Porous and nonporous Ag nanostructures fabricated using cellulose fiber as a template

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Porous and nonporous metallic Ag nanostructures were fabricated with ease by using cellulose fiber as a template.

Metallic materials on the nanometer scale are now attracting wide attention due to their unique physical and chemical properties and potential applications. Typical examples are metallic nanospheres,[1] nanocubes,[2] nanoprisms,[3] nanowires,[4] nanorods,[5] and nanotubes.[6] They can be synthesized in solution using structure-directing reagents, and employed as building blocks for constructing more sophisticated nanostructures by the so-called bottom-up approach. For example, 1D arrangements,[7,8] 2D surface patterns[9,10] and 3D superlattices[11] were assembled from nanospheres of different sizes. Additional physicochemical treatments can further transform discrete nanoparticles into semicontinuous and continuous nanostructures.[12,13] Alternatively, Meldrum and co-worker prepared porous gold structures that have nearly regular 15 μm channels using the calcium carbonate skeletal plates of echinoids (sea urchins) as templates.[14] In their procedure, a commercial gold paint was used to coat the echinoid skeletal plates, followed by annealing and removal of calcium carbonate in acid. Apparently, finer metallic structures on the nanometer scale are not available by using this approach. In the present work, we propose a facile approach to the fabrication of metallic nanostructures by *in situ* synthesis of metal nanoparticles in or on organic templates and subsequent removal of the template. As examples, porous and nonporous Ag nanostructures were fabricated by using cellulose fiber as the template.

Recently, we reported the *in situ* synthesis of noble metal nanoparticles using cellulose fibers as a nanoreactor.[15] Cellulose fibers have hierarchical porous structures, in which metal nanoparticles can be readily synthesized and stabilized. In a typical preparation, a lint free cellulose sheet (PS-2, Bemcot, 100% cellulose, Asahi Kasei, Japan) was used, which is composed of long uniform cellulose fibers of *ca.* 11 μm in a network morphology. The surface of each fiber is rough and has pores of 30–70 nm in size. The cellulose sheet was immersed in 100 mM aqueous $AgNO_3$ for 1 min, and rinsed with ethanol for 30 sec. The incorporated Ag^+ ions were bound to cellulose macromolecules *via* electrostatic (*i.e.*, ion-dipole) interactions and homogeneously distributed in the fibers. After reduction in 200 mM aqueous $NaBH_4$ for 10 min, it was rinsed with Milli-Q water and dried in a vacuum. In this particular specimen, the width of the cellulose fibers is *ca.* 11 μm, the same as that of the original fibers. Silver nanoparticles have a diameter of 7.9 ± 2.4 nm, and are aligned along the cellulose fibers.

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The composite was calcined in a programmable KDF-S70 furnace to remove the organic components. The temperature was raised at a rate of 2.4 K min^{-1} from room temperature to 450 °C, and kept at this temperature for 3 h. After it was allowed to cool down to room temperature, a piece of yellow silver sheet was obtained, as shown in the inset of Fig. 1a. It is flexible and is much shrunk from the original cellulose sheet. Scanning electron microscopy (SEM) observations† (Fig. 1a) show that it is in fact a network of Ag metallic fibers that is clearly inherited from the cellulose template. Magnified images show that wires of the network are nonporous and have a width of *ca.* 500 nm, *i.e. ca.* one twentieth of the width of the original cellulose fiber (*ca.* 11 μm). They assume a hemisphere-on-wire morphology (Figs. 1b and c) and the diameter of the hemispheres is also *ca.* 500 nm. Wavelength dispersive spectroscopy (WDS) studies‡ by focusing the electron beam on the hemisphere and wire confirmed that both of them are composed of metallic silver (>97%), indicating complete removal of the organic components by calcination. These observations suggest that silver nanoparticles fused with their neighboring particles along the cellulose fiber during calcination, without losing the network morphology of the template. Silver nanoparticles on the surface of the composite fiber might have fused faster than those inside the fiber, resulting in the formation of hemispherical Ag particles attached on the Ag wire.
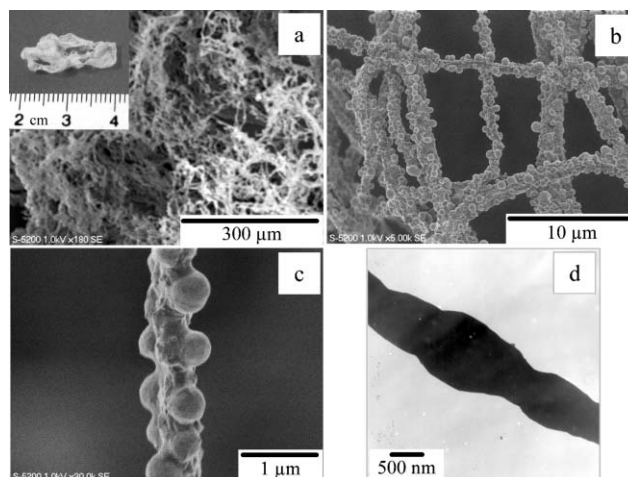
Fig. 1 (a–c) SEM images of a silver network fabricated using PS-2 as the template and aqueous $AgNO_3$ (100 mM) as the precursor solution *via* reduction and calcination: (a) overview, inset: digital camera image of the silver sheet, (b) magnified image, (c) single wire with hemispheres, and (d) TEM image of a single wire.
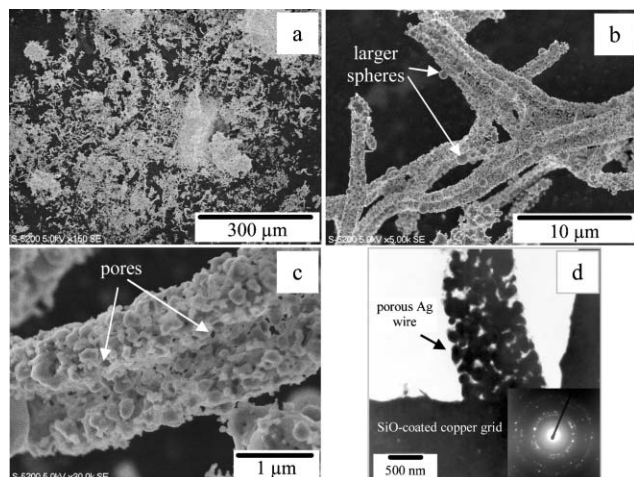
Transmission electron microscopy (TEM) observations§ also confirmed that the Ag wire is nonporous, as shown in Fig. 1d.

