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Room temperature growth of SnSe nanorods from aqueous solution

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Semiconductor nanostructures have attracted tremendous interest in the past few years because of their special physical properties and their potential for applications in micro- and opto-electronic devices [1]. Particularly, nanoscale one-dimensional structures have attracted considerable attention due to their unique electronic, optical, and mechanical properties [2, 3], such as nanowire light-emitting devices with extremely low power consumption [4]. In recent years, the synthesis of one-demensional semiconductor materials such as nanowires, nanorods, or fibers has been the focus of research work [5, 6]. Tin (II) selenide, as a IV–VI compound semiconductor, with a band gap of about 0.9 eV, can be widely used in infrared optoelectronic devices, holographic recording systems and memory switching devices [7–9]. Different methods have been used for the preparation of nanocrystalline SnSe, such as the chemical vapor transport technique [10], solid-state reaction [11], solid-state metathesis [12], Bridgman method [13], self-propagating high-temperature synthesis [14], and brush plating technique [15]. Generally, these methods have some limits; for example, the requirement of a special device, toxic reagents and high temperature. Recently, solution routes, such as hydrothermal [16], solvothermal [17], and organometallic precursor methods [18] have been developed for the synthesis of SnSe. Solution routes to inorganic materials avoid some of the above-mentioned undesirable characteristics. Solution techniques show a high degree of compositional control inherent in the synthesis of multielement inorganic materials [19].

Here, an aqueous solution route to synthesize SnSe nanorods, based on a chemical reaction between a selenium alkaline aqueous solution and tin (II) halide in the presence of the complexing agent at room temperature is reported. Compared with previous reports, the

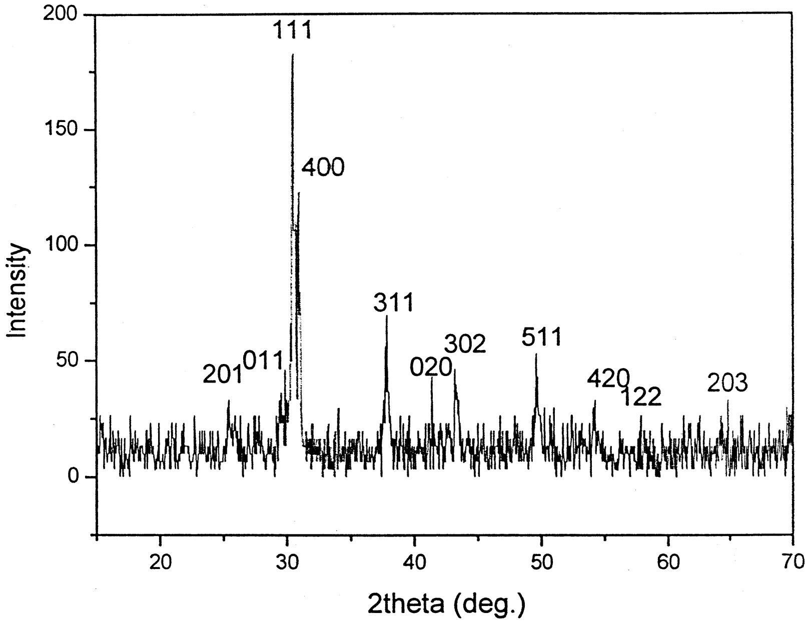

Figure 1 XRD pattern of the product SnSe.

