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One-Pot Silver Nanoring Synthesis

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Abstract Silver colloidal nanorings have been synthesized by reducing silver ions with $NaBH_4$ in trisodium citrate buffers. pH increase, by addition of NaOH, was used to speed up reduction reaction. The UV–vis absorption spectra of resulting silver nanorings showed two peaks accounting for transverse and longitudinal surface plasmon resonance, at $\approx$400 nm, and between 600 and 700 nm, respectively. The shapes of these silver nanoparticles (nanorings) depended on $AgNO_3/NaBH_4$ ratio, pH and reaction temperature. Particles were analysed by transmission electron microscopy, scanning electron microscopy and X-ray diffraction. A reaction pathway is proposed to explain silver nanoring formation.

Keywords Nanorings · Silver · Nanoparticles · Synthesis

Introduction

Nanoscale materials and structures for high value applications is an emerging area of nanoscience and nanotechnology. Nanomaterials, usually ranging from 1 to 100 nanometers (nm), may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine and water treatment [1]. Among such materials, silver nanoparticles have been intensively studied because of their intriguing optical, electronic, mechanical and bactericidal properties [2]. Several techniques have been employed for the synthesis of noble metal nanoparticles, such as gas evaporation, arc plasma, sputtering, electrochemical methods, laser ablation [3], etc. This communication describes the synthesis of silver nanoparticles by chemical reduction of silver ions by $NaBH_4$ [4]. We report herein the formation of ring-shaped silver nanoparticles synthesized in a one-pot experiment. Extraordinary optical properties from noble metal such as gold and silver are termed surface plasmon resonance induced by the collective oscillation of electron density [5]. It is known that the optical response of silver nanospheres exhibits a single absorption peak corresponding to surface plasmon resonance at about 400 nm. However, aggregated silver nanospheres give rise to two surface plasmon bands corresponding to transverse and longitudinal resonance [6]. Several techniques are already known for the elaboration of silver nanoparticles of different shapes like rods, triangular or hexagonal plates by varying the conditions of reduction and capping agent [7–10]. In contrast, little work has been done on the influence of pH conditions on the production of silver nanoparticles [11].

Experimental

Materials

Trisodium citrate was obtained from Alfa Aesar; sodium hydroxide, silver nitrate and sodium borohydride were purchased from VWR and used as received. Photomicrographs of nanoparticles were obtained with a JEOL 7400 FEGSEM and a JEOL 2010 TEM operated at 400 KV accelerating voltage. XRD pattern was obtained with JEOL

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2010 TEM. UV–Vis spectra of nanoparticle suspensions were recorded with a Perkin Elmer λ 25 UV–Vis spectrophotometer.

Methods

Seven pill boxes containing 4 mL of 10^{-3} M trisodium citrate and variable amounts of sodium hydroxide were maintained at 21 ± 0.5 °C under stirring. Identical volumes of 5.10^{-3} M silver nitrate (0.35 mL) and 10^{-2} M $NaBH_4$ (0.15 mL) were quickly added simultaneously to each pill box under vigorous stirring. Pill boxes were then stored in the dark. The same experiment was repeated at 25± 0.5 °C.

Results and Discussion

Numerous studies describe to the reduction of silver nitrate in the presence of ammonium hydroxide [1] in which NH_3 plays the double role of base and silver ion complexing agent. In contrast, very little interest has been devoted the influence of sodium hydroxide on the reduction of silver nitrate to obtain silver nanoparticles [11]. So, we decided to investigate systematically the influence of pH on the reduction of silver nitrate by $NaBH_4$ (Table 1). Reactions were realized at 21 ± 0.5 °C by quick and simultaneous addition of silver nitrate and $NaBH_4$ under vigorous stirring to the solutions of trisodium citrate containing various amounts of NaOH. Tested pH ranged from 7.7 to 9.8.

Colors of nanoparticle suspensions changed in the function of reaction pH: scattered light (Fig. 1a) varied from yellow to green with increasing pH, while transmitted light changed from yellow to purple through dark blue (Fig. 1b). Corresponding UV–Vis spectra are displayed in Fig. 1c. Sample 1 (pH 7.7) presents a plasmon resonance peak at 400 nm as reported in the literature [12]. Samples 2, 3 and 4 corresponding to pH 8.4–9.3 (Table 1) present a plasmon resonance peak at the same wavelength but with a much more intense absorbance. Then, increasing pH to 9.6–9.75 leads to a decrease in 400 nm absorbance, to the level of the first sample, and to the appearance of an additional broad band around 660 nm. This fact is probably due to an aggregation of the nanorings [13, 14].

