



Reduction effect of pore wall and formation of Au nanowires inside monolithic mesoporous silica

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Abstract

This Letter reported reduction effect of pore wall on AuCl_4^- ions at low temperature ($<100\text{ }^\circ\text{C}$) and formation of Au nanowires within pores of monolithic mesoporous silica. Such nanostructured Au/silica assembly was obtained by soaking the silica into HAuCl_4 solution, drying and annealing at $\leq 300\text{ }^\circ\text{C}$, without any special reduction treatment. Further experiments, revealed that the reducing groups OH^- on pore walls are responsible for reduction of Au^{3+} ions at low temperature. The formation of Au nanowires can be attributed to the low nucleation rate, uni-directional diffusion of Au atoms along pore channels and the size confinement of pore channels.

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1. Introduction

Since the introduction of mesoporous silica in 1992 by Mobil researchers [1], mesoporous materials have generated a surge of interest, because of their potential applications over a wide technological range, such as filtration, biological separation and catalysis support [2–7]. Despite their interesting structural and synthetic aspects [8–11], properties of mesoporous materials have not been fully investigated. Understanding the properties of mesoporous materials, for example, high chemical activity is of great importance. Recently, we have synthesized Au/ SiO_2 assembly

by soaking monolithic mesoporous silica into HAuCl_4 aqueous solution and subsequent treatment. It was found that Au^{3+} ions are reduced to Au^0 at a low temperature $<100\text{ }^\circ\text{C}$ in air without any special reduction treatment. Subsequent annealing at the temperature $\leq 300\text{ }^\circ\text{C}$ results in formation of Au nanowires inside the monolithic porous silica. Such nanostructured Au/silica assembly assumes tunable optical properties, from near infrared to visible region, simply by subsequent annealing in air at different temperatures, which has been reported elsewhere [12]. In this Letter, we focus on the reduction effect of pore wall on Au^{3+} ions and formation of Au nanowires within pores of the monolithic mesoporous silica from optical measurements and micro structural characterization.

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2. Experiment

The plate-like monolithic mesoporous silica (about 1 mm in thickness) was first prepared by the sol-gel technique with precursors; tetraethyl-orthosilicate, water, alcohol (catalyzed by HNO_3), followed by ageing, drying and finally annealing at 700 °C for 1 h, as previously described [13]. The mesoporous silica prepared in this way, whose pores are inter-connected and open to ambient air, had the porosity about 50%, a specific surface area of 510 m^2/g , and pore diameters mainly distributed in the range less than 30 nm, determined by isothermal N_2 adsorption measurement, as described previously [13]. The pre-formed silica host was then immersed into 0.010 M HAuCl_4 aqueous solution for more than 2 weeks, which is long enough to soak the host [14]. The soaked sample (0.08% Au in weight, or 100:0.24 in molar ratio of Si to Au, determined by the soaking solution concentration and host porosity [13]), was washed using deionized water and dried at 80 °C for about 14 h, followed by annealing at 300 °C for about 2 h. For reference, HAuCl_4 solution was directly added into the precursor solution of the mesoporous silica. After gelation, ageing and drying at 80 °C for 2 weeks, a plate-like (also about 1 mm in thickness) HAuCl_4 -doped silica, or reference sample, was obtained. The molar ratio of Si to Au is also close to that of the soaked sample by controlling addition amount of the HAuCl_4 solution. Subsequently, the reference sample was annealed at 300 °C for 2 h. All the experiments were performed in air atmosphere.

Optical absorption spectra for the samples were recorded at room temperature on a Cary 5E UV-Vis spectrophotometer. The HAuCl_4 aqueous solution was diluted to 50 times and measured at 10 mm of path length (in a quartz cell). Isothermal nitrogen sorption measurement was conducted using an Omnisorp 100CX specific surface area and porosity analyzer. X-ray diffraction (XRD) was carried out on an X-ray diffractometer (Phillips PW 1700). For transmission electron microscopic (TEM) observation, the samples were ground into powders and dispersed in ethanol in a test tube, followed by ultrasonic vibration in a bath for 20 min. A few drops of the liquid were

placed on a carbon coated copper grid. After evaporation of the alcohol, the copper grid was mounted on TEM (H-800) or a high-resolution transmission electron microscope (HRTEM) (JEOL 2010) equipped with energy-dispersive X-ray spectrometer (EDS).

