Formation of Silver Nanowires in Aqueous Solutions of a Double-Hydrophilic Block Copolymer

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Recently, much effort has been devoted to the controlled synthesis of one-dimensional (1D) nanostructured materials, such as nanorods, nanowires, and nanotubes.[1−3] In particular, metal nanowires have attracted considerable and increasing attention due to their unique magnetic, optical, electrical, and catalytic properties and their potential applications in nanoelectronics.[4,5] For the preparation of silver nanowires, "hard templates", such as carbon nanotubes[6] and mesoporous silica,[7] and "soft templates", such as DNA[8] and rodlike micelles,[9] have been used. Interestingly, several wet chemical routes to silver nanowires in the absence of 1D-structured templates have also been reported, which include ultraviolet irradiation photoreduction,[10] solid−liquid-phase arc discharge,[11] and a pulse sonoelectrochemical method.[12] However, the exploration of novel wet chemical methods for the synthesis of metal nanowires is still a challenging research area.

Some recent studies have revealed that the so-called double-hydrophilic block copolymer (DHBC),[13] which consists of one hydrophilic block interacting strongly with appropriate inorganic materials and another hydrophilic block mainly promoting solubilization in water, can exert very effective control on the morphology of inorganic crystals such as $CaCO_3$,[14] $BaSO_4$,[15] and calcium phosphate.[16] Specifically, unusual bundles of $BaSO_4$ nanofibers can be easily prepared in aqueous solutions of a phosphonated DHBC.[15] Herein, we show that the ability of DHBC in inorganic morphology control can be further applied to the synthesis of potentially technologically important silver nanowires.

A commercial DHBC poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-*b*-PMAA, PEO = 3000 g/mol, PMAA = 700 g/mol, Th. Goldschmidt AG, Germany)[14,15] was used for the facile synthesis of silver nanowires in aqueous solutions. The PMAA block of the copolymer carries carboxylic acid groups capable of coordinating with Ag^+ ions whereas the PEO block does not interact strongly with Ag^+ ions and mainly promotes solubilization in water. In a typical synthesis, 0.2 mL of 0.02 M $AgNO_3$ was added to 1.8 mL of 2 g/L PEO-*b*-PMAA solution. After mixing, the solution was allowed to stand at room temperature for 54 h and the formation of silver particles was manifested by a gradual yellowish coloration of the solution. The resultant silver colloidal dispersion was characterized directly by UV−vis spectroscopy (Shimadzu UV-250, 1-cm path length) and the product particles were characterized with transmission electron microscopy (TEM, JEOL JEM-200CX, 200 kV) and high-resolution TEM (HRTEM, Hitachi H-9000HAR, 300 kV). It is worth noting that, in the synthesis, silver nanowires formed spontaneously and no additional reductant, ultraviolet irradiation, or electrochemical method was required. It was reported that PEO-type nonionic surfactants can slowly reduce Ag^+ ions to metal Ag through oxidation of their oxyethylene groups,[17] indicating that the PEO block of the copolymer may play a similar role in the reduction of Ag^+ ions in the present case.

Figure 1 presents typical TEM images of silver nanowires after aging for 54 h. Figure 1a shows the presence of a large number of silver nanowires, which range in diameter from 20 to 40 nm and usually exhibit curved or distorted morphologies. The crystalline nature of the Ag nanowires was revealed by the corresponding electron diffraction pattern. The observed diffraction spots/rings with d spacings of 0.236, 0.202, 0.141, 0.121, and 0.117 nm can be indexed as (111), (200), (220), (311), and (222) reflections, respectively, according to the cubic structure of Ag. A relatively long and nearly straight silver nanowire, which had a diameter of 25−40 nm and was larger than 1 μm in length, is shown in Figure 1b. In contrast, Figure 1c presents a shorter and curved silver nanowire with a diameter of about 20 nm. A HRTEM image (Figure 1d), which shows continuous lattice fringes over a large area, was obtained by enlargement of a selected area of this nanowire. The

