

Preparation of Silver Nanoparticles via Ionomer Clusters

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ABSTRACT

This work focuses on preparing silver nanoparticles by using a novel technique, which is simple, fast and economical. Silver nanoparticles were produced by using a sulfonic acid polystyrene ionomer as a template, and these were then characterized by UV-visible spectrophotometer, wide angle X-ray diffraction, and transmission electron microscopy. Two different levels of acid groups of ionomers were used, 30 and 50 mole %. The results show that silver nanoparticles prepared from an ionomer containing 30 mole % of acid groups provided a smaller particle diameter, about 14.8 nm. Furthermore, using partially neutralized ionomers as a template, an even smaller diameter of silver nanoparticles was achieved. Particles 10.1 nm and 14.3 nm were observed from the partially neutralized ionomers containing 30 and 50 mole% sulfonated groups respectively.

Keywords: silver nanoparticles, ionomer clusters, ionomer templates, sulfonated ionomers, nanoparticle preparation

1 INTRODUCTION

Nanotechnology has played a key role in both academia and industry for the past two decades. This is due to the unique properties and potential applications for nano-scale materials, especially metallic nanoparticles. Metallic nanoparticles can be used for catalytic, optoelectronic and biomedical applications. Particularly, silver nanoparticles have exhibited antimicrobial properties and also been used as biosensing materials for surface enhanced Raman spectroscopy and metal-enhanced fluorescence [1-4]. A variety of procedures have attempted to synthesize nanoparticles. Nanoparticles of silver have been prepared via a microemulsion of water in supercritical CO₂ [5-6] and via a rapid expansion of a supercritical solution into a liquid solvent [7-9]. Oleic acid has been used as a stabilizer for silver nanoparticle synthesis under various pH conditions via the solvent exchange method, in which silver nitrate was reduced and transferred into organic solvent by reorientation of oleic acid [10].

The ion solvent exchange method provides a simple and reproducible technique to prepare silver nanoparticles. For example, the formation of silver nanoparticles embedded in Nafion® membranes [4,11], natural rubbers [12], polysaccharides [13], liquid crystalline polymers [14] and dendrimers [15] are based on a standardized ion exchange process. By utilizing ionomers that contain a nanoscale

morphology of ionic clusters [16], which are typically viewed as roughly spherical aggregates about 3-15 nm in size [17], this allows the formation of metallic nanoparticles using the cavities of ionic clusters. Therefore, in this work, silver nanoparticles were prepared by reducing silver nitrate with sodium borohydride within the clusters of the ionomers. UV-visible spectroscopy (UV-vis), wide angle X-ray diffraction (XRD), and transmission electron microscopy (TEM) were employed to characterize the formation and the morphology of silver nanoparticles.

2 EXPERIMENT

2.1 Materials

Silver nitrate (AgNO₃), sodium borohydride (NaBH₄), sulfuric acid, sodium hydroxide (NaOH) and methanol were purchased from Qrec and used without further purification. General purpose polystyrene (PS) with number average molecular weight of about 130,000 was obtained from Siam Polystyrene Co., Ltd. Propionic anhydride was obtained from Fluka. Sulfonic acid polystyrene (SPS) was synthesized from propionyl sulfate according to a procedure reported in a previous article [18]. The degree of sulfonation of SPS was determined by titration with a standard 0.05 M NaOH solution in methanol. Sulfonation levels of the SPS were 30 and 50 mol%, which will be referred to as SPS30 and SPS50, respectively. The partially neutralized SPS was obtained via an ion exchange process with NaOH [19]. The partially neutralized versions of SPS30 and SPS50 will be referred to as SPS30Na and SPS50Na, respectively.

2.2 Preparation of Silver Nanoparticles

In a typical ion exchange/silver reduction process, 1 g of SPS was dissolved in 20 mL of methanol before adding 5 mL of 1 M AgNO₃ solution with continue stirring and heated to 60 °C for 1 hr. Then 20 mL of 1 M of NaBH₄ solution was added into the sample. Silver particles were precipitated and rinsed with water and methanol several times. The sample was dried in the oven at 90 °C for 48 hrs. The silver particles prepared via ionomers of SPS30, SPS50, SPS30Na and SPS50Na are denoted as AgH30, AgH50, AgNa30 and AgNa50, respectively.

2.3 Characterization

UV-vis absorption spectra of the silver colloid solution were acquired using a UV-4100 spectrometer. Silver powders were measured using a Bruker D8 X-ray diffractometer with a Cu K α radiation monochromatic filter in the 2θ range of 30-80°. The morphology of synthesized silver nanoparticles was observed on a Philips Tecnai 20 transmission electron microscopy. The samples were prepared by dropping the silver colloid on carbon-coated Cu grids and allowing them to dry in air at 60 °C for 24 hrs. They were observed at an accelerating voltage of 100 kV and magnification of 620,000x.

