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Synthesis in aqueous phase and characterization of silver nanorods and nanowires

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Silver nanorods and nanowires have been synthesized via a chemical process in aqueous phase by using ascorbic acid as a reducing agent and anionic surfactant dodecyl benzene sulfonic acid sodium (SDBS) as a capping agent. The products were characterized by X-ray diffraction (XRD) techniques and transmission electron microscopy (TEM). Experimental results indicated that the concentration of ascorbic acid played a critical role in the formation of the silver nanorods and nanowires. The optical properties were investigated. The prepared nanostructures displayed a very strong absorption band at room temperature.

Key words: *nanomaterials; optical properties; X-ray technique*

1. Introduction

One-dimensional (1D) nanostructures are expected to play an important role in fabricating nanoscale devices. As a result, the synthesis and characterization of 1D nanostructures have recently attracted much attention due to their interesting physical properties and their potential applications in fabricating optoelectric, thermoelectric, and magnetic devices [1–7]. Silver nanorods and nanowires with well-defined dimensions and aspect ratios are particularly interesting to fabricate and study because they exhibit high electrical conductivity, thermal conductivity and unusual optical properties among all the metals. Recently, much effort has been devoted to syntheses of silver nanorods and nanowires. For example, silver nanorods and nanowires have be prepared by using DNA [8], carbon nanotubes [9, 10], polymers [11, 12] and mesoporous silica [13] as templates, respectively. Murphy and coworkers have successfully synthesized high-quality silver and gold nanorods and nanowires by using a rod-like micellar template of cetyltrimethylammonium bromide

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(CTAB) instead of hard template [14, 15]. Tian and his collaborators have synthesized silver nanorods and nanowires by using a surfactant-assistant route [16]. They used sodium dodecylsulfonate as a capping agent but not as a soft template. Xia and Sun have demonstrated a polyol process that generated silver nanowires by reducing silver nitrate with ethylene glycol in the present of poly (vinyl pyrrolidone) (PVP) [17]. Murphy reported a seedless and surfactantless wet chemical approach to produce silver nanowires in the present of NaOH [18]. However, the final products of all these chemical methods were characterized by problems such as relatively low yields, low aspect ratios, irregular morphologies, non-uniformity size, or polycrystalline domain structure.

In this paper, we report a solution-phase method that generated silver nanorods and nanowires by reduced silver nitrate with ascorbic acid in the presence of anionic surfactant SDBS, which served as a capping agent. It was found the ascorbic acid concentration plays a key role in the formation of these nanocrystals.

2. Experimental

$AgNO_3$ and ascorbic acid (Shanghai Chemistry Co.) of analytical grade purity were used as starting materials without further purification. All solutions were made with distilled water. In a typical experiment, 1 dm^3 of 10 mM $AgNO_3$ solution and 1 dm^3 of 50 mM SDBS solution were added to 48 dm^3 of distilled water in a flask. 10 min of vigorous stirring was necessary to ensure that all the reagents were dispersed homogeneously at room temperature. 6 dm^3 of 10 mM ascorbic acid solution was then added drop-wise to the above solution under a continuous stirring. After the ascorbic acid addition was completed, the mixture was heated to 100 °C and refluxed for 30 min. The colour of the reaction solution changed to orange-yellow due to formation of silver nanorods and nanowires. Prior to characterization, the precipitate was separated by a centrifuge at 3000 rpm for 20 min and carefully washed repeatedly with distilled water and absolute ethanol to remove the remaining SDBS, and then dried in a vacuum oven at 60 °C for 5 h. The X-ray diffraction (XRD) patterns were recorded using a Japan Rigaku D/Max 2200PC diffractometer with graphite monochromatized CuK_α radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) studies were carried out using a Japan JEM-100CX Ⅱ transmission electron microscope. UV-visible spectra were measured on a Varian Cary-100 spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

The X-Ray diffraction (XRD) pattern (Fig. 1) taken from the sample prepared using 1.2 mM ascorbic acid in the presence of 1 mM SDBS (the final concentration) indicates that the crystal structure of the nanorods and nanowires is face-centred cubic (fcc), space group $Fm3m$, and cell lattice parameters: a = 4.086 Å (JCPDS file number: 04-0783). The high peaks indicate that the as-prepared samples are well crystallized.

