

*Brief communication*

## Network structure consisting of chain-like arrays of gold nanoparticles and silica layer prepared using a nonionic reverse-micelle template

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### Abstract

A nonionic reverse-micelle based approach is described for fabrication of a network structure consisting of chain-like arrays of gold nanoparticles, followed by coating process with a uniform silica layer using a sol-gel method. The hexadecyl-poly (ethylene oxide-15) ether (designated C<sub>16</sub>E<sub>15</sub>) is used as a template for this study. The effects of a water-to-surfactant molar ratio (*w*) as well as the concentration of tetraethyl orthosilicate ([TEOS]<sub>oil</sub>) are investigated on the resulting organized structures.

### Introduction

Controlling an arrangement of metal nanoparticles is one of the central issues in the field of nanomaterial science (Schmid, 2004). To construct an ordered nanoparticle assembly, a template-patterning method has been demonstrated to be very effective; for example the use of a carbon nanotube and the nanochannel of a porous alumina as a hard template (Fullam et al., 2000; Wyrwa et al., 2002). A certain “soft template” consisting of organic material such as amphiphile provides us a confined microreactor for controlled synthesis of well-defined inorganic materials as well as for their self-assembly into unique superstructures (Li et al., 1999). However, these superstructures cannot be always regulated because the shape of a micellar template changes continuously even by a subtle change of a condition, and may be transformed to unfavorable one. To suppress these

difficulties, we propose a novel method consisting of a soft-template patterning for assembling nanoparticles and a sol-gel technique for stabilizing their assembly with a hard-material such as metal oxide. Liz-Marzán and co-workers (1996) has been studied the metal-oxide-coating of the isolated metal nanoparticles. In addition, we have developed a reverse microemulsion based approach for synthesis of core-shell type nanoparticles consisting of various inorganic nanoparticles and metal oxides (Kishida et al., 2000; Tago et al., 2003). However, there are only limited reports on the coating of nanoparticle-assembly (Stella et al., 1998; Yonezawa et al., 2003). In this paper, we demonstrate synthesis of the novel Au/SiO<sub>2</sub> nanocomposite consisting of the network chain of gold nanoparticles and a uniform silica layer using a microemulsion template. The morphology of the resulting structure is controlled by a water-to-surfactant molar ratio (*w*)

or the concentration of tetraethyl orthosilicate ( $[\text{TEOS}]_{\text{oil}}$ ) in the microemulsion system.

### Experimental procedure

Au/SiO<sub>2</sub> nanocomposites were prepared in the polar core of nonionic reverse microemulsion of C<sub>16</sub>E<sub>15</sub>/cyclohexane/water. The procedure was composed of 5 steps; formation of NH<sub>4</sub>AuCl<sub>4</sub> salt nanoparticles, control of micellar shapes, silica-coating of the nanoparticles, purification and reduction of the aurate salt into metallic gold. Typical preparative procedure is as follows; the reverse emulsions was prepared by solubilizing 0.4 ml of 0.85 M HAuCl<sub>4</sub> aq. into the stirred C<sub>16</sub>E<sub>15</sub>/cyclohexane solution at 50°C ( $[\text{C}_{16}\text{E}_{15}]_{\text{oil}} = 0.125$  M, total volume 20 ml). After several minutes, a small portion of 30 wt% NH<sub>3</sub> aq. was added until pH increased to 8–9. The color of the solution changed from yellow to orange, which implied the formation of NH<sub>4</sub>AuCl<sub>4</sub> salt nanoparticles. The amount of AuCl<sub>4</sub><sup>-</sup> was constant for all the samples described in this paper. After aging for 5–10 min, appropriate amount of NH<sub>3</sub> aq. was added into the solution to control the micellar shape of C<sub>16</sub>E<sub>15</sub> and to align the nanoparticles. For silica-coating, 1 g of TEOS was added as a silica source, and then aged for 1 h. To remove the C<sub>16</sub>E<sub>15</sub> surfactant and the residual TEOS, the centrifugation and rinsing process with 2-propanol were repeated several times. Finally, the obtained products were dried in an oven at 80–90°C overnight. During drying process, the color of the product changed from light orange to pink. UV-Visible spectra of the Au/SiO<sub>2</sub> nanocomposites showed the surface plasmon resonance band at around 520 nm, which is characteristic of a nano-sized metallic gold. The reaction of Au<sup>3+</sup> → Au<sup>0</sup> occurred probably due to thermal decomposition of the aurate salts, or to reduction by the oxygen or 2-propanol that diffused into the nanoparticles through the pores of the silica shell layer. For TEM study, the Au/SiO<sub>2</sub> nanocomposites were redispersed in 2-propanol with the aid of 2-dimethylaminoethanol, and the portion of the dispersion was dropped on a carbon-film-supported Cu-grid. The micellar shapes were estimated from an electric conductivity (EC) measurement (CM-14P, TOA Electrics Ltd.).

