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Synthesis and characterization of indium monoselenide nanosheets: A proposed pseudo top-down mechanism

Mildred A. Airo [a], Siziwe Gqoba [a], Mubiayi P. Kalenga [a], Stefan Govindraju [a], Makwena J. Moloto [b], Nosipho Moloto [a,*]

[a] Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, South Africa
[b] Department of Chemistry, Vaal University of Technology, Private Bag X021, Vanderbijlpark 1900, South Africa

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ABSTRACT

Rhombohedral InSe nanocrystals have been synthesized by the refluxing of $InCl_3$ and Se in oleylamine (OLA) in one pot, at a temperature of 200 °C and a mole ratio of 1:1. The role of OLA in this method is to reduce the selenium while acting as both a solvent and a capping agent. The optical properties of the resulting nanoparticles have been studied by obtaining their absorption and photoluminescence spectra. The morphology and phase structure of the InSe nanoparticles have also been determined by X-ray diffraction and transmission electron microscopy (TEM). The TEM images show that the nanoparticles developed from large layered structures at the beginning of the synthesis, then later disintegrated to smaller particles as the time of synthesis is prolonged. This is confirmed by the UV–vis absorption spectra as they show that the nanoparticles obtained after 60 min are blueshifted compared to the ones obtained after 10 min. The formation mechanism of the nanoparticles resembles the top-down approach though the particles are first constructed chemically to form bulk InSe which then self-digest by breaking down chemically to form smaller particles; hence we call it the pseudo top-down approach.

1. Introduction

Majority of the techniques that exist for the fabrication of nanoparticles have included the top-down approach, using processes such as etching and photolithography to create patterned nanostructures [1]. More promising results have been obtained in the bottom-up approach, [1] where nanoscale structures are built by the manipulation of individual atoms and by controlled nucleation and growth processes. Most researchers have used the wet chemical synthesis technique, which is an example of the bottom-up approach to successfully synthesize quantum dots semiconductors [2–5]. However no studies have been reported to confirm if layered semiconductors such as indium monoselenide InSe and GaSe ever adhere to the bottom-up approach. Indium monoselenide, InSe is a group III–VI layered compound semiconductor which has attracted researchers mainly due to its potential application in photovoltaic fabrication [6,7]. It has an energy gap of 1.3 eV at room temperature which is near the theoretical optimum for solar energy conversion and has transport and photo-transport properties that are highly anisotropic [8–10]. Due to its interesting electronic and optical properties, it has been used as an absorber material as well as a precursor to $CuInSe_2$ for solar cell and ionic battery applications [11–13]. Herein we therefore seek to synthesize InSe nanosheets using the colloidal method and elucidate their formation mechanism.

2. Experimental

2.1. Chemicals

Indium (III) chloride, 99% selenium powder, 70% oleylamine (OLA), chloroform and 96% ethanol were obtained from Sigma-Aldrich.

2.2. Synthesis of nano-sized InSe

InSe nanoparticles were synthesized by a simple one pot method. In a typical experiment, the mole ratio was selected to be 1:1. About 0.3948 g (5 mmol) of indium chloride and 1.1059 g (5 mmol) of selenium powder were placed into a three neck flask with a capacity of 50 mL, and 10 mL of OLA was added in as a solvent, surfactant and a reductant to reduce selenium. The mixture was then heated rapidly to 200 °C under nitrogen gas and strong magnetic stirring. During the heating process, the

* Corresponding author. Tel.: +27 117176774; fax: +27 865228349.
E-mail address: Nosipho.Moloto@wits.ac.za (N. Moloto).

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mixture, which appeared to be homogenous, changed the color from black to yellow then to dark brown when the temperature of 200 °C was attained. At this temperature, aliquots were obtained at different time intervals and then allowed to cool to 80 °C naturally. The samples were washed with ethanol to flocculate the particles. The particles were then collected by centrifugation for 10 min at 3000 rpm. The washing was done several times in order to remove lingering impurities and the products were left to dry at room temperature for 12 h to obtain dark brown powders. The time intervals used were 10 min, 30 min and 60 min respectively.

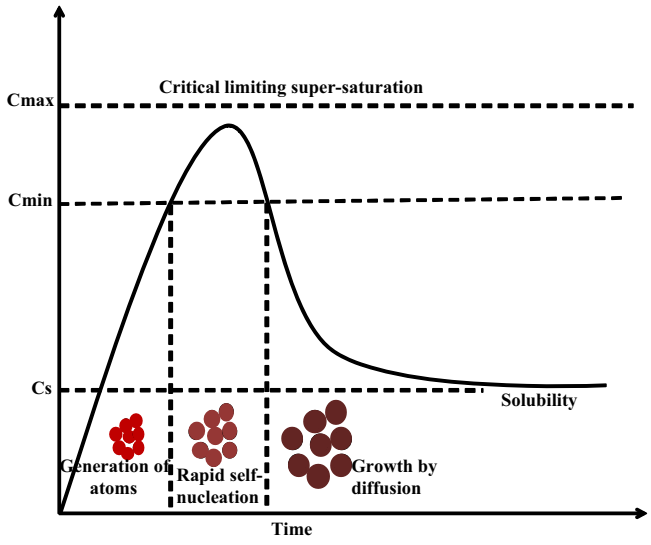
2.3. Characterization

2.3.1. Optical characterization

A Varian Cary Eclipse (Cary 50) UV–vis spectrophotometer was used to carry out the absorption measurements. A Varian Cary Eclipse EL04103870 fluorescence spectrophotometer with a medium PMT voltage at an excitation wavelength of 200 nm was used to measure the photoluminescence of the particles. For both spectral analysis, the powders were dissolved in chloroform and placed in quartz cuvettes (1 cm path length).