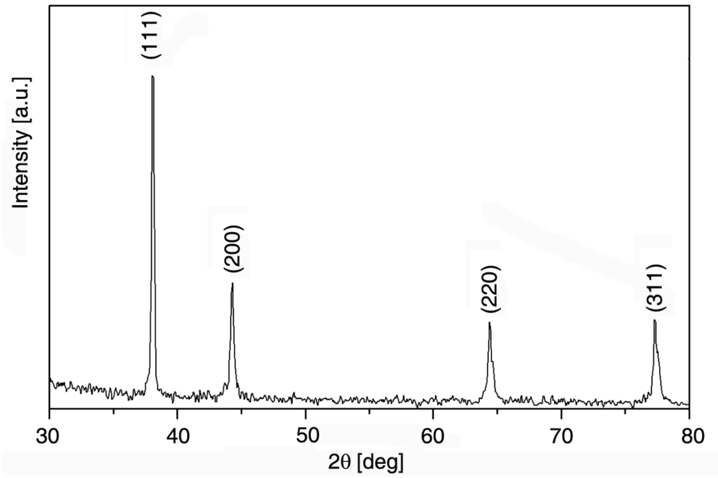

Fig. 1. XRD pattern of the as-prepared silver samples

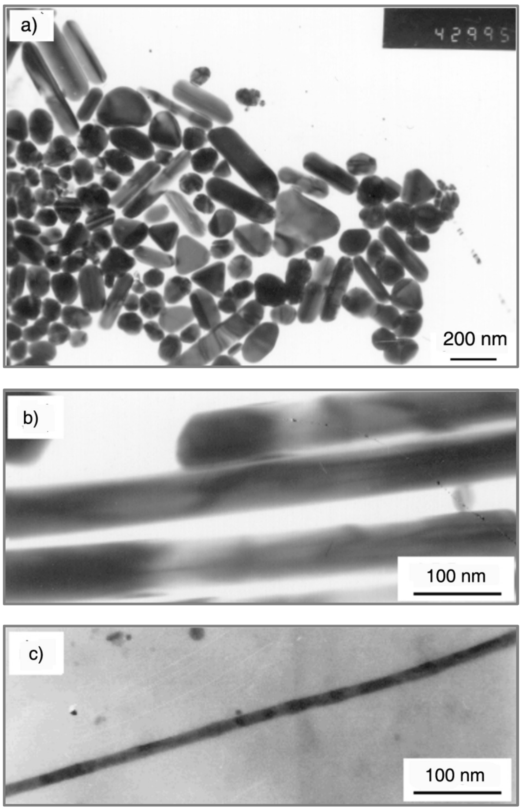

Fig. 2. TEM images of silver nanorods and nanowires
prepared with 1.2 mM ascorbic acid in the presence of 1mM SDBS (a)
and typical SEM image of individual nanorods (b) and nanowires (c)

The morphologies and structures of the products were investigated by the transmission electron microscopy (TEM); Figure 2a shows a typical TEM image taken from the orange-yellowish colloidal solution obtained using 1.2 mM ascorbic acid. It was clearly seen that the as-prepared samples consisted of an abundance of nanorods and nanowires, and relatively few spherical nanoparticles. The length of the nanorods ranges from 500 nm to 1.5 μm. The TEM of individual nanorods (Fig. 2b) shows that the average width of the nanorods is ca. 50–60 nm. The smallest aspect ratio of the rods is about 10 and the largest exceeds 40. The length of the nanowires ranges from 600 nm to 2.5 μm. The TEM of individual nanowires (Fig. 2c) shows that the average width of the nanowires is about 10–15 nm.

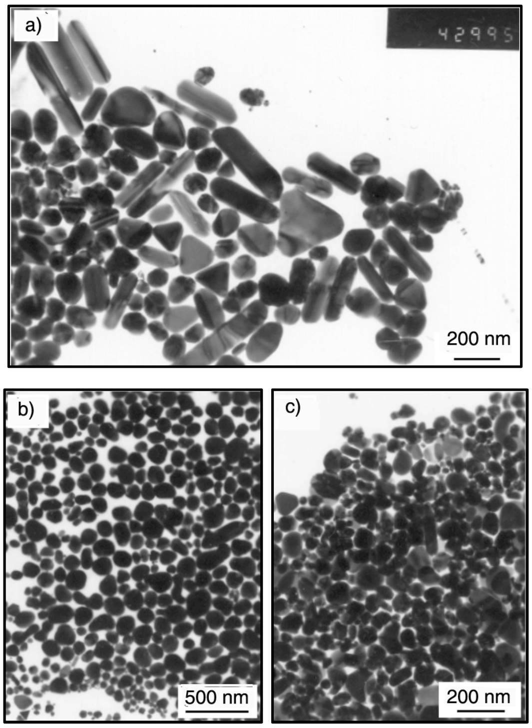

Fig. 3. TEM images of silver samples prepared using: a) 0.2 mM ascorbic acid in the presence of 1mM SDBS, b) 1.8 mM ascorbic acid in the presence of 1mM SDBS, c) 1.2 mM ascorbic acid in the presence of 10 mM SDBS

