

# Fabrication of chiral silver nanoparticles and chiral nanoparticulate film *via* organogel†

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**Chiral silver nanoparticles and chiral nanoparticulate films were prepared through the *in situ* reduction of an organogel formed by a newly designed silver(I)-coordinated organogelator.**

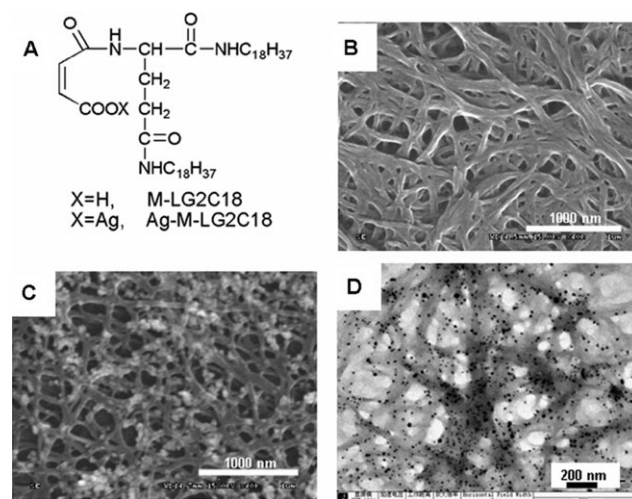
The synthesis and preparation of chiral materials have been attracting great interest in the past decades because of the potential applications of chiral materials in enantioselective separation, asymmetric catalysis and non-linear optics.<sup>1</sup> So far, most of the chiral materials have been derived from the organic and inorganic chiral species, while chiral metals or metal clusters are very limited. Recently, there has been a surge of interest in the chirality of metal surfaces and metallic nanoparticles (NPs).<sup>2–7</sup> For example, Yao *et al.*<sup>3</sup> and Gautier and Bürgi<sup>4</sup> have reported the formation of the metal nanoclusters capped by chiral organic molecules, respectively. Markovich, Kotlyar and co-workers<sup>5</sup> have reported the synthesis of optically active silver NPs using DNA as a template. Naaman and Avnir<sup>6</sup> have observed the chirality induction in bulk gold and silver. These new findings have led to renewed interest in the synthesis and functions of chiral metals or chiral NPs. In this communication, we report the preparation of the chiral silver NPs using an organogel as the template and further built the nanoparticles into the solid films through the organogel route for the first time.

Low molecular weight gels (LMWGs) are an important type of soft matter and have been attracting great interest in recent years.<sup>8</sup> Organogels generally contain a three-dimensional network which can immobilize organic solvents. The organogel is a physical gel in which organic molecules and solvents are held together through non-covalent interactions such as hydrogen bonds,  $\pi$ - $\pi$  stacking and van der Waals interactions. One of its important merits is that the nanostructures in the organogel can be fabricated in a large quantity. In addition, the nanostructures of the gels can be tailor-made through the modification of organic molecules. These “soft” nanostructures can be further used to synthesize other notable nanomaterials.<sup>9,10</sup> Besides organic molecules, metal complexes and organometallics<sup>11</sup> have also been shown to form organogels and exhibit unique properties. The metal complex gels can

be further functionalized. In some cases, the metal ions in the complex can be transformed to metal or metal oxide. In this paper, we designed a Ag(I)-coordinated organogelator and fabricated the organogel with different solvents. Further reduction of the gel led to the formation of the chiral Ag NPs. We have built up the organogel into solid films and an *in situ* reduction of the film produced a chiral nanoparticulate thin film.

The gelator was designed using the glutamic acid moiety because we have found that this moiety is capable of forming various organogels easily.<sup>12</sup> Previously, we have designed a organogelator containing the Boc group. We further changed this Boc to a maleic acid and then made the silver salt. The molecular structure of the gelator is shown in Fig. 1.