3. Results

For treated soaked sample, the existence of doped particles inside pores of silica has been confirmed by the fact that the nitrogen sorption isotherm for dried or annealed soaked sample is lower than that for SiO_2 host, as previously illustrated [13,15]. Fig. 1 illustrates the optical absorption spectra of both soaked and reference samples, after drying and subsequent annealing. The absorption spectrum of HAuCl_4 solution is also included for comparison. For the dried soaked sample (see Fig. 1a), a broad absorption band with a maximum around 970 nm appears, accompanied by two other peaks at 225 and 305 nm, respectively, (a small peak at 1400 nm is from silica and not discussed here). Subsequent annealing at 300 °C induces the enhancement of the broad band and red-shift to 1030 nm, together with appearance of a shoulder around 535 nm and disappearance of the peaks in ultraviolet region, as shown in inset of Fig. 1a. In contrast, the dried reference sample shows no absorption peak in visible region, except two much stronger peaks around 225 and 320 nm, respectively, together with a sharp peak at 234 nm, as illustrated in Fig. 1b. Subsequent annealing at 300 °C results in a peak around 525 nm (see inset of Fig. 1b), which originates from the normal surface plasmon resonance (SPR) of Au nanoparticles [16]. Both samples show completely different optical spectra in the region from visible to near infrared. For HAuCl_4 solution, in the ultraviolet region there are three absorption peaks located at 228, 240 and 310 nm, respectively, similar to those of the dried reference sample, as indicated in Fig. 1c.

Fig. 2 shows the XRD results of the soaked and reference samples. After drying at 80 °C for more than 10 h, we can see, for the soaked sample, that a diffraction peak at ca. $2\theta = 38^\circ$, corresponding to

