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Size discrimination of colloidal nanoparticles by thiol-functionalized MCM-41 mesoporous molecular sieves

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Thiol-functionalized MCM-41 mesoporous materials with a well-defined pore size of 40 Å may be used to discriminate between colloidal gold and silver particles in a mixture. More specifically, the thiol-functionalized MCM-41 material selectively entraps colloidal gold particles (size 35 Å) in the pores from a mixture of the gold and silver particles of size 70 Å. The gold particles are held in the matrix *via* thiolate linkages and this process has been studied using UV-vis spectroscopy and thermogravimetry/differential thermal analysis. This approach is promising for application in bioseparation methodologies as well as in the generation of one-dimensional superstructure assemblies.

Ordered *mesoporous* materials,[1,2] like MCM-41 with pore dimensions in the range 20–100 Å, have been considered to be interesting materials with potential applications involving host–guest interactions[3,4] often requiring modification of the surface composition of the mesoporous material by attaching organic functional groups to the surface wall.[5] This process of surface-modification may be accomplished either by grafting the functional groups of interest to hydroxy groups present on the inorganic supports[5] or by direct incorporation of the reactive functional groups during synthesis of the mesoporous support.[3,6]

We demonstrate here an interesting application of thiol-functionalized MCM-41 mesoporous silicates prepared by the direct synthesis approach in the size-selective extraction of nanoparticles from a colloidal-solution mixture. This approach is likely to have important applications in the polydispersity reduction of colloidal nanoparticle-size distributions,[7] in bioseparation methodologies as well as application of the MCM-41-nanoparticle composites in non-linear optics where hitherto polymers have been used as the host.[8]

The synthesis of thiol-functionalized MCM-41 material[9] was carried out as follows: 3-mercaptopropyl-propyltrimethoxysilane (MPTS) was used along with TEOS in a 1 : 10 molar ratio as the silica sources. The gel composition was 1.0 MPTS : 10.0 TEOS : 0.42 CTMABr : 0.96 NaOH : 272 H_2O : 66 MeOH. Methanol was used in the initial gel mixture to reduce and control the fast hydrolysis of MPTS. The reaction mixture was first stirred at room temperature for 12 h and then heated in autoclave at 95 °C for 36 h under static conditions. The product obtained was filtered and washed several times, first with distilled water, and then with acetone. The product was dried at 95 °C for 4 h. The surfactant was removed by solvent extraction with a mixture of solvents containing methanol, water and HCl. In a typical extraction process, 85 g of methanol and 3.25 g of HCl (35.4%) were used for 24 h under reflux for the extraction/removal of the surfactant from 1.0 g of the solid product. X-ray diffraction analysis of the thiol functionalized MCM-41 mesoporous

material yielded weak 110 and 200 Bragg reflections along with the main 100 reflection indicating hexagonal ordering of the pores in the mesoporous material. Chemical analysis of the thiol–MCM-41 material yielded a C : H : S composition ratio of 8.44 : 2.38 : 4.28. Thus, chemical analysis of the sample, after extraction of the surfactant, confirms the presence of propyl–thiol functionality in the organo-MCM-41 mesoporous material. The specific surface area of the extracted samples was determined by the BET method using the adsorption of N_2 measured with an Omnisorb CX-100 instrument. Prior to the adsorption experiment, all the samples were activated at 150° C for 6 h at 10^{-4} Torr. The BET measurements on the thiol functionalized MCM-41 mesoporous material yielded a mean pore size of 40 Å and a BET surface area of 926 m^2 g^{-1}. Silver (size = 70 ± 13 Å) and gold (size = 35 ± 7 Å) colloidal particles were synthesized in aqueous medium by borohydride reduction as described in detail elsewhere (refs. 10 and 11, respectively).

Fig. 1A shows the UV-vis spectrum of a 1 : 1 (by volume) mixture of the silver and gold colloidal solutions (blue curve) as well as the spectra recorded from the individual solutions (green and red curves).[12] The strong resonance at 400 nm (green curve) is due to excitation of surface plasmon vibrations in the silver colloidal particles[10] while the weaker absorption at *ca.* 520 nm is the corresponding excitation occurring in the gold (red curve) particles.[11] The strong signatures of silver and gold colloidal particles in the visible region of the electromagnetic spectrum, together with their strong binding with thiol molecules[10,11] make them ideal candidates for encapsulation in thiolated matrices.

