Highly Dispersed Gold Nanowires within the Pore Channels of Mesoporous Silica Thin Films Prepared From Organic–Inorganic Hybrid Films Functionalized with Basic Moieties

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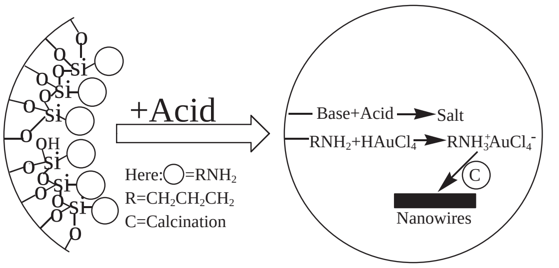
Combined a surface modification scheme with a neutralization reaction, accompanied with reduction procedure, highly dispersed gold nanowires within the pore channels of mesoporous silica thin films were prepared from organic–inorganic hybrid films modified with basic moieties.

Metallic nanowires have been the focus of many researchers because of their current and potential applications in fields such as electronics, optics, and chemical sensors.[1] Ordered mesoporous hosts with a uniform porous structure could provide excellent molds for the fabrication of these kinds of novel materials.[2] However, up to date, most work are centered on the growth of nanowires inside mesoporous powder[3] rather than mesoporous thin films (MTFs), which would find attractive applications in making nano-ordered devices.[4] Even so, all the previous MTFs with metal nanowires loaded were prepared with electrochemical method, in which a conduct substrate should be used for electrochemical deposition[5a] or a complicated process should be employed to introduce catalysis centers for electroless deposition.[5b,5c] Herein, we develop a facile and simple strategy to incorporate highly dispersed gold nanowires into the pore channels of MTFs.



Scheme 1. Pictorial representation of the strategy to incorporate gold nanowires into the pore channels of MTFs.

The synthetic protocol is shown in Scheme 1. After the basic organosilane of aminopropyltrimethoxysilane (APS) was modified on the inner surface, the $HAuCl_4$ could be introduced into MTFs via neutralization reaction.[6] Followed by reduction procedure, the Au nanowires could be formed within MTFs. It should be emphasized that using this strategy, MTFs not only served as a confined template, a function for traditional wet impregnation method,[3b,3c] but also a reactor for neutralization reaction. Specifically, the MTFs were prepared as a previous report on the quartz substrate.[7] Surfactant was extracted using ethanol with a little concentrated HCl being added under refluxed condition. The resultant films were extensively washed with ethanol and deionized water. The obtained films were then dipped into 200 mL of toluene solution. After half an hour, 20 mL of APS was poured into the above toluene solution and refluxed for 12 h to obtain base-functionalized MTFs.[8] It should be noted that trace of adsorbed water in MTFs and impurity water in toluene could effectively enhance the grafted number of basic $-NH_2$-bearing organosilane because of the formation of dense monolayer from the slightly hydrolyzed APS as shown in Scheme 1.[9] The modified films were dipped into a 5 mM $HAuCl_4$ aqueous solution for ca. 2 h. $HAuCl_4$ could be effectively adsorbed owing to the strong interaction of neutralization reaction. The resultant films were calcined under H_2 atmosphere at 350 °C for 2 h.

The assembly process was investigated by UV–vis spectroscopy. Figure 1 shows the UV–vis absorption of $HAuCl_4$ aqueous solution and composite films with $HAuCl_4$ being bonded. Pure solution shows two intense charge-transfer bands, peaking at 212 and 234 nm (not shown), and a moderate d–d transition band at around 310 nm as shown in Figure 1a.[10] After the $HAuCl_4$ has reacted with $-NH_2$, the *d–d* transition band undergoes a significant red shift to ca. 330 nm ascribed to the strong interaction between $-NH_2$ and $HAuCl_4$,[6,10] which indicates that $HAuCl_4$ has been successfully introduced into the pore channels of MTFs.

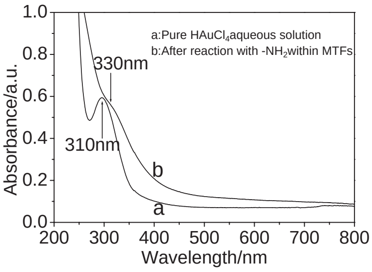


Figure 1. UV–vis spectra of the (a) pure $HAuCl_4$ aqueous solution and (b) functionalized MTFs bonded with $HAuCl_4$.

