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Synthesis of Silver Selenide Bicomponent Nanoparticles by a Novel Technique: Laser–Solid–Liquid Ablation

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A novel laser–solid–liquid ablation technique has been developed to synthesize Ag_2Se nanoparticles from silver nitrate and selenium powder in a mixed solvent of 2-propanol and ethylenediamine. The products were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The XRD indicated that the products were the single phase of silver selenide. The TEM images revealed that the as-prepared Ag_2Se grains were homogeneous and spherical, and their average size was about 30 nm. This novel technique can be extended to prepare other nanoparticles of various compositions. © 2001 Academic Press

Key Words: **silver selenide; laser–solid–liquid ablation; nanoparticles.**

INTRODUCTION

Due to their novel characteristics determining their bulk properties and allowing a variety of applications, nanoscale particles are receiving much attention in both basic science and advanced technological research. Among the variety of syntheses for producing metallic or nonmetallic nanoparticles, the capability of a laser as a tool has already been demonstrated (1, 2). Use of lasers as the energy source has been found to be more efficient than conventional heat-energy sources (3, 4). In addition, the output of a laser can be manipulated by varying both the laser pulse width and the spot area, providing an additional flexibility to the synthetic process.

Most of these applications, however, were performed under a low-pressure inert gas atmosphere. In these processes, a laser beam is directed onto a solid surface or is adsorbed by gaseous species (5–8). Besides the processes in the gaseous environment, a liquid medium can also be applied to the synthesis of the nanoparticles and has its unique advantage. The particles produced in liquid are generally expected to be uniform in size and shape, and the synthesis rate is relatively high. In addition, no vacuum system is required for the process. Until now, however, a few laser-assisted syntheses of nanoscale materials have been tried using liquid media. Fojtik and Henglein first used the 694 nm light of a ruby laser to perform laser ablation of mental films immersed in various solvents to from colloidal solutions (9). Later, Yeh *et al.* employed a laser ablation technique to generate Cu nanoparticles from CuO power in 2-propanol (10). Subramanian and co-workers employed the laser–liquid interaction to synthesize silver nanoparticles from silver nitrate solution in distilled water (4). Yang *et al.* prepared nanocrystalline diamonds by etching graphite with a high-power pulsed laser in water (11). Recently, we developed a novel technique for synthesis of silver selenide nanocrystalline particles by laser ablating selenium powders suspended in the solution of silver nitrate. This work is the first example of synthesizing binary component nanoparticles via laser-induced reaction.

The synthesis and characterization of metal selenides have attracted considerable attention because of their brilliant application prospects. They are widely used as sensor and laser materials, optical recording materials, and thermoelectric cooling materials (12). Silver selenides is a well-known superionic conductor. It has been widely used in solar cells and as an optical filter (13). Many techniques have been applied to prepare silver selenide, including a mechanical alloying method using a high-energy ball mill (14), electrolysis (15), sonochemical synthesis (16), and a hydrothermal route at elevated temperature and pressure (17). Ag_2Se nanoparticles have been synthesized through the reaction of $AgNO_3$, Se, and KBH_4 in pyridine (18). The synthesis reported herein shows that the nanoparticles can also been prepared by the technique of laser ablation.

EXPERIMENTAL

In a typical experiment, 1×10^{-4} mol of Se powder and 2×10^{-4} mol of $AgNO_3$ were added into a 20-ml mixed

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solvent of 2-propanol and ethylenediamine, and the container was bubbled with argon to keep the system out of air. $AgNO_3$ was dissolved into the solution, and some of the Se powder was also dissolved in the mixed solvent, the other Se powder was suspended in the solution with stirring. The fundamental output of a Q-switched Nd:YAG laser (Quantary DCR 130), 1064 nm in wavelength and 7 ns in pulse width, was gently focused on the powders and the solution by a long focal-length lens. Ablation of the pulsed laser beam lasted 30 min at 10 Hz and its power density on the surface of the solution was near 10^9 W/cm^2.

All reagents used in the reaction were of analytical grade. After the reaction, black precipitate was separated from the solution by a centrifuge, and washed with ethanol. The final product was dried in vacuum at 60–70°C for 4 hours.