The UV-vis spectra recorded from the thiol-functionalized MCM-41 material before (red curve) and after immersion for 12 h in the 1 : 1 silver–gold colloidal solution mixture (blue curve) are shown in Fig. 1B. The mesoporous material was washed with copious amount of water after recovering it from the colloidal solution. While strong absorption in the ultraviolet is observed for the mesoporous material (red curve, Fig. 1B), there are no observable resonances in the visible region of the spectrum where the
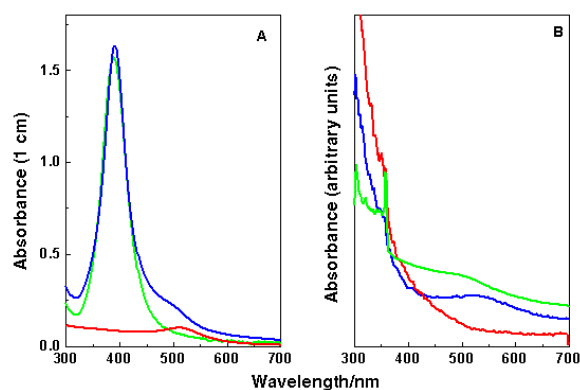
Fig. 1 (A) UV-vis spectra of the 1 : 1 (by volume) gold and silver colloidal solution mixture (blue curve) as well as the pure silver (green curve) and gold (red curve) colloidal solutions. (B) UV-vis spectra of the as-prepared thiolated MCM-41 mesoporous material (red curve), the mesoporous material after immersion in the 1 : 1 gold–silver colloidal solution mixture (blue curve) and the MCM-41–gold nanoparticle composite film after heating in air at 475 °C for 1 h (green curve).
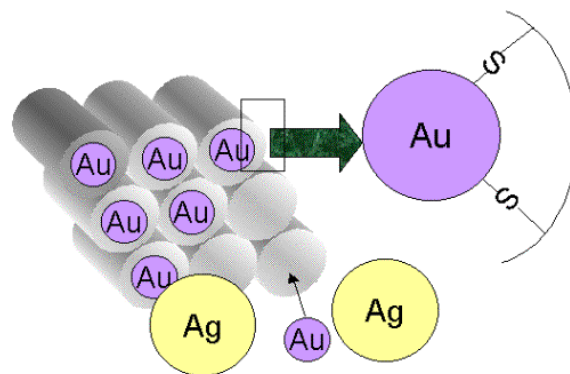
colloidal gold and silver nanoparticles absorb strongly. It is observed from the figure that after immersion of the thiol-functionalized mesoporous material in the colloidal solution mixture, gold colloidal nanoparticles are entrapped in the cavities of the MCM-41 material (resonance at 533 nm). It is also to be noted that there is no evidence for the presence of silver in the solid matrix, in spite of the very strong absorption cross-section for Ag particles compared to that of Au.

A control experiment was also carried out wherein the MCM-41 mesoporous material without thiol functionality was immersed in the gold–silver colloidal solution mixture and subjected to UV-vis analysis after washing of the powder. No evidence of either silver or gold nanoparticles in the matrix was observed, indicating the necessity of suitable functional groups to be present in the organo-inorganic matrix for successful selective entrapment of nanoparticles.

The colloidal gold nanoparticles have dimensions (35 Å) commensurate with the pore size (40 Å) of the thiol functionalized MCM-41 material and coordinate *via* thiolate linkages with the mesoporous material. The silver particles, on the other hand, are far too large to fit within the framework and are not entrapped within the mesoporous matrix. The above results clearly indicate that there is size selective entrapment of the colloidal particles in the mesoporous network and moreover, thiol functional groups play a crucial role in extracting and binding the colloidal particles to the mesoporous framework. This process is illustrated in Scheme 1.

Another possibility for the entrapment of gold particles in preference to silver particles may be the significant differences in covalent interactions of the thiol molecules in the MCM-41 matrix with gold and silver particles. However, it is well known that the covalent-bond energies of alkanethiols with gold and silver thin films is nearly the same[13] and hence this factor may be ruled out in the separation of the gold and silver particles observed.

The thiol functionalized MCM-41 material with and without the entrapped gold nanoparticles was subjected to thermogravimetric (TGA) and differential thermal analysis

Scheme 1 Diagram showing the size selectivity of thiolated MCM-41 mesoporous material (40 Å pore size) in entrapping gold nanoparticles (35 Å size) from a mixture of gold and silver (size 70 Å) colloidal particles. A magnified view of the thiolate linkage of gold nanoparticles with the MCM-41 framework is also shown.