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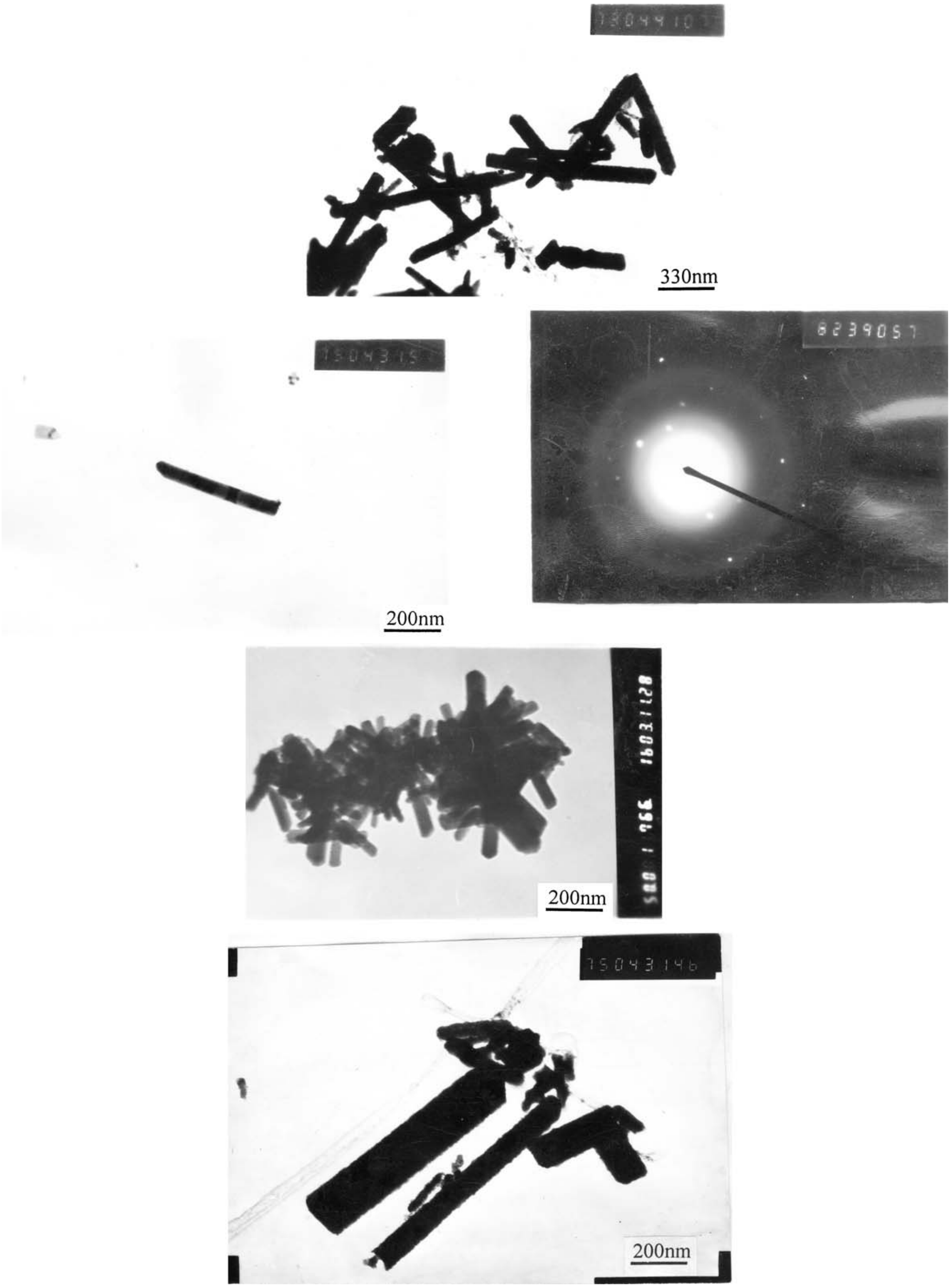

Figure 2 TEM photographs of the product SnSe prepared at the molar ratio of TSC/Sn 20:1 (a) and a selected area (b), 10:1 (c) and 25:1 (d).

present method is relatively simple and rapid, and provides a new strategy for the synthesis of metal chalcogenides with special morphology.

All reagents were of analytical grade and used without further purification. Manipulation and reactions were carried out in air. The selenium alkaline aqueous solution was prepared as follows: NaOH (24 g, 0.60 mol) and elemental Se (0.20 g, 0.0025 mol) were added to 30 ml of distilled water. The mixture was heated slightly for a few minutes till selenium dissolved completely, and a deep-red aqueous solution was obtained. $SnCl_2{\cdot}2H_2O$ (0.59 g, 0.0027 mol) was added to 30 ml of distilled water with trisodium citrate (TSC) (14.7 g, 0.05 mol), and then NaOH was added until a transparent solution was observed. The selenium alkaline aqueous solution was added to the mixture slowly through rapid stirring, and a black precipitate formed. The precipitate was separated by centrifugly and washed with distilled water, diluted HCl and absolute ethanol several times to remove any possible impurities. The final product was dried in vacuum at 60 °C for 5 h.

The X-ray diffraction (XRD) pattern of the product is shown in Fig. 1. The diffraction peaks in the pattern correspond to the (111), (400), (311) and (511) planes, which can be indexed to the orthorhombic structure of SnSe. The positions and intensities of the peaks are consistent with that of the JCPDS card file (no. 32-1382). The average diameter of the SnSe nanorods was about 90 nm, which was calculated from the half-width of the diffraction peaks using the Scherrer equation.

Nanorods with diameters of 80–100 nm and lengths up to 1000 nm were observed using a transmission electron microscope (TEM) (Fig. 2a). Fig. 2b shows a single SnSe nanorod and the selected area electron diffraction pattern furthermore indicates that the SnSe nanorods are crystallize.

The products were characterized by X-ray photoelectron spectroscopy (XPS) for evaluation of their composition and purity. Fig. 3 shows XPS spectra of Se (3d) and Sn (3d). The peak measured in the Se energy region detected at 53.4 eV is attributed to the Se (3d) transition. The two strong peaks taken for the Sn region detected at 485.5 and 494.0 eV are assigned to the Sn (3d) binding energy. The atomic ratio of Sn/Se calculated on the basis of the Sn (3d) and Se (3d) spectra is approximately 1.1. No obvious peaks for tin oxides or elemental selenium were observed indicating high purity of as-synthesized product.