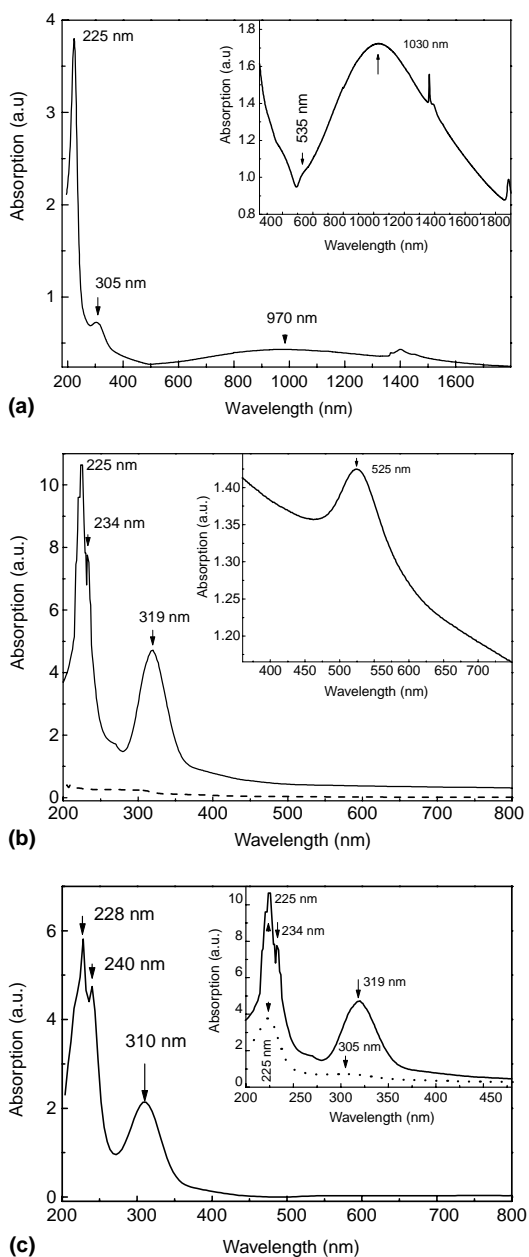


Fig. 1. Optical absorption spectra of the soaked (a) and reference samples (b) after drying at 80 °C, and HAuCl₄ solution (c). Insets of (a) and (b) are their spectra after subsequent annealing at 300 °C for 2 h, respectively. Dash line in (b) is the absorption spectrum of the solvent perspired from the wet-gel of the reference sample during aging. Inset of (c): absorption spectra of the dried reference sample (solid line) and dried soaked sample (dotted line) (from (a) and (b)).

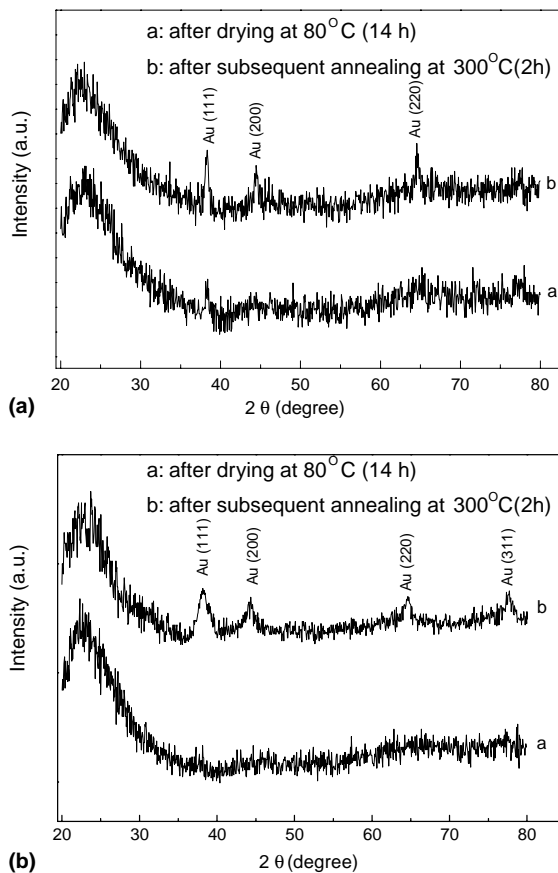


Fig. 2. XRD results of the soaked sample (a) and the reference sample (b) after drying and subsequent annealing.

(111) plane of Au crystal, seems detectable (see curve, as in Fig. 2a). The corresponding EDS measurement has confirmed the existence of Si, O, Au peaks but only a mere trace of Cl (not shown here). Subsequent annealing at 300 °C induces the obvious diffraction peaks of Au crystal planes (111), (200) and (220). However, there are no such diffraction peaks in the dried reference sample until it was annealed at 300 °C, as illustrated in Fig. 2b.

TEM examination indicates that Au nanowires are formed together with some roughly spherical Au nanoparticles in annealed soaked sample. Most nanowires in the experiment are 10–20 nm in diameter and curved with branches although we also found some are straight and uniform in diameter. Fig. 3 presents the typical TEM images of Au

