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A facile route to well-dispersed single-crystal silver nanoparticles from $[AgSO_3]^-$ in water

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ABSTRACT

Well-dispersed single-crystal Ag nanoparticles (NPs) were synthesized through a simple hydrothermal strategy in an aqueous solution of $[AgSO_3]^-$. The obtained Ag NPs are quasispherical in shape and the diameter of particles is ranging from 35 to 50 nm with a narrow size distribution. The proper choices of $[AgSO_3]^-$ as precursor and PVP as stabilizer are the keys to the formation of Ag NPs. A possible formation mechanism was proposed. And the optical absorption property of the obtained Ag NPs was also investigated. The as-prepared Ag NPs exhibit an absorption band at ca. 430 nm, which is the characteristic surface plasmon resonance of spherical/quasispherical Ag NPs.

1. Introduction

Noble metal nanoparticles (NPs) are of current research interest because of their distinctive properties that are significantly different from those of bulk materials, but they retain many of the microelectronic, optical, electronic, catalytic, nonlinear optical switching and surface-enhanced Raman scattering (SERS) [1–6]. Thanks to the efforts from many research groups, shape-controlled synthesis has been achieved for a number of metals, including Ag, Au, Pt, and Pd [7–10]. Among them, Ag NPs have drawn particular attention, due to their unusual physical properties, especially due to their sharp plasmon absorption peak.

Hitherto, much effort has been devoted to the syntheses of silver nanomaterials, such as nanocubes [11], triangular nanoplates [12,13], nanoparticles [14,15], nanowires [16,17], and so on. However, truncated nanocubes and multiple twinned particles (MTPs) have the lowest free energy for fcc silver metal. To obtain single crystalline spherical/quasispherical Ag NPs, the kinetics of nucleation must be carefully controlled. It still remains a challenge to prepare single-crystal Ag NPs with controllable size with high yield via a facile method. In this communication, well-dispersed single-crystal Ag NPs ranging from 35 to 50 nm in size were synthesized through a simple hydrothermal strategy in an aqueous solution of $AgNO_3$ and Na_2SO_3. The proper choices of $[AgSO_3]^-$ as precursor and PVP as stabilizer are the keys to the formation of well-dispersed Ag NPs. A possible formation mechanism was proposed and the UV–vis absorption behavior was also discussed.

2. Experimental

The chemicals involved in the work were silver nitrate ($AgNO_3$), sodium sulfite (Na_2SO_3) and poly(vinylpyrrolidone) (PVP, MW ≈ 40,000). All the chemicals were of analytical grade and used as received without further purification. In a typical process, 0.5 mmol silver nitrate and 2 mmol PVP were firstly dissolved into 40 mL distilled water in a Teflon vessel with 50 mL capacity. 1 M Na_2SO_3 aqueous solution was then added dropwise into the solution under magnetic stirring until a transparent solution was obtained. The resulting transparent solution was sealed in a stainless steel autoclave and maintained at 120 °C for 8 h. After the reaction completed, the autoclave was cooled down to room temperature naturally. The final product was collected by centrifugation, washed repeatedly with distilled water and absolute ethanol, vacuum-dried at 60 °C, and kept for further characterization.

The crystalline structure was identified by X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 1.54178$ Å). The morphology of the sample was observed by a JEOL-2010 transmission electron microscopy at an acceleration voltage of 200 kV. Infrared (IR) absorbance measurement of the product was carried out on a Nicolet 560 FTIR. The optical absorption spectra were recorded on a Shimadzu UV-2450 UV–vis recording spectrophotometer.

3. Results and discussion

A typical X-ray diffraction (XRD) pattern of the products is shown in Fig. 1. Four distinct diffraction peaks were observed, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of *fcc* silver accordingly. The cell parameter calculated from this pattern was 4.085 Å, in agreement with that found in the literature (JCPDS No.

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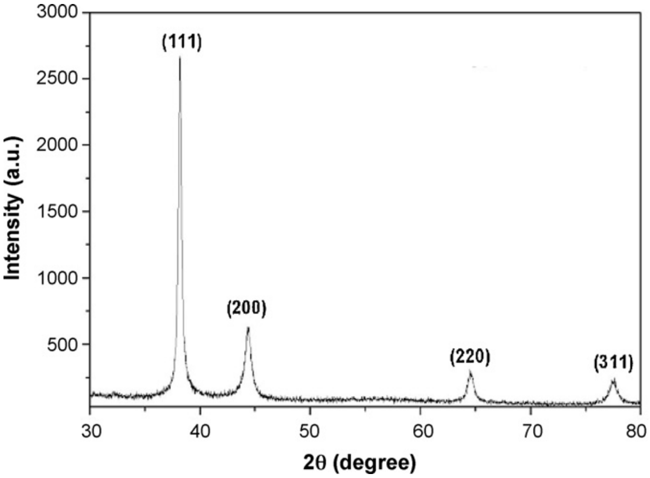

Fig. 1. A typical XRD pattern of Ag NPs obtained at 120 °C for 8 h.

