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Facile route for preparation of silica–silver heterogeneous nanocomposite particles using alcohol reduction method

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Abstract

Silica–silver heterogeneous nanocomposite particles were successfully prepared by facile route including alcohol reduction method. Thiol groups were employed as a chemical protocol to make a binding between silver nanoparticle and silica surface. After the reaction for 10 min, a large number of quasi-spherical silver nanoparticles with an average size of 6.9 nm in diameter were homogeneously formed on the surface of silica particles. The immobilized silver nanoparticles grew to large ones with an average size of 10.6 nm in diameter after additional reaction for 2 h. The resulting nanocomposite particles were characterized by transmission electron microscopy (TEM), energy-dispersive X-ray (EDX), UV–vis spectrophotometer, and X-ray diffraction (XRD) analysis.

Keywords: Nanocomposite; Alcohol reduction; Silica; Silver nanoparticles

1. Introduction

In recent years, many preparation routes [1–7], by which metal nanoparticles are immobilized onto various inorganic supports, have been developed by many scientists to expand the application area and to control the morphology and the behavior of nanomaterials. Among them, composite materials containing silver have great potential applications in biochemistry for chemical sensors [8] and antibacterial materials [9]. Especially, silver-supported silica materials [10,11] are expected to be excellent candidates for antibacterial materials due to their good chemical durability and high antibacterial activity. Moreover, these hybrid materials can prevent metal nanoparticles from agglomerating without the use of a stabilizer and be easily retrieved owing to the relatively large size of the supporting materials. As a result, they make it easy to handle metal nanoparticles.

Alcohol reduction method [12] has been known as a chemical reducing agent free preparation method for colloidal dispersion of metal nanoparticles. In this method, metal ions are mainly reduced by alcohol via redox reaction between the metallic precursor and alcohol; the reduction of metal ions is greatly governed by ΔE, the difference between the oxidation potential of alcohol and the reduction potential of metal species at a given temperature [13]. Generally, monoalcohol aqueous solutions such as ethanol/water mixture are frequently used as a reducing agent and a solvent for the reduction reaction in alcohol reduction method. In a typical procedure, the metal precursors are suspended or dissolved in an ethanol/water mixed solvent. The resultant metal precursor suspensions or solutions are heated with reflux at a given temperature for a few hours in the presence of water-soluble polymeric stabilizer like poly(*N*-vinyl-2-pyrrolidone), and then colloidal metallic particles are formed. This method seems to be proper for attaching metal nanoparticles to the surface of the support materials due to its slower reduction rate compared to the direct reduction method by a chemical reducing agent in solution. It is well known that the fast reduction rate makes it difficult to control the system.

Recently, in order to easily prepare the nanocomposite materials, we have suggested novel preparation routes including the polyol process or alcohol reduction method for the first time [14–16]. In the present study, as a continuation of our previous researches, silica–silver heterogeneous nanocomposite particles were prepared by alcohol reduction method. Silver nanoparticles

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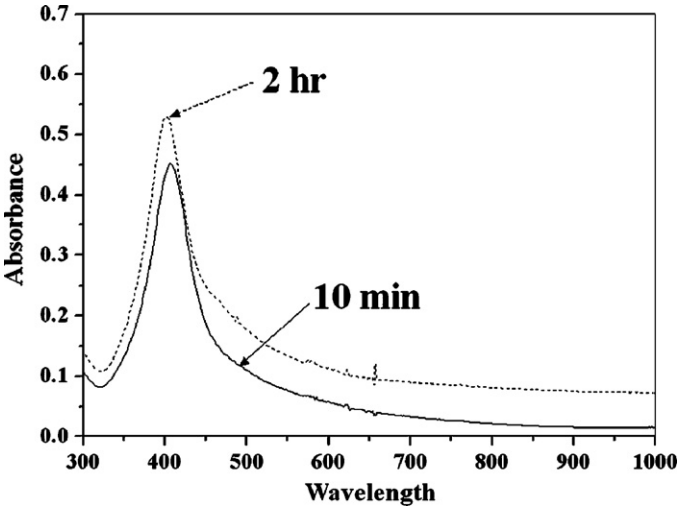

Fig. 1. UV–vis absorption spectra of the silica–silver nanocomposite particles prepared by the alcohol reduction method.

with narrow size distribution were homogeneously and quickly immobilized onto the silica surface with thiol groups. The resulting composite particles were characterized by transmission electron microscopy (TEM), energy-dispersive X-ray (EDX), UV–vis spectrophotometer, and X-ray diffraction (XRD) analysis. Also the mechanism for the preparation steps was briefly discussed on the basis of experimental results.

