Noble metal nanochains through helical self-assembly†

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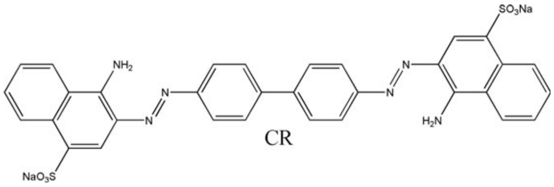
Silver nanochains composed of nanoparticles were prepared by photoreduction *in situ* under assistance of a helical self-assembly originating from coordination of Congo red and Ag^+. The special hierarchical nanostructures with different surface plasma resonance compared with silver nanoparticles have potential applications for electrical nanodevices.

Over the past decade, one-dimensional nanostructures have attracted much attention because of the beneficial influence of their dimensionality on electronic and optical materials properties.[1–6] Exciting examples involve the chemical vapor deposition preparation of carbon nanotubes (CNTs),[1] semiconductor nanowires, nanotubes and nanobelts,[2,3] and the self-assembly of cyclindrical micelles,[4,5] ribbons,[6] and peptide nanofibers and nanobelts.[7,8] Particularly, self-assembly of small molecules offers many opportunities for obtaining one-dimensionally hierarchical nanostructures.[9–18] Pioneered by Braun, Belcher and their coworkers, there have been numerous examples of DNA or viruses as scaffolds for complex nanostructured inorganic materials.[19]

Noble metal nanostructures, such as nanoparticles, nanoplates, nanowires and nanobelts, have attracted extensive research interest due to their potential applications in catalysis, electronics and biology.[20–23] As a typical noble metal, various silver nanostructures are obtained by different methods.[24–27] Special structures such as helical nanostructures could result in interest and unique optical and electromagnetic properties.[28] In this paper, Ag chainlike hierarchical nanostructures based on helical small-molecular self-assembly of $AgNO_3$ and Congo red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$) were introduced.



CR

In a typical experiment, 10 mL of 2.5 mM $AgNO_3$ was mixed with 20 mL of Congo red (100 mg mL^{-1}) in a flask. As shown in Fig. S1†, obviously, the colour of the solution was changed from red to purple. Fig. S2† presents the solution Uv-vis spectra before and after mixing. There was only little difference in the ultraviolet region, indicating that Ag(I) and Congo red might have interacted by coordination effect between Ag^+ and –N=N–, $-NH_2$, $-SO_3^-$. A drop of the mixture (Fig. 1Sb†) was put onto silicon plates and dried under vacuum at room temperature (25 °C). The experiment was operated in a dark room. Meanwhile, after 24 h, the solution (Fig. 1Sb†) was under vis-light for 48 h. At this time the colour had disappeared and there was a yellow substance at the bottom of the flask. After concentration and purification, the samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atom force microscopy (AFM), X-ray diffraction (XRD) and UV-vis spectroscopy.

From Fig. 1a, large-scale helical precursors were shown. The diameter of the precursor was 100–200 nm and the width of them was about 40 nm (Fig. 1b). Some of them had branched structures, shown in Fig. 1c. TEM image also showed the helical nanobelt microstructures (Fig. 1d). Our understanding of CR ligation was further complicated by the fact that CR might exist in two different forms: as unimolecular and supramolecular ligand species.[29] In our case, in the presence of Ag^+, elongated symmetric polyaromatic ring molecules with planar structure forming the hydrophobic center and charged terminals make CR prone to self-aggregation in helical aggregates.[30] The result of the energy dispersive X-ray (EDX) analysis (Fig. S3†) confirmed that the helical precursor consisted of the elements of C, N, O, S and Ag, a chemical composition that agreed with the $C_{32}H_{22}N_6Ag_3O_6S_2$ circuitously. It indicated that in the precursor, the ratio of Congo red and Ag^+ was about 1 : 3.

