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Catalytically active gold nanoparticles confined in periodic mesoporous organosilica (PMOs) by a modified external passivation route

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ABSTRACT

A modified external passivation route was performed to control the distribution of gold nanoparticles in periodic mesoporous organosilica (PMOs). The surfactants were first removed completely to ensure enough space in the mesopores. The external surface was then functionalized with *n*-octadecyltrimethoxysilane (C_{18}TMS), and finally the internal surface was modified with aminopropyltrimethoxysilane (APTMS) to enhance the adsorption of $(HAuCl_4)^-$ complex, followed by the reduction under hydrogen atmosphere. The external passivation aims to prevent the formation of large aggregated gold particles on the exterior surface. The aminopropyl groups at the internal surface ensure the incorporation of gold nanoparticles with a size about 5 nm inside the pore channels of PMOs. A combination of high-resolution TEM/STEM and SEM shows that the selective surface functionalization can effectively avoid the growth of large gold particles at the external surface and strictly confine the gold nanoparticles within the pore channels of PMOs. The confined gold nanoparticles in PMOs exhibit good catalytic properties in the reduction of methylene blue (MB) dye with sodium boron hydride as reducing agent.

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1. Introduction

Gold nanoparticles on appropriate supports have attracted much attention due to their potential applications in catalysis [1,2] and biology [3,4]. The confinement of gold particles (1–5 nm in diameter) within the channels or at the surface of mesoporous silica have gained considerable attention due to MCM-41 analogous shell properties, including large surface area, highly ordered mesopores, tunable pore size and large pore volume [5–10]. There have been many publications about gold nanoparticles confined in mesoporous silica by various methods, such as aerosol-assisted self assembly [6], organometallic approach [11], electroless deposition [12] and sonochemical reduction [13] or low temperatures hydrogen reduction of $(HAuCl_4)^-$ complex [14–19]. Gold particles coarsen considerably without the restriction of silica wall if they are located at the external surface of mesoporous silica. This is difficult to be avoided especially in the hydrogen reduction of $(HAuCl_4)^-$ complex since a fraction of $(HAuCl_4)^-$ can be adsorbed on the external surface of mesoporous silica particles and then gold will grow into large particles. However, a particle size small enough is preferable for catalysis application, for example, gold particles with diameter lower than ~5 nm show higher activity in CO oxidation [1,20,21]. Therefore it is of great significance to stabilize nanoparticles in the 2–5 nm size range. The external passivation of mesoporous materials [22–24], where external functionalization with hydrophobic groups such as methyl is performed prior to removal of the structure-directing agents (surfactants), has proven to be highly effective to avoid the potential to form large aggregated particles on the exterior surface. The selective surface functionalization, including the external passivation and the internal modification with other silanes, has been successfully used in the inclusion of II–VI nanomaterials such as CdSe or CdS within mesopores of MCM-41 and SBA-15 [25–28] or metal deposition in micropores of SBA-15 [29]. The hydrophobic groups at the external surface prevent while the ones at the inner surface facilitate the adsorption of metal precursor, so that nanoparticles will grow within the pore channels of mesoporous silica instead of aggregating at the external surface. However, if short chain hydrophobic groups are used and the surfactants have not been removed prior to the external passivation, this method is impossible to be used in the case of introducing gold nanoparticles into the mesopores of silica materials by the reduction of $(HAuCl_4)^-$ complex because during the external passivation, the surfactants will dissolve in organic solvent and then the short chain hydrophobic groups will enter the mesopores and bind to the inner surface of silica materials. It is obvious that such observation does not facilitate the incorporation of gold nanoparticles into the pore channels since the hydrophobic groups hinder the adsorption of $(HAuCl_4)^-$ complex. A modified external passivation route is performed in

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our work to control the distribution of gold nanoparticles in periodic mesoporous organosilica (PMOs) instead of ordered mesoporous silica materials. PMOs are synthesized by the supramolecular-assembly route in the presence of structure-directing agents using a silsesquioxane of the type $(EtO)_3Si–R–Si(OEt)_3$ as the sole precursor, therefore the organic groups R are located within the channel walls as bridges between Si centers [30–32]. These homogenously distributed organic groups provide PMOs materials with many of the favorable properties associated with organic polymers [33,34]. As a novel class of organic–inorganic nanocomposites, PMOs have potential applications in host-guest inclusion so that there are also appropriate candidate hosts to confine gold nanoparticles in the pore channels [35].

2. Experimental

2.1. Synthesis of periodic mesoporous organosilica

Periodic mesoporous organosilica was prepared using 1,2-bis(triethoxysilyl)ethane (BTESE, 96%) as the precursor and poly(ethylene glycol)-B-poly(propylene glycol)-B-Poly(ethylene glycol) (P123) as the structure-directing agent. For the synthesis, a molar ratio of BTESE, 1; P123, 0.034; HCl, 11.7; H_2O, 326 was applied. BTESE was added dropwise into a solution of P123, HCl and water at 40 °C. The mixture was stirred for 24 h until white precipitates formed, and then the products were moved into Teflon-lined autoclaves and aged for 72 h at 100 °C. The white precipitates were recovered by filtration, washed with water until reaching a pH of 6–7, and then dried at atmosphere. The surfactant template was removed from the organosilica materials through solvent extraction. An as-synthesized sample (0.5 g) was gently stirred for 6 h in a solution of HCl (36 wt%, 5 g) and ethanol (100 g) in a 50 °C water bath. This procedure was repeated several times until the surfactants were totally removed. The powder was filtered, washed with ethanol, and air-dried at 60 °C for 12 h to obtain the pure periodic mesoporous organosilica.

