Synthesis of Nanowires and Coral-Shaped Nanostructures of Ag by an Ultraviolet Photo-Reduction Technique at Room Temperature

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Nanowires and coral-shaped nanostructures of Ag were prepared by an ultraviolet photo-reduction technique at room temperature.

Physical and chemical properties of metal nanocrystals strongly depend on particle size, size distribution and morphology.[1] Synthesis of well-controlled shape and size of metal nanoparticles can be crucial for their application.[2] In the recent years, much effort has been contributed to morphology-controlled growth of metal nanoparticles.[3–6] El-Sayed and coworkers reported a beautiful example of controlling the shape of Pt nanoparticles by changing the ratio of the concentration of the capping polymer materials to the concentration of the platinum cations used in the reductive synthesis of colloidal particles in solution at room temperature.[7] Antonietti et al. prepared noble-metal colloids of nonclassical shapes by the use of “microgel”, spherical polymer gel particles with a well-defined diameter in the nanometer range and an adjustable chemical functionality.[8] However, definite shape-controlled synthesis of metal nanoparticles is still difficult to achieve. Exploration of a novel technique for the fabrication of shape-controlled metal nanoparticles is a challenging research area.

In our previous works, we reported the shape-controlled growth of single-crystalline Ag nanorods and dendrites,[9] and gold nanoparticles of plate-like triangle, hexagon and quasi-ellipsoid[10] by a novel ultraviolet irradiation photo-reduction technique. In this paper, extending the convenient ultraviolet photo-reduction technique, we synthesized novel Ag nanowires and coral-shaped nanostructures of Ag by virtue of alternative of the capping materials.

The preparation procedure of the shaped Ag nanoparticles by the ultraviolet photo-reduction technique has been detailed in our previous reports.[9,10] Briefly, a 30-W low pressure, column-like mercury lamp (λ = 253.7 nm) was employed as an ultraviolet light source. $AgNO_3$ aqueous solutions of various concentrations containing capping materials in 1 cm × 1 cm × 4.5 cm quartz cells were purged with nitrogen gas for removal of oxygen and then were irradiated by the ultraviolet source for 48 h at room temperature. The products obtained were centrifuged, washed with distilled water and absolute ethanol repeatedly, dried at 60 °C for 5 h under vacuum, and then redispersed in ethanol solution for morphology observation. The transmission electron microscopy (TEM) image was taken with a Hitachi model H-800 TEM, using an accelerating voltage of 200 kV.

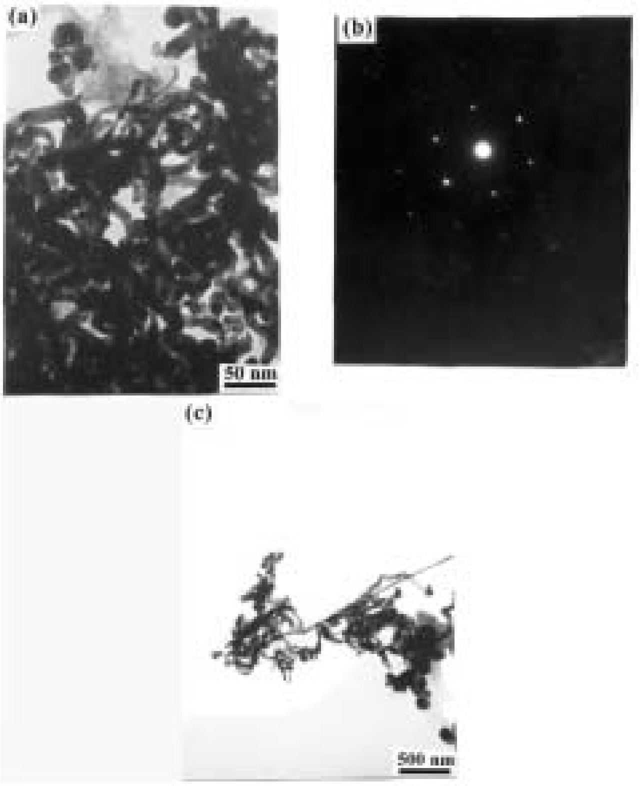

Figure 1 (a) The TEM image of Ag nanowires prepared by irradiating a 10^{-3} M $AgNO_3$ aqueous solution using 3 wt% sodium stearate (SS, $C_{17}H_{35}COONa$) as capping materials. (b) The corresponding electron diffraction (ED) for (a). (c) The TEM image of Ag nanowires prepared by irradiating a 10^{-2} M $AgNO_3$ aqueous solution using 3 wt% sodium stearate (SS, $C_{17}H_{35}COONa$) as capping materials.

Figure 1 (a) showed the TEM image of Ag nanowires prepared by irradiating a 10^{-3} M $AgNO_3$ aqueous solution using 3 wt% sodium stearate (SS, $C_{17}H_{35}COONa$) as capping materials. The nanowire was about 10 nm in diameter and up to 200 nm in length. The corresponding selective area electron diffraction (SAED) of a single nanowire in Figure 1 (b) revealed that only a hexagonal diffraction spot pattern was observed, indicating that the Ag nanowire prepared using the 3 wt% SS as capping materials was single crystal and has a preferential growth direction along the Ag [111] axis. The corresponding lattice constant is a = 0.4061 nm, consistent with the previous result[9] and reported data (JCPDS File No. 4-0783). Furthermore, when $NaBH_4$ as reduction agent was exploited in the similar system, only spherical Ag nanoparticles were observed. It demonstrates that the very slow ultraviolet irradiation photo-reduction process was favorable for the highly preferential growth of the Ag nanowire.[11] Further results demonstrate that the present Ag nanowries gradually grew longer and thicker with the increase of $AgNO_3$ concentrations, much different from the development of the previous Ag nanorods prepared using the PVA as capping materials into the dendritic nanostructure.[9] A typical TEM image of the Ag nanowires prepared by irradiating a 10^{-2} M $AgNO_3$ aqueous solution containing 3 wt% SS was presented in Figure 1 (c). It is clear that the produced Ag nanowire was 50 nm in average diameter and reached a maximum length up to 2.5 μm with an aspect ratio of 50.

