SETSCI Conference Indexing System,
Volume 3 (2018), 193-195

ISAS 2018-Winter
2nd International Symposium on Innovative Approaches in Scientific Studies
November 30 – December 2, 2018, Samsun, Turkey

The Hot-Injection Method for Synthesis of Nano- and Microparticles

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Presentation/Paper Type: Oral / Full Paper

Abstract **–** The hot-injection is one of the most used chemical synthesis methods to be able to produce nano- and/or micron sized particles in a liquid medium. Synthesis of nanoparticles of group II-VI semiconductors such as ZnO, ZnSe, CdSe and IV and V metals such as Pb, Sn, Bi has been achieved successfully with this method. The synthesis of CdSe and Bi particles including both their nano-sized forms such as nanocrystals, nanoplates and nanowires and also the micron-sized forms obtained via hot-injection is exhibited in this study. Transmission electron microscopy (TEM) images of these nanostructures are supported by their energy dispersive X-ray (EDX) measurements. The X-ray powder diffraction (XRD) is used to determine their composition. The crystal structure of the Bi microparticles is determined. The classical growth model of the colloidal nanoparticles is given. Some superior aspects of this synthesis procedure relative to the others are shown and discussed with the help of the experimental findings.

Keywords – Hot-injection, chemical synthesis, nanoparticles, microparticles, X-ray diffraction, electron microscopy

I. INTRODUCTION

The hot-injection method was first introduced to synthesize cadmium chalcogenide (CdS, CdSe and CdTe) nanocrystals and afterwards enormously expanded to the others [1]-[3]. In this method, precursors of the particle to be synthesized are fast injected into a hot solvent and allowed to decompose and then combine in the medium and so the particle is created [4]. There are a lot of factors affecting the fundamental physical properties of the particles during the synthesis. For instance, synthesis temperature, synthesis time interval and also capping ligands determine the size and size distribution of the particles as well as their shapes [5]. The quality grades of the reactants might affect the properties of the particles.

In this paper, hot-injection synthesis procedures of cadmium selenide (CdSe) and bismuth (Bi) nano- and microparticles are given and explained.

II. EXPERIMENTAL

First, a trioctylphosphine and selenium complex (TOP-Se) was prepared. Later, this complex was injected into a sufficiently hot non-coordinating octadecene solvent including cadmium oxide and bismuth acetate along with stearic acid for the production of CdSe and Bi particles, respectively. The simplified representation of the synthesis system is shown in Fig. 1. All synthesis operations were carried out under a controlled argon gas flow and the temperature of the solvent was monitored and controlled well before and after the injection.

Transmission electron microscopy (TEM) images of the samples were taken by using an electron microscope JEOL JEM-2100F operating at 200 kV. The powder form of the samples was obtained with centrifugation and then drying under argon gas for X-ray powder diffraction (XRD) analysis. A Rigaku SmartLab X-ray diffractometer was used to measure XRD patterns.

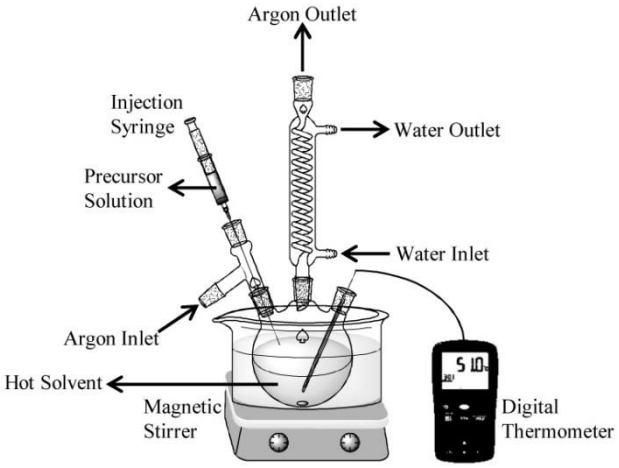

Fig. 1 The synthesis system of the nano- and microparticles.

III. RESULTS AND DISCUSSION

In Fig. 2, two TEM pictures belong to CdSe nanocrystals and a Bi microparticle, respectively, are shown. These particles are nucleated and growth according to the classical nucleation and growth model. After the injection, a lot of nuclei are formed in the non-coordinating solvent and later growth towards to the particle around a constant temperature. The synthesis reactions can be written for both particles as follows.

$$\begin{matrix} Cd(St)_2 + TOPSe \rightarrow CdSe\ NCs \\ Bi(St)_3 + TOPSe \rightarrow Bi\ MPs \end{matrix} \quad (1)$$

where St, NCs, MPs mean stearate anion, nanocrystals and microparticles.

