Journal of Colloid and Interface Science 324 (2008) 216–219

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

One-step synthesis of silver nanoparticles by sonication or heating using amphiphilic block copolymer as templates

Zhongli Lei *, Liang Zhang, Xiangyu Wei

Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, School of Chemistry and Materials Science, Xi'an 710062, People's Republic of China

ARTICLE INFO

Article history:
Received 20 October 2007
Accepted 23 April 2008
Available online 3 June 2008

Keywords:
Self-assembly
Sonicating
Templates

ABSTRACT

Block copolymer-supported Ag Nps (nanoparticles) have either a "cherry"-like or "raspberry"-like morphology [Antonietti, et al., Adv. Mater. 7 (1995) 1000–1005] depending on the amount of silver nitrate loading and the external conditions. Sonication favors silver nitrate and polyethyleneimine diffusion; the nucleation sites are well distributed in the micellar cores, so it is easy to form the cherry-like Ag NP colloids. However, when the amount of silver nitrate is decreased, it is heating that induces the formation of raspberry-like Ag NP colloids. The Ag NP colloids were investigated by transmission electron microscopy to demonstrate the nanosize dimensions and the location of the Ag NPs in the micelles. X-ray diffraction was employed to determine the crystal structure of the Ag NPs. UV–vis spectroscopy was employed for further qualitative characterization of the optical properties of Ag NPs.

1. Introduction

The versatility of physical and chemical properties of transition metal Nps (nanoparticles) renders them promising materials in fields such as catalysts [1–5], sensors [6–8], magnetism [9,10], and photoelectronics [11,12]. Especially for noble metal NPs such as silver (Ag), interest is mostly focused on their catalytic applications, because these NPs can serve as a bridge between homogeneous and heterogeneous catalysis and bring new opportunities for catalysis [13,14]. Various methods for the preparation of Ag NPs including wet and dry atmospheres have been developed [15–28], and some excellent reviews are available [29]; however, the chemical reduction of metal ions in solution is the most common preparative route. Unfortunately, unprotected Ag NPs are susceptible to irreversible aggregation in solution due to their small size and shape. One of the effective strategies is to protect NPs with agents such as thiols, surfactants, polymers, and polyelectrolytes that can spontaneously adsorb onto the particle surface to prevent agglomeration, resulting in stable particles [30,31].

The using of block copolymers as templates has been recognized as an effective approaches to creating nanopatterned materials. In principle, the first step is constructing a "stable" precursor that consists of micelles, metal ions, and reductant; the second is transforming this precursor into polymer–nanoparticle composites. The resulting polymer–nanoparticle composites are promising candidates to exploit or enhance the unique properties of Nps, while the polymer matrix can control host–guest interactions to ensure the well-defined spatial distribution of NPs [32].

Ultrasound has become an important tool in chemistry in recent years. It is well known that ultrasonic radiation in liquids has a variety of physical and chemical effects that are derived from acoustic cavitation, which can provide a unique method for driving chemical reactions under extreme conditions [33,34]. In this paper, we report a facile and efficient method for Ag NP synthesis. The whole experiment procedure is outlined in Fig. 1. The approach described here is based on the self-assembly of a diblock copolymer to micelles, which serve as a compartment for the formation of NPs with the aid of sonicating or heating. Judicious selection of auxiliary conditions can further lead to control of the morphology of Ag NPs colloids. The results demonstrate that template growth of NPs with the aid of sonication or heating can be used to fabricate configurations that are otherwise inaccessible.

2. Materials and methods

2.1. Materials

The amphiphilic block copolymer polystyrene-*block*-poly(acrylic acid) (PS_{54}-*b*-PAA_{135}) was synthesized by atom transfer radical polymerization (ATRP) as described in the literature [35]. The M_n of the PS-*b*-PAA is 15,380; the M_w/M_n is 1.19. Polyethyleneimine (PEI, $M_n = 600{,}000$–$1{,}000{,}000$) was purchased from Aldrich and was used without further purification. Silver nitrate ($AgNO_3$) was purchased from Xi'an Chemical Regent Corporation. Toluene was purchased from commercial sources and distilled from sodium be-

* Corresponding author. Postal address: College of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, China. Fax: +86 29 85307774.
E-mail address: zhllei@snnu.edu.cn (Z. Lei).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2008.04.050

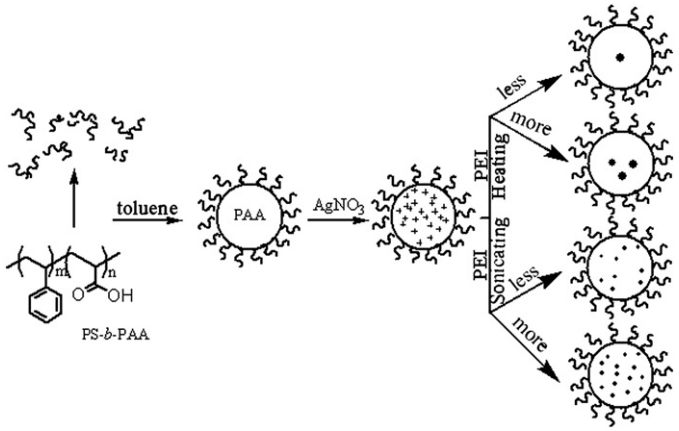

Fig. 1. Scheme of the formation of Ag NPs colloids.

fore using. The water used throughout these experiments was prepared by a Milli-Q Academic purification system. The ultrasonator (KQ-250DE 40KHZ) was purchased from KunShan Corporation of China.

