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Article

Bottom-up preparation of gold nanoparticle-mesoporous silica composite nanotubes as a catalyst for the reduction of 4-nitrophenol

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ABSTRACT

Gold (Au) nanoparticle (NP)-mesoporous silica (SiO_2) composite nanotubes were prepared by a bottom-up approach, in which Au NPs were anchored to the inner wall of mesoporous SiO_2 tubular shells. In this composite, the agglomeration, exfoliation, and grain growth of Au NPs were restricted, and the loading and size of the catalyst NPs were easily tuned. The mesoporous shell, open ends, and one-dimensional passage of the SiO_2 nanotubes all promote the diffusion of reactants, which enhanced the catalytic efficiency of this composite in the reduction of 4-nitrophenol. The Au NP-mesoporous SiO_2 composite nanotubes also demonstrated good reusability, and no leaching or agglomeration of the Au NPs was observed during the catalytic reaction.

1. Introduction

Noble metal nanoparticles (NMNPs) composed of metals, such as Au, Ag, Pt, and Pd, that range in size from several to dozens of nanometers are effective heterogeneous catalysts for various chemical reactions, including degradation of organic molecules [1–5], oxidation [6,7], hydrogenation [8], and C–C coupling [9,10]. Because bare NMNPs tend to aggregate, which decreases their catalytic activity, supportive platforms are usually required to load, stabilize, and separate these nanocatalysts. Recently, carbon materials like activated carbon, carbon nanotubes, and graphene have been frequently used as supports because of their high specific surface area, mechanical strength, and chemical stability [11–14]. The exfoliation and grain growth of loaded NMNPs, and the poor control of their dispersity are urgent issues that need to be resolved. Mesoporous silica ($mSiO_2$) materials can also host NMNPs inside their periodic, size-fixed channels. For example, NMNPs have been generated *in situ* within the pores of MCM-41 and SBA-15 by strategies such as chemical vapor deposition [15], supercritical fluids [16], impregnation [17], and ion exchange [18]. Although the exfoliation and grain growth of NMNPs can be substantially confined in $mSiO_2$, other crucial parameters including size, morphology, and loading of nanocatalyst are still difficult to control.

Bottom-up strategies developed in recent years may help to overcome these limitations [19–22]. For example, the surface of polymer latex and silica colloidal nanospheres can be decorat-

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ed with certain functional moieties like amino or thiol groups. As a result, NMNPs capped with suitable modifiers may attach onto these core templates through coordination or electrostatic interactions. Coverage of such complex by an $mSiO_2$ shell using sol-gel methodology would produce sandwich-like “core-NMNP-shell” structures. The advantages of such design are obvious: (1) NMNPs with determined composition, size, and morphology can be produced; (2) the loading of the nanocatalyst can be tuned simply by changing the concentration of their corresponding dispersion; (3) the agglomeration, exfoliation, and grain growth of NMNPs can be largely restricted because they are sandwiched between the core and shell; (4) reactants are easily transported across the $mSiO_2$ shell to react with the internal NMNP catalysts.

Compared with a spherical $mSiO_2$ shell, $mSiO_2$ nanotubes with open ends and a one-dimensional passage are thought to allow more efficient reactant transportation. Unfortunately, because of the lack of readily dispersible nanowire templates, the bottom-up fabrication of $mSiO_2$ nanotubes loaded with NMNPs is still challenging. Recently, the synthesis of aniline oligomer-based organic nanowires (ONWs) by self-assembly was reported [23]. Their unique water dispersity and surface charge means that these ONWs may be used as templates for the facile production of NMNP-$mSiO_2$ composite nanotubes. Herein, gold (Au) nanoparticles (NPs) are anchored to the inner wall of $mSiO_2$ nanotubes. The catalytic performance of these Au-$mSiO_2$ composite nanotubes is also examined by their ability to reduce the representative organic dye 4-nitrophenol (4-NP).