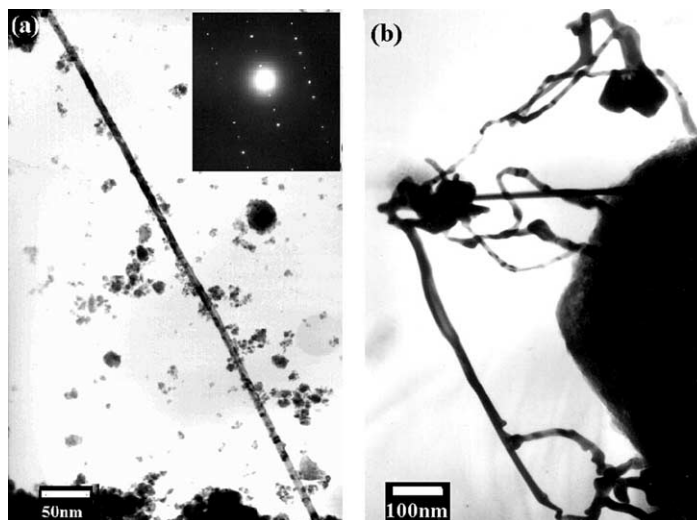


Fig. 3. TEM images of dried soaked sample after annealing at 300 °C, showing a straight and uniform Au nanowire (a) and Au nanowires with branches and curvature (b). The inset of (a) is the SAED pattern of the Au nanowire.

nanowires together with some smaller Au particles, removed from silica host by ultrasonic vibration during preparation of TEM specimen, and silica aggregates on the carbon film. The selected area electron diffraction (SAED) reveals the single crystalline characteristic of the Au nanowires. However, for annealed reference sample, only approximately spherical Au nanoparticles were observed uniformly dispersed in mesoporous silica (not shown here), as illustrated in Fig. 3 of [17].

4. Discussion

4.1. Absorption peaks of AuCl_4^- ions

The absorption peaks in the ultraviolet region directly originate from AuCl_4^- ions. The two peaks in the range of 225–240 nm are attributed to charge transfer of AuCl_4^- ions, and the peak around 310 nm originates from d–d transition of the ions, which are unique ‘fingerprints’ for the AuCl_4^- ions and have been reported [18]. Decrease of these peaks indicates reduction of AuCl_4^- ion concentration in sample. Hence after drying at 80 °C, there still exist AuCl_4^- ions in both soaked and reference samples, but the ion concentration in the

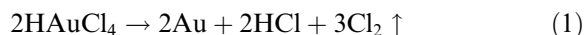
former is much lower than that of the latter, due to much weaker AuCl_4^- ion peaks (see inset of Fig. 1c). Combining XRD and EDS measurements, we can know that most AuCl_4^- ions within pores of the mesoporous silica host have been reduced and even some Au crystals have been formed for the soaked sample after drying at 80 °C for >10 h.

For the reference sample, however, the opposite is true. Most Au ions have not been reduced after drying at 80 °C from optical measurements and XRD data (see Figs. 1b, 2b). According to its synthesis process, when the reference sample was in wet gel state (or before drying), it seems that AuCl_4^- ions should exist both in the silica skeleton and solvent within pores of the wet gel. But further experiments, revealed that there are no detectable AuCl_4^- ions in the solvent within the pores. As we know, ageing of a wet gel will result in extrusion of solvent from the gel due to contraction of gel skeleton. Dash line in Fig. 1b is the absorption spectrum for this solvent perspired from the reference sample during aging after completion of gelation. It shows no detectable absorption peaks of AuCl_4^- ions. This means that in the reference sample most of AuCl_4^- ions enter silica skeleton during sol–gel, instead of the solvent within pores after gelation as we usually expected.

Compared with those of HAuCl_4 solution, for the dried reference sample, the two charge-transfer bands, blue-shift to about 225–234 nm, respectively, but the d–d transition band undergoes a significant red-shift to about 320 nm. As for the dried soaked sample, the two charge-transfer bands of AuCl_4^- ions merge into one band at 225 nm, accompanied by blue-shift of the d–d transition band. These band shifts are indicative of the environmental changes of AuCl_4^- ions, or formation of some adduct by an interaction between the Si–O groups, and the negative charge on the AuCl_4^- ions. Obviously, the interaction should be stronger for the reference sample than that in HAuCl_4 solution, due to the ions in the silica skeleton, resulting in the red shift of d–d transition to 320 nm [16]. For the soaked sample, after drying, remaining unreduced AuCl_4^- ions should be coordinated with silica on pore wall. It is evident that the interaction is weaker than that of AuCl_4^- ions in aqueous solution and in silica skeleton, and hence the d–d transition blue shifts.

