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FABRICATION AND CHARACTERIZATION OF SILVER-TIN DIOXIDE CORE-SHELL STRUCTURED NANOCOMPOSITE PARTICLES

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Abstract. Core-shell structure nanoparticles with silver core and tin dioxide shell were synthesized via a facile soft-chemical process. Optical absorption spectra of tin dioxide deposited silver core nanoparticles, obtained by UV-Visible spectroscopy, showed distinct shifts, both in peak position and its intensity, compared with bare silver nanoparticles, which indicated that silver-tin dioxide core-shell nanoparticles appeared to be formed. The core-shell structure formation was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD pattern showed distinct major peaks corresponding to cubic silver and minor peaks due to tetragonal tin dioxide phases. TEM results, from which we could estimate the nanoparticles size as well as their shell thickness, demonstrated that thin tin dioxide shells encapsulated the silver core particles.

1. Introduction

Core-shell nanoparticles have recently been the focus of a lot of scientific efforts because of the combination of different properties in one particle based on different compositions of the core and the shell. Furthermore, many interesting technological applications can be foreseen for this kind of material, in addition to others in analytical chemistry (chromatography), separation technology (ion exchange), catalysis, biochemistry and medicine, etc. [1, 2]. These types of particles can be defined by their different core and shell compositions. The core often (though not always) shows the relevant property (e.g. semiconductors, metals, magnetic oxides, encapsulated molecules), while the shell can stabilize the core; create compatibility between the core and the environment; or can change the charge, functionality, or reactivity of the surface as well as modification of particular properties of the core [3-7]. This is especially important if the shell is a polymer and the final core-shell particle can be homogeneously

dispersed in a polymer on the nanoscale [8]. In recent years, especially for medical purposes, the shell has become more and more important (e.g., for drug delivery applications) [9].

Core-shell architectures are the result of either a two-step approach, consisting of preparation of nanoparticles and then modification of their surface, or an *in-situ* approach during particle formation. The shell can be formed by surface chemical reactions, by simple adsorption of molecules or small nanoparticles or the whole core-shell nanoparticle can be formed by subsequent self-assembly and crosslinking of macro molecules.

In the present study, we have investigated the synthesis of Ag-SnO_2 nanocomposite particles with core-shell morphology. The surface plasmon absorption band and the morphology of the synthesized Ag-SnO_2 core-shell nanoparticles were examined and the attained results were discussed.

2. Experimental section

The Ag-SnO_2 core-shell nanoparticles were synthesized by using a simple hydrothermal method according to the procedure reported elsewhere [10]. Details of a typical experiment are as follows. 97 mL of deionized water was placed in a 250 mL glass beaker in an ice bath. One millilitre of 1 mM silver nitrate followed by 1 mL of 100 mM sodium borohydride and 1 mL of 34 mM tri-sodium citrate were added to the above beaker under vigorous stirring. A transparent bright yellow color was observed immediately due to the formation of the silver colloid. This colloid was aged for few hours at room temperature. The pH of a 20 mL aliquot of prepared 1 mM silver colloid was increased to 10.5 by the addition of 0.1 mM sodium hydroxide solution. This colloid was transferred to a 50 mL conical flask and placed in a water bath at 60 °C. This solution was stirred vigorously for 5 min followed by the rapid addition of fresh sodium stannate trihydrate solution (1 mL, 9 mM). Afterwards, the solution was heated to 60 °C for 10 minutes in a water bath and then maintained at 60 °C with rapid stirring for 1 h. This process was repeated to obtain large amount of colloid. Then this colloid was concentrated by centrifugation at 10000 rpm and washed with deionized water to remove the unreacted species and impurities. Then nanoparticles were redispersed in appropriate amount of deionized water by ultrasonication.

