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## SYNTHESIS OF CdIn<sub>2</sub>S<sub>4</sub> MESOCRYSTALS

M. V. Carević<sup>1</sup>, M. I. Čomor<sup>1</sup>, T. D. Savić<sup>1</sup>, S. P. Ahrenkiel<sup>2</sup> and N. D. Abazović<sup>1</sup>

<sup>1</sup>*Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia, (kiki@vin.bg.ac.rs)*

<sup>2</sup>*South Dakota School of Mines and Technology, 501 E. Saint Joseph Street, Rapid City, SD 57701, USA*

### ABSTRACT

Ternary nanosized sulfide CdIn<sub>2</sub>S<sub>4</sub> was synthesized using hot-injection method in oleic acid/oleylamine mixture as reaction media at 270°C. TEM images have shown that obtained material grows through multistep process, forming marigold structures built out from mesocrystals. Influence of oleic acid and oleic acid/oleylamine mixture as reaction media on mesocrystal formation is tracked and discussed.

### INTRODUCTION

Classical crystallization theory explains material growth through three separated steps: nucleation, normal growth and competitive growth (Ostwald ripening). In nucleation step, elementary building units (atoms, ions or molecules) form clusters. Primary formed clusters then grow during normal growth step.[1] In a third step, all clusters that reach critical size (nanocrystals) will continue to grow through Ostwald ripening at the expense of smaller ones, that will dissolve, giving on that way additional material.[1] Briefly, this process can be represented as: ions/atoms/molecules → clusters → nanocrystals → single crystal.

In the past decade, new, non-classical theory of crystal growth emerged, mainly to explain formation of mesocrystals (*mesoscopically structured crystals*), new class of nanostructured solid materials[2]. This theory starts from nanocrystals as primary building blocks. In the basis of the theory lays oriented attachment, i.e. alignment of nanocrystals in such a manner that they share common crystal plane forming larger units-*mesocrystals*. If surface of primary nanocrystals is covered with organic molecules as surfactants, in the process of nanocrystals merging these organic molecules will be included in final mesocrystal, forming defects.[2]

What is needed to be underlined here is that mesocrystals mainly have characteristics inherited from primary building units, but also can have new,

improved ones. In order to meet needs for different applications, it is necessary to understand mesocrystals formation mechanism, to design proper synthetic methods and to fully characterize obtained structures.

Here, attempts to synthesize mesocrystals of ternary sulfide  $\text{CdIn}_2\text{S}_4$  (CIS) are presented. CIS is direct band-gap semiconductor, with the bulk band-gap energy of about 2.1 eV, which places its absorption threshold deep in visible part of solar spectrum (~560 nm). This characteristic makes it interesting for applications where light-semiconductor interaction can be utilized, like photocatalysis or photovoltaics.

In synthesis of nanosized chalcogenide materials (sulfides, selenides, tellurides) method that in last 30 years gave the most impressive results is hot-injection method, which is, basically, injection of precursor solution in hot ( $T > 200^\circ\text{C}$ ) pre-heated coordination solvent. Wide choice of precursors, surfactants, coordination solvents and reaction media gives freedom to manipulate with shape, size, crystal phase and overall characteristics of outcome materials. All previous facts supports decision to use hot-injection method as method of choice in synthesis of CIS mesocrystals. In order to minimize number of factors that can have influence on characteristics of obtained material, oleic acid and oleylamine were simultaneously used as coordinating agents, surfactants and reaction media.

## EXPERIMENTAL

Chemicals: cadmium acetate dihydrate ( $\text{Cd}(\text{Ac})_2$ ), indium-acetate ( $\text{In}(\text{Ac})_3$ ), oleic acid ( $\text{OA}-\text{C}_{17}\text{H}_{33}\text{COOH}$ ), oleylamine ( $\text{OLAM}-\text{C}_{18}\text{H}_{35}\text{NH}_2$ ) and 2-mercaptoethanol ( $2\text{ME} - \text{HS}-\text{C}_2\text{H}_4-\text{OH}$ ) were purchased from Sigma - Aldrich. Sulfur powder was obtained from Alfa Aesar. Toluene and acetone were purchased from JT Baker.

Cadmium precursor solution was prepared as follows: 0.0177g of  $\text{Cd}(\text{Ac})_2$  and 2 ml of OA were loaded in three-neck flask and heated at  $200^\circ\text{C}$  under constant Ar flow. After about 30 min, brown solution is formed, and was left at room temperature to cool down.