Figure 2 presents the low angle XRD of the as-synthesized and Au nanowire-loaded MTFs, and the inset shows the high angle patterns. Two intense diffraction peaks of the as-synthesized MTFs at $2\theta = 1.06$ and 2.10°, indexed as (100) and (200) reflections, are characteristic of a two-dimensional hexagonal structure with d_{100} spacing of ca. 8.4 nm as shown in Figure 2a. The absence of the (110) reflection is typical in the XRD patterns for the hexagonal unit cells with the *c* and *a* axes parallel to the film substrate.[5] After the extraction, the peaks shift toward the higher angle and further shift during the calcination process because of the further contraction of silica framework. An apparent decrease of the small angle peak intensity can be found after the incorporation of gold, which indicates that Au nanowires have been indeed formed within MTFs since the pore filling would reduce the scattering contrast between the pores and the walls, and result in the reduction of the peak intensity.[5] The presence of characteristic diffraction peaks at $2\theta = 38°$, assigned to (111)

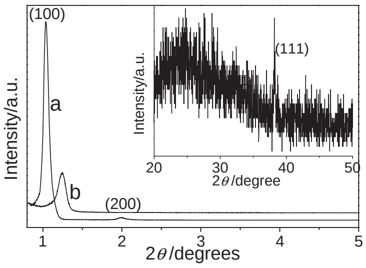


Figure 2. Small angle XRD of (a) the as-synthesized, (b) Au nanowire-loaded MTFs. The inset shows the wide angle XRD patterns of gold nanowire-loaded composite films.

planes of the face-centered cubic (fcc) structure of gold, indicates that gold has well crystallized as shown in the inset.

The morphology and distribution of Au within the MTFs were directly observed by transmission electron microscopy (TEM). The highly dispersed and homogenous synthesized nanowires are shown in Figure 3a as dark rodlike objects between the walls of MTFs. It can be clearly seen that gold nanowires have a uniform size of ca. 7 nm equal to the pore diameters of the MTFs. These measurements suggest the feasibility of controlling the diameters of the nanowires via the pore sizes of the templates. The selected area electron diffraction (SAED) in the inset also supports the fact that gold has crystallized. In order to observe the morphologies of the incorporated gold nanowires directly, HF/H_2O/ethanol solution added with alkanethiols as a stabilizing ligand was employed to remove the silica framework.[11] Figure 3b shows the isolated Au nanowires with diameter of ca. 7 nm and an aspect ratio higher than 10. The corresponding SAED is very clear and the rings can be indexed to (111), (200), (220), and (311) reflections of crystallized Au. The corresponding HRTEM image of a single Au nanowire in Figure 3c shows {111} lattice fringe across the width of the entire nanowire, with an interplanar spacing of ca. 0.24 nm similar to that of fcc structured gold.

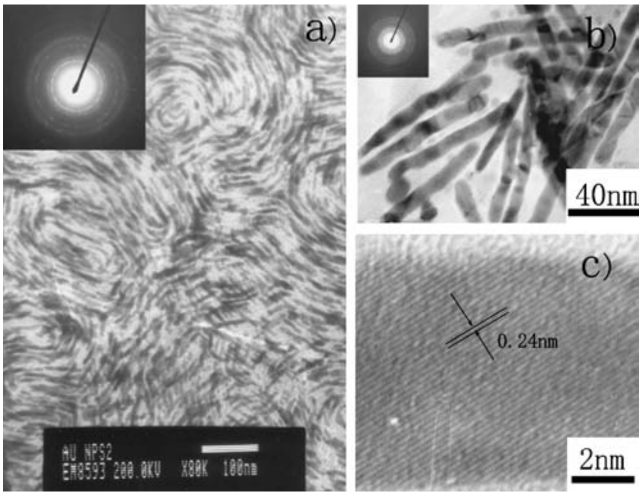


Figure 3. Typical TEM images of (a) the MTFs loaded with gold nanowires and the inset shows the corresponding SAED; (b) unsupported gold nanowires after the removal of silica framework; (c) is a HRTEM of a single gold nanowire.

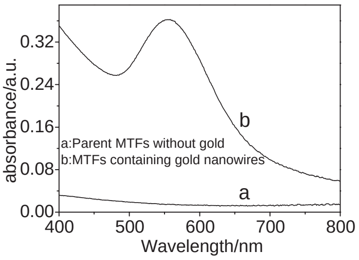


Figure 4. UV–vis spectra of (a) the parent MTFs without gold, and (b) the MTFs loaded with gold nanowires.

Figure 4 shows the optical absorption of the parent MTFs and the composite films. Though the parent films show no absorption in the wavelength region >400 nm, the composite films containing gold nanowires reveal an surface plsamon resonance absorption peak at 565 nm along with the increased backgrounds which are originated from an interband transition of the d band to the Fermi surface.[12] These results further indicate the presence of the gold nanowires within MTFs.[5c]

In summary, a new strategy has been developed to synthesize highly dispersed Au nanowires within MTFs. The key point of the used method was the modification of the inner surface of MTFs with basic moieties, which served as reactants to effectively adsorb acidic metal precursors via neutralization reaction. The synthesized composite films could have attractive applications in optical fields, such as nonlinear optics. This method can be extended to the preparation of other metal nanowire-loaded composite films via the selection of the different acidic metallic precursor compounds.

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