In Figure 2a, the nanocrystals have mainly spherical shape and are well separated from each other. The nanocrystals

being at the edges of the image were omitted to be able to evaluate an average size. The average size was calculated over the leaving nanocrystals behind which are 63 particles by using image processing program ImageJ. The average diameter of the nanocrystals was found to be 3.2 nm. These nanocrystals are in the strong confinement regime because their average radius is smaller than the exciton Bohr radius of the bulk sample [6]. It means that the optical properties of these nanocrystals strongly depend on their sizes. A size determination was made for one spherical Bi microparticle seen in Figure 2b. It is about 639 nm. These calculated values are listed in Table 1.

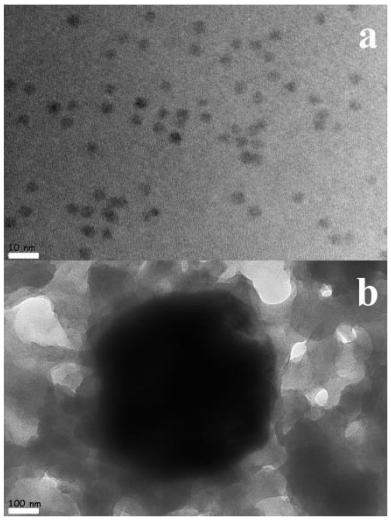

Fig. 2 TEM photos of CdSe nanocrystals and a Bi microparticle. Scale bar is 10 nm for (a) and 100 nm for (b).

Table 1. Average sizes of the synthesized particles.

Synthesized Nanoparticle	Average Diameter (nm)
CdSe Nanocrystals	~3.2
Bi Microparticle	~639

Characteristic X-ray energy peaks refer to Cd and Se elements have been seen in the energy dispersive X-ray (EDX) spectrum of CdSe NCs. In addition, elemental Bi has been determined in that of Bi MPs (not given in the paper). The XRD spectrum of the Bi MPs is shown in Figure 3.

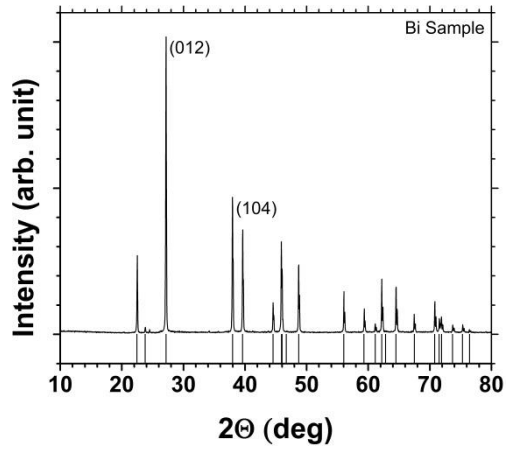

Fig. 3 XRD spectrum of synthesized Bi MPs. Powder diffraction data of hexagonal bismuth from the JCPDS are shown with vertical lines at the bottom.

The detailed XRD measurement data of these MPs are listed in Table 2. The XRD peaks of the synthesized Bi sample match well with those of hexagonal Bi having PDF card JCPDS 85-1330. The lattice constants of the hexagonal sample (a and c) can be derived by putting the data in Table 2 into Equations 2 and 3 [7].

$$d_{hkl} = 0.5\frac{\lambda}{\sin\theta} \quad (2)$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2} \quad (3)$$

where h, k, l are the miller indices of the plane, d is the distance between adjacent planes, λ is the wavelength of incident X-rays onto the sample and θ is the angle of incidence relative to the planes. Here, λ is 1.54059 Å, that is copper K-α, for this experiment.

Table 2. XRD data of the synthesized Bi particles.

hkl	2θ (º)	FWHM (º)
003	22.503	0.090
101	23.820	0.10
012	27.182	0.098
104	37.973	0.088
110	39.630	0.084
015	44.573	0.080
006	45.889	0.087
202	48.717	0.081
024	56.0316	0.064
107	59.347	0.079
205	61.142	0.094
116	62.199	0.080
122	64.525	0.084
018	67.458	0.075
214	70.803	0.086
009	71.544	0.106
300	71.901	0.090
027	73.734	0.084
125	75.349	0.082
033	76.412	0.084

The miller indices of the most intense two peaks are (012) and (104) in Figure 3. The hexagonal lattice constants of the Bi MPs are calculated as a=4.5424 Å and c=11.8587 Å if the values of (012) and (104) are used in the above equations.

IV. CONCLUSION

CdSe and Bi particles were synthesized at nano- and microscale by using the hot-injection method. Their compositional and physical characterization was made by using TEM, EDX and XRD. Construction of the experimental setup of the hot injection is more easier and cheaper relative to the other production methods of nanoparticles such as physical vapour deposition and it can be employed to obtain other metallic and semiconductor particles.

ACKNOWLEDGMENT

This research was done under Toros University's Scientific Research Project 2015-01-01-01-BAP-MUHF.

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