In contrast, when a composite prepared by using more dilute aqueous $AgNO_3$ (1 mM) was calcined under otherwise identical conditions, a small amount of residues with aggregated structures was formed. Clearly, the population of silver nanoparticles was not large enough to maintain an extended network morphology after calcination. Even so, imprints of the original cellulose fibers were observed by SEM on the surface of the residue. Nanoparticles of 20–97 nm were attached on the surface of these imprints.

It is known that $AgNO_3$ decomposes at 440 °C into metallic silver, nitrogen, oxygen and nitrogen oxides. In order to test if the direct conversion is effective, we conducted calcination after incorporation of metal ions without applying the reduction process. This altered procedure yielded only a metallic powder (Fig. 2a). Magnified images show that it consists of short (several microns) porous Ag wires of *ca.* 1 μm diameter (Figs. 2b and c). This diameter is two times as large as those obtained by applying the reduction process, but is again much shrunk from the original cellulose fibers. Clearly, Ag particles of *ca.* 170 nm in diameter (Fig. 2c) are produced and assembled along the template fiber, forming highly porous wires (Fig. 2c). Larger particles of 470 nm– 1 μm were also noticed on the wire (Fig. 2b, indicated by arrows). The nanoporous morphology was also confirmed by TEM. As shown in Fig. 2d, the pores are several tens of nanometers in size and they appear to be voids formed by the fusion of silver particles. Selected area electron diffraction patterns (SAED) match well with that of cubic metallic silver, indicating that the porous fiber consists of metallic silver. Without the reduction process, $AgNO_3$ decomposes to give Ag particles during calcination and gases of nitrogen, oxygen and nitrogen oxides are evolved. Such thermal conversion and gas release should be responsible for the formation of the porous morphology.

It is clear that the size and morphology of the metallic network depend on those of the template and on the fabrication process. Organic objects on the nanometer scale thus become useful templates for the fabrication of metallic nanostructures. It is known that individual cellulose fibers consist of microfibrils (10–30 nm) and their bundles. They can be separated from each other by mechanical disintegration, maceration, and chemical digestion. For example, commercial filter paper (Toyo Roshi Kaisha, Japan) contains separate microfibrils and their bundles ranging in width from 10–30 nm up to micrometers, as revealed by SEM. In order to obtain finer Ag wires, we used this material as a template in our preliminary trials. The results showed that silver nanowires of ten to several tens of nanometers became obtainable. Currently, more efforts are being devoted in our lab to explore further possibilities.

In summary, we have developed a novel method to fabricate metallic nanostructures. The method includes the *in situ* synthesis of metal nanoparticles in an appropriate organic template and subsequent removal of the organic components by calcination. As metal particles on the nanometer scale are formed *in situ* in organic templates, the current approach can produce much finer metal nanostructures than that reported by Meldrum and co-worker.[14] This approach is facile, and would provide ready access to metallic nanostructures of desired morphology and size, if appropriate templates are available. We can envisage many attractive applications for such metallic structures.

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Notes and references

† SEM observations were carried out on a Hitachi S-5200 field emission scanning electron microscope (FE-SEM) at 1 kV without metal coating.
‡ Wavelength dispersive spectroscopy (WDS) studies were carried out on a JEOL EPMA JXA-8200.
§ TEM observations were carried out on a JEOL JEM-2000EX transmission electron microscope at 120 kV.

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Fig. 2 (a–c) SEM images of powder obtained using PS-2 as the template and aqueous $AgNO_3$ (100 mM) as the precursor solution (a) overview, (b)–(c) magnified images, (d) TEM image of a single porous Ag wire, inset: SAED pattern. Calcination was carried out directly after the incorporation of Ag^+ ions without applying the reduction process.