04-0783). The broad nature of the XRD peaks could be attributed to the nanosize of the particles.

The morphology of the sample was observed by TEM, which are shown in Fig. 2. In Fig. 2a, the low-magnification TEM image displays that the morphology of the sample is of well-dispersed. The Ag NPs are quasispherical in shape and the average diameter of particles is ranging from 35 to 50 nm with a narrow size distribution (Fig. 2b and c), which might be due to the surfactant PVP as stabilizer. Fig. 2d shows the selected area electron diffraction (SAED) pattern of a typical individual nanoparticle. It can be concluded that Ag NPs are single crystalline and the incident electron beam is perpendicular to {1 1 1} facets of the NPs resulting from the sixfold rotational symmetry spots. The inner set consisting of the strongest six spots (triangle) is due to the allowed {2 2 0} reflection of fcc silver. The outer spots (square) with the weakest intensity could be assigned to the allowed {4 2 2} reflection.

Fig. 3 shows the high-magnification TEM image of Ag NPs, from which the contrast can be obviously observed. The surrounding polymer is about 2–3 nm in thickness. From the HRTEM image (as shown in Fig. 3b), the observed interplanar spacing of approximately 0.235 nm corresponds to the (1 1 1) planes of fcc Ag. The well-resolved interference fringe patterns confirmed the crystallinity of the silver particles.

FT-IR measurements have also been conducted to show the existence of the PVP molecules on the surface of the NPs. As shown in Fig. 4, the wavenumbers at 2952, 2920 and 2852 cm^{-1} are usually thought to originate from C–H stretching, and the asymmetric and symmetric H–C–H stretching in PVP molecules. The