2. Experimental procedure

2.1. Materials

Tetraethyl orthosilicate (TEOS 98%, Aldrich), absolute ethanol (HPLC grade 99.9%, DUKSAN Pure Chemical Company, Korea) and ammonia solution (NH_4OH 25%, Wako Pure Chemical Industries, Japan) were used to prepare silica particles. The 3-mercaptopropyltrimethoxysilane (MPTMS) was purchased from Sigma-Aldrich chemical company (97%) and used as a chemical protocol to make a binding between silica and silver particles. Silver nitrate ($AgNO_3$ 99.995%, Aldrich) was used as a silver ion source. Also, ethanol and poly(vinylpyrrolidone) (PVP, K-15, Mw 10,000, Junsei Chemical Company, Japan) were used to reduce silver ions by alcohol reduction method. All materials were used as received. The water used in this study was deionized by the Milli-Q Plus system (Millipore, France), having an 18.2 MΩ electrical resistivity.

2.2. Preparation of silica particles functionalized with thiol groups

Spherical silica particles were prepared by the sol–gel process on the basis of the Stöber method [17]. For the MPTMS-functionalization of the surface of silica particles, a procedure similar to that described by Philipse and Vrij was employed [18]. A 10.6 g of 25% ammonia solution was mixed with 125 g of absolute ethanol under mild stirring. After 20 min, the sol–gel reaction for the formation of silica particles was initiated by adding 5 g of TEOS into the solution. After 1 h, 1 g of MPTMS was added into the solution. The resulting solution was kept for 6 h under mild stirring. After the reaction, the reactant was centrifuged at 3000 rpm for 30 min to separate the silica particles functionalized with thiol groups. The separated particles were washed with ethanol to remove un-reacted reagents. Then, the washed particles were collected and dried at 40 °C for 1 day in an incubator.

2.3. Preparation of silica–silver heterogeneous nanocomposite

To immobilize the silver nanoparticles onto the silica surface modified with thiol groups, alcohol reduction method was employed. The typical process is as follows: 0.1 g of silica particles functionalized with thiol groups was dispersed in ethanol using sonication and agitation. And then, 4 g of PVP was dissolved in the mixture under mild stirring to prevent distortion of the polymer chain. After the complete dissolution of PVP, 0.1575 g of $AgNO_3$ was added into the solution and the solution

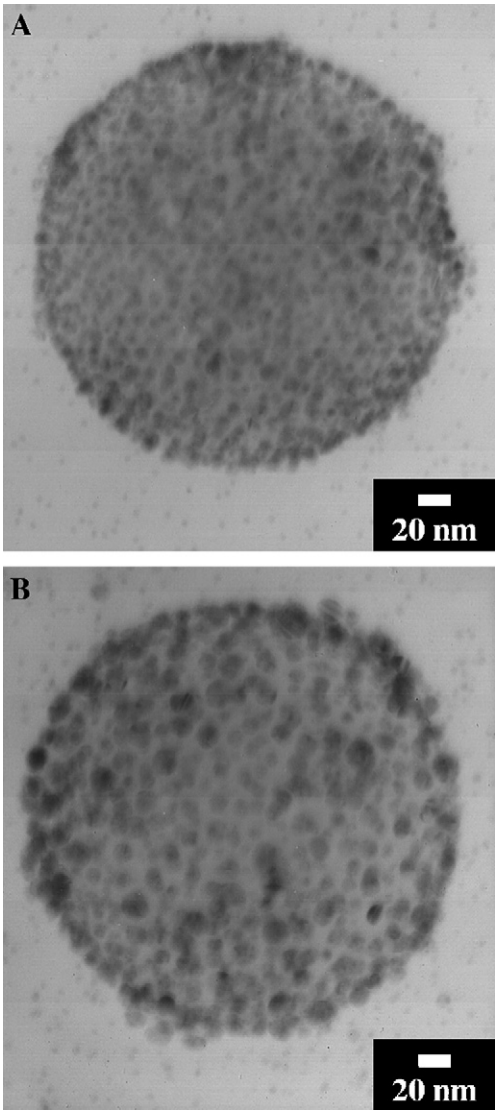

Fig. 2. TEM images of the silica–silver nanocomposite particles prepared by the alcohol reduction method at different reaction times: (A) 10 min and (B) 2 h.