### Results and discussion

Figure 1(a) shows the TEM image of the nanocomposite prepared at  $w=9$ . No visible silica layer was observed probably due to too small content of water for the hydrolysis of TEOS. The purified nanoparticles become the random aggregates because of absence of template or silica shell. At  $w=23$ , isolated, spherical nanoparticles was observed (Figure 1b). Each particle consists of 5-nm-sized, single nanoparticle and uniform silica layer with 20 nm in thickness. In earlier works using the other metal salts such as RhCl<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub> or PdCl<sub>3</sub> as a core metal source, the similar isolated core/shell particles were obtained, when prepared at  $w=23$  in the C<sub>16</sub>E<sub>15</sub>/cyclohexane/water microemulsion (Kishida, 2000). Further increase in  $w$  from 23 provides the organized structure of nanoparticles. At  $w=60$ , the organized 1D-chains appeared, but the several chains were observed in the single silica rod (Figure 1c). Figure 1(d) shows the TEM image of the product prepared at  $w=200$ . The TEM analysis revealed that the colloidal network structure consisting of chain-like arrays of the 5 nm-sized gold nanoparticles. Each particle along the chain was separated by the interparticle spacing of 5–10 nm. The chain-like array partially branched into two or three lines, and was surrounded with a uniform silica layer. The uniform layer indicates the heterogeneous deposition of the silicate species onto the nanoparticle surface at an initial stage of the silica formation. Finally, the well-separated network structure consisting of the 1-D chains and the uniform layer was obtained at  $w=200$ . The branched structure of 1-D chains is very unique, although there were some reports on the straight alignment of nanoparticles (Nakao et al., 2002). The result indicates that the morphology of the C<sub>16</sub>E<sub>15</sub> template varies from a spherical to a rod-like structure upon  $w$  increase.

A relationship between  $w$  and the morphology of the C<sub>16</sub>E<sub>15</sub> reverse-emulsion template in a solution was investigated using EC measurement. Figure 2 shows EC data of the samples prepared at various  $w$  by solubilizing 0.85 M aqueous solution of NaCl, instead of HAuCl<sub>4</sub> aq., into the C<sub>16</sub>E<sub>15</sub>/cyclohexane solution. In the  $w$  range between 5 and 43, EC was small and increased monotonically upon  $w$  increase, but increased sharply by 2–3 orders of magnitude from  $w=55$ .