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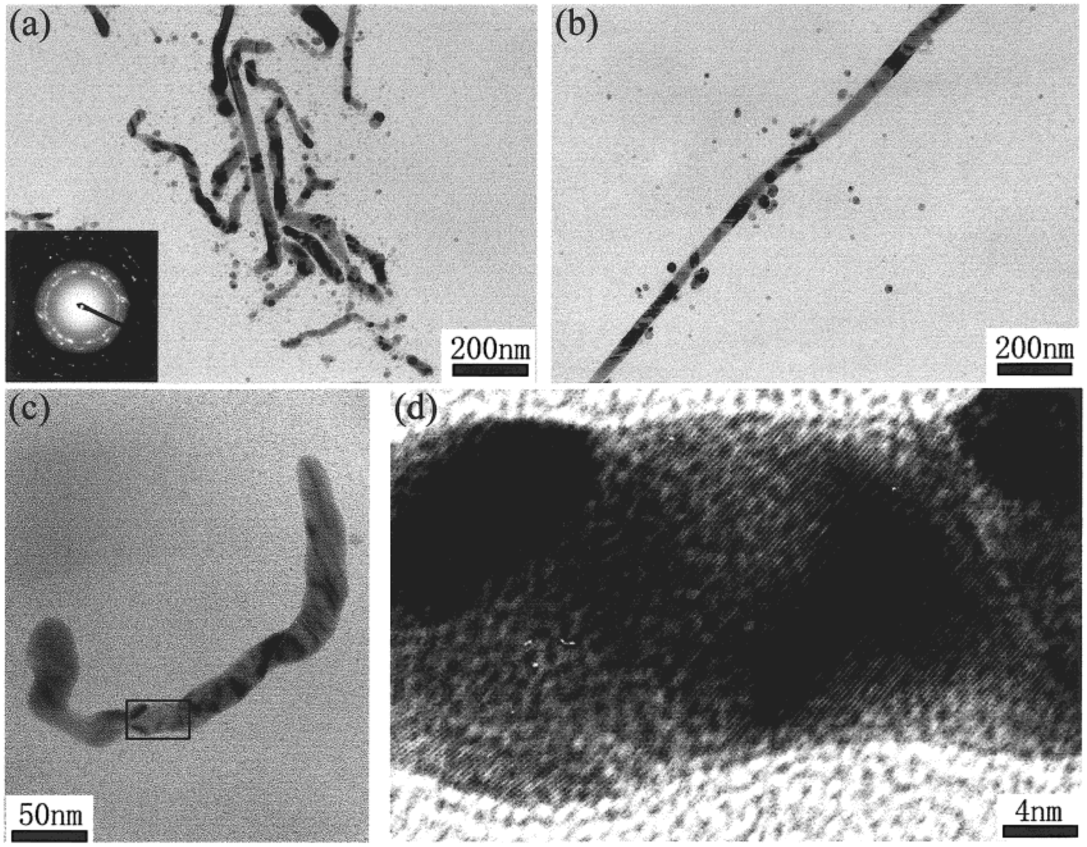

Figure 1. TEM (a−c) and HRTEM (d) images of Ag nanowires formed after 54 h of aging. Inset of (a) shows the corresponding electron diffraction pattern. Plate (d) corresponds to a high-resolution image of the framed area in (c).

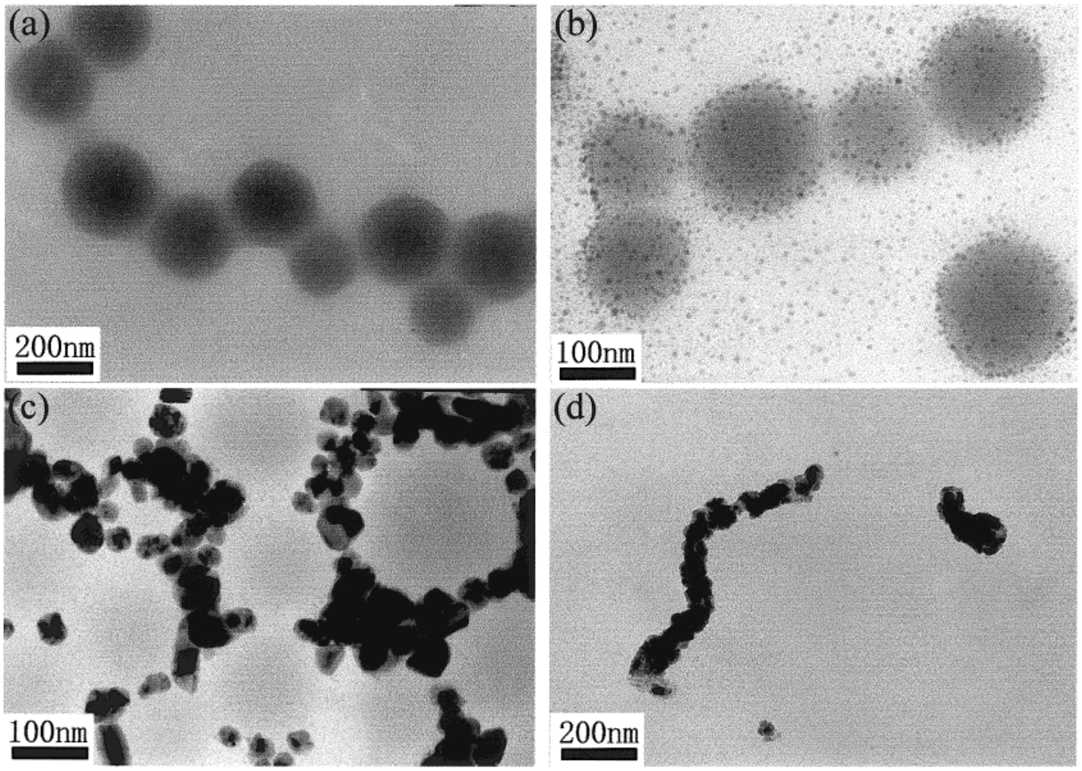

Figure 2. TEM images of the products obtained at earlier stages of Ag nanowire formation. Aging time: (a) 1, (b) 5, (c) 15, and (d) 25 h.