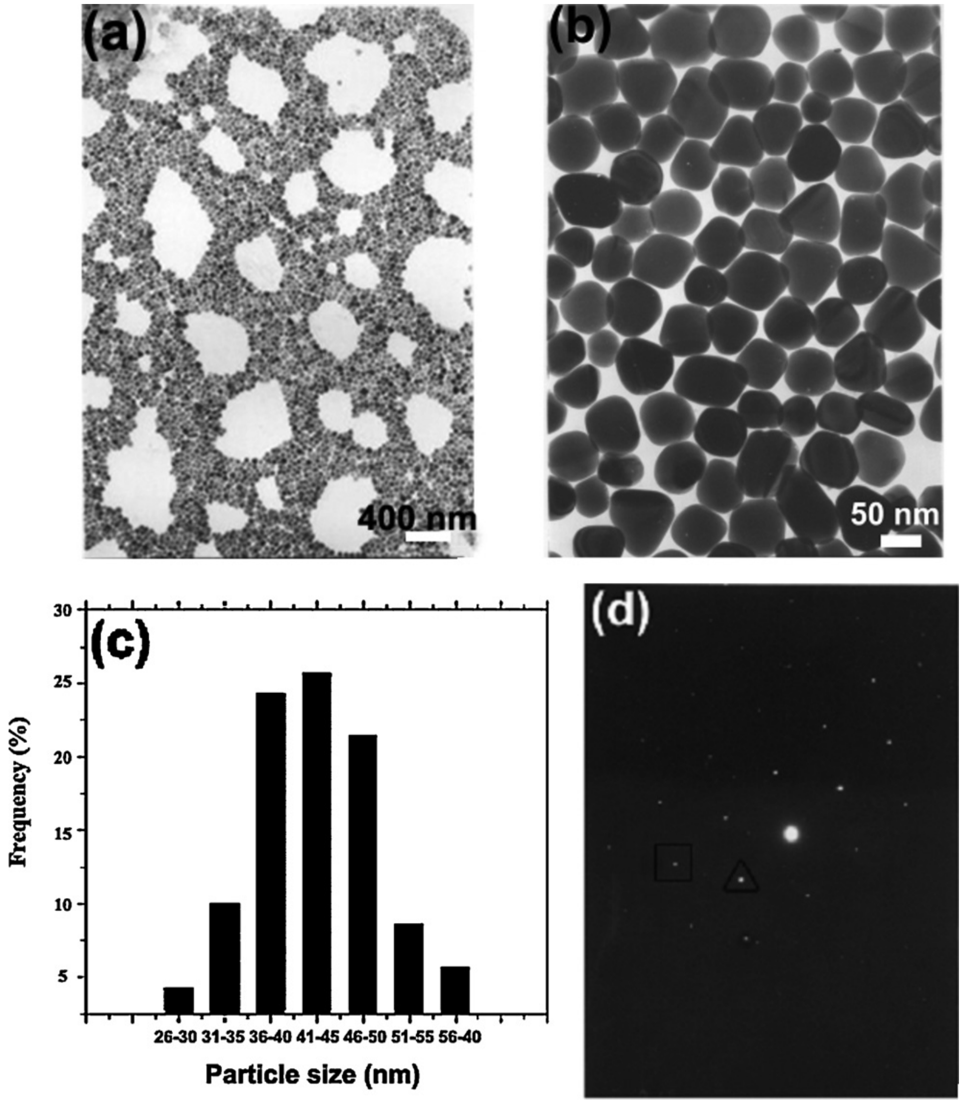

Fig. 2. (a) and (b) TEM images and (c) the size distribution (histogram) for the as-obtained Ag NPs. (d) A typical corresponding SAED pattern.

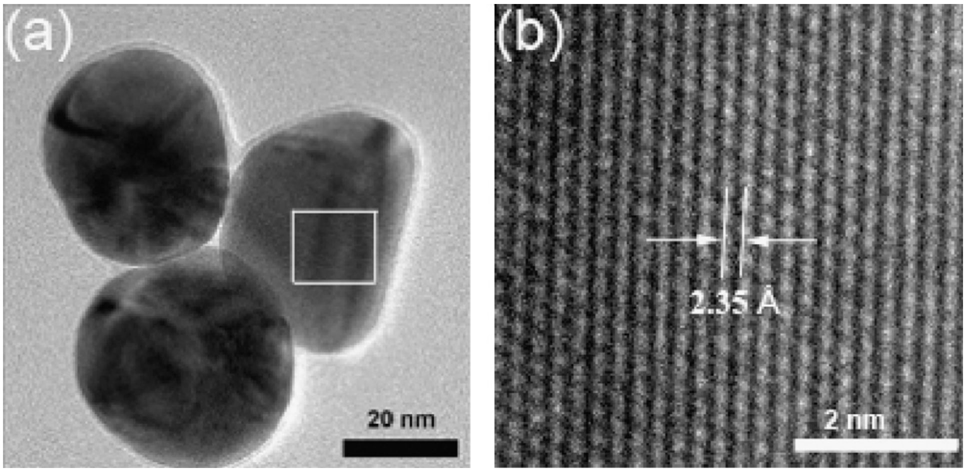

Fig. 3. (a) High-magnification TEM image of Ag NPs, clearly showing the surrounding polymer. (b) A typical HRTEM image of a selected area of an individual Ag NP shown in (a).

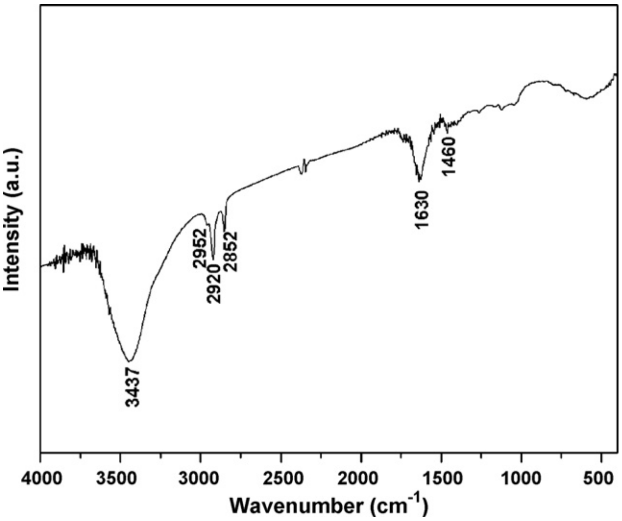

Fig. 4. FT-IR spectrum of the resulting products.

band at 1664 cm^{-1} corresponding to the C=O and C–N stretching vibrations of the pyrrolidone ring is found to shift to lower wavenumber (1630 cm^{-1}) for the PVP-capped Ag NPs. It is implied that PVP molecules strongly adsorb on the surface of silver nanoparticles through the coordination bond between the silver atom and oxygen atom of the carbonyl group, preventing the Ag NPs from aggregation. The FT-IR results further elucidate the role of PVP as stabilizer or capping agent in the formation and growth of the Ag NPs.

