

Nano-Au/silica composite synthesized using nitrated SBA-15 as a host

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Abstract

Nano-Au/silica composite has been synthesized by using nitrated mesoporous silica material as host. The nitration treatment of mesoporous silica, i.e. SBA-15, with ammonia caused the generation of $-\text{NH}_x$ groups on its surface. After impregnation with aqueous solution of HAuCl_4 and following reduction, highly-dispersed gold nanoparticles with uniform sizes were formed in the channels of the nitrated host. The samples were characterized by FTIR, XRD and TEM techniques. The results showed that the nitration treatment was an alternative and effective way to modify the surface properties of the silica host for immobilizing gold nanoparticles. It was supposed that the interaction between the surface $-\text{NH}_x$ groups and gold precursors was the key to immobilizing gold in the channels.

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1. Introduction

Nano-metal/host composites have received much attention due to their special characteristics on optics, electronics and catalysis [1]. Porous materials, such as carbon nanotubes [2], anodic alumina membranes [3] and many mesoporous materials [4] are often used as hosts to incorporate metal nanostructures. Among these hosts, mesoporous silica, like MCM-41 and SBA-15, are widely used owing to their high surface areas and narrow pore sizes distributions. Most importantly, the metal growth could be effectively confined into the channels of the mesoporous silica, and thus the size of the formed metal particles or wires was limited to nano-scale [5,6]. However, it is still a great challenge to immobilize metal particles into the channels of the silica hosts due to weak interaction between the silica surface and the metal precursors. During impregnation and followed drying and reduction treatment, the metal particles are apt to migrate on the outer surface and cause bulky agglomerates [7]. One usual approach to dissolve this problem is to modify the host surface with organic compounds containing certain functional groups,

such as amines or thiols. Then the metal species can be immobilized in the channels of the host by stronger interactions between the metals and these functional groups [8,9]. Shi et al. used organic amines, including *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (TPED) and aminopropyltrimethoxysilane (APS) to modify mesoporous silica and finally incorporate Au nanoparticles into its channels [10]. They argued that the introduction and immobilization of the Au species should be attributed to a neutralization reaction between the basic amine groups and the acidic HAuCl_4 precursor. Up to now, the modification of the host surface was usually achieved by using toxic organic amines or thiols.

In the present work, we used nitrated SBA-15 as host to embody highly-dispersed Au nanostructures. Recently, nitrated mesoporous silica has been studied as a solid base. The basic property was derived from the surface $-\text{NH}_x$ species, which was initiated from the partial replacement of oxygen atoms by nitrogen atoms. These surface $-\text{NH}_x$ groups were expected to play a similar role as the amine groups did in immobilizing metals.

2. Experimental

SBA-15 was synthesized in accordance with the published procedure [11] using tri-block copolymer poly(ethylene oxide)–

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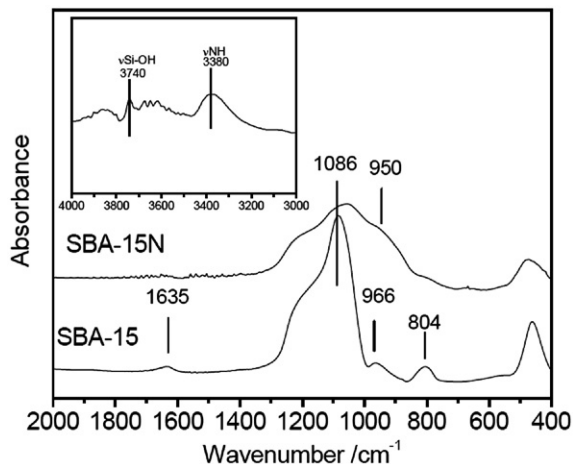


Fig. 1. Infrared spectra (in KBr) of SBA-15 and SBA-15N. Inset: Infrared spectrum of SBA-15N under vacuum.

poly(propylene oxide)–poly(ethylene oxide) [(EO)₂₀(PO)₇₀(EO)₂₀] as template in acidic conditions. In brief, a solution of (EO)₂₀(PO)₇₀(EO)₂₀:HCl:TEOS:H₂O=2:60:4.5:15 (mass ratio) was prepared, stirred for several hours at 40 °C, and then heated under autogenous pressure in a sealed autoclave at 100 °C for 20 h. The solid product was collected by filtration and calcined at 500 °C for 6 h.

SBA-15 was nitrated with ammonia as reported in literature [12]. SBA-15 powder was placed in a tubular quartz furnace with pure nitrogen flushed to remove air before nitridation. Afterwards, ammonia atmosphere was introduced. Then the temperature of the furnace was raised to 1000 °C and held for 20 h for nitridation reaction. After that, the sample was cooled to room temperature. The obtained white sample was denoted as SBA-15N.

For preparing Au nanoparticles inside the mesoporous channels, SBA-15N was first impregnated with 0.1 M HAuCl₄ aqueous solution under stirring for 70 h, then washed with deionized water to remove the excess HAuCl₄ and finally dried at 120 °C in air for 30 min. The obtained sample was reduced with NaBH₄ solution to obtain the final product, which was denoted as Au/SBA-15N.

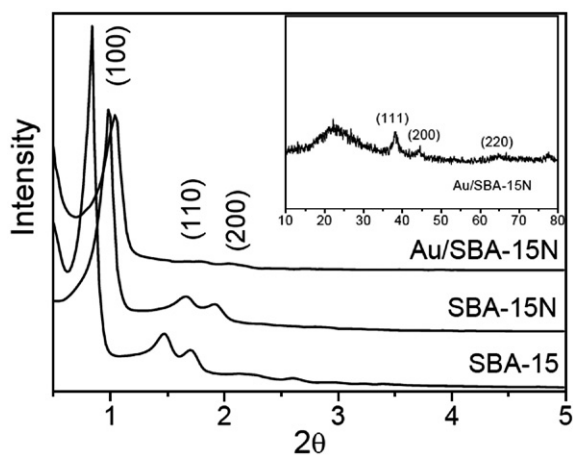


Fig. 2. Small-angle XRD patterns of mesoporous samples. The inset shows the wide-angle XRD patterns of SBA-15 loaded with gold nanoparticles.