The X-ray powder diffraction (XRD) pattern of the product was recorded on a Rigaku D/Max-C X-ray diffractometer using Cu$K\alpha$ radiation. A transmission electron microscopy (TEM) image of the product was recorded with a JEM-100CX II microscope using an accelerating voltage of 100 kV. Its X-ray photoelectron spectrum (XPS) was obtained on a VG X-ray photoelectron spectrometer, with nonmonochromatized Mg$K\alpha$ X-ray used as the excitation source.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of a typical sample synthesized by the laser ablation reaction in the mixed solution of 2-propanol and ethylenediamine (1:1 in volume). All peaks can be indexed as the orthorhombic Ag_2Se phase (JCPDS cards no. 24-1041). The peak due to possible impurities such as Ag, Ag_2O, and Se is not observed. Based on the half-width of the peaks, the average particle size is determined by the Scherrer equation in the range of 25 nm. Production of silver selenide is confirmed by the XPS characterization. The strong peak at 53.4 eV corresponds to Se 3*d* binding energy for Ag_2Se (Fig. 2a). The peak at 367.8 eV corresponds to Ag $3d_{5/2}$ binding energy for Ag_2Se (Fig. 2b). Further evidence was obtained by the Auger electron spectra of the products (Fig. 2c). The kinetic energy of Ag $M_4N_{45}N_{45}$ is 357.4 eV, which is consistent with that of bulk

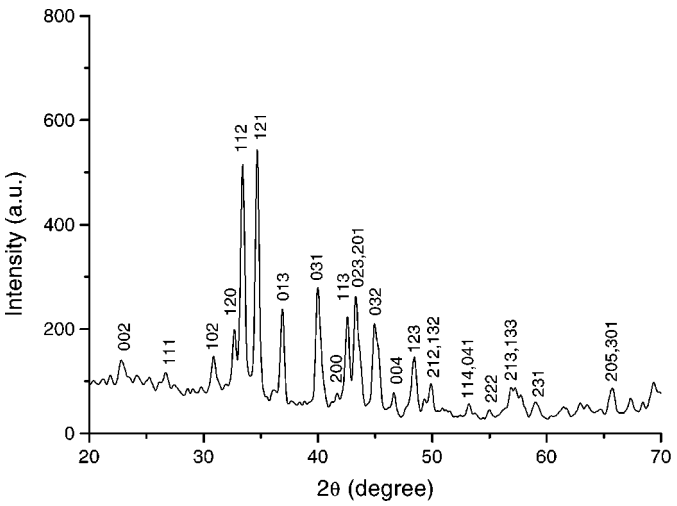

FIG. 1. XRD pattern of as-prepared Ag_2Se nanoparticles.