The compound was found to form organogels with many kinds of organic solvents such as methanol, ethanol or DMSO. In a typical method, 5 mg Ag-M-LG2C18 were dissolved in 1 mL ethanol under heating. After cooling to room temperature a white gel formed. The formed gel was dispersed in 20 mL ethanol under vigorous stirring at room temperature and 6.5 mg hydroquinone was added to the mixture. Then the mixture was stirred for 3 h in the dark and a yellow silver colloid was obtained. The gel formation was confirmed by the inverted test tube method and SEM observation. Fig. 1(B) shows the SEM image of the xerogel of Ag-M-LG2C18 with ethanol. Network structures composed of many fibers, whose



**Fig. 1** Molecular structure of the gelators (A) and SEM images of the as-prepared xerogel (B) and reduced xerogel (C) formed by Ag-M-LG2C18, respectively. TEM image of the reduced xerogel (D).

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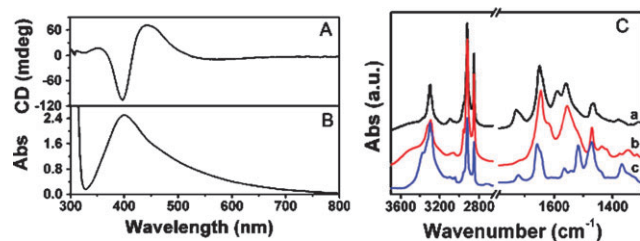
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width is about 50–60 nm and with length up to several micrometers, were obtained.

Since the ethanol gel contains silver(I) ion, we tried to prepare the silver nanoparticles in the organogel by *in situ* reduction of silver(I) ions. We used hydroquinone to reduce the silver(I) containing ethanol gel. The mixture turned yellow after stirring for 3 h and the colour did not change further. To get a clear insight into the formed silver nanoparticles we observed the reduced sample with SEM and TEM. Fig. 1(C) shows the obtained SEM image in which many silver nanoparticles are attached on the fibers. The diameter of these particles is about 20 nm. From the image the fibrous structure of the gel was also apparent which implied that the microstructures of the gel have not been damaged during the reduction process. TEM observation confirmed the formation of silver nanoparticles in the gel network. From Fig. 1(D) we observed that many nanoparticles were embedded in the networks of the fibers. The size of the nanoparticles varied from about 10 to 20 nm, which is consistent with SEM observation.

The gel formation of the compound and the generation of the silver nanoparticles in the organogel were further examined by FT-IR spectra. The xerogel of Ag-M-Glu2C18 shows four main vibrations in the range 1400–1800  $\text{cm}^{-1}$  at 1645, 1619, 1554 and 1470  $\text{cm}^{-1}$ . These bands can be assigned to amide I band, C=O stretching of silver carboxylate, amide II band and  $\text{CH}_2$  scissor vibration, respectively. Six bands appear in the same range after reduction at 1720, 1657, 1564, 1541, 1516 and 1472  $\text{cm}^{-1}$ . To aid comparison, we also measured the FTIR spectrum of M-LG2C18, which is the carboxylic acid form of the gelator, and there were five main peaks in the range at 1728, 1649, 1589, 1558 and 1465  $\text{cm}^{-1}$ . The disappearance of the peak at 1619  $\text{cm}^{-1}$  and the appearance of the peak at 1720  $\text{cm}^{-1}$  after reduction of the gel indicated the silver carboxylate was reduced. The vibration of  $\text{COO}^-$  at 1516  $\text{cm}^{-1}$  after reduction proved the existence of free  $\text{COO}^-$  in the reduced xerogel. The vibration of the C=O bond in the carboxylic acid group shifted from 1728  $\text{cm}^{-1}$  in the M-Glu2C18 to 1720  $\text{cm}^{-1}$  in the reduced gel illustrated that there are interactions between carboxylic acid groups and silver nanoparticles. This explained the stability of the silver nanoparticles in the gel.

The UV-Vis spectrum of the nanoparticles shows a broad absorption band with the maximum at 408 nm, which is typical of the plasmon absorption of silver NPs (Fig. 2(B)). We have also measured the CD spectrum of the silver



**Fig. 2** CD (A) and UV-Vis spectra (B) of the prepared silver nanoparticles and FT-IR spectra (C) of M-LG2C18 (a), and of the xerogel of Ag-M-LG2C18 before (b) and after reduction (c), respectively.