The nitrogen content of the samples was determined by alkaline digestion with molten NaOH. The detailed procedure was as described in literature [13]. In the present work, the content of nitrogen in SBA-15N was 10.8 wt.%. The infrared spectra were recorded on a Bruker EQUINOX 55 spectrometer by KBr pellet method in the range between 400 and 4000 cm⁻¹ at 4 cm⁻¹ resolution and 32 scans. To avoid the influence of air, the self-support pellet of the nitrated sample was treated at 400 °C under vacuum for 1 h, and then cooled to room temperature under vacuum before infrared measurement. X-ray diffraction (XRD) patterns were collected on a D/Max-βb X-ray diffractometer equipped with Cu Kα radiation and graphite monochromator. Transmission electron microscopy (TEM) images were obtained on a JEOL-2000EX electron microscope operating at the accelerating voltage of 120 kV.

3. Results and discussion

Fig. 1 gives the IR spectra of the parent and nitrated silica hosts. For parent SBA-15, the two absorption bands centered at 1086 cm⁻¹ and 804 cm⁻¹ are ascribed to the asymmetric and symmetric stretching of Si–O–Si. The peaks at 1635 cm⁻¹ and 966 cm⁻¹ are corresponding to δ (HOH) of physisorbed water and Si–O stretching vibration of the surface Si–OH groups [14]. After nitridation, a new band appeared at 950 cm⁻¹ and the Si–O–Si stretching band at 1086 cm⁻¹ was broadened. This should be attributed to a greater disturbance and a bond strain caused by the incorporation of nitrogen into the framework [12]. When the sample was measured under vacuum (Fig. 1, inset), the intensity of the typical OH stretching band (3740 cm⁻¹) was found weaker than that for the parent silica, while a broad band appeared at about 3380 cm⁻¹. This new absorption band can be assigned to ν (NH) of Si–NH–Si on the surface of SBA-15N [15]. Thus it can be seen that the partial replacement of the oxygen atoms by nitrogen atoms after nitridation leads to generation of new –NH_x groups on the surface, which further results a modification of the surface properties of the silica host.

The XRD patterns of the parent and nitrated hosts, as well as the Au incorporated material, are shown in Fig. 2. The diffractions of all samples exhibited three clear peaks, which is in well accordance with 2D hexagonally ordered structures. In the diffraction pattern of SBA-15N, three peaks shifted slightly to the high-angle region, implying a shrink of mesostructure after nitridation. The same phenomenon has also been reported by other researchers [12,15]. Although the XRD peaks intensity of Au/SBA-15N slightly decreased, it is clear that the ordered mesostructure of the host was still remained after loaded with Au species. The wide-angle XRD pattern of Au/SBA-15N, as given in

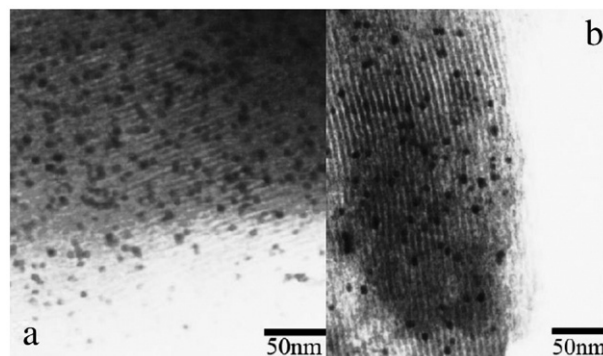


Fig. 3. TEM images of Au/SBA-15N.

Fig. 2 (inset), shows the existence of incorporated Au. Three weak diffraction peaks appeared at about 38.0° , 44.3° and 64.5° , respectively, corresponding to the (111), (200) and (220) reflections of cubic Au.

Fig. 3 presents TEM images of the Au/SBA-15N composite. In accordance with the XRD results, the mesoscopic order of the host could be clearly identified in the TEM views of Au/SBA-15N. Au nanoparticles appearing as dark dot-like objects could be observed between the walls of the channels. These nanoparticles are evenly distributed in the channels with a uniform size, which is close to the pore diameter of SBA-15N.

For comparison, non-nitrided SBA-15 was also used as a host in the same conditions. But no Au particles could be found in the channels as we have investigated through TEM observation (not given). This phenomenon indicates that nitridation is the key to immobilizing Au species into the channels. Basic $-\text{NH}_x$ groups were generated on the surface of the silica host during nitridation, which might increase the interaction between surface and gold species. The interaction that might result from the neutralization and/or coordination between surface $-\text{NH}_x$ groups and gold species led to the immobilization of Au nanoparticles in the channels. We suppose that the nitrided surface exhibit similar function as the organic amine groups does, the latter have been used by other researchers to modify mesoporous silica in immobilizing metal species [10,16].

4. Conclusion

An alternative strategy has been developed to synthesize highly-dispersed Au nanoparticles within the channels of nitrided SBA-15. After nitridation, the surface properties of

the host were modified with the generation of $-\text{NH}_x$ groups on the surface. The stronger interactions between the $-\text{NH}_x$ groups and the Au precursor would help to immobilize Au species into the host's channels. The method is expected to be generally applied to incorporate other metal nanostructures within the channels of mesoporous materials.

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