2.3.2. X-ray diffraction

XRD patterns on powdered samples were measured on a Bruker MeasSrv (D2-205530)/D2-205530 diffractometer using secondary graphite monochromated CuKα radiation (λ 1.54060 Å) at 30 kV/30 mA. Measurements were carried out using a glancing angle of incidence detector at an angle of 2°, for 2θ values over 10–90° in steps of 0.026° with a step time of 37 s and at a temperature of 25 °C.



Scheme 1. Lamer and Dinegar mechanism describing nucleation and growth of the nanocrystals as a function of time and precursor concentration [24].

2.3.3. Electron microscopy

The transmission electron microscopy (TEM) was carried out on a FEI Technai T12 TEM microscopy operated at an acceleration voltage of 200 kV with a beam spot size of 20–100 nm in TEM mode. The HRTEM images were obtained from a JEOL JEM-2100 microscopy with a LAB6 filament and an EDS detector, operated at 200 kV. The samples were prepared by placing a drop of the suspended nanoparticles in chloroform, on a carbon–copper grid. The grid with the sample was then allowed to dry at room temperature.

3. Results and discussion

The simple solution phase reaction system used in this paper provides a feasible and homogeneous environment for the formation of layers of InSe which later break down into the nanosized particles. In addition, it provides an environment conducive to study the effect of the reaction time on the size of the InSe nanoparticles, which has rarely been reported. The effect of duration of synthesis on the size of II–VI nanoparticles has been well studied [2,21–23]. The usually quoted growth mechanism of nanoparticles from colloidal synthesis is the Lamer and Dinegar's mechanism [24]. This growth mechanism involves the formation of the nuclei from the precursors, followed by the growth of the nuclei through the Ostwald ripening process and the termination of growth when the precursors are depleted (Scheme 1).

However this mechanism is contrary to the observed results below. The digestive mechanism depicted in Scheme 2 is also contrary to the observed findings illustrated below as it involves the post-treatment of polydispersed nanoparticles rather than the formation of the nanoparticles during the reaction [25].

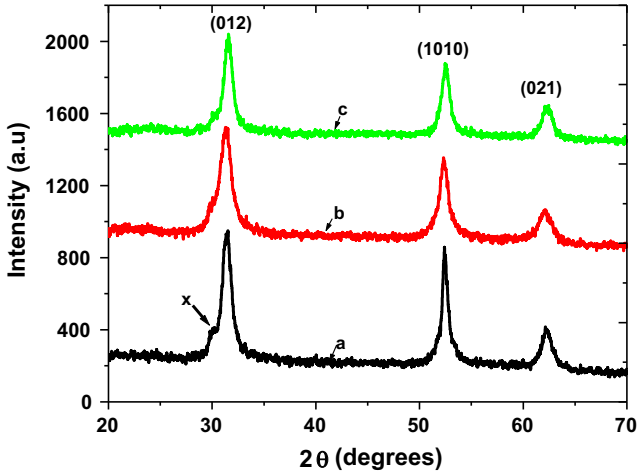
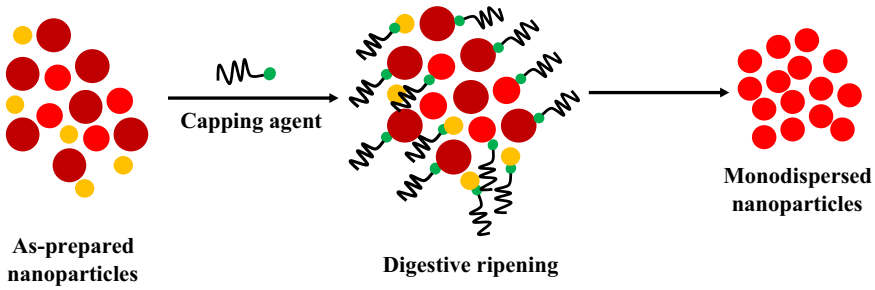


Fig. 1. XRD patterns of InSe nanoparticles synthesized at temperature of 200 °C with a mole ratio of 1:1 ($InCl_3$:Se) after: (a) 10 min which gave the InSe layers, (b) 30 min and (c) 60 min.



Scheme 2. Digestive ripening mechanism showing the size tuning of a poly-dispersed sample [25].