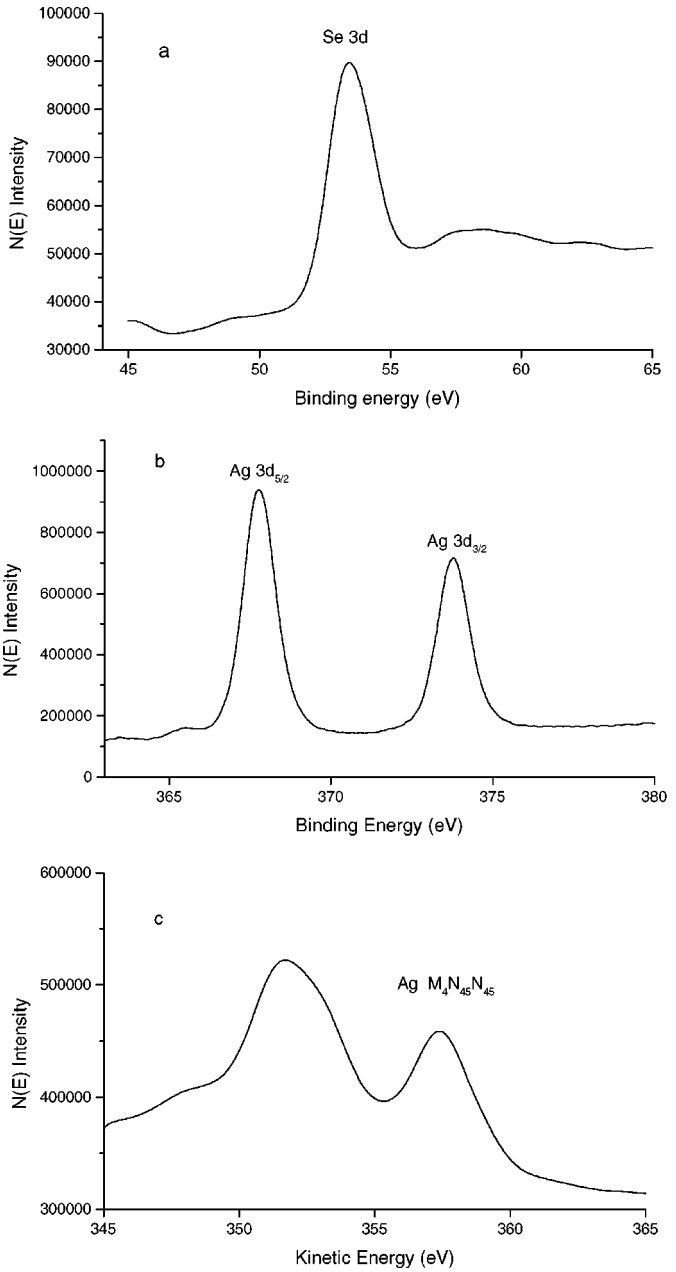

FIG. 2. XPS pattern of as-prepared products. (a) Se 3*d* electron spectra of as-prepared Ag_2Se products; (b) Ag 3*d* electron spectra of as-prepared Ag_2Se products; and (c) Ag Auger electron spectra of as-prepared Ag_2Se products.

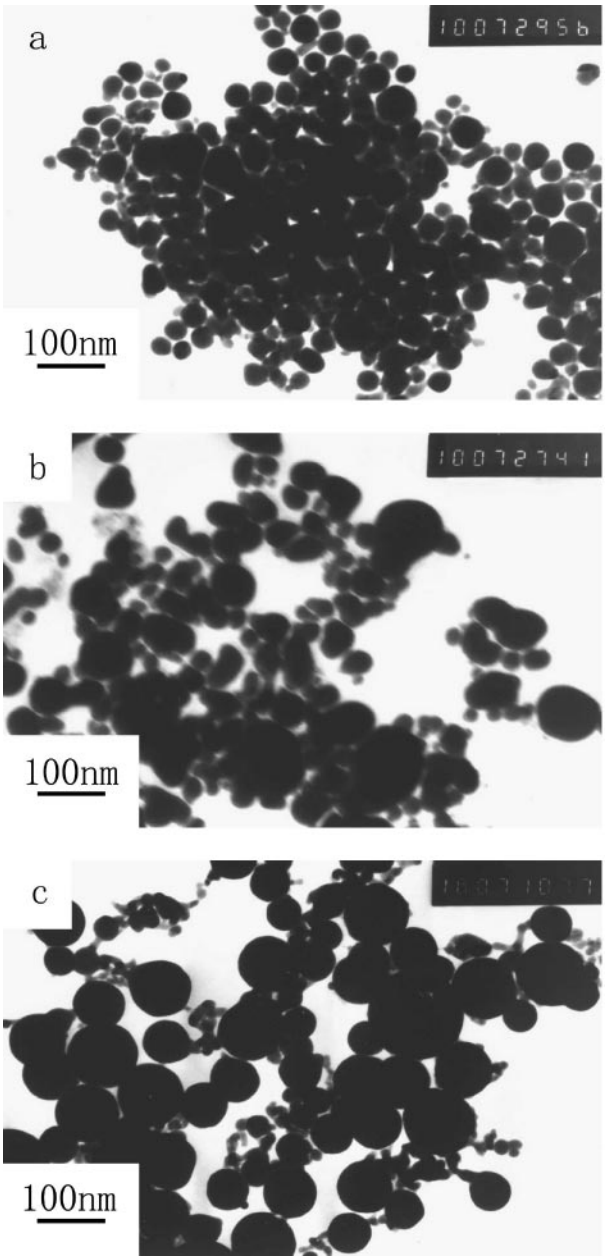

FIG. 3. TEM images of the Ag_2Se products prepared under different conditions: (a) in a mixed solvent of 2-propanol and ethylenediamine after 30 min of laser ablation; (b) in 2-propanol solvent and after 30 min of laser ablation; and (c) in a mixed solvent of 2-propanol and ethylenediamine after 90 min of laser ablation.

