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Communications

Synthesis of Gold Nanoparticles via Electroless Deposition in SBA-15

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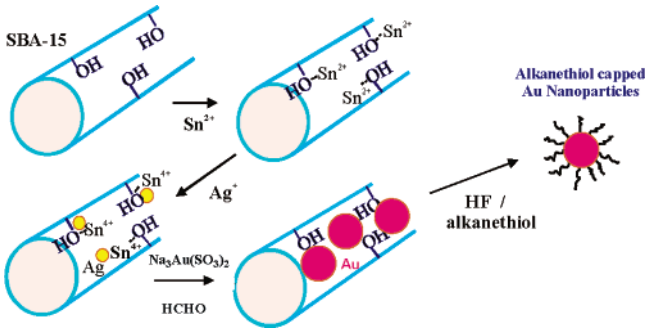
The synthesis and fabrication of nanostructured materials are currently of great fundamental, scientific, and technological interest.[1] Mesoporous materials are one class of nanostructured materials whose ordered pore structures are in the 2−30 nm scale. They have been expected to feature in the development of other nanoscale materials and devices either directly or by acting as templates.[2] With regard to their use as templates, nanocomposite and nanoscale materials have been prepared using the pores of mesoporous materials via four routes. The first involves the impregnation of metal salts in the pores of mesoporous materials and subsequent reduction (thermally, chemically, or photochemically) or reaction with appropriate reagents to produce metal or semiconductor nanoparticles and nanowires.[3] The second method involves the addition of metal salts or organometallic reagents during the initial synthesis of the mesoporous material. Follow-up chemical reduction or thermal treatment leads to the formation of nanoparticles inside the pores or walls of the material.[4] The third method involves encapsulation of pre-made nanoparticles during the synthesis of the mesoporous material.[5]

Scheme 1. Synthesis Scheme of Electroless Synthesis Au/SBA-15 Nanocomposite and Alkanethiol-Capped Gold Nanoparticles



Here, we report the synthesis of monodisperse samples of gold nanoparticles ranging from 5 to 9 nm in SBA-15 using a fourth method: silver-catalyzed electroless deposition (Scheme 1). The synthesis resulted in a Au/SBA-15 nanocomposite material with a very large loading level of monodisperse gold nanoparticles aligned in the channels. Extraction of the SBA-15 entrapped gold from the nanocomposite by etching the SBA-15 framework with HF in the presence of alkanethiols results in milligram quantities of gold nanoparticles with low polydispersity. To the best

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of our knowledge, this is the first time that SBA-15 materials have been used to exclusively produce 5−9 nm metal nanoparticles and in large quantity. Two reports of metal-catalyzed electroless deposition in mesoporous materials used Pd-catalyzed synthesis and both reports claimed the synthesis resulted in nanowires.[6] Furthermore, the electroless deposition of Ni and Cu did not include dissolution of the silicate framework[6a] while the electroless deposition of Au in SBA-15 thin film did include dissolution only for the purpose of TEM imaging and it was done in the absence of alkanethiol. The quantity of Au nanowires collected from thin films in the latter is very minute and the resulting nanowires are in a corrosive HF solution.[6b]