2.2. Fabrication of Ag NPs colloids using block copolymer micelles as templates

The procedure is performed by simple mixing of the block copolymer solutions in toluene with the metal salt and reductant in turn. First, a predetermined amount of block copolymer PS-*b*-PAA was dissolved in 10 ml of toluene. The PS-*b*-PAA formed spherical micelles in which the polar poly(acrylic acid) (PAA) heads constituted the center and the nonpolar polystyrene (PS) tails extended outward. After the solution was stirred for 10 h, 0.5 ml of $AgNO_3$ solution was added to the solution under vigorous stirring and continued for 36 h in the dark to allow complete dissolution of the silver nitrate within the cores of the block copolymer micelles. Next, 0.5 ml water containing 0.02 g PEI was added to the former solution with stirring. Due to its polarity, PEI was also solubilized preferentially in the cores of the micelles, where it induced the reduction of the Ag NPs. Finally, the resulting solutions were sonicated for 3 h under nitrogen or heated for 3 h at 80 °C. The formation of Ag NPs in the micellar cores was directly seen by color change of the dispersion solution from colorless to yellow.

2.3. Sample characterization

Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-600 electron microscope at an accelerating voltage of 75 kV. The samples were prepared by depositing 20 μl of the aggregate solution on 200-mesh carbon-supported copper grids, followed by solvent evaporation at atmospheric pressure and room temperature. All samples were dried under atmosphere without staining. X-ray diffraction (XRD) measurements was obtained using a Rigaku Model D/max 2000 PC X-ray diffractometer operating with a Cu anode at 40 kV (acceleration voltage) and 50 mA (electric current) in the range of 2θ value between 20° and 80° with a speed of 2°/min. Prior to peak width measurement, each diffraction peak was corrected for background scattering and was stripped of the $K\alpha_2$ portion of the diffracted intensity. The UV–vis adsorption measurements were performed on a Perkin–Elmer Lambda 950 spectrometer.

3. Results and discussion

In recent years, the use of amino-containing compounds for preparing metal NPs has been widely investigated because of their simplicity and wide variability. With the use of linear PEI to serve as a reducing agent and a protective agent, $HAuCl_4$ was reported to be induced to form gold NPs and nanoplates spontaneously [36,37], whereas in this paper silver ions in reverse micellar cores are reduced into Ag NPs by PEI with the aid of sonicating or heating. Fig. 2 shows typical TEM images of the "cherry"-like Ag NP colloids produced with the aid of sonication. It is apparent that the as-synthesized Ag NPs are almost spherical and have diameters of 20 ± 5 nm in Fig. 2a, 30 ± 5 nm in Fig. 2b. Fig. 3 shows TEM images of the corresponding Ag NP colloids produced with the aid of heating. As can be seen in this figure, when the concentration of silver nitrate is 80 mg/ml, it is easy to form "raspberry"-like Ag NP colloids, and the diameter of Ag NPs is about 30 ± 10 nm (Fig. 3a). When the concentration of the silver nitrate increases from 80 to 200 mg/ml, the cherry- and raspberry-like Ag NPs colloids can be seen in one image (Fig. 3b).

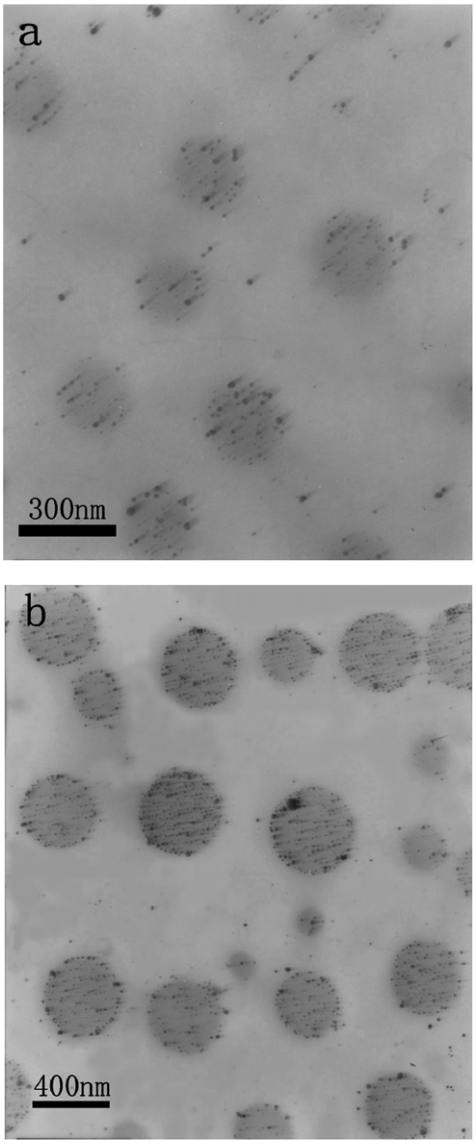

Fig. 2. TEM images of the Ag NPs colloids with sonicating sonication. The initial concentrations of silver nitrate and PS-*b*-PAA were 90 and 1.1 mg/ml ml for sample (a), and 200 and 2.2 mg/ml ml for sample (b), respectively.

As the formation of microphase-separated block copolymer phases is a thermodynamic phenomenon, templating is governed to a great extent by numerous physical parameters, and together with solvent effects, the combination makes it difficult to predict the structure [38]. Temperature is a important physical parame-