4.2. Reduction effect of pore wall

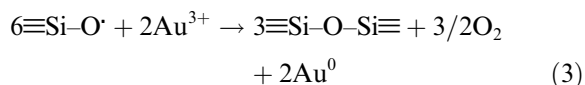
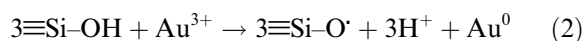
As we know, the decomposition of HAuCl_4 into Au usually occurs in air at a temperature higher than 170 °C according to the following reaction [19]:



Preparation of nanostructured Au in porous solids is usually conducted at the temperature higher than 250 °C or under H_2 atmosphere [17,20,21]. Obviously, the results of the soaked sample in this Letter are beyond our expectation. Here, we attribute it to the reduction effect of pore wall in monolithic mesoporous silica.

The as-prepared mesoporous silica has high specific surface area and a large number of defects (such as unsaturated bonds) on the surface of pore wall, which result in high surface energy and in turn high chemical activity [22–24]. Due to the existence of unsaturated bonds, Si on the pore wall bonds with hydroxyl (–OH) by dissociative adsorption of water molecules, and forms silanol groups, i.e., $\equiv\text{Si-OH}$. Thus, when the pore wall is in contact with HAuCl_4 solution, AuCl_4^- ions will

adsorb on the pore wall via ligand exchange [25], and ion exchange between H^+ in $\equiv\text{Si-OH}$ and Au^{3+} in AuCl_4^- will occur. The adsorption of the gold ions on the wall will change their redox potential. During the subsequent drying process, the $\equiv\text{Si-OH}$ groups on pore wall provide the capability required for the reduction of the AuCl_4^- ions [11,26]. Accordingly, Au^{3+} reduction can proceed under the surface-mediated reduction processes:



Therefore, HAuCl_4 can be reduced during drying at 80 °C in air, which has been confirmed by XRD, EDS and optical measurements of the soaked sample.

In order to further confirm, the reduction effect of silica pore wall on Au^{3+} ions, we drop some HAuCl_4 solution on the surface of a piece of glass slide without pores, followed by treatment in the same way. The results are different from those of the soaked sample, but similar to the reference sample, i.e., after drying process, the optical spectrum shows two strong AuCl_4^- peaks in ultraviolet region and XRD shows no trace of Au crystal diffraction peaks, as illustrated in Fig. 4. This indirectly confirms the reduction effect of silica pore

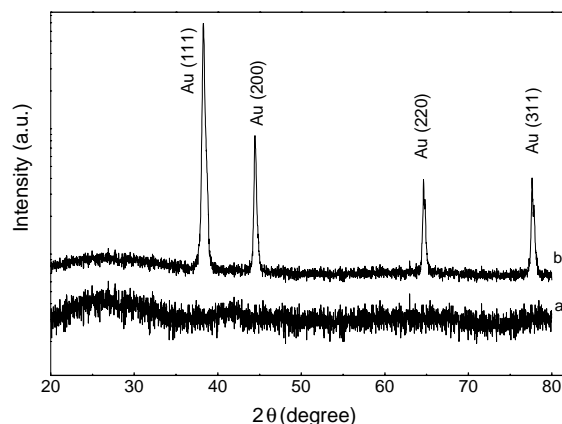


Fig. 4. XRD for HAuCl_4 solution dropping-glass slide after drying (80 °C for 14 h) (a) and subsequent annealing at 300 °C for 2 h (b).

wall on Au^{3+} ions. Subsequent annealing at 300 °C results in similar optical absorption spectrum and XRD result to the reference sample, as shown in inset of Figs. 1b, 4b.

As for the reference sample, because most of AuCl_4^- ions were embedded in silica skeleton during the sol–gel and there are no detectable AuCl_4^- ions in the solvent within pores after gelation (wet gel) (dash-line in Fig. 1b), as mentioned above, the surface-mediated reduction process like reactions (2) and (3) cannot occur during drying process.

