Preparing silver nanoparticles in supercritical water

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ARTICLE INFO

Article history:

Received 5 September 2008

Accepted 5 November 2008

Available online 12 November 2008

Keywords:

Silver nanoparticles

Nanomaterials

Catalysts

Silver microparticles

Supercritical water

Reaction time

ABSTRACT

Silver (Ag) nanoparticles were prepared using Ag microparticles as precursors in supercritical water (SCW). The effect of reaction time on preparing Ag nanoparticles was investigated. The obtained products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. The results indicated that, with the increase of reaction time, Ag microparticles prepared by calcination method with the sizes $>2\ \mu\text{m}$ remained after SCW treatment because of their high crystallinity, but those with the sizes $<1\ \mu\text{m}$ were destroyed and formed many Ag nanoparticles due to the destructive effect of SCW.

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1. Introduction

Silver (Ag) nanoparticles have been applied in many areas because of their good surface plasma resonance (SPR), surface-enhanced Raman scattering (SERS) effects, antibacterial capability, catalytic property and high reactivity [1–3]. Up to now, many methods have been developed to prepare Ag nanoparticles. Among them, polymer-protected reduction method and microemulsion method are widely used [4–7]. Polymer-protected reduction method has been used for preparing Ag nanoparticles in the presence of polymer-protectors by reducing silver nitrate (AgNO_3). However, the size and dispersion of prepared Ag nanoparticles are greatly affected by the species and concentrations of polymer-protectors, the molar ratio of polymer-protectors to AgNO_3 . Ag nanoparticles with the sizes smaller than 30 nm have been successfully obtained by microemulsion method, but the process of synthesizing microemulsions is extremely complex and there are many influencing factors during the preparation of Ag nanoparticles.

Supercritical water (SCW) has been used in many fields of chemistry due to its unique properties such as high diffusivity, low viscosity and lack of toxicity. SCW provides an excellent reaction medium for hydrothermal synthesis of metal and metal oxide nanoparticles. Ziegler et al. reported copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2$) hydrolyzed to form polydisperse copper (I) oxide (Cu_2O) particles with diameters from 10 to 35 nm without alkanethiol ligands in SCW. However, in the presence of 1-hexanethiol, copper nanocrystals

(Cu, $\sim 7\ \text{nm}$ in diameter) were obtained. In addition, they studied the effects of different precursors on the morphologies of prepared particles [8]. Viswanathan et al. obtained zinc oxide nanoparticles (ZnO , 39–320 nm) by oxidation of zinc acetate in SCW. The effects of flow rate and feed concentration were also studied in their work [9]. To our knowledge, however, very limited literatures have reported Ag nanoparticles obtained in SCW [10]. And there are no reported studies of using Ag microparticles as precursors to prepare Ag nanoparticles in SCW thus far. In this paper, Ag microparticles were prepared by calcination method. Ag nanoparticles were subsequently obtained in SCW using these Ag microparticles as precursors. The effect of reaction time on preparing Ag nanoparticles in SCW was extensively investigated.

2. Experimental

2.1. Preparation of Ag samples

The experimental process was as follows: Firstly, 1.0 g of silver chloride (AgCl) and 2.0 g of sodium carbonate (Na_2CO_3 , keeping in excess) were mixed homogeneously in ceramic crucible. Then the crucible was placed in a muffle and heated at $550\ ^\circ\text{C}$ for 3 h. After that, the muffle was cooled down to room temperature and the product was filtrated and washed with deionized water to remove the by-products. The product was dried at $80\ ^\circ\text{C}$ under vacuum for 2–3 h. S-1 was obtained by this procedure.

Secondly, 2 ml 0.1 mol/L sodium hydroxide (NaOH) solution was added to 75 ml deionized water (the pH value of the obtained solution was 8.5), then 5 ml of hydrogen peroxide (H_2O_2) was dissolved into the solution. The mixture was stirred for a short time and transferred into a stainless steel autoclave with a capacity of 100 ml. After 0.25 g of

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Fig. 1. XRD patterns of Ag samples (a) S-1; (b) S-2; (c) S-3.

