Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio†

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Using a seed-mediated growth approach in a rodlike micellar media, silver nanorods of varied aspect ratio were prepared from nearly spherical 4 nm silver nanoparticles.

The physical and photophysical properties of metals on the nanometer scale are influenced by the shape of the nanoparticle.[1] Well defined silver nanorods and nanowires are desirable for their optical and electronic properties.[2,3] However, preparation of silver nanoparticles by chemical reduction methods generally yields a wide range of sizes and morphologies.[4] Silver nanorods and nanowires have been prepared by ultraviolet irradiation–photoreduction,[5] solid–liquid phase arc-discharge,[6] a pulsed sonochemical method,[7] templated by DNA,[8] with a carbon nanotube template,[9] in mesoporous silica,[10] in polymer films,[11] and in membrane templates.[12] Here, a new strategy is applied. A preformed silver seed was used to promote silver growth in solution, by chemical reduction of a silver salt. The presence of a rodlike micelle in solution promoted silver rod formation. We have been able to reproducibly make silver nanorods of aspect ratio 2.5–15 (10–15 nm short axes) and nanowires of 1–4 micrometer length with 12–18 nm short axes, and effectively separate the rods or wires from spheres and other shapes by centrifugation. Our method is not electrochemical and requires no nanoporous membrane, and thus may be more amenable to large-scale preparation of these materials.

The Ag seeds, 4 nm in diameter on average, were prepared by chemical reduction of $AgNO_3$ by $NaBH_4$ in the presence of trisodium citrate to stabilize the nanoparticles.‡ To make nanorods§ and wires¶ of varying aspect ratio, $AgNO_3$ was reduced by ascorbic acid in the presence of seed, the micellar template cetyltrimethylammoniun bromide (CTAB), and NaOH. The seed concentration and base concentration relative to the Ag^+ concentration are key to making larger aspect-ratio nanomaterials. CTAB is also necessary to produce a high yield of rods. Rods and wires can be separated from spheres by centrifugation.‖

The electronic absorption spectra of silver nanorod solutions show the conventional 400 nm peak observed for spherical silver nanoparticles and another peak at longer wavelengths, due to the longitudinal plasmon band of rod-shaped particles (ESI†).[1a,c,13–15] Decreasing the amount of seed in the nanorod preparation led to a further red shift of longer-wavelength longitudinal plasmon bands in the nanorod products, implying that the silver rods increased in average aspect ratio as the seed concentration decreased. Our optical data are in accord with what others have observed for metallic nanorods for transverse and longitudinal plasmon bands.[1a,c,13–15] In the absence of CTAB, spheroidal nanorods (aspect ratio < 2.5) were unstable and reverted to spheres (as judged by the disappearance of the long-wavelength absorption band) within 10 min. In the absence of seed, silver ion reduction by ascorbic acid in the presence of CTAB yielded only a few rods, which varied in aspect ratio.

Transmission electron microscopy (TEM) was performed on centrifuged solutions that had additional long wavelength peaks in their optical absorption spectra.** Figs. 1 and 2 show micrographs of particles prepared from 4 nm seeds after shape separation. The elongated rods shown in Fig. 1 were of uniform length (42 ± 3 nm) and aspect ratio (3.5). Interestingly, these rods self-assemble in a manner resembling a two-dimensional smectic liquid crystal upon gradual solvent evaporation. Depending on seed concentration, rods of aspect ratio 10–15 can also be seperated.§¶‖ Fig. 2 shows a micrograph of silver nanowires, 1–4 μm long with aspect ratio 50–350, mostly separated from spherical side-products. EDAX analysis of the samples confirmed that the particles were silver (not silver oxide) with a considerable amount of CTAB still present.

The only difference between the preparation of nanorods and the preparation of nanowires was the relative amount of NaOH in solution. For the nanorods, the pH of the reaction solution was slightly higher than the pK_a of the second proton of ascorbic acid (≈ 11.8), suggesting that the ascorbate dianion is a significant component of the solution. In the case of the nanowires, the pH of the solution was slightly lower than this pK_a, sugggesting that the monoanion of ascorbic acid (first $pK_a \approx 4.1$) is predominant in solution. It is reasonable that silver ion complexes of these two different forms of the reducing agent, in conjunction with their complexation with the cationic CTAB and silver seed in solution, are important in nanorod and nanowire formation. Mechanistic studies are in progress. Nonetheless, our new wet chemical synthetic method of silver

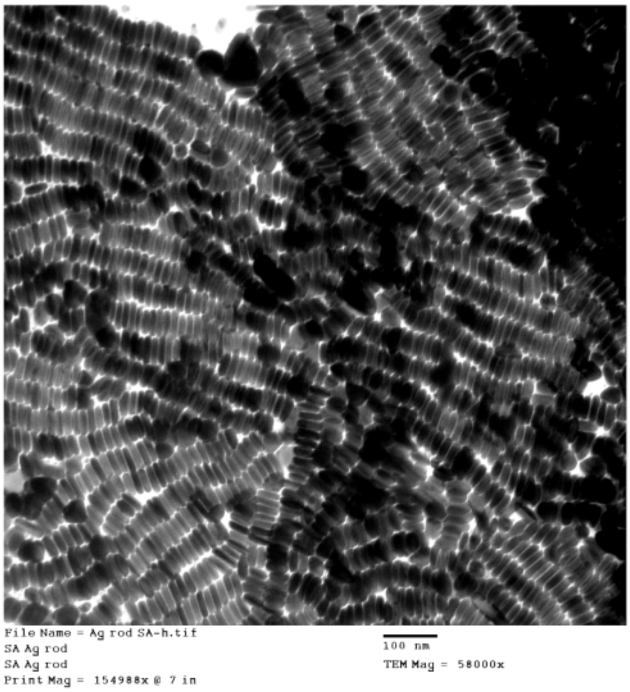

Fig. 1 TEM image of shape-separated silver nanorods from a preparation with 0.06 mL seed; scale bar = 100 nm.