The synthesis of gold nanoparticles in SBA-15 was addressed using an electroless deposition method[7] as follows. SBA-15 was prepared as per literature reports.[8] The as-synthesized SBA-15 material was treated with hexamethydisilazane (HMDS)/toluene (5 mL/60 mL) solution under N_2 for 12 h to cap (and thus passivate) the external surface silanols with trimethylsilyl groups. The surfactant was then removed via solvent extraction. Five hours of stirring of 0.5 g of SBA-15 in 100 mL of diethyl ether:ethanol (1:1) solution yields the mesoporous material. After filtration and air-drying, ca. 0.5 g of the material was stirred in an aqueous $SnCl_2$ (20 mL, 26 mM/70 mM trifluoroacetic acid) solution for 20 min. This process allows Sn^{2+} to complex to the pore walls.[9] Filtration was followed by washing the precipitate several times with water:ethanol solution and air-drying. The resulting Sn^{2+}-loaded materials was stirred in aqueous ammonical $AgNO_3$ solution (40 mL, 0.029 M) for 3 min resulting in a yellow-brown powder. The resulting Ag clusters formed on the pore walls then serve as nucleation and growth sites for gold nanoclusters. The precipitate was then dispersed in 10 mL of H_2O, to which 3 mL of gold plating solution ($Na_3Au(SO_3)_2$, Oromerse Part B, Technic Inc.) was added and the solution was sonicated for 1 min, then centrifuged, and decanted. Under sonication conditions, 4 mL of aqueous formaldehyde (0.625 M) was immediately added, leading to the reduction of the infiltrated Au(I). After filtration and washing of the precipitate with EtOH:H_2O (1:1), a dark red-brown gold nanoparticle/SBA-15 nanocomposite (Au/SBA-15) powder was isolated. A likely reaction sequence is as per Reference 7.

The Au/SBA-15 nanocomposite material (0.045 g) was then dispersed in 25 mL of ethanol containing 5 g of 11-mercapto-1-undecanol. The silicate host was etched by adding 5 mL of aqueous HF solution (48 wt %) to the dispersion followed by sonication for 30 min. [*Caution: HF is highly toxic and extreme care has to be exercised while handling it!*] A light red-wine supernatant and a dark red-brown colored precipitate were obtained after centrifugation. The HF-containing supernatant was discarded and the precipitate was rinsed carefully with ethanol:water (1:1). The washed precipitate was then dispersed in various solvents under sonication, resulting in purple to dark red-wine colored solutions which usually remain stable for several months.

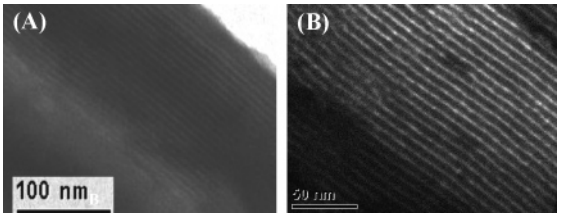

Figure 1. Representative TEM image of mesoporous SBA-15 (A) *before* electroless deposition of Au and (B) *after* electroless deposition of Au. Dark contrast in (A) originates from the *walls* of the SBA-15, where 80 keV imaging conditions are used. Dark contrast in (B) originates from Au deposits formed in the *voids*, where 80 keV imaging conditions are used.

The TEM images (Figure 1) of SBA-15 and Au/SBA-15 show well-ordered channel structures that are characteristic of mesoporous materials. The channel volumes are less electron dense before electroless deposition (Figure 1A) but they clearly become more electron dense than the silica wall due to the encapsulated gold nanoparticles after the electroless deposition (Figure 1B). The center wall-to-center wall distance of a channel pore obtained from TEM is ca. 8.1 nm. The powder XRD patterns (see Supporting Information) show a low-angle Bragg reflection that is characteristic of ordered mesoporous materials and several wide-angle reflections that correspond to gold nanoclusters when indexed. When the low-angle XRD reflections were indexed on a hexagonal symmetry ($a_0 = 2d100/\sqrt{3}$), the unit cell of the mesoporous material was found to be ca. 11.1 nm before and 11.9 nm after the electroless deposition. These are slightly greater values than the center-to-center distance of the channels obtained from the TEM image.[10] The unit cell sizes are consistent with the largest particle core size obtained from the materials. This indicates that the particle size is clearly controlled by the pore size of the mesoporous material and that the particles grow exclusively in the channel walls after the external silanols are capped with HMDS (see Supporting Information).[11]

The alkanethiol-capped nanoparticles obtained after etching the composite materials with HF in alkanethiol solutions are dispersible in various solvents such as ethanol, THF, and water:ethanol (1:1). TEM images of the gold nanoparticles resulting from exposure to 11-mercapto-1-undecanol and then dispersion in ethanol:water (1:1) are shown in Figure 2. The resulting particles are 5−9 nm in diameter and are less polydisperse (±15.0%) (Figure 2 inset) than those obtained

