typical distillation-precipitation polymerization process.

2.4. Preparation of the $\text{SiO}_2/\text{Au}/\text{PEGDMA}$ core–shell microspheres

0.05 g $\text{SiO}_2/\text{PEGDMA}$ microspheres were dispersed in 1.0 mL of HAuCl_4 aqueous solution (0.10 M) and incubated for 24 h at room temperature. Then, the microspheres loaded with gold species were centrifuged from the solution and washed with water through repeating centrifugation, decantation, and suspension for 5 times. At last, the microspheres loaded with gold species were suspended in 5 mL of de-ionized water under ice bath. Then, 1.0 mL of NaBH_4 aqueous solution (0.10 M) was added dropwise to the above suspension to reduce the loaded gold species to the nanoparticles. The deep purple color was observed for the resultant APS-modified $\text{SiO}_2/\text{Au}/\text{PEGDMA}$ core–shell microspheres. The final products were purified by repeating centrifugation, decantation, and suspension in water for three times and dried in a vacuum oven at room temperature till constant weight. The loading capacity of the gold nanoparticles was 1.56% after the reduction as determined by ICP.

2.5. Catalytic reduction of 4-nitrophenol to 4-aminophenol in an aqueous medium

Catalytic properties of $\text{SiO}_2/\text{Au}/\text{PEGDMA}$ microspheres were investigated via the reduction in 4-nitrophenol (4-NP) to 4-aminophenol (4-AnP) with NaBH_4 as the reductant under ambient temperature in aqueous solution as a model reaction. A typical experiment was carried out as follows: 1.0 mL of 4-NP aqueous solution (5 mM, 5×10^{-7} mol), 1.0 mL of NaBH_4 (0.2 M, 2×10^{-4}

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