After photo-induced reduction under visible light for 48 h, a typical TEM image (Fig. 2a) shows that there still was similar morphology of the precursor. In detail, compared with

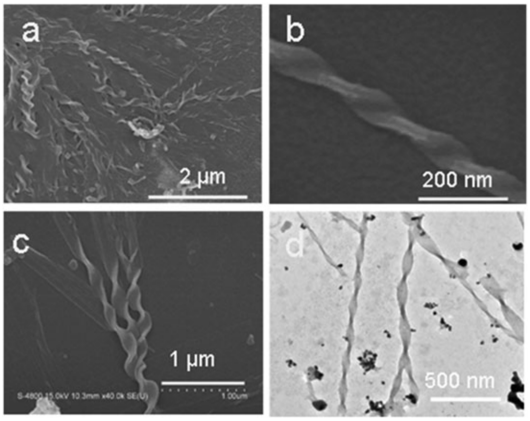


Fig. 1 (a) Low-magnification SEM image of the precursor; (b) higher-magnification SEM image of single precursor; (c) SEM image of branched microstructure; (d) TEM image of the precursor.

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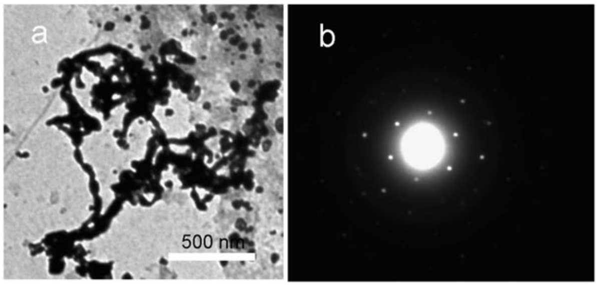

Fig. 2 (a) TEM image of the final product; (b) relevant SAED pattern.

Fig. 1d, in the terms of contrast between the substrate (Cu grid) and the products, it could be induced that there was more heavy element in the final product than that in the precursor. Selected area electron diffraction (SAED) of the final product was shown in Fig. 2b. It indicates that the product was cubic single crystalline. From the XRD pattern (Fig. 3), the peaks of the product can be attributed to the bulk cubic Ag patterns. The diffraction features appearing at about 38.1°, 44.1° and 64.4°, correspond to the (111), (200) and (220) planes of the cubic phase of Ag, respectively.[24] Based on the pattern, the lattice constant was 0.4091 nm, which is very close to the reported data (JCPDS File 04-0783).

In order to obtain more details, atom force microscopy (AFM) was employed to investigate the morphology of the Ag nanochains prepared. As shown in Fig. 4a, there were many Ag nanochains with the length of 300–400 nm on the surface of the Si substrate, which were shorter than the initial helical organic template nanofibres. The reason may be the structural shrinkage and partial fracture after photoreduction *in situ*. In detail, Ag nanochains were composed of caved Ag nanoparticles with the diameter of about 40 nm (shown Fig. 4b), which was near to the width of the Ag–Congo red complex nanohelix (Fig. 1). So, it could be proposed that Ag nanochains were evolved from the nanohelices by reduction under vis-light.

Silver nanomaterials show unique optical properties as a result of surface plasmon resonance. It is well known that spherical silver nanoparticles exhibit a single absorption band at 420 nm, whereas anisotropic silver particles show two surface plasmon resonance absorption peaks that are characteristic of the short (transverse band) and long (longitudinal band) axes of these systems.[31,32] Spectrum a in Fig. 5 shows the UV-vis absorption spectrum of silver nanochains suspended in water. One peak corresponding to the short axes of the nanochains appears at about 420 nm; the other peak occurs at about 650 nm, which can be attributed to the short aspect ratio of the Ag nanochains. As a comparison, for Ag nanoparticles with a diameter of approximately 40 nm synthesized in the presence of citrate acid, the characteristic surface plasmon band is observed at 420 nm (spectrum b in Fig. 5). Thus, the appearance of the absorption band actually mirrors the appearance of the different nanostructures of silver.