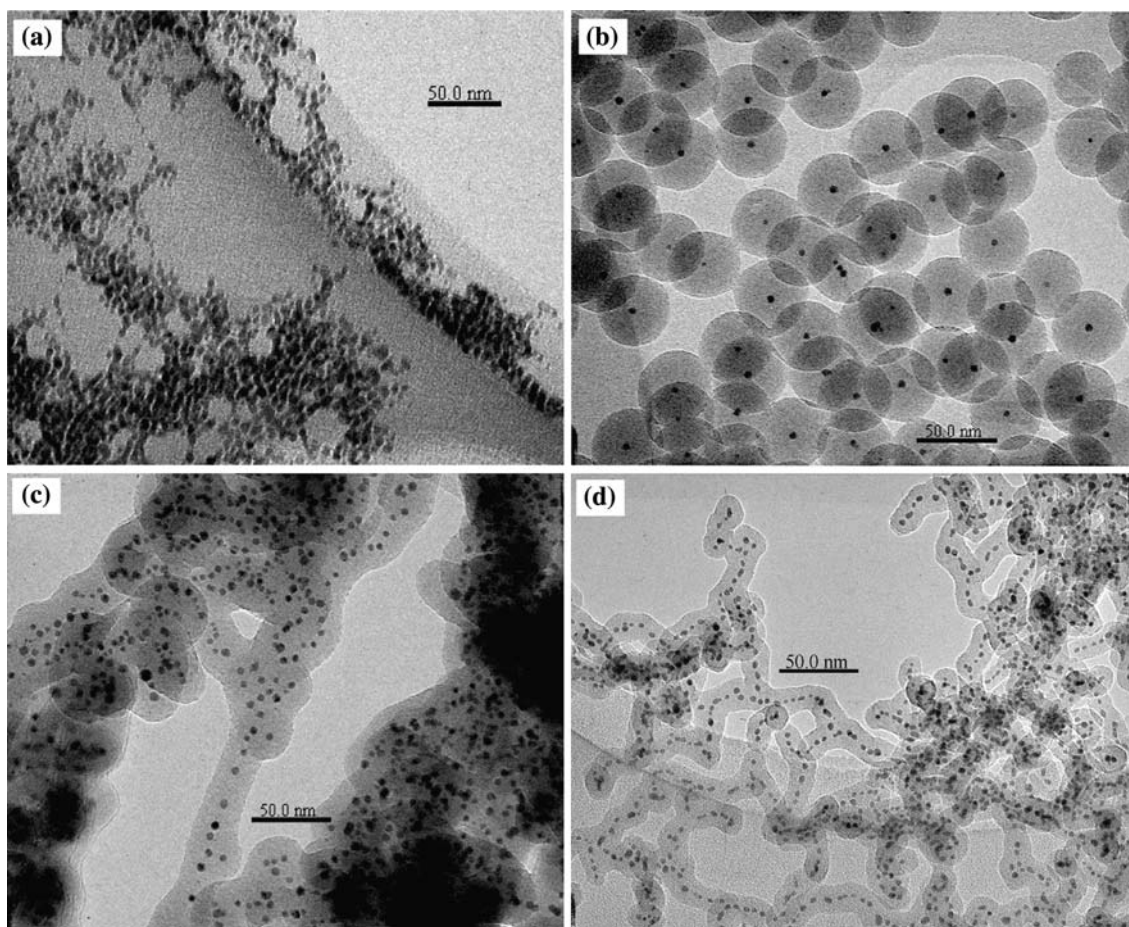


Figure 1. TEM images of Au/SiO<sub>2</sub> nanocomposites prepared at various water-to-surfactant molar ratios ( $w$ ) in the C<sub>16</sub>E<sub>15</sub>/water/cyclohexane system. ([C<sub>16</sub>E<sub>15</sub>] = 0.125 M, [TEOS]<sub>oil</sub> = 0.24 M) (a)  $w=9$ , (b)  $w=23$ , (c)  $w=60$ , and (d)  $w=200$ .