Table 1 pH values of the different mixtures

Entry	1	2	3	4	5	6	7
NaOH (μL)	35	70	105	140	175	210	245
pH	7.73	8.45	9.01	9.28	9.57	9.69	9.75

Each assay contained 4 mL of sodium citrate (10^{-3}M), 0.35 mL of $AgNO_3$ (5.10^{-3} M), 0.15 mL of $NaBH_4$ (10^{-2} M) and, from 1 to 7, increasing volumes of freshly made 1 M NaOH

Transmission electron microscopy (TEM) was used to visualize the size and shape of the resulting silver nanoparticles (Fig. 2a, e). Reaction mixtures from pH 8.4–9.7 showed a great abundance of nanorings (Fig. 2c). As shown in Fig. 2b histogram, these nanorings have a mean external diameter of 70 nm and an internal diameter of 30 nm. The aggregation of the nanorings shown in Fig. 2e can explain the apparition of a second absorbance peak at 660 nm. XRD spectra showed a diffraction pattern characteristic of the face-centered-cubic structure of crystalline metallic silver.

Experimental conditions strongly influenced nanoparticle characteristics. For example, in these series of experiments, nanorings were obtained at temperatures comprised between 19 and 22 °C. At 25 ± 0.5 °C and the same concentration conditions, spherical hollow nanoparticles with ~100 nm diameter were obtained (Fig. 3).

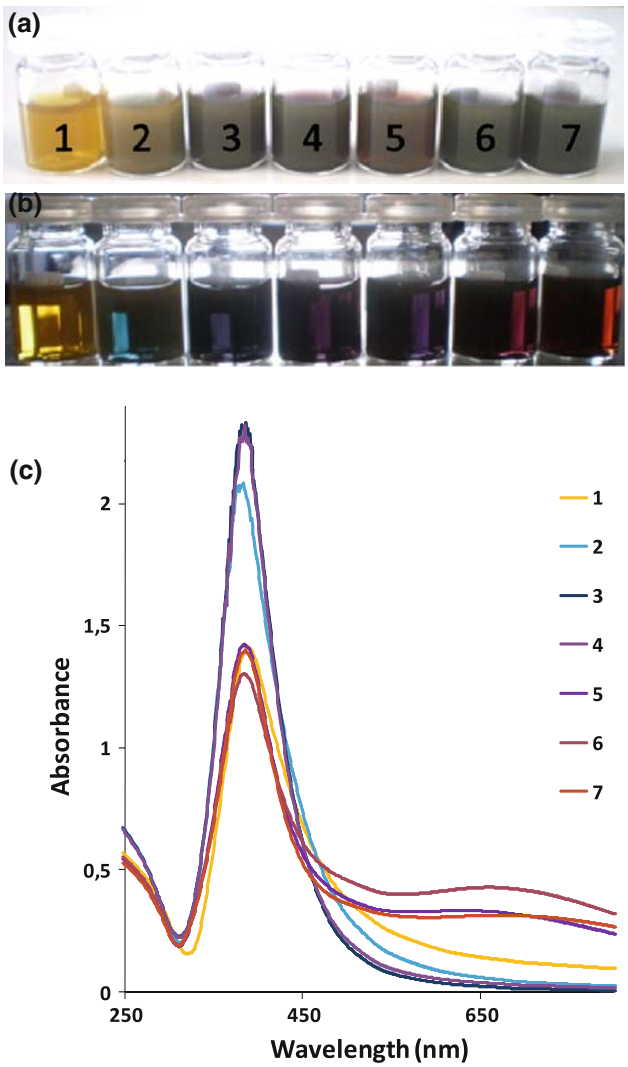

Fig. 1 **a** Colors observed of scattered light; **b** colors of transmitted light; **c** UV–Vis spectra (for conditions see Table 1)

