



Characterization of chalcogenides nanostructures for industrial application

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Metal chalcogenide hierarchical nanostructures as energy conversion devices were studied in this chapter. Cd-chalcogenide nanostructures were chosen as sample study due to their unique properties as energy converter. In the first step, different methods were introduced to grow this type of nanostructures. It was discussed three low cost-effective methods to grow the Cd-chalcogenide nanostructures such as thermal evaporation (chemical and physical vapor depositions), chemical bath deposition, and electrochemical methods. However, it was observed that samples were grown by a pulsed laser deposition method as a complex method. In addition, effects of growth conditions on morphology and optical properties of the nanostructures were investigated. In the second step, the fundamentals of solar energy conversion were described. Furthermore, quantum physics of semi-conductor solar cells was studied. Finally, the Cd-chalcogenide nanostructures were introduced as solar energy conversion and important factors that can affect the efficiency of this type of solar cells were introduced.

Keywords: Chalcogenide; Nanostructures; Energy conversion.

1. INTRODUCTION

From 2004 to 2030, the annual global consumption of energy is estimated to rise by more than 50%. Assuming current policies and practices remain in place, most of the increased energy production is expected to come from the combustion of fuels such as oil, ethanol, natural gas, and coal. A commensurate increase in CO₂ (a prominent greenhouse gas) emissions is anticipated, much of which is due to burning coal the fastest growing source of energy globally. Despite projected persistent increases in oil and gas prices, less than

10% of the global energy production in 2030 is predicted to come from renewable energy sources, such as hydroelectric, solar, wind, hydrothermal, and biomass. In order to moderate global reliance on exhaustible natural resources and their environmentally hazardous combustion, more scientific efforts should be directed toward reducing the cost of energy production from renewable sources [1].

There exist many potential renewable energy technologies in the form of solid-state devices, such as solar cells, which convert solar energy in the form of light to the more practical form of electricity. In addition, a large collection of condensed matter phenomena involves the conversion of energy from one form to another, and some proceed with efficiency near unity. Consequently, the study of energy conversion in materials is a field full of opportunities for practical and socially significant applications. Solar energy reaching the Earth's surface provides an energy supply potential surpassing the power consumption of our civilization by three orders of magnitude. Still, this immense energy resource has not been harvested to an extent that can yield a tangible environmental or economic impact. Collectively, fulfillment of these conditions should enable competitive solar energy installations in terms of cost per watt, compared to traditional energy sources, even without governmental subsidies [2].

Over the past decade, semiconductor nanostructures have played a significant role in the development of nanotechnology applications. In fact, these are the most attractive classes of materials for functional nanodevices, including gas and biological sensors [3], field effect transistors [4], light-emitting diodes (LED) [5, 6], solar cells [7, 8], nanogenerators, and optoelectronic devices [9]. These new properties and applications of semiconductor nanostructures have attracted both scientific and industrial communities. In fact, in semiconductor nanostructures, the huge surface-to-volume ratio ($\sim 10^8 \text{ m}^{-1}$ for nanowires compared to $\sim 10^2 \text{ m}^{-1}$ for bulk materials) results in strong sensitivity of the excitons to surface states and as well as defects caused by their reduced size.

Metal chalcogenide semiconductors have attracted much attention because of potential for above applications. In general, metal chalcogenides are compounds consisting of a metal and an element which is a member of the chalcogen column (oxygen group) of the Periodic Table. While oxygen is a member of the chalcogens, so all metal oxides are technically metal chalcogenides, but the term is commonly used only refer to compounds of a metal with sulfur (S), selenium (Se), and tellurium (Te). In fact, semiconducting metal chalcogenide nanocrystals (II–VI and IV–VI) are a class of materials that exhibit band gap energies spanning from the mid-to-near infrared (PbS, PbSe, and PbTe) to the visible (CdS, CdSe, and CdTe) and into the ultraviolet (ZnS and ZnSe) regions. In particular, CdE (E = S, Se, Te) nanocrystals have been of great interest to nanomaterial scientists due to their relatively easy synthesis, the ability to produce high-quality nanocrystals in terms of size and shape, and the associated capability to tune the absorption and emission throughout the visible region. According to these applications and properties, recently research about synthesis and application of semiconducting metal chalcogenide nanocrystals is one of the hot topics. These properties make them particularly important for optical devices and finding a good alternative instead of silicon solar cells. Therefore, this chapter is a short review of results on preparation, characterization, and applications of semiconducting of Cd-chalcogenide nanocrystals (CdE; E = S, Se, Te) that are as one of the best materials for solar cells energy conversion.