Such a transition from a low to a high conducting state has been frequently observed in oil-rich microemulsions based on nonionic amphiphiles, and this phenomenon has been explained as a transformation of the microemulsion containing the isolated droplets in the nonconducting organic solvent into the system-spanning bicontinuous network. The freeze fracture electron microscopy images of H<sub>2</sub>O-*n*-octane-C<sub>12</sub>E<sub>5</sub> system by Jahn et al. (1988) showed the transition from the droplets to the three-dimensional network of tubules toward the water-rich side, and their morphology is similar to the rod-like silica involving gold nanoparticle chains shown in Figure 1(d). We note that the value of  $w$  for the transformation of the C<sub>16</sub>E<sub>15</sub> emulsion is in accordance with that for the appearance of the

chain-like arrays of the nanoparticles, as shown in Figure 1c ( $w=60$ ). The result suggests that spontaneous 1-D assembly of the gold nanoparticles occurred in the C<sub>16</sub>E<sub>15</sub> emulsion fluid.

Figure 3 shows the Au/SiO<sub>2</sub> nanocomposite prepared at various [TEOS]<sub>oil</sub> in the C<sub>16</sub>E<sub>15</sub> emulsion ( $w=60$ ). Reducing [TEOS]<sub>oil</sub> from 0.24 M to 0.057 M resulted in decrease in thickness of the silica layer from  $\sim 7$  nm to  $\sim 2$  nm, which indicates that the layer thickness can be tuned in a controlled way, and that network of 1-D chains can be stabilized even by the silica layer as thin as 2 nm even after the template removal. In addition, the roughness of the thin silica layer in Figure 3(c) implies such a formation process of the nanocomposite that the isolated gold nanoparticles uniformly coated with silica layer of a few nanometers,



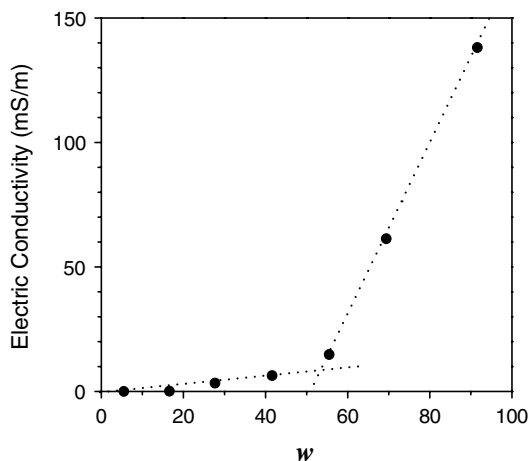


Figure 2. Electric conductivity data of the  $C_{16}E_{15}$ /water/cyclohexane microemulsion as a function of a water-to-surfactant molar ratio ( $w$ ) (closed circle). The samples were prepared using 0.85 M NaCl aq. instead of  $H AuCl_4$  ( $[C_{16}E_{15}] = 0.125$  M).

aggregate into the 1-D linkage of the nanoparticles inside the  $C_{16}E_{15}$  cylinder network, followed by further silica growth on the surface of the 1-D arrays, and resulted in the final rod-like silica with the smooth surface, as seen in Figure 3(a).

In conclusion, the novel, three-dimensional network structures consisting of the gold nanoparticle chains was constructed by the use of the  $C_{16}E_{15}$  reverse-micelle template when prepared at  $w > 60$ , and subsequently could be coated with the silica layers by the sol-gel method. The silica layer played a role preventing the organized structure of the gold nanoparticles to coagulate into a bigger random aggregation of the nanoparticles even after removing the template. The branched structure of the 1-D chain is very unique. A conclusive mechanism on the formation process of the network is now on progress.