Ag_2Se (19). Qualification of the peak areas verifies the composition of the product as Ag_2Se.

The TEM micrograph (Fig. 3a) reveals the morphology and grain sizes of the particles. As shown in the image, the as-prepared Ag_2Se nanoparticles are uniform spherical crystallites with sizes ranging from 10 to 50 nm, which is in good agreement with the XRD measurement.

The solvents, the mixture of 2-propanol and ethylenediamine, water, ethanol, 2-propanol, and their combinations have been used in the synthesis. Unlike other methods (18), synthesis of the Ag_2Se particles seems not to be very sensitive to the solvents in the technique of laser–solid–liquid ablation. Changing the solvents only affects the shape and the size distribution of particles. For instance, the Ag_2Se particles produced in 2-propanal are ellipsoidal with size ranging from 10 to 110 nm, as shown in Fig. 3b. The optimum solvent for producing the nanoparticles is found to be the mixture of 2-propanol and ethylenediamine.

Blank experiment shows that no Ag_2Se product could be obtained without applying the ablated laser beam. The interaction time of the laser beam also affects the size distribution of nanoparticles. Longer interaction time creates more products, but induces further coalescence of the particles. The particles shown in Fig. 3c are the products after 90 min of laser ablation, in which a much broader size distribution (10–130 nm) is found from the TEM image.

Synthesis of the silver selenide is a reduction reaction and can be represented by the following equation:

$$2Ag^+ + Se + 2e \rightarrow Ag_2Se.$$

In the previous reduction synthesis of silver selenide nanoparticles, KBH_4 was selected as the reactant (18). In a similar experiment to generate Cu nanoparticles from CuO power in 2-propanol, a small amount of oxidized product, acetone, was confirmed by gas chromatography (10, 20), which suggest that 2-propanol may react as the reactant. In our case, the Se powders absorb the photon energy from the laser beam, producing temperatures of several kilokelvin and strong light emission. Such a condition is similar to a plasma discharge. In such a hot plasma region, 2-propanol is excited. The Se atom is reduced to Se^{2-} by accepting the electron transferred from 2-propanol, and the excited state of 2-propanol is oxidized to acetone, as it was in the formation of Cu nanoparticles from CuO (10, 20). Se^{2-} then reacts with Ag^+ in the solution homogeneously, forming Ag_2Se nanoparticles. Figure 4 illustrates this formation process of the Ag_2Se particles.

On the other hand, as has been reported (4, 21), Ag^+ can be reduced to Ag particles by laser ablation in the solution of $AgNO_3$ in water, ethylene glycol, diethylene glycol, and 2-ethoxyethanol. Therefore, in our cases, the $AgNO_3$ could be also reduced to Ag clusters. Furthermore, the Se powders can be partially dissolved in ethylenediamine and produce a complex (22). The newly formed Ag grains have a high surface area and are very active. They could react with the solved Se atoms, forming Ag_2Se nanoparticles (18). Under some special conditions, Ag clusters could be incompletely reacted and left as impurities in the products. In our experiment, by varying the ratio of 2-propanol and ethylenediamine, the composition of the products varies a little bit.

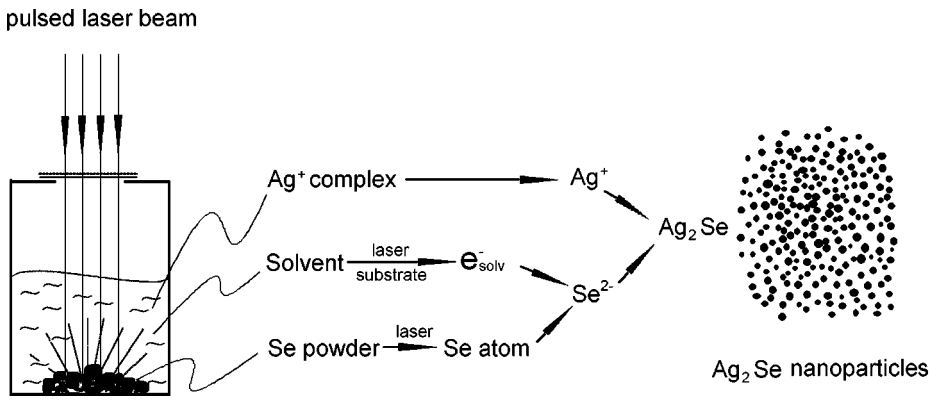

FIG. 4. Schematic illustration of the proposed machanism for the homogeneous formation of Ag_2Se nanoparticles by a novel laser–solid– liquid ablation technique.