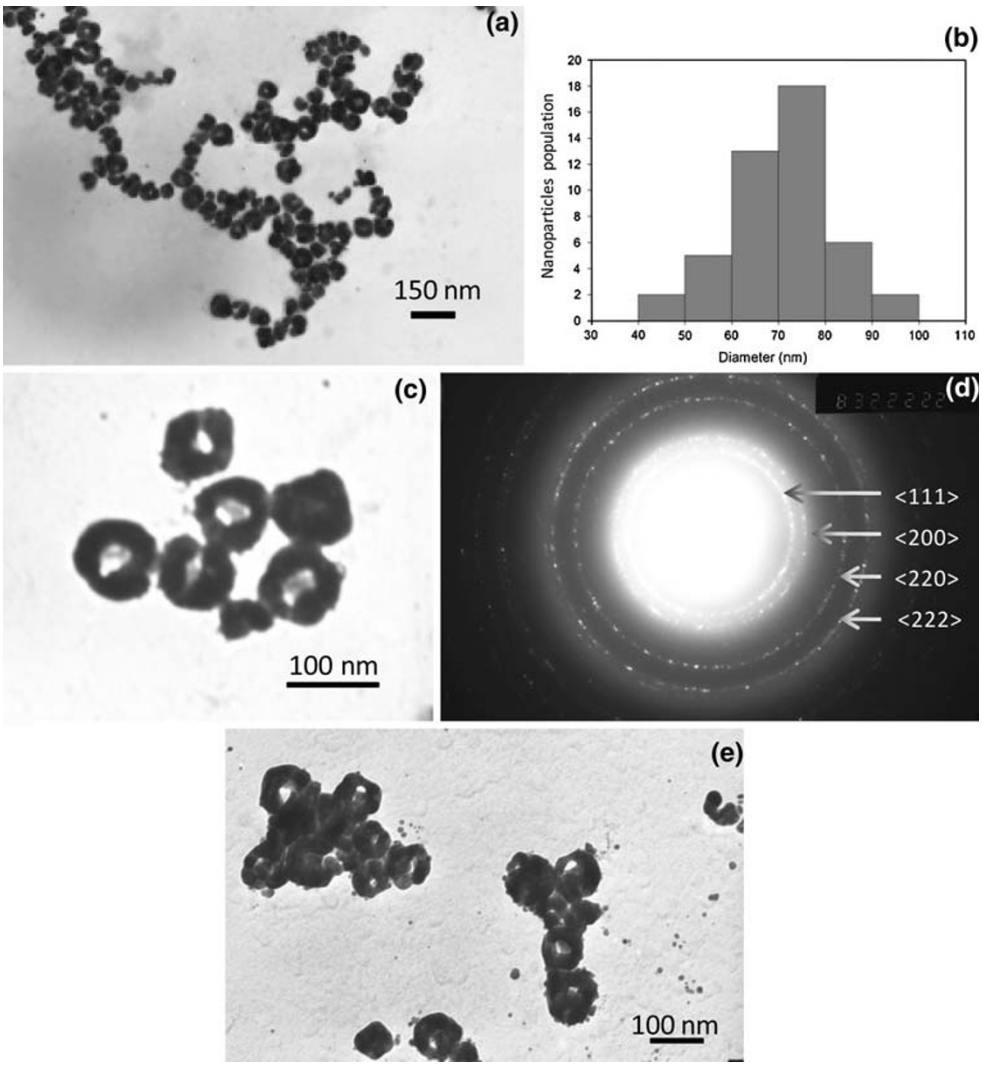

Fig. 2 **a**, **c** TEM photomicrograph of silver nanoring suspension 2; **b** histogram of nanoring external diameters; **d** XRD of nanorings; **e** TEM photomicrograph of silver nanoring suspension 7

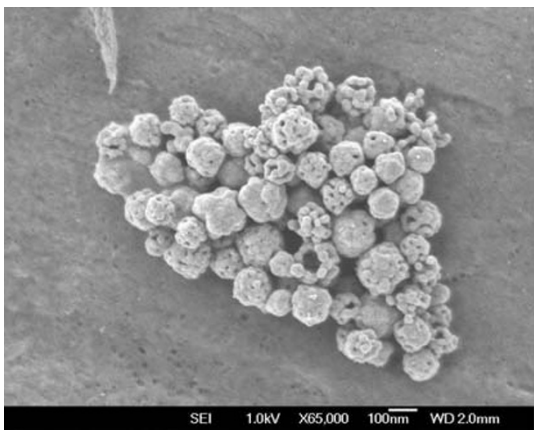

Fig. 3 FEGSEM photomicrograph of silver spherical hollows suspension obtained at 25 ± 0.5 °C

To elucidate the mechanism of such nanoring, cryo FEGSEM experiments were conducted. A solution of citrate 4 mL (10^{-3} M) and NaOH 70 µL (pH 8.5) was stirred vigorously, and 0.35 mL of $AgNO_3$ 5.10^{-3} M was quickly added. Before the reduction stage, a drop of the solution was quickly cryogenized by quenching into liquid nitrogen. Scanning electron microscopy shows preformed nanorings before the addition of the reducer (Fig. 4). The photomicrograph in Fig. 4 shows a nanoring shape that could be due to an aggregation of small Ag_2O nanoparticles resulting from the reaction of NaOH on silver nitrate. These

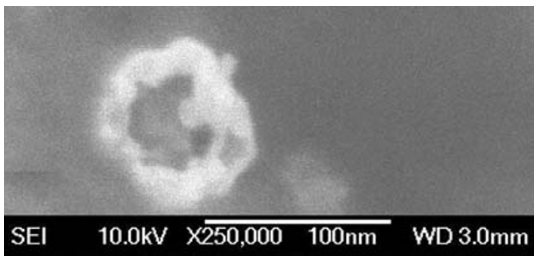

Fig. 4 Cryo FEGSEM photomicrograph of preformed silver nanoring before the addition of $NaBH_4$

entities should be further reduced by $NaBH_4$ to give silver nanorings.

Conclusion

We have realized for the first time a one-pot synthesis and structure characterization of silver nanorings. Uniformly sized silver nanorings are characterized by well-defined crystalline structure along the whole ring as shown by XRD patterns. These crystalline structures have unique plasmonic properties that would find applications in nanoscaled photonics, plasmonic devices and optical manipulation.

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