S-1 was added into the mixture, the autoclave was sealed and heated at 450 °C for 15 min, while the reaction pressure was kept at 33.5 MPa. The autoclave was cooled down to room temperature, and the product was filtrated and washed with deionized water. The product was then dried at 80 °C under vacuum for 2–3 h, and the obtained product was nominated as S-2.

In order to investigate the effect of reaction time on preparing Ag nanoparticles in SCW, the other parallel experiment was conducted following the same process as that of sample S-2, except that the reaction time was 30 min. The sample thus prepared was denoted as S-3.

2.2. Characterization

The phase of the samples was identified by XRD patterns, which were taken on a Philip X'pert X-ray diffractometer (Cu K_{α} , $V=40$ kV, $I=40$ mA). Prior to the measurement, the samples were ground thoroughly in an agate mortar. The morphologies of the samples were taken on a Hitachi H-7500 TEM, with an accelerating voltage of 80 kV. Prior to TEM measurement, the samples were ultrasonically treated in methanol for 30 min.

3. Results and discussion

XRD patterns of S-1, S-2 and S-3 are shown in Fig. 1. As demonstrated in Fig. 1, only diffraction peaks of cubic Ag can be observed, indicating that cubic Ag is the only crystalline phase in the samples.

Generally, TEM can be used to observe the morphologies of the samples. Fig. 2 illustrates the TEM images of S-1 prepared by calcination method. These particles in Fig. 2(a) and (b) are quasi-circular and the sizes of them are bigger than 2 μm . Furthermore, most of these microparticles aggregate together. In Fig. 2(c) and (d), there are many circular particles and the sizes of them are smaller than 1 μm . Similar to the large quasi-circular particles, these circular particles also aggregate together. XRD result indicates that these particles are all Ag microparticles.

Fig. 3 shows the TEM images of S-2 prepared in SCW for 15 min. As can be seen, there are also many large quasi-circular particles with the sizes bigger than 2 μm .

Fig. 2. TEM images of S-1 prepared by calcination method.

Fig. 3. TEM images of S-2 prepared in SCW for 15 min.

Compared with Fig. 2, some small particles with irregular shapes are obtained. And the sizes of them are smaller than 1 μm . In addition, circular particles (shown in Fig. 2(c) and (d)) disappear in Fig. 3.

Fig. 4 illustrates the TEM images of S-3 prepared in SCW for 30 min. Similar to Fig. 3, there are many large quasi-circular particles in Fig. 4(a) and (b), and the sizes of them are bigger than 2 μm . These Ag microparticles also aggregate together. Circular particles

Fig. 4. TEM images of S-3 prepared in SCW for 30 min.

with the sizes smaller than 1 μm also disappear in Fig. 4. Furthermore, compared with Fig. 3, a lot of small particles with irregular shapes can be found. As can be seen from Fig. 4(c) and (d), these small particles are composed of many Ag nanoparticles (with the sizes smaller than 100 nm). However, these Ag nanoparticles aggregate together. Then Ag nanoparticles are obtained after SCW treatment.

The forming process of Ag nanoparticles can be explained as follows:

In the work, Ag microparticles (shown in Fig. 2) were previously prepared by calcination method. When Ag microparticles were treated in SCW, the large Ag microparticles with the sizes bigger than 2 μm remained because of the high crystallinity. On the contrary, the small Ag microparticles with the sizes smaller than 1 μm were destroyed due to the destructive effect of SCW. In this study, SCW provided a highly destructive environment. Moreover, with the increase of reaction time, the small Ag microparticles were destroyed further and Ag nanoparticles were obtained.

4. Conclusions

A novel approach for preparing Ag nanoparticles using Ag microparticles as precursors in SCW was found. It was believed that, the highly destructive ability of SCW could cause Ag microparticles to

break down into Ag nanoparticles with regular shape and small size by optimizing the parameters such as the reaction time, temperature and pressure. In addition, the conditions of preparing Ag precursors also need to be optimized in the future.

Acknowledgment

This research was financially supported, in part, by the National Key Technology R&D Program (2008BAC32B03) of China.

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