measured *d* spacing is 0.23 nm, which corresponds to the *d*(111) spacing for *fcc* Ag (0.236 nm), confirming the crystalline nature of the produced silver nanowires. To the best of our knowledge, this is the first report of obtaining lattice fringes for silver nanowires synthesized by wet chemical methods. Occasionally, short single-

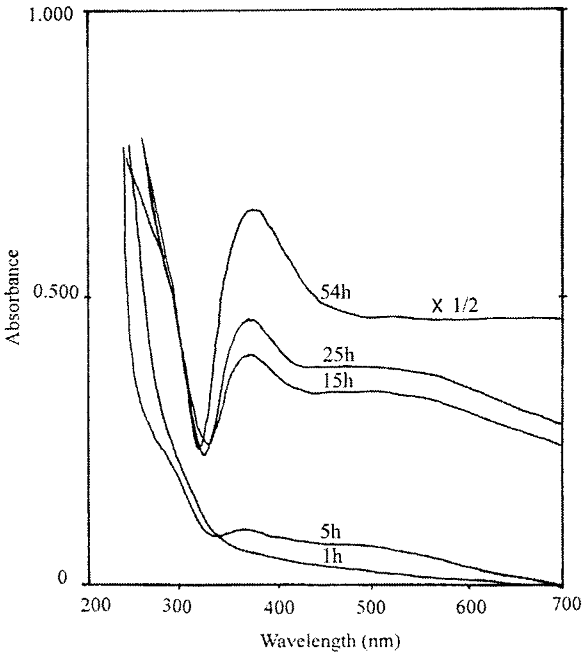

Figure 3. Absorption spectra of silver nanowires (aged for 54 h) and earlier products with various aging times.

crystal nanowires exhibiting continuous lattice fringes over the whole wires can be observed. However, in most cases, each nanowire was comprised of several single-crystal nanowires that were linked together through crystal defects between them. The HRTEM results also revealed that the nanowires were almost continuous and there were no visible polymers present within the nanowires, suggesting the formation of pure silver nanowires instead of a polymer/silver nanowire composite.

Some insight into the formation mechanism of the silver nanowires has been obtained by examining TEM images (Figure 2) and absorption spectra (Figure 3) of the products obtained at earlier stages of Ag nanowire formation. As shown in Figure 2a, the sample aged for 1 h exhibits large spherical particles (140−260 nm) with low contrast. The corresponding electron diffraction result has revealed the amorphous nature of these particles, excluding the formation of metallic silver. This is consistent with its absorption spectrum, which shows no plasmon band characteristic of metallic silver particles. It has been documented that micelle formation can be induced when the strongly interacting block of a DHBC coordinates with specific metal ions to become a hydrophobic block or a core-forming block in water.[13] For example, DHBC complex micelles with sizes up to several hundred nanometers formed when noble metal ions were added to aqueous solutions of poly(ethylene oxide)-*block*-poly(ethyleneimine) (PEO-*b*-PEI) where the PEI block strongly interacts with the metal ions by complexation.[18] Therefore, it can be reasonably deduced that the observed spherical particles are DHBC complex micelles formed upon complexation of the PMAA block with silver ions.

After an aging time of 5 h, in addition to the large low-contrast DHBC complex particles, a large number of tiny high-contrast particles (<10 nm) were observed, indicating the formation of silver nanoparticles (Figure 2b). Accordingly, a weak absorption peak around 366 nm, which can be attributed to the surface plasmon excitation of the silver particles, appeared in the absorption spectrum. When the aging time was prolonged to 15 h, the sizes of the silver nanoparticles increased to several tens of nanometers during the course of the gradual reduction reaction (Figure 2c). Meanwhile, many silver nanoparticles apparently adhered to the surfaces of the DHBC complex micelles and started directed aggregation growth. In the corresponding absorption spectrum, the plasmon band of silver particles increased greatly in intensity, indicating a considerable increase of the amount of reduced silver. The position of the plasmon band was slightly red-shifted to 370 nm, possibly due to the increase of the particle size. After being aged for 25 h, silver nanowires exhibiting coarse surfaces, which resulted from directed aggregation growth of primary particles, can be clearly observed (Figure 2d). When the aging time was further prolonged to 54 h, these coarse nanowires finally developed into the smooth silver nanowires shown in Figure 1, the absorption spectrum of which shows an intense plasmon band at 377 nm (Figure 3).

In summary, a novel wet chemical method for the synthesis of silver nanowires has been developed by using PEO-*b*-PMAA as a directing and reducing agent. It is revealed that the formation of DHBC complex micelles may play an important role in the directed aggregation growth of the silver nanowires. However, the detailed formation mechanism still needs further investigation. It is also worthwhile to explore the extension of the present technique to the preparation of other metal nanowires.

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