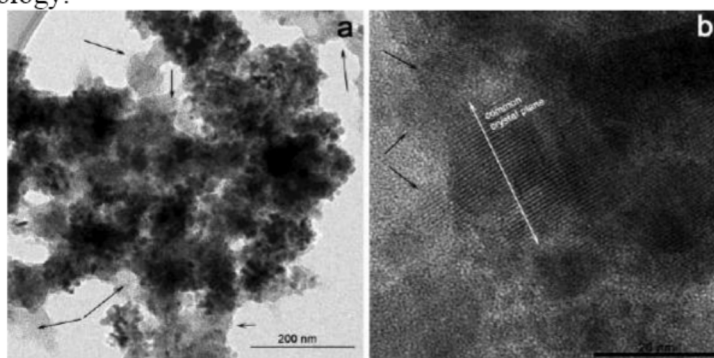
Indium precursor solution was prepared as follows: 0.0584 g of  $\text{In}(\text{Ac})_3$  and 2ml OA were loaded in three-neck flask and heated at  $270^\circ\text{C}$  under constant Ar flow. After about 30 min, pale yellow solution is formed.

Sulfur precursor solution was prepared as follows: 0.0128g of sulfur powder and 2ml of OA or 1ml of OLAM were loaded in three-neck flask and heated at  $90^\circ\text{C}$  under constant Ar flow. After about 30 min solution was left at room temperature to cool down. After preparation of the precursor solutions, Cd and S solutions were swiftly injected in. In solution at  $270^\circ\text{C}$ , and reaction mixture was kept at that temperature for 4h (S1 in pure

OA) or 1h (S2 with addition of 1ml OLAM). TEM and STEM images are obtained using JEOL JEM-2100 LaB6 microscope (200kV acceleration voltage).

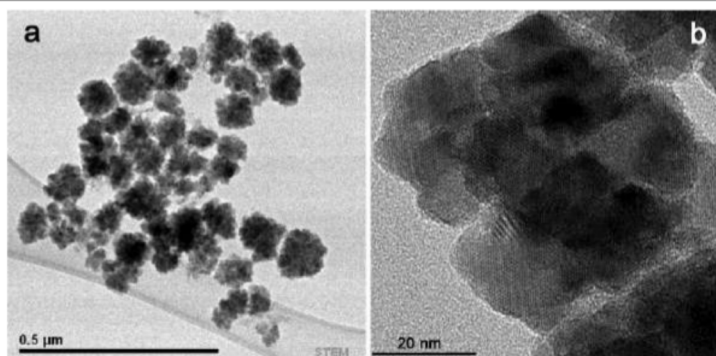
## RESULTS AND DISCUSSION

In order to confirm formation of ternary semiconductor CIS, XRD measurements (not presented) were performed. It was revealed that sample S1 is a mixture of hexagonal binary sulphide CdS and ternary cubic CIS (which was a dominant phase). TEM images (Fig.1) have confirmed existence of two materials characterized with different particle sizes and morphology.



**Figure 1.** TEM images of sample S1 at different magnifications

In Fig 1a, by arrows are indicated areas where small spherical particles (average size  $\sim 4$  nm) are clearly visible. Their particle size distribution is very uniform, and it was confirmed that these particles are hexagonal CdS. Larger, irregularly shaped particles belong to cubic CIS. At higher magnifications (Fig. 1b), it became clear that particles of CIS start to orient along a common crystal plane, forming larger structures (white arrow). However, the fact that in the sample S1 there are still present separated particles that are not oriented in a common manner (black arrows) along with the presence of binary sulphide in the sample, indicated that even after 4h of reaction mesocrystal formation is not finished. In order to speed up the reaction we have added OLAM to the reaction mixture (see Experimental). OLAM as an organic base, provides conditions for faster decomposition of the cation-oleic acid complex [3], accelerating in that way subsequent formation of the desired sulphide. After only 1h of reaction, as XRD measurements (not presented) confirmed, pure CIS was formed. STEM image (Fig. 2a) revealed that complex marigold-like structures were formed, with sizes ranging from around 50 to 200 nm.



**Figure 2.** a) STEM and b) TEM image of sample S2

From image at higher magnification (Fig 2b) it is clear that marigolds are made of flake-like structures, which are formed from even smaller sub-units, with sizes in range from 8 to 14 nm. Such multi-levelled architecture is, as explained by non-classical nucleation theory, characteristic for mesocrystals. In presented experimental conditions, their formation was easier, since after initial acceleration of reaction by addition of OLAM, system have enough time to arrange in complex manner. Presence of organic molecules (as capping agents) at nanocrystal surface provided their easier rotation in process of oriented attachment.

### CONCLUSION

Hot-injection method of  $\text{CdIn}_2\text{S}_4$  mesocrystals is proposed. It was shown that addition of OLAM was crucial for formation of pure cubic CIS in given experimental conditions. TEM images revealed that material is characterized with multi-levelled structure: primary nanocrystals through oriented attachment process form mesocrystals that than are arranged in marigold-like structures.

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