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† Electronic supplementary information (ESI) available: UV–VIS spectra of silver nanorods. See http://www.rsc.org/suppdata/cc/b1/b100521i/

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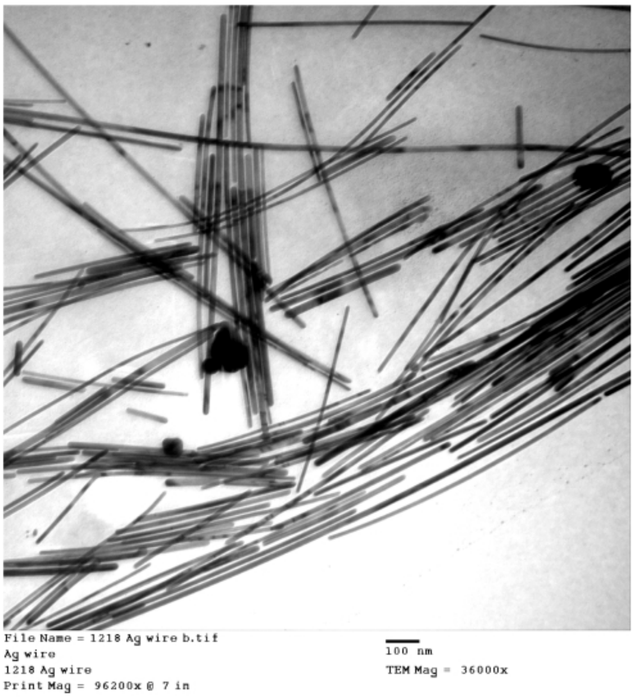

Fig. 2 TEM image of shape-separated silver nanowires; scale bar = 100 nm.

nanorods and nanowires is relatively simple to perform, and requires no nanoporous membrane.

Notes and references

‡ Preparation of 4 nm seed: a 20 mL solution with a final concentration of 0.25 mM $AgNO_3$ and 0.25 mM trisodium citrate in water was prepared. While stirring vigorously, 0.6 mL of 10 mM $NaBH_4$ was added all at once. Stirring was stopped after 30 s. This seed was used 2 h after preparation but could not be used after 5 h, as a thin film of particles appeared at the water surface. According to transmission electron microscopy, seed diameters were 4 ± 2 nm. For capping action of citrate see: A. Henglein and M. Giersig, *J. Phys. Chem. B*, 1999, **103**, 9533.

§ Procedure for Ag rods: first, six sets of solutions were prepared containing 0.25 mL of 10 mM $AgNO_3$, 0.50 mL of 100 mM ascorbic acid, and 10 mL of 80 mM CTAB. Next, a varied amount of 4 nm seed solution (2 mL, 1 mL, 0.5 mL, 0.25 mL, 0.125 mL or 0.06 mL) was added. Finally, 0.10 mL of 1 M NaOH was added to each set. NaOH must be added last to obtain the desired nanorods in decent yield. After adding the NaOH, the solution was gently shaken just enough to mix the NaOH with the rest of the solution. Within 1–10 min a color change occurred varying from red, to brown, to green depending on seed concentration. Each solution contained a mixture of rods and spheres with the aspect ratio of the rods increasing with decreasing seed concentration.

¶ Procedure for Ag wires: a solution containing 2.5 mL of 10 mM $AgNO_3$, 5.0 mL of 100 mM ascorbic acid and 93 mL of 80 mM CTAB was prepared. Next, 2.5 mL of the 4 nm seed solution was added. Finally, 0.5 mL of 1 M NaOH was added. After adding the NaOH, the solution was gently shaken just enough to mix the NaOH with the rest of the solution. A yellow color appeared within 15 min.

‖ Rods were concentrated and partially separated from spheres and surfactant by centrifugation. For solutions containing 0.25 mL of seed or more, 10 mL of solution was centrifuged at 6000 rpm for 30 min. The supernatant, containing mostly small spheres and platelets, was removed and the solid, containing some platelets and more rods with aspect ratio of 3–4, were redispersed in 0.5 mL of deionized water. For solutions containing 0.125 mL or 0.06 mL of seed, 10 mL of the solution was centrifuged at 2000 rpm for 6 min. The supernatant, containing short rods, spheres, and platelets, was separated from the solid which contained rods of aspect ratio 3–4 and a few larger rods (aspect ratio 10–15). Wires were partially separated from spheres and surfactant by centrifugation. For wires, 10 mL of the solution was centrifuged at 6000 rpm for 30 min. The supernatant was removed and the precipitate, containing silver nanowires, was redispersed in 0.5 mL of deionized water.

** All TEM grids were prepared from the solutions that were separated by centrifugation. 1.5 μL of solution was added to each grid. The grids and a small beaker of water were placed under a glass dish. The beaker of water provided a water vapor atmosphere to allow for slow drying (1–2 h) of the rod or wire solutions on the grid.

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