4.3. Growth-confinement effect of pore channels

The formation of Au nanowires can be attributed to the confinement growth of Au nuclei in the pore channels. During drying process, the reduction of AuCl_4^- ions in the soaked sample is followed by clustering of Au atoms and formation of Au crystal nuclei within pore channels. Due to diminishing atomic activity at low temperature, both nucleation rate and growth of Au crystal should be very low [27]. Moreover, only some special sites inside pores would be beneficial to form Au nuclei in energy [23]. Most of the reduced Au^0 atoms located at other sites are in atomic state or oligomers, and they diffuse onto the formed nuclei due to existence of Au atomic concentration gradient around them. Obviously, this diffusion is uni-directional along the channels, and hence the Au crystallites grow into nanowires within the channels even at 80 °C, which can be deduced from the broad absorption peak in Fig. 1a (SPR peak position of Au nanoparticles red-shifts with increasing their aspect ratio [12,28]). Subsequent annealing at 300 °C leads to growth of formed nanowires, corresponding to the increase of optical absorption and red-shift of the peak position. The existence of nanowires and aspect ratio distribution result in a broad SPR at lower energy region, which was discussed elsewhere [12]. For the reference sample, subsequent annealing at 300 °C in air gives rise to reduction of HAuCl_4 into Au according to reaction (1), but there is no such growth condition for Au nanowires as the soaked sample (no Au atoms in the pore channels). Therefore Au nuclei form in silica skeleton and grow into ultra-fine Au nanoparticles with high dispersion.

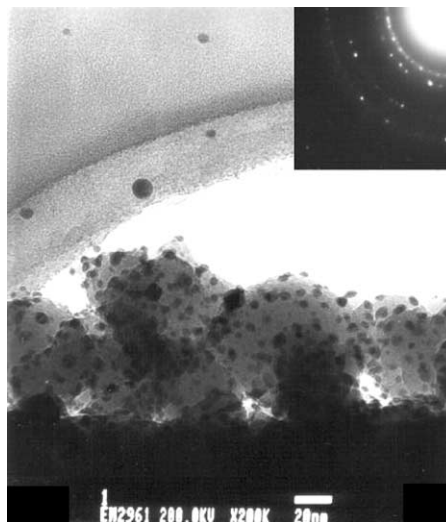


Fig. 5. TEM micrograph of soaked silica powders after annealing at 300 °C. Inset: the corresponding SAED pattern.

For further verification, that the pore channels in the monolithic mesoporous silica play a crucial role in formation of Au nanowires, we sufficiently grind the as-prepared mesoporous silica into powders. 0.01 M HAuCl_4 , aqueous solution is added to the silica powders and mixed until a uniform yellow color is observed. Then the composite is dried at 80 °C in air for about 14 h, followed by annealing at 300 °C for 2 h. TEM examination shows that the spherical Au nanoparticles with 5–7 nm in diameter uniformly disperse on the surface of silica spheres, as shown in Fig. 5. Obviously, when the mesoporous silica is ground into powders, most of long pore channels are destroyed. Thus, without the confinement of the pore channels, HAuCl_4 is reduced and Au nuclei grow into nanoparticles on the surface of silica particles.

5. Conclusions

In summary, reduction effect of pore wall on HAuCl_4 and formation of Au nanowires within pore channels of the monolithic mesoporous silica have been demonstrated from optical measurements and micro structural characterization. Only soaking monolithic silica host and subsequently

drying at $<100\text{ }^{\circ}\text{C}$ for enough long time, can we obtain 1D nanostructured Au/silica assembly. Monolithic porous host and drying at low temperature for enough long time, not a single one of these conditions can be dispensed with. Otherwise, spherical Au particles will be obtained. We believe that the surface-mediated reduction effect of silica pore wall induces the reduction of HAuCl_4 in mesoporous silica during drying at $80\text{ }^{\circ}\text{C}$ in air atmosphere. The low nucleation rate (at low temperature), uni-directional diffusion of Au atoms along pore channels and the size confinement of pore channels lead to formation of the Au nanowires.

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