2. Experimental

2.1. Materials

Poly(diallyldimethylammonium chloride) (PDDA, 20% aqueous solution) was purchased from Sigma-Aldrich. Poly(vinylpyrrolidone) (PVP, molecular mass = 58000 g/mol), ammonium persulfate (APS, 98.5%), and trimethoxy(octadecyl)silane (C_{18}TMS, 90%) were obtained from Aladdin Reagent Co. Aniline, xylene, hydrogen tetrachloroaurate ($HAuCl_4$), trisodium citrate (Na_3Cit), $NaBH_4$, tetraethyl orthosilicate (TEOS), ammonia (28%), and 4-NP were purchased from Sinopharm Chemical Reagent Co. Deionized water was used throughout the experiments.

2.2. Synthesis of PDDA-modified ONWs

Water-dispersible ONWs were synthesized according to the literature [23]. In a typical experiment, PVP (0.5 g) and APS (0.1 g) were dissolved in deionized water (50 g). The solution was covered with xylene (20 g) to construct an oil-water interface. Aniline (0.1 g) was added dropwise into the upper xylene phase, and then the system was left undisturbed at room temperature for 24 h. ONWs formed in the bottom aqueous phase. The ONWs were separated by centrifugation and rinsed with deionized water.

The ONWs were modified with PDDA as follows. ONW powder (90 mg) and PDDA solution (1.0 g) were added to deionized water (20 g) and stirred at room temperature for 10 min. The PDDA-modified ONWs were separated by centrifugation and rinsed with deionized water three times before further usage.

2.3. Synthesis of ONW-Au composites

Au NPs (diameter = 12 nm) were synthesized by a reported method [24]. An aqueous solution of $HAuCl_4$ (5 mL, 3 mmol/L) was mixed with deionized water (10 mL) and heated to boiling point. Na_3Cit solution (10 mL, 5 mmol/L) was added, and then the mixture was reacted for 30 min to form a violet-red solution. Au NPs (diameter = 5 nm) were synthesized using a similar procedure [25]. An aqueous solution of $HAuCl_4$ (5 mL, 3 mmol/L), deionized water (25 mL), and Na_3Cit solution (10 mL, 5 mmol/L) was mixed at room temperature. $NaBH_4$ solution (10 mL, 2 mmol/L) was added dropwise under vigorous stirring, giving a pale red solution after 30 min.

To synthesize ONW-Au composites, a solution of Au NPs (12 nm, 1 mL) was slowly injected into a solution of the PDDA-modified ONWs (90 mg) in water (20 g). The mixture was stirred for 20 min before centrifugation and rinsing with water. Au NPs with a diameter of 5 nm were attached onto the PDDA-modified ONWs in the same manner. The loading of Au NPs can be tuned by varying the volume of their solution mixed with ONWs.

2.4. Synthesis of ONW-Au-SiO_2 composites

ONW-Au composite (90 mg) was added to deionized water (20 g), ammonia (0.3 g), and ethanol (2.0 g). TEOS (0.3 g) and C_{18}TMS (0.1 g) were added, and the mixture was stirred at room temperature for 12 h. The product was isolated by centrifugation, rinsed with deionized water and then ethanol, and dried at 80 °C to give an ONW-Au-SiO_2 composite as a pale yellow powder.

2.5. Synthesis of Au-$mSiO_2$ composite nanotubes

ONW-Au-SiO_2 composite was heated at a rate of 2 °C/min to 550 °C and then maintained at this temperature for 2 h. During heating, both the ONWs and pore-directing agents (the alkyl chain of C_{18}TMS) within the SiO_2 shell were removed to generate Au-$mSiO_2$ composite nanotubes as a pink powder. The Au-$mSiO_2$ composite nanotubes contained approximately 4% Au NPs when 1 mL of the 12-nm Au NP solution was used, as measured by inductively coupled plasma (ICP) spectroscopy. For comparison of catalytic performance, an analogue of the Au-$mSiO_2$ composite nanotubes was also prepared without using the pore-directing agent C_{18}TMS. This analogue is denoted as Au-SiO_2 composite nanotubes.

2.6. Reduction of 4-NP

The reduction of 4-NP by $NaBH_4$ using Au-$mSiO_2$ composite nanotubes as a catalyst was performed in a quartz cuvette at