Like most fcc noble metal, cubooctahedra and multiple twinned particles of silver have the lowest surface energy and are therefore favored by thermodynamics. To obtain a shape other than the thermodynamic ones, the kinetics of nucleation must be carefully controlled. In our case, the single-crystal morphology of Ag NPs must be controlled by the proper choice of the precursor $[AgSO_3]^-$ and the hydrothermal process, through which the reduction of silver ions can be proceed in a mild way. Furthermore, the complex of PVP and Ag$^+$ ions and the protection of PVP as a steric stabilizer or capping agent lead to the formation of Ag NPs with good dispersity [16,18]. The formation mechanism was displayed as Fig. 5. The main chemical reactions involved in the process were expressed as below [19]:

$$Ag^+ + SO_3^{2-} \rightleftharpoons Ag_2SO_3 \downarrow$$
$$Ag_2SO_3 + SO_3^{2-} \rightleftharpoons 2[AgSO_3]^-$$
$$2[AgSO_3]^- \rightleftharpoons 2Ag^0 + SO_4^{2-} + SO_2 \uparrow$$

Due to that their size-dependent optical properties become of fundamental importance, Fig. 6 shows the UV–vis absorption spectra of Ag NPs maintained hydrothermally for 8 and 24 h, respectively. Both the spectra show a minimum at 320 nm due to the intraband transition in the metal that damps the plasma oscillations in this spectral region [20]. The quasispherical NPs show an absorption band at ca. 430 nm (solid line), which is the characteristic surface plasmon resonance of spherical Ag NPs [21]. Increasing the reaction time to 24 h (dash line), It is

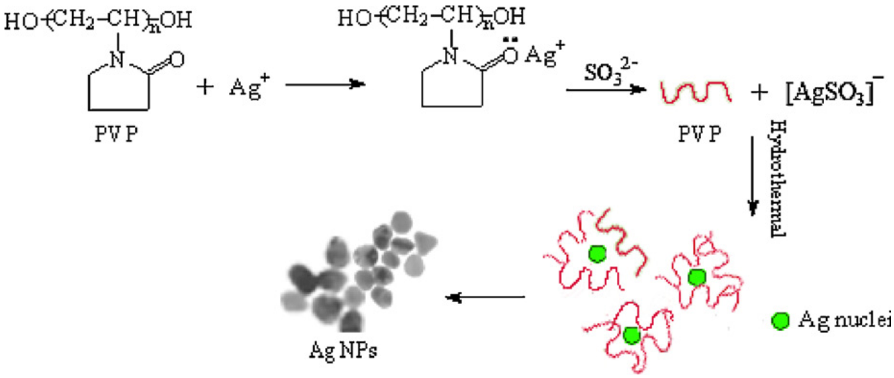

Fig. 5. Schematic sketch of the formation mechanism of PVP-capped Ag NPs.

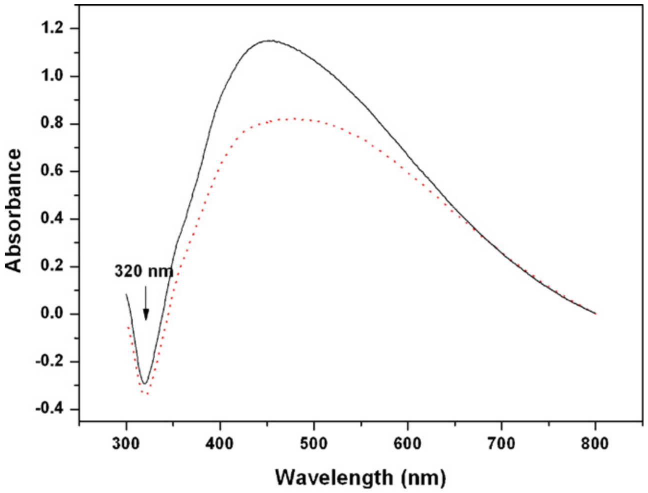

Fig. 6. UV–vis absorption spectra of the NPs prepared for 8 (solid line) and 24 h (dash line).

interesting to note that a broad absorption peak centered at ca. 520 nm developed, which is a result of the longitudinal plasmon resulting from the aggregation of the silver clusters [22]. Further work is under way to delineate the exact growth mechanism and the detailed optical behaviors of single crystalline Ag NPs.

4. Conclusions

In summary, well-dispersed single-crystal Ag NPs with diameter ranging from 35 to 50 nm in size have been successfully synthesized through a simple hydrothermal strategy in an aqueous solution of $AgNO_3$ and Na_2SO_3. The products were examined by a variety of characterization techniques. The proper choices of $[AgSO_3]^-$ as precursor and PVP as stabilizer or capping agent are the keys to the formation of Ag NPs. A possible formation mechanism of the single-crystal Ag NPs was proposed and the optical absorption property was investigated and discussed.

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