(DTA). Fig. 2A shows the percentage weight (red curve, left axis) and heat flow (blue curve, right axis) recorded for the as-prepared thiolated MCM-41 powder and the corresponding data for the mesoporous material with the gold nanoparticles is shown in Fig. 2B. While the mass loss with heating clearly shows a significant loss at *ca*. 330 °C in both cases and may be attributed to loss of the thiol groups from the framework, the major features in the TGA curves for the two materials are similar. Significant differences, however, are observed in the heat flow patterns (DTA data) for the bare and gold coordinated mesoporous samples in the high temperature regime. An exothermic process is observed at *ca*. 440 °C for the thiolated MCM–41 sample containing gold nanoparticles (Fig. 2B) which is clearly absent in the as-prepared mesoporous sample (Fig. 2A). It is to be noted that this exothermic process is not accompanied by a detectable weight loss (DTA curve, Fig. 2B, left axis). We attribute this exothermic reaction to sintering of the colloidal gold nanoparticles within the porous framework. The decomposition of the thiol functional groups at *ca*. 330 °C enables facile diffusion of the now free colloidal gold particles within the porous network and thereafter, sintering. This was conveniently cross-checked by UV-vis spectroscopy measurement of the gold entrapped mesoporous material after heating at 475 °C for 1 h (green curve, Fig. 1B). There is considerable change in the optical absorption spectra of the mesoporous framework–gold nanoparticle composite before and after
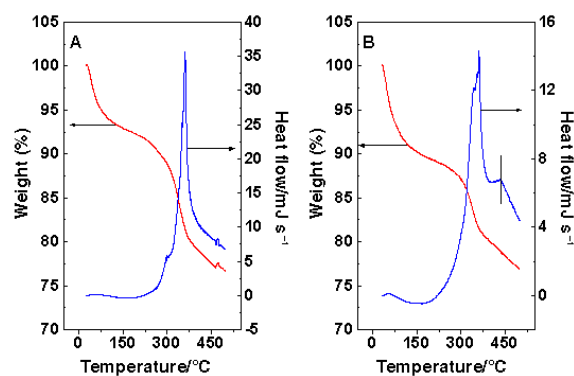

Fig. 2 (A) TGA data (red curve, left axis) and the DTA data (blue curve, right axis) plotted as a function of temperature for the as-prepared thiolated MCM-41 mesoporous material. (B) TGA data (red curve, left axis) and the DTA data (blue curve, right axis) plotted as a function of temperature for the thiolated MCM-41 mesoporous material entrapped with gold nanoparticles. The exothermic peak at *ca*. 440 °C is indicated in the figure.

the heating process (compare blue and green curves, Fig. 1B). The plasmon resonance due to gold at *ca*. 530 nm is blue-shifted, reduced in intensity and broadened. This is clearly indicative of cross-linking of the colloidal gold nanoparticles.[14] It should be noted that the spectra in Fig. 1B have been displaced vertically for clarity.

The possibility of entrapping colloidal metal nanoparticles in a quasi-1D topology and thereafter, effectively cross-linking them to form nanowires is another attractive aspect of the present work which opens a new strategy for the formation of superstructures of colloidal nanoparticles with controllable geometry.[14] The MCM-41 framework thus provides a template rather similar to that used for the generation of nanowires of gold by entrapment of colloidal gold particles within the pores of alumina as demonstrated by Feldheim *et al*.[14]

In summary, it is demonstrated that thiol-functionalized MCM-41 mesoporous materials may be used to size-selectively extract and entrap colloidal nanoparticles from a mixture of colloidal nanoparticles of varying sizes. The anchoring of the colloidal particles within the porous framework is accomplished *via* thiolate linkages. It is also demonstrated that the topology of the MCM-41 framework may be utilized to generate quasi-1D superstructures of the entrapped nanoparticles. This method may be extended to the incorporation of ionizable functional groups in the MCM-41 framework and entrapment of charged colloidal particles *via* electrostatic interactions. In such an entrapment protocol, the particles may be extracted from the MCM-41 matrix by reversal of the electrostatic interaction. This approach also shows promise for species-specific entrapment of particles from a mixture of similarly-sized nanoparticles by incorporation of functional groups in the MCM-41 framework that selectively bind to one component of the mixture. These exciting possibilities will be addressed in future reports.

Acknowledgements

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12 UV-vis spectroscopy measurements of the colloidal solutions were carried out on a Hewlett-Packard 8542 A diode array spectrophotometer operated at 2 nm resolution while measurements on the thiol-functionalized MCM 41 powder with and without entrapped colloidal nanoparticles were performed in the reflection mode on a Shimadzu UV-2101 PC instrument using barium sulfate as a standard for background correction.

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