3 RESULTS AND DISCUSSION

UV- vis. The absorption spectra of AgH30, AgH50, AgNa30 and AgNa50 were similar. Provided in Figure 1 is an absorption spectra of AgNa30, which serves as a typical example. The absorption band λ_{max} , which ranged from 400 to 480 nm, corresponds to the surface plasmon resonance of the nanoparticles, and indicate that the silver nanoparticles are well dispersed in a colloidal suspension. Some degree of unsymmetrical spectra were observed, which may be due to a slight distribution in the size of the silver particles.

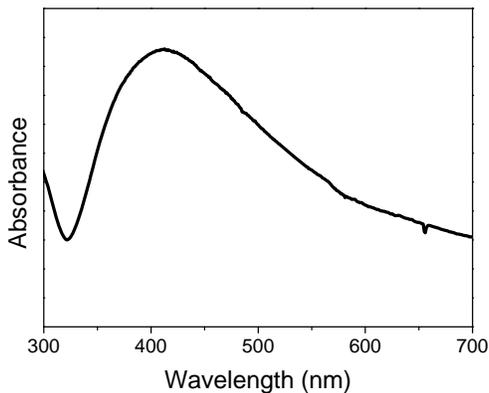


Figure 1: UV-vis absorption spectra of AgNa30.

XRD. The formation and size of solid silver nanoparticles were obtained from the X-ray diffraction analysis. As provided in Figure 2, the XRD pattern of the four prominent peaks at 2θ values of about 38, 44, 64 and 78° matches well with that of the bulk FCC silver in the JCPDS database and in the literature [4, 9]. These peaks can be attributed to the (111), (200), (220) and (311) planes. The broadness of the peaks is due to the particles being nanoscale. Peak broadening can be used to estimate the average silver particle size, based on the Debye-Scherrer equation [20]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is an average particle diameter, K is a constant related to the crystal shape (equal to 1 here), β is the corrected band broadening parameter, λ is wavelength of the x-ray source and θ is the diffraction angle.

According to Debye-Scherrer equation, the average diameters for silver nanoparticles prepared via AgH30, AgH50, AgNa30 and AgNa50 are 14.8, 17.7, 10.1 and 14.3 nm, respectively.

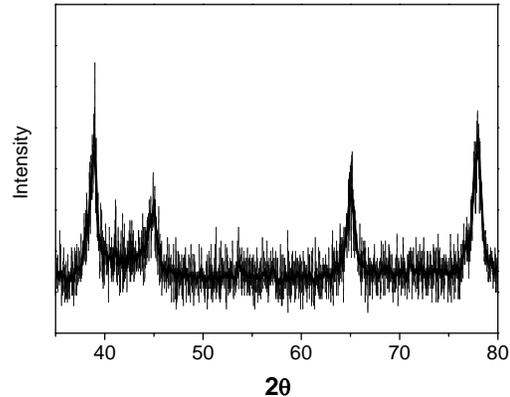


Figure 2: Wide angle X-ray diffraction pattern for silver nanoparticles of AgNa30.

TEM. To obtain further information on the particle size of the nanoparticles, TEM was employed. Figure 3 shows the TEM micrograph of silver nanoparticles of AgNa30. A spherical shape and excellent distribution in the colloid can be observed. The size of silver nanoparticles obtained from TEM image agrees well with the result from XRD.

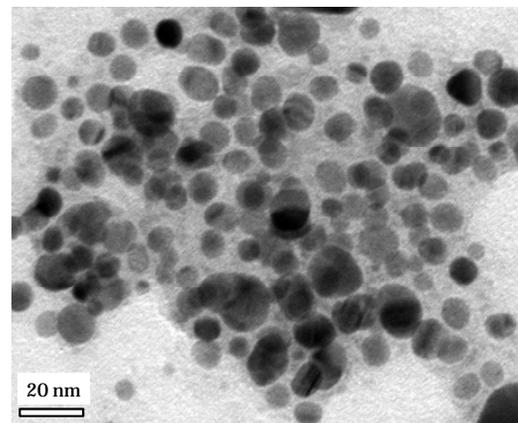


Figure 3: TEM image of silver nanoparticles, prepared from AgNa30.

4 SUMMARY

Silver nanoparticles were prepared by the ion solvent exchange method via the clusters of the ionomers acting as a media. The average diameter for silver nanoparticles prepared from AgH30, AgH50, AgNa30 and AgNa50 is 14.8, 17.7, 10.1 and 14.3 nm, respectively. At the same degrees of sulfonation, the size of silver nanoparticles prepared from partial neutralized ionomers is smaller than that of without neutralization.

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