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(10) Although no significant change in the lattice spacing of the material has occurred during the electroless deposition process, the value of center wall-to-center wall distances for the SBA-15 material obtained from TEM image is 3.0−3.8 nm less than that obtained from the XRD analysis. This discrepancy for the value may arise from the lower TEM resolution or the relatively higher degree of change in *d*-spacing (subsequently larger percentage of error) of XRD measurements at very low angles, 2θ. Such slight differences are in fact not uncommon in SBA-15 materials (see ref 3b).
(11) If the external surface hydroxyl groups are not capped with trimethylsilyl to inhibit the formation and growth of particles on the external surfaces, rather large particles (>20 nm in diameter) form (see Supporting Information also).

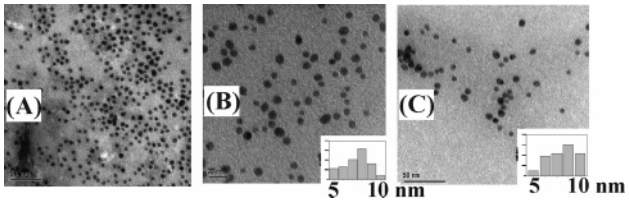

Figure 2. Representative TEM images of gold nanoparticles after being extracted from SBA-15 and dispersed in an ethanol:water solution. Insets: Size distributions for the corresponding TEM images.

via the conventional Brust/Schiffrin[12] solution synthesis (typically ±30%).

The composition of the materials was established using energy-dispersive X-ray spectroscopy (EDX) during TEM imaging (see Supporting Information). The EDX of Au/SBA-15 before HF etching exhibits large silicon and oxygen peaks. After HF etching, these peaks are either very minor or are absent and a large Au peak is observed. Materials treated for shorter periods of Au electroless plating yield a substantial Ag signal. The corresponding solutions are also yellowish-brown in color after HF etching, suggesting the substantial presence of Ag nanoparticles exist in these solutions.

Electroless deposition methods (of Cu, Ni, and Au) in SBA-15 have previously been reported to result in nanowires.[6] A significant number of gold nanorods were indeed obtained from some of the syntheses procedures used here, especially when either a longer reaction time was used or if a larger concentration of Ag^+ or Au^+ was used (Supporting Information). Furthermore, "necklace"-type aggregates of gold nanoparticles and structures that appear to be nanowires in TEM images in some of the Au/SBA-15 samples were observed. However, upon etching with HF, only nanoparticles with a few nanorods were obtained (Supporting Information). The etching of Au/SBA-15 in the absence of alkanethiols results in aggregated particles or aggregate resembling corrugated nanowires (see Supporting Information) These observations suggest that (i) aggregates or corrugated nanowires within the channels break up into nanoparticles upon sonication in the presence of HF/alkanethiols or (ii) nanowire-like aggregates form under the electron beam during imaging. However, since the Au/SBA-15 is visually red-brown in solid form or when dispersed in solution, it clearly does not contain a nanoparticle aggregate (typically blue-purple). Moreover, the 3 nm walls of SBA-15 isolate the rows of particles from one another. UV−Vis−NIR spectra of the solid samples exhibited only a plasmon peak around 523 nm and no peak in the near-IR region (Supporting Information), ruling out the presence of nanorods.

In conclusion, this work demonstrates that the electroless deposition of Au in SBA-15 is practical for the synthesis of milligram quantity of Au nanoparticles per unit gram of SBA-15 in the pores. It is noteworthy that the pores of SBA-15 are fully occupied by the nanoparticles. Au/SBA-15 is expected to have interesting optical, electrical, and magnetic properties such as waveguides,[13] magnetic coupling,[2c] and heterogeneous catalysis[3c] because it has aligned arrays of gold nanoparticles, where each lined array is electronically isolated from neighbors by virtue of the silica framework.

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Supporting Information Available: TEM images, XRD patterns, EDX spectra, and UV−Vis spectra of Au/SBA-15 nanocomposites and Au nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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