2.2. Functionalization of periodic mesoporous organosilica

To synthesize amino-functionalized PMOs, 3 g of PMOs was mixed with 1.5 g of aminopropyltrimethoxysilane (APTMS) in 100 ml of chloroform. This mixture was stirred at room temperature for 24 h and then filtered. The samples were washed with chloroform to remove the residual APTMS and then air-dried at 80 °C for 24 h. The samples were denoted as NH_2-PMOs. Long chain alkyl-functionalized PMOs were synthesized by suspending 3 g of PMOs in 100 mL distilled water and fluxing for 6 h at room temperature. The samples were then centrifuged and air-dried at 80 °C for 24 h. This hydrated PMOs and 1.5 g of *n*-octadecyltrimethoxysilane (C_{18}TMS) were mixed in 100 mL of chloroform. The reaction mixture was filtered after having been stirred for 24 h at room temperature. The solid product was washed copiously with chloroform to completely remove the residual C_{18}TMS and dried under ambient atmosphere (the sample was denoted as C_{18}TMS–PMOs). The synthesis of amino-functionalized C_{18}TMS–PMOs was conducted according to the procedure of the NH_2–PMOs sample described above. The samples were labeled as NH_2–C_{18}TMS–PMOs.

2.3. Impregnation and reduction of Au complex

The samples NH_2–PMOs, C_{18}TMS–PMOs and NH_2–C_{18}TMS–PMOs were mixed with the aqueous solution of $HAuCl_4 \cdot 4H_2O$, respectively. The extent of the adsorption of $(HAuCl_4)^-$ complex was estimated by the change of the absorbance band in ultraviolet–visible (UV–vis) spectra or the variation of the color of solutions after a certain time. The mixture was stirred for 3 h in dark and then filtered. The impregnated samples were reduced under H_2 atmosphere at 373 K for 2 h. The obtained samples were labeled as Au–NH_2–PMOs and Au–NH_2–C_{18}TMS–PMOs, respectively.

2.4. Catalysis testing

The preliminary catalytic testing for Au–NH_2–C_{18}TMS–PMOs was carried out by reduction of 2 mL methylene blue (MB) (2×10^{-5} mol/L) in water using 1 mL $NaBH_4$ (0.05 mol/L) as the reducing agent and 0.005 g Au–NH_2–C_{18}TMS–PMOs sample as the catalyst. The concentration of MB was monitored by UV–vis spectra.

2.5. Characterization of the samples

High resolution scanning electron microscopy (HRSEM) images were obtained on a JEOL JSM 6500F microscope equipped with an energy-dispersive X-ray analyzer (EDX). HAADF (high angle annular dark field) scanning transmission electron microscopy (STEM) and TEM images were obtained on a FEI TECNAI F30 microscope operating at 300 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8/advance diffractometer using a high power Ni-filtered Cu Kα radiation (1.541 Å) source. Nitrogen adsorption measurements were carried out at 77 K on a Micromeritics ASAP 2020M volumetric adsorption analyzer. Before the measurements, the samples were outgassed under vacuum at 90 °C for 5 h. The pore size distribution was obtained from the adsorption branch of isotherms using BJH approach. The solid state ^{13}C cross-polarized magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectra were recorded on a Bruker DSX300 spectrometer according to the following measurement conditions: 75.47 MHz resonance frequency, 2.0 s delay time, π/2 pulse, 3.55 μs pulse width, 4 kHz MAS rate, and 2048 times the number of acquisitions. Chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm. UV–vis spectra were measured on a Thermo Evolution 600.

3. Results and discussion

The location control of gold nanoparticles in periodic mesoporous organosilica is performed according to Scheme 1. The surfactants (P123) in as-prepared PMOs were completely removed in advance, and then external passivation with hydrophobic octadecyl groups, followed by internal functionalization with aminopropyl groups were conducted on the extracted PMOs, and finally $(HAuCl_4)^-$ complex was adsorbed into PMOs and reduced under hydrogen atmosphere. As shown in the solid state ^{13}C CP MAS NMR spectra (Fig. 1), the complete removal of P123 from PMOs by the extraction treatment has been confirmed since there are no detectable signals at 17 and 73 ppm assigned to the remnant P123 surfactants in all samples [36]. The signals at 5.0 and 22.7 ppm are related to the carbon atoms linked to silicon atoms, and the presence of these signals indicates that no Si–C bond cleavage occurs during either the synthesis or the surfactant extraction process. The resonance at 30.0 ppm can be assigned to the carbon atoms of octadecyl groups, indicating that C_{18}TMS have been functionalized into PMOs. In addition, a resonance attributed to the carbon atoms of aminopropyl groups appears at 43.8 ppm for the NH_2–C_{18}TMS–PMOs, suggesting the successful functionalization with APTMS. The signals at 18.2 and 58.3 ppm represent the carbon of unreacted surface methoxy groups ($Si–OCH_3$) [37].

All samples display a type IV nitrogen adsorption-desorption isotherm, indicative of a typical mesoporous structure (Fig. 2), and exhibit a narrow pore size distribution (PSD) (Fig. 3). The iso-

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