In the present study, the concentration of ascorbic acid plays a critical role in the formation of silver nanorods and nanowires. The silver nanoparticles with various morphologies were obtained as shown in Fig. 3 by changing the concentration of ascorbic acid from 1.2 mM to 0.2 mM and 1.8 mM. When the concentration of ascorbic acid was decreased to 0.2 mM, many nanorods, with a few triangular prisms and some nanoparticles were found in the products (Fig. 3a). It can be clearly seen that the aspect ratio of nanorods decreases upon decreasing concentration of ascorbic acid.

When it was increased to 1.8 mM, the products were dominated by spherical or irregular nanoparticles (Fig. 3b).

In addition, the SDBS concentration is another important parameter influencing the information on silver nanorods and nanowires. When no SDBS was introduced, $AgNO_3$ cannot be reduced by ascorbic acid and the reaction solution was still transparent after refluxing for 30 min at 100 °C. No silver nanoparticles were found in the solution by TEM. When the SDBS concentration is increased to 10 mM, spherical nanoparticles are the major products (Fig. 3c).

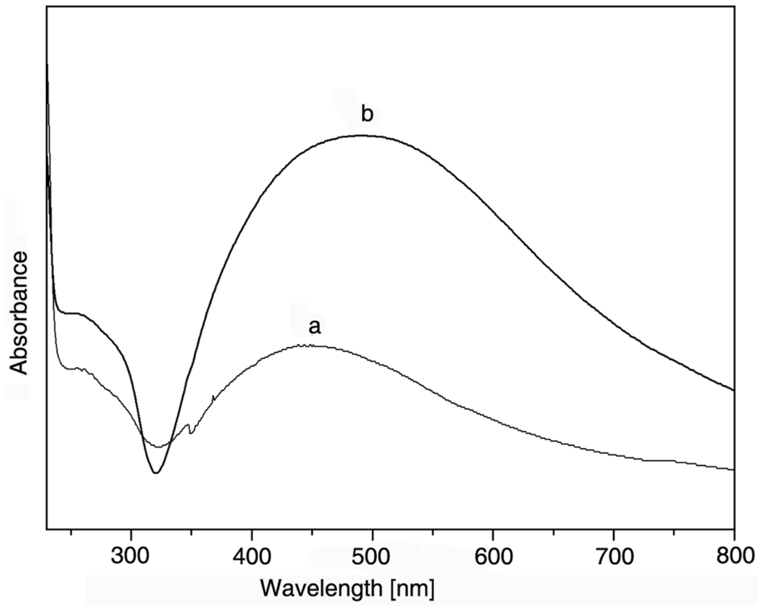

Fig. 4 UV-Vis absorption spectrum of silver nanocrystals prepared using: a) 0.2 mM, b) 1.2mM ascorbic acid in the presence of 1 mM SDBS.

It is well known that gold, silver, and copper nanoparticles display plasmon absorption in the visible region, and silver nanoparticles usually have an absorption maximum at 404 nm [19]. The UV-visible spectra of the silver nanocrystals fabricated using various concentrations of ascorbic acid (0.2 mM and 1.2 mM) are shown in Figs. 4a, b, respectively. The optical properties of silver nanoparticles depend on shape, as shown in Fig. 4. This is due to the absorption of visible light both along the length of the nanorods (the longitudinal plasmon band) and along the width of the nanorods (the transverse plasmon band). The larger the aspect ratio, the more red-shifted the longitudinal plasmon band, as theory predicts [20] and experiment confirms [21–23]. Figure 4a displays an absorption maximum at 447 nm red-shifted by about 43 nm compared to the reported results. The reason is that the obtained nanocrystals consisting of some spherical nanoparticles and nanorods, which have smaller aspect ratio, are abundant. Since the silver nanorods and nanowires prepared using 1.2 mM ascorbic acid have larger aspect ratio, Figure 4b shows absorption maximum at 495 nm, which is red-shifted by about 91 nm. As the shape of silver nanocrystals changed from spheres to rods and wires, the red-shift increased with the increasing aspect ratio. These experimental results strongly confirm the results predicted by the theory.

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