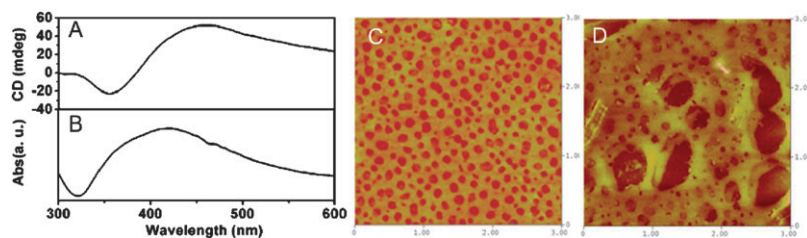
nanoparticles (Fig. 2(A)), which showed a positive and negative Cotton effect at 442 and 398 nm, respectively with a crossover at 416 nm. This means that the formed silver NPs are chiral. In comparison with the work of Markovich, Kotlyar and co-workers, it was found that the shape of our CD spectrum resembled their spectrum.<sup>5,13</sup> This indicated that our chiral silver nanoparticles were formed by a similar mechanism. Taking into account the polydisperse property of our silver nanoparticles observed by TEM, it can be suggested that our chiral silver NPs were related to formation of the chiral fiber structure in the organogel rather than individual gelator molecules.<sup>5</sup> We have also used the solution of Ag-M-Glu2C18 to generate silver nanoparticles. It has been found that although Ag NPs can be produced in the solution, they did not show any CD signal. Previously, Schaaff and Whetten have suggested three possibilities of the origin of the chirality of metal NPs.<sup>7</sup> On the basis of our results and comparing these with the work of Schaaff and Whetten,<sup>7</sup> and that of Markovich, Kotlyar and co-workers,<sup>5</sup> it seemed that the chirality of our synthesized Ag NPs would probably be related to the chiral nanofibers formed by the gelator.

It should be mentioned that the selection of the reduction agents is very important also. When we applied the sodium borohydride as reducing reagent, although the silver NPs were produced rapidly, they separated from the gel. In addition, we have also tested UV-irradiation and found that the mixture is colourless even after 36 h of irradiation. This suggests that it is only through the gel formation that the chiral silver NPs were fabricated.

We also investigated the formation of chiral silver NPs in ultrathin films. Although the gel could be dried on solid substrates to form a xerogel, it was unstable and did not form uniform film. To solve this problem, we embedded the gel into PMMA<sup>14</sup> and cast them together to obtain a uniform film. The compound was found to form a co-organogel with PMMA and this was then cast onto a solid substrate to build up into a stable film. Upon exposure of the film to  $\text{H}_2\text{NNH}_2$  for 24 h the film turned yellow. This implied that the silver(I) ion was reduced in the film. Fig. 3 shows the UV-Vis, CD spectra and AFM images of the film before and after exposure to  $\text{H}_2\text{NNH}_2$  gas. In the AFM image, a porous film containing the gelator molecules was evident. Upon exposure to  $\text{H}_2\text{NNH}_2$ , NPs were found in the film, suggesting the formation of silver NPs in the film. The UV-Vis spectrum also indicated the formation of the silver nanoparticles in the film. In addition, a similar CD spectrum to the case in the organogel was observed, confirming the chiral nature of the formed silver NPs. If we only cast the mixture of the compound and PMMA onto solid substrate, although the silver NPs could be generated in the film, no chiral NPs could be detected. Thus, only through the co-gel formation of Ag-M-Glu2C18 with the PMMA, could a film embedded with chiral silver NPs be obtained.

It should be further noted that the use of silver salt in the formation of chiral silver NPs is very important. If we simply doped the gel with the preformed silver nanoparticles, no chiral signals could be detected.

In conclusion, we have prepared chiral silver nanoparticles and chiral silver nanoparticulate films using a silver(I)



**Fig. 3** CD (A) and UV-Vis spectra (B) of the silver nanoparticles embedded film and AFM images of the film before (C) and after reduction (D), respectively.

ion-coordinated organogel as template by *in situ* reduction. The formation of the organogel process played an important role in the formation of the chiral nanoparticles. It is suggested that the formation of the chiral silver NPs is related to the formation of the chiral organogel rather than the chiral gelator molecules. This work clearly extends the means to obtain chiral metal materials.

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