The mechanism for the formation of SnSe may be summarized as follows:

$$3\mathrm{Se} + 6\mathrm{NaOH} \rightarrow 2\mathrm{Na_2Se} + \mathrm{Na_2SeO_3} + 3\mathrm{H_2O} \quad (1)$$

$$\mathrm{SnCl_2}\cdot 2\mathrm{H_2O} + 4\mathrm{OH}^- \rightarrow [\mathrm{Sn(OH)_4}]^{2-} + 2\mathrm{Cl}^- + 2\mathrm{H_2O} \quad (2)$$

$$[\mathrm{Sn(OH)_4}]^{2-} + 2\mathrm{TSC} \rightarrow \mathrm{Sn(TSC^*)}_2^{2-} + 4\mathrm{NaOH} \quad (3)$$

$$\mathrm{Na_2Se} + \mathrm{Sn(TSC^*)}_2^{2-} + 2\mathrm{Na}^+ \rightarrow \mathrm{SnSe} + 2\mathrm{TSC} \quad (4)$$

Here, TSC* means citrate which may have dissociated two sodium ions. Excessive OH^- is necessary to make elemental Se dissolve completely [20]. Elemental Se will precipitate when the concentration of OH^- is lower than 10 M. A higher concentration of NaOH will make the post-treatment of the final product difficult. The amount of $\mathrm{SnCl_2}\cdot 2\mathrm{H_2O}$ is slightly excessive relative to that of elemental Se, which ensures that elemental Se reacts completely. Otherwise, unreacted Se in the product will be difficult to remove.

The complexing agents play an important role in the formation of SnSe nanorods. Bulk SnSe with an irregular morphology formed without any complexing agents. When potassium nitrilotriacetate (NTA) was used as the complexing agent, the product was in an aggregated state. SnSe with various morphologies such as rod-like, sheet-like and particle-like were obtained

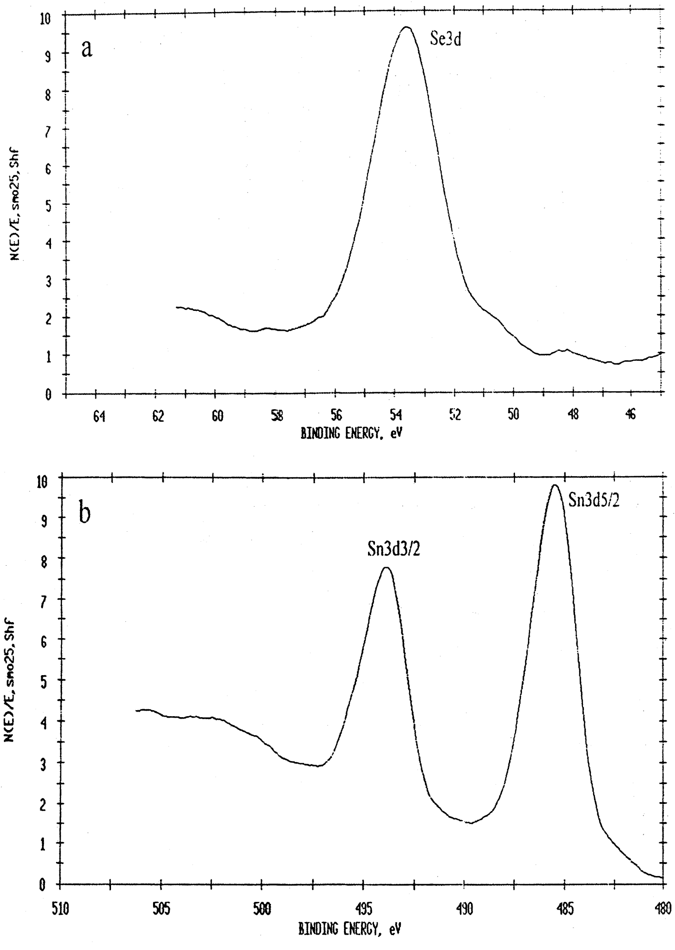

Figure 3 XPS analysis of the product SnSe: Se 3d (a) and Sn 3d (b).

using ethylene-diamine-tetra-acetic acid (EDTA) as the complexing agent. It has been reported that sheet-like SnSe formed in the presence of tartaric acid [20]. The results may be explained by the complexing strength of various ligands. A detailed study of the influence of different complexing agents on the morphologies of SnSe is still in progress. Furthermore, the amount of TSC also has an influence on the morphology and size of the product. If the concentration of TSC was changed to 0.9 M (TSC/Sn molar ratio is 10:1) and all the other preparation conditions remained unchanged, the diameter of SnSe nanorods decreased to about 50 nm and the nanorods were in an aggregated state (Fig. 2c). A higher concentration of TSC (TSC/Sn $=$ 25:1) resulted in slightly thicker SnSe nanorods with a diameter of 100–160 nm (Fig. 2d). The complexing agent can reduce the concentration of free Sn^{2+} in the solution and affect the reaction rate. When the ratio of TSC/Sn increases, the concentration of free Sn^{2+} ions in the solution decreases. As a result, the nucleation rate of SnSe becomes slower, which is favorable for the nuclei to grow into the rods with larger size.

In summary, SnSe crystalline nanorods can be easily synthesized in alkaline aqueous solution in the presence of the complexing agent (TSC). The influence of various ligands on the morphologies of SnSe and the possible reaction mechanism have been discussed.

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