The ultraviolet-visible absorption spectra were taken by a UV–visible double beam spectrometer (UVD-2950, LaboMed.). For the UV–Visible spectra, the Ag and Ag-SnO_2 colloids were used. The transmission electron microscopy (TEM) images were taken on a Leo 912 AB instrument at an accelerating voltage of 120 kV by placing a drop of Ag-SnO_2 colloid on a carbon coated copper grid. The crystallographic structure of the solid sample was determined using a Philips PW1800 X-ray diffractometer equipped with graphite monochromatized Cu-Kα (λ = 1.5405 Å) radiation. Solid sample for XRD analysis was prepared by dip coating of Ag-SnO_2 colloid on a glass substrate which was then heat treated at 200 °C.

3. Results and discussion

Figure 1 shows the UV–visible absorption spectra of the Ag colloid and Ag-SnO_2 nanoparticle solution during the deposition process of tin dioxide. The surface plasmon (SP) band of the Ag nanoparticles was red-shifted from 400 to 410 nm after a 1 hour reaction time. The solution changed from a bright yellow to an intense straw yellow color. A growth in the absorption intensity is also evident, which, along with the displacement of the peak position, is attributed to the increase in the refractive index of the surrounding medium due to the deposition of SnO_2 shell over Ag nanoparticles.

The structural and morphological properties of the prepared core-shell particles were examined. The morphology of the synthesized Ag-SnO_2 core-shell structure nanoparticles was examined by TEM (Fig. 2). Figure 2 shows TEM images of the Ag-SnO_2 nanoparticles

synthesized at 60 °C with a reaction time of 60 min. The core Ag particles are about 18-20 nm in diameter, and resultant core-shell structure of the Ag-SnO_2 nanoparticles is clearly observed in this image. The thickness of SnO_2 shell is about 5 nm. However, the particle size of SnO_2 in the shell layer was about 1–2 nm (which can be estimated from XRD data according to Scherrer formula for crystallite grain size).

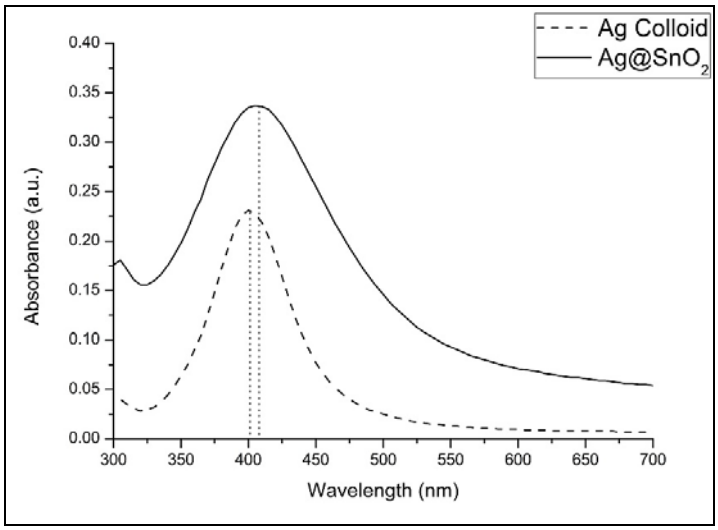

Fig. 1. UV-Vis absorption spectra of the Ag colloid and Ag-SnO_2 core-shell nanoparticles colloids. A 10 nm red-shift in the peak position and an increase in the absorbance of nanoparticles are observed due to shell formation.

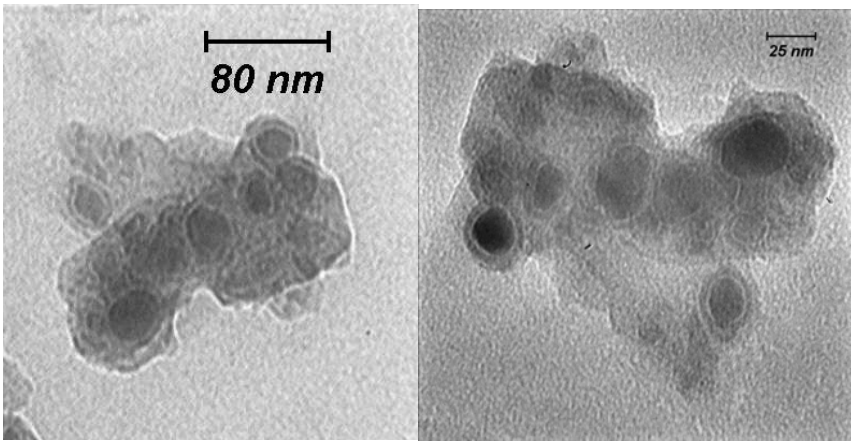

Fig. 2. TEM images of the Ag-SnO_2 core-shell structure nanoparticles.