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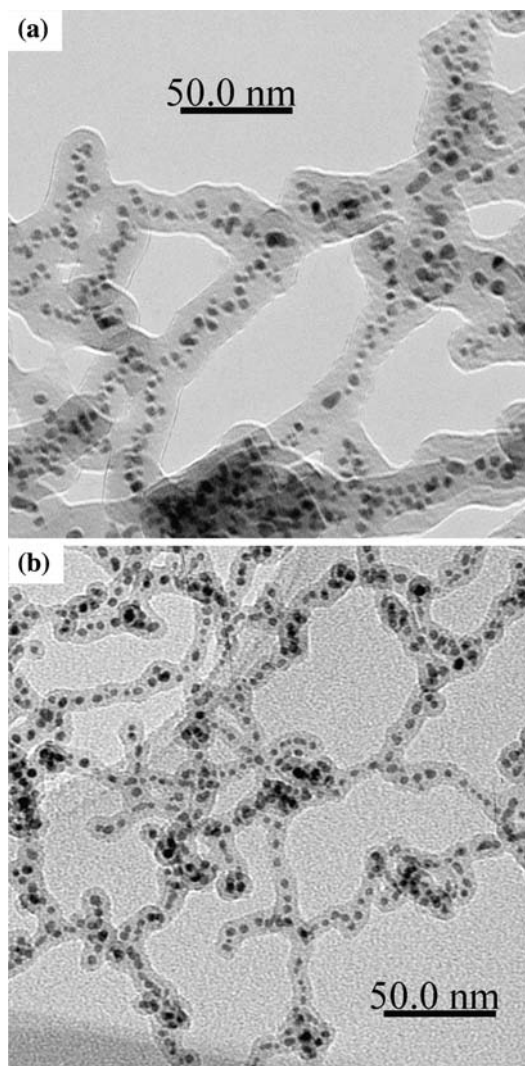


Figure 3. TEM images of  $Au/SiO_2$  nanocomposites prepared at various concentrations of TEOS ( $[TEOS]_{oil}$ ) in the  $C_{16}E_{15}$ /water/cyclohexane system. ( $w = 60$ ,  $[C_{16}E_{15}] = 0.125$  M) (a)  $[TEOS]_{oil} = 0.17$  M, (b)  $[TEOS]_{oil} = 0.057$  M.

### References

- Fullam S., D. Cottell, H. Rensmo & D. Fitzmaurice, 2000. Carbon nanotube templated self-assembly and thermal processing of gold nanowires. *Adv. Mater.* 12, 1430–1432.
- Jahn W. & R. Strey, 1988. Microstructure of microemulsions by freeze fracture electron microscopy. *J. Phys. Chem.* 92, 2294–2301.
- Kishida M., T. Tago, T. Hatsuta & K. Wakabayashi, 2000. Preparation of silica-coated rhodium nanoparticles using water-in-oil microemulsion. *Chem. Lett.* 29, 1108–1109.

- Li M., H. Schnablegger & S. Mann, 1999. Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization. *Nature* 402, 393–395.
- Liz-Marzán L.M., M. Giersig & P. Mulvaney, 1996. Synthesis of nanosized gold-silica core-shell particles. *Langmuir* 12, 4329–4335.
- Nakao S., K. Torigoe, K. Kon-No & T. Yonezawa, 2002. Self-assembled one-dimensional arrays of gold-dendron nanocomposites. *J. Phys. Chem. B* 106, 12097–12100.
- Schmid G., 2004. *Nanoparticles: From Theory to Application*. New York: John Wiley & Sons.
- Stella M., L.C. Brousseau III, A. Jones & D.L. Feldheim, 1998. Template synthesis of one-dimensional Au, Au-Poly(pyrrole), and poly(pyrrole) nanoparticle arrays. *Chem. Mater.* 10, 1214–1219.
- Tago T., S. Tashiro, Y. Hashimoto, K. Wakabayashi & M. Kishida, 2003. Synthesis and optical properties of SiO<sub>2</sub>-coated CeO<sub>2</sub> nanoparticles. *J. Nanoparticle Res.* 5, 55–60.
- Wyrwa D., N. Beyer & G. Schmid, 2002. One-dimensional arrangements of metal nanoclusters. *Nano Lett.* 2, 419–421.
- Yonezawa T., H. Matsune & N. Kimizuka, 2003. Formation of an isolated spherical three-dimensional nanoparticle assembly as stable submicronmeter-sized units by using an inorganic wrapping technique. *Adv. Mater.* 15, 499–503.