Cubic Mercury Selenide Nanoparticles: Sonochemical Synthesis and Characterization

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A convenient sonochemical process for the preparation of HgSe nanoparticles by using Hg(CH₃COO)₂ and SeCl₄ in the presence of hydrazine as reductant agent has been discovered. Three capping agents have been used that including TEA (triethanolamine), SDS (sodium dodecyl sulfate) and TGA (thioglycolic acid). The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL) and X-ray energy dispersive spectroscopy (EDS). The effects of capping agent and reaction time on the morphology, particle size and phase of nano-sized HgSe products have been investigated.

Keywords: Nanoparticles, Sonochemical synthesis, HgSe, Hydrazine, Triethanolamine, Thioglycolic acid.

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1. INTRODUCTION

In recent years, there has been considerable interest in semiconductors of nanometer dimensions due to the quantum size effect that they exhibit. Semiconductor selenides have already found applications as sensors, laser materials, optical filters, solar cells, and many other devices [1]. HgSe is a semimetal, characterized by high electron mobility, large electron concentration and a variation of band gap with temperature [2]. It is one of the very interesting II–VI materials to be investigated for its applications in IR emitters, IR detectors and tunable lasers [3]. The electrical properties of HgSe leads to the wide applications in optoelectronic technology including photoconductive photovoltaic, IR detector, IR emitter, tunable lasers and thermoelectric coolers.

A wide range of techniques have been developed to synthesize mercury chalcogenides with control of the nanostructure and particle size. These developments include solvothermal or solvent-based approaches, sonochemical method [4], microwave-assisted heating [5], electrochemical method [6], emulsion, thermal decomposition [7] and thermolysis of mercury precursors [8]. The sonochemical method has been used extensively to produce nanosized materials with unusual properties, since the unique conditions facilitate the formation of smaller particles and different shapes of products compared to other methods. The chemical effects of ultrasound arise from the phenomenon called acoustic cavitation, i.e., the formation, growth and implosive collapse of bubbles in an ultrasonically irradiated liquid. The unique reaction conditions, temperatures of 5000 K, pressures of about 500 bar and rapid cooling rates in excess of 1010 K/s [9] enable the synthesis of metastable phases that are difficult to prepare in other ways.

In this work, we develop a facile method to prepare HgSe nanoparticles in an aqueous solution under sonochemical conditions. This method is a simple and convenient procedure that provides an effective way for the synthesis of selenide and telluride materials. Recently, our group reported synthesis of nanostructures containing selenide and telluride ions [10].

2. SYNTHESIS AND CHARACTERIZATION

2.1 Method of Sample Manufacturing and Analysis

HgSe nanoparticles were synthesized according to this procedure: an aqueous solution of Hg(CH₃COO)₂ in the presence of capping agent was mixed with SeCl₄ aqueous solution. Then the solution was irradiated with an ultrasonic horn, and hydrazine was added drop-wise. The black precipitates obtained were centrifuged and washed by distilled water and ethanol in sequence and dried in vacuum at 60 °C. The as-synthesized HgSe nanoparticles were characterized by SEM, TEM, PL, EDS, and XRD analyses.

3. RESULTS AND DISCUSSION

The room temperature PL spectrum of the HgSe (sample No 2) was measured with an excitation wavelength of 261 nm. Fig. 1a shows a broad emission band centered at 393 nm. The determined band gap of this sample is 3.15 eV, while that of bulk HgSe is ~ 0.24 eV [11]. The sample No 2 shows a blue-shifted emission compared to bulk sample. This further confirms the larger variation of particle sizes. The band gaps increase with the decreasing of the particle sizes. The EDS analysis measurements were used to characterize the chemical composition of the products (Fig. 1b). The results for HgSe (sample No 2) show that only the elements Hg and Se exist and therefore indicate a pure HgSe phase in the particles.

Fig. 2a-c shows SEM images of the as-prepared HgSe in the presence of different capping agents. In the presence of TEA (Fig. 2a), agglomerated nanoparticles with a semispherical shape are observed. With exchange of the capping agent from TEA to SDS (Fig. 2b), the particle size increases and agglomeration of the nanoparticles decreases. When SDS is substituted with TGA and other reaction parameters remain unchanged, nanoparticles show dense agglomeration (Fig. 2c). Fig 2d shows the TEM image of the sample prepared
Fig. 1 – PL spectrum (a) and EDS spectrum (b) of sample 2

Fig. 2 – SEM images of samples 1 (a), 2 (b), 3 (c) and TEM image (d) of sample 2

Fig. 3 – XRD patterns of samples 1 (a), 2 (b), 4 (c)

For investigating the effect of sonication time, the reactions carried out in the presence of TEA and hydrazine for 15, 30, 45 and 60 min. With decreasing aging time from 30 min (Fig. 2a) to 15 min (Fig. 4a), microspheres were obtained. With increasing aging time to 45 min (Fig. 4b) and then 60 min (Fig. 4c), the microspheres were broken and agglomerated nanoparticles were formed. With respect to above mentioned, sonication time is one important parameter controlling the morphology of the products.
4. CONCLUSION

In summary, we have demonstrated the synthesis of HgSe nanoparticles from Hg(CH₃COO)₂ and SeCl₄ in the presence of TEA, SDS and TGA as capping agents and hydrazine as reductant via a sonochemical method. This method is introduced as an inexpensive, fast, reproducible process for the large-scale synthesis of HgSe nanoparticles. We expect that this method could be used for the future preparation of some other nanosized sulfides, selenides andtellurides.

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REFERENCES