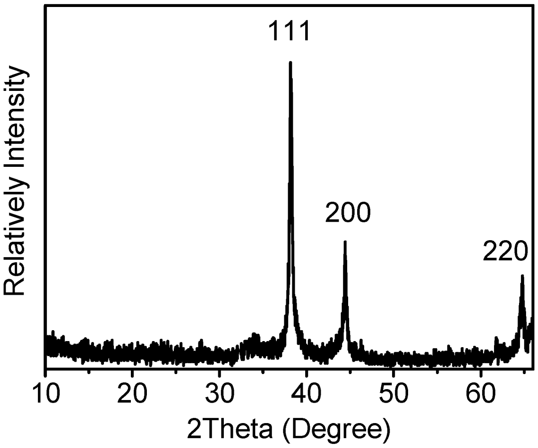

Fig. 3 XRD pattern of the final product prepared.

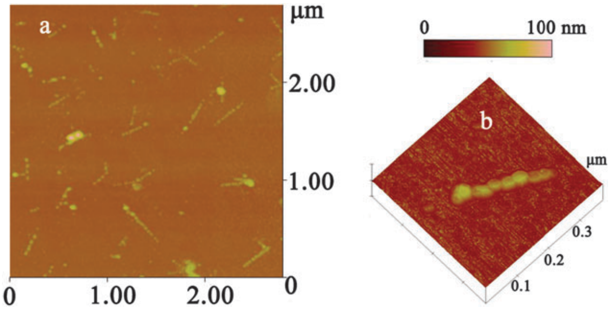

Fig. 4 AFM images of Ag nanochains (a) low-magnification; (b) higher-magnification.

It is further noted that metal ions in the subphase can affect the precursor helical formation. Among Cu(II), Ni(II), Cd(II), Ca(II), Zn(II), and Ag(I), only in the case of Ag(I) did we get the helical nanostructures (data not shown). This suggested that all these metal ions except Ag(I) block the propagation of the assembly backbone in a helical sense. Furthermore, no helical precursors can be obtained from Congo red solution. After all, a proposed mechanism was as follows (Fig. 6): Ag(I)–Congo red helical nanobelts were formed by small molecular self-assembly. Then, under visible light, Ag nanochains were reduced from the helical nanobelts.

In conclusion, we have successfully synthesized silver nanochains based on supramolecular co-assembly. This method is simple, convenient and economical and can be performed under ambient conditions. The Ag nanochains have the potential for incorporation into functional electronic, optoelectronic, or sensing devices, which could lead to extreme miniaturization and enhanced performance. In addition, such

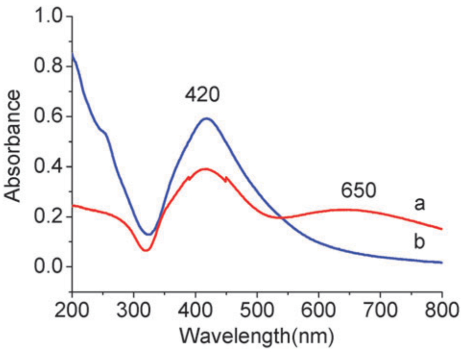

Fig. 5 The UV-vis spectra of (a) Ag nanochains and (b) Ag nanoparticles dispersed in water.

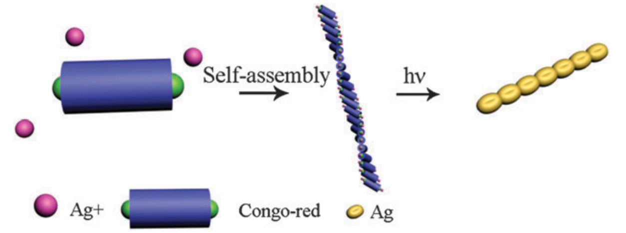

Fig. 6 The schematic illustration of the formation process of Ag nanochains.

Ag nanochains can be used as building blocks to form a variety of functional nanostructures.

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