Soft template mechanisms have been widely proposed for the formation of one-dimensional metallic nanowires in solutions.[12] In the present case, a similar 3 wt% of SS aqueous solution in absence of Ag^+ was dropped on the copper grid coated with carbon films for the TEM observation. The TEM image shows that the partial SS capping materials can self-assemble to form rod-like micelles in the aqueous solution. Therefore, it can be proposed that by irradiating the present ultraviolet source, the aqueous solution containing Ag^+ and SS generated hydrated electrons and radicals such as ${}^{\bullet}H$ radicals, which subsequently reduced the Ag^+ into Ag atoms.[13] The produced Ag atoms further aggregated into Ag clusters. One or some small Ag clusters adsorb on the surface of rod-like micelle of the SS and then grew into the nanowire by diffusion of the Ag ions onto the micellar surface. The photo-reduction process of the Ag^+ and formation mechanism of the Ag nanowire using SS as capping materials by the ultraviolet irradiation technique can be described as follows:

$$H_2O \xrightarrow{\text{Irradiation}} {}^{\bullet}H,\ {}^{\bullet}OH,\ e^-_{aq},\ H_3O^+,\ \cdots\cdots\ (e^-_{aq}\ \text{represents hydrated electrons})$$

$$Ag^+ + e^-_{aq}, {}^{\bullet}H \longrightarrow Ag^o$$

$$Ag^+ + Ag^o \longrightarrow Ag_2^+$$

$$2\,Ag_2^+ \longrightarrow Ag_4^{2+}$$

$$Ag_4^{2+} \xrightarrow[\text{Plus } Ag^+ \text{ and } NO_3^-]{\text{Agglomeration}} Ag_n^{m+}(NO_3^-)_x \longrightarrow \text{Ag atoms}$$

$$\xrightarrow{\text{Nucleate}} \text{Ag clusters} \xrightarrow{\text{SS rod-like soft template}} \text{Ag nanowires}$$

With concentration increase of the Ag^+ in the solution, more and more Ag atoms were produced, leading to growth in length and thickness of the Ag nanowire. The similar soft-template mechanism has been proposed by Esumi et al. for the formation of gold nanowires using gemini surfactants as capping materials under ultraviolet irradiation.[14]

It is well known that the selection of an appropriate protective polymer can lead to various colloidal morphologies by controlling the growth and handling of the agglomeration process.[15] In the present case, dramatic morphology variation of Ag nanoparticles was observed when sodium dodecyl sulfate (SDS) was used as capping materials for synthesis of the shaped Ag nanostructure under the ultraviolet irradiation. Figure 2 (a) shows the TEM image of Ag nanopaticles produced by irradiating 10^{-2} M $AgNO_3$ aqueous solution using 3 wt% SDS as capping materials. From the image, it can be seen that the Ag nanoparticle displayed coral-like nanostructure. The branches of the particle grew in the way of extending around with the same center. The corresponding SAED (Figure 2b) shows polycrystalline diffraction rings of silver, revealing that the coral-shaped Ag nanostructure consisted of small Ag clusters. The formation mechanism of the coral-shaped Ag nanostructure is unclear currently and needs further investigation. However, it is noteworthy that to our best of knowledge, although many authors have reported preparation of the Ag nanowire and dendritic nanoparticles, the coral-like Ag nanostructure was first synthesized until now.

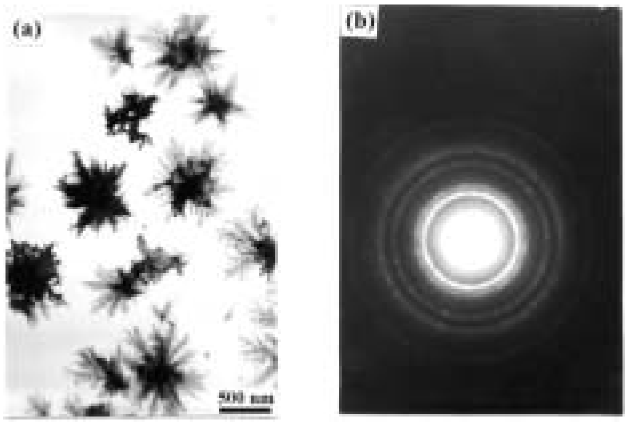

Figure 2. (a) The TEM image of coral-shaped Ag nanostructures produced by irradiating 10^{-2} M $AgNO_3$ aqueous solution using 3 wt% $C_{12}H_{25}NaSO_4$ as capping materials. (b) The corresponding electron diffraction.

In summary, nanowires and coral-shaped nanostructures of Ag were prepared by an ultraviolet photo-reduction technique at room temperature. The Ag nanowries gradually grew longer and thicker with the increase of $AgNO_3$ concentration. These novel Ag nanostructures are anticipated to have important applications in electronics such as the miniaturization of electronic devices and the progress of ultra-large-scale integrated circuits, and in physical and electrical fields.

References and Notes

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