Figure 5 shows the slight change of the products. The solvent with 30% to 50% (in volume) ethylenediamine gives pure Ag_2Se phase, as shown in Figs. 1 and 5a. However, when the compostion of ethylenediamine is over 70%, the XRD pattern shows a small peak at 38 deg, as marked by the arrow in Fig. 5b. It can be found that this peak appears at higher intensity with the increase of the composition of ethylenediamine. Figure 5c shows the case of 90% ethylenediamine, in which the peak at about 38 deg is higher. This small peak can be attributed to Ag particles. The 2-propanol was thought to stabilize metal clusters (10, 23). Ethylenediamine can coordinate to Ag^+ to form a stable complex, and the $AgNO_3$ can be dissolved easily in the mixed solvent. While the composition of 2-propanol decreases (i.e., the composition of ethylenediamine increases), which decreases the time of the reaction between the Ag clusters and Se atoms solved in the solution, the Ag clusters congregate to Ag particles. However, with the increase of 2-propanol (the composition of ethylenediamine decreases), the solubility of $AgNO_3$ decreases. The optimum ratio is 30% to 70% of ethylenediamine. Although this process could occur during the laser–solid–liquid ablation, the first process as shown in Fig. 4 is though to be the main process, because the Se powders are mainly kept as solids in the solution at the beginning.

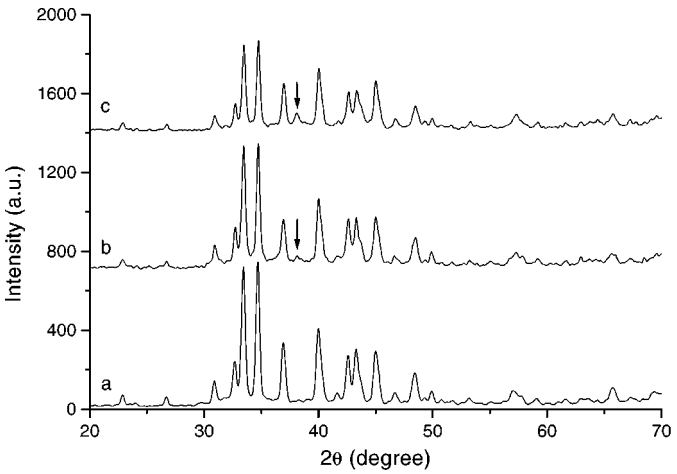

FIG. 5. XRD pattern of as-prepared products: (a) 1×10^{-4} mol of Se powder and 2×10^{-4} mol of $AgNO_3$, mixture of 10 ml of 2-propanol and 10 ml of ethylenediamine, 30 min of laser ablation; (b) 1×10^{-4} mol of Se powder and 2×10^{-4} mol of $AgNO_3$, mixture of 6 ml of 2-propanol and 14 ml of ethylenediamine, 30 min of laser ablation; and (c) 1×10^{-4} mol of Se powder and 2×10^{-4} mol of $AgNO_3$, mixture of 2 ml of 2-propanol and 18 ml of ethylenediamine, 30 min of laser ablation.

In the laser–solid–liquid ablation technique, a physical method, pulsed laser beam, is combined with solution reaction, the traditional chemical synthesis. Two solid reagents are involved in the reaction. Among them, one is suspended in the solution as the target of laser ablation, and the other is dissolved in the solution. The experiment takes place at room temperature and under the normal pressure. The result of synthesizing Ag_2Se shows that the technique is efficient in preparing the nanoparticles. The technique can certainly be applied to synthesize the nanoparticles of other binary components, which are difficult to obtain by other conventional methods.

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