Figure 3 shows the electron diffraction pattern of Ag-SnO_2 core-shell structure nanoparticles synthesized by a simple hydrothermal method. As seen from Fig. 3, the sample has shown three distinct peaks at 33.94, 36.60, and 51.74 corresponding to (101), (200), and (211) Bragg reflections of the tetragonal rutile structure of tin dioxide. Moreover, three intense reflections at 38.28, 44.49, and 64.60 can be attributed to (111), (200) and (220) planes of face-centered cubic structure of silver metal. The crystal structure of the SnO_2 coated on the Ag nanoparticles is consistent with cassiterite (JCPDS card no.: 41- 1445). There was a slight sharpening of the bands for the sample heat treated at 200 °C. Small intensity of the tin dioxide nanoparticles is may be due to the very small size of the nanocrystallites. Any peak corresponding to Ag-Sn compound was not observed, which

corroborated that the materials retain their physical structures and hence are expected to form a nanocomposite rather than alloy.

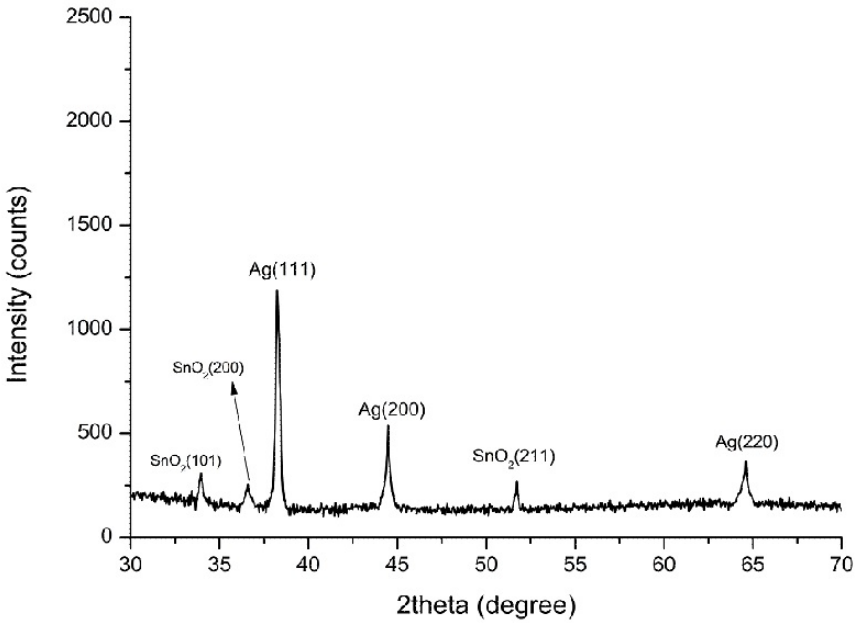

Fig. 3. XRD pattern of Ag-SnO2 core-shell nanoparticles.

4. Conclusions

To sum up briefly, Ag-SnO_2 core-shell structure nanoparticles were successfully synthesized by a facile hydrothermal process. The thickness of the SnO_2 shell was about 5 nm, and the primary crystallite size of the SnO_2 was estimated from XRD data to be 1-2 nm. The peak position of the SP absorption band of the Ag nanoparticles was red-shifted from 400 to 410 nm, due to the formation of the SnO_2 shell. The increasing intensity of the SP band of Ag-SnO_2 core-shell nanoparticles during the reaction was attributed to an increase in the crystallinity of the SnO_2 shell, as well as an increase in the refractive index of the medium around Ag cores.

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