2. EXPERIMENTAL

Cd-chalcogenide nanocrystals and thin films have been grown using physical and chemical methods, such as thermal evaporation methods (physical vapor deposition (PVD) and chemical vapor deposition (CVD)), electro-chemical deposition, sol-gel, solvothermal, hydrothermal, molecular beam epitaxy (MBE), chemical bath deposition (CBD), and pulsed laser deposition (PLD). However, chemical methods have been used more than physical methods to grow these types of nanostructures. In this part, we present some popular methods for growth of Cd-chalcogenide nanocrystals and thin films that are included thermal evaporation, CBD, and electrochemical methods as three of the cost-effective and simple techniques. In addition, it will be presented PLD method as one of the advanced methods to grow Cd-chalcogenide nanocrystals.

Comparing to the various methods available for synthesizing nanostructures, thermal evaporation is one of the simplest techniques for growing semiconductor nanostructures. In addition, thermal evaporation provides a particularly cost-effective and high-quality equilibrium process, in which the morphology of nanostructures can be controlled by the content and melting points of the sources and substrates used [19, 20]. Thus, this process is frequently found in the literature, where researchers have presented the use of this model for growing semiconductor nanostructures. Thermal evaporation has proven to be very successful and versatile in the fabrication of nanobelts and nanowires that have various characteristics. Gao and Wang grew CdS nanobelts by using a thermal evaporation method [21]. They used a CVD setup to grow CdS nanobelts via vapor–liquid–solid (VLS) by the assistance of gold as metal catalyst and vapor–solid (VS) process.

3. RESULTS AND DISCUSSION

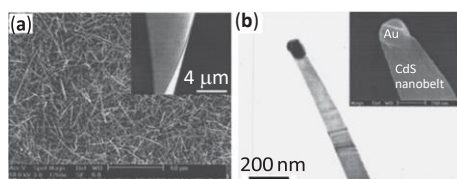


Figure 1 (a) SEM image of the CdS nanobelts. The inset shows a high-magnification SEM image of a curved belt, with typical thickness of 40 nm. (b) TEM image of a CdS nanobelt capped by an Au nanoparticle. Inset shows a similar result in SEM observation.

Figure 1 shows SEM and transmission electron microscope (TEM) images of the CdS nanobelts that were grown by Gao and co-workers. They used these nanobelts as photoconductors. Fu et al. also used Au as catalyst to grow CdS nanowires by using a thermal evaporation method [23]. Figure 2 shows the CdS nanowires that were grown by the VLS process by this group.

Addition of Au, the other metals also can be used as catalyst to grow Cd-chalcogenide nanocrystals. Dai et al. used Sn as metal catalyst to grow ultra-long CdS nanowires by using a thermal evaporation method [24]. Figure 3 reveals the CdS nanowires that were grown by assistance of the Sn metal as the catalyst.

However, no metal droplet at tip of the nanowires can be seen. The hexagonal shape of the tip indicates that the growth direction of nanowires has been [0001] and high-resolution transmission electron microscope (HRTEM) results also confirmed this claim. They used the nanowires as optical waveguide.

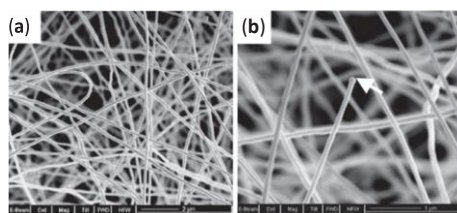


Figure 2 (a and b) Typical SEM images of the products. The products demonstrate a uniform wire-like morphology. The wires are about hundreds of microns in length and average about 100 nm in diameter.

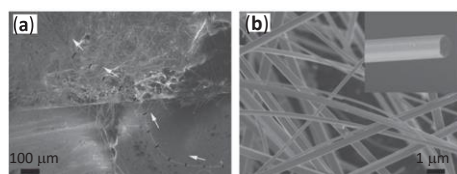


Figure 3 (a) Low-magnification and (b) medium-magnification SEM images of CdS nanowires, inserted image in (b) is the end faces of a typical nanowire.

In some cases, metal chalcogenide or metal oxide, such as ZnS, ZnO, CdS, and CdO, has high melting points; therefore, the use of a catalyst in the source material can decrease the melting point of the source. Owing carbothermal effects, graphite can cause a decrease in the melting point of a source material. Therefore, graphite powder is usually added as a catalyst to

metal chalcogenide or metal oxide powders to reduce the melting point of the source materials for the thermal evaporation method. The role of graphite should be similar to that when it was used in the catalytic growth of ZnO nanowires through vapor transportation [25]. Here, it can be described this method to grow Cd-chalcogenide nanocrystals, for example, CdS nanostructures. Under the adopted conditions, CdS is reduced by carbon into Cd according to the following reactions [26]:



The Cd vapor was transported to the substrates by carrier gas and reacted with the metal catalyst at a lower temperature to form alloy droplets. As the droplets became supersaturated with Cd, there was the generation of crystalline CdS nanostructures, plausibly according to reaction (4) below:



It is known that several factors are important to obtain nanostructures via thermal evaporation method, where substrate temperature is one of them. Zhang *et al.* studied the effect of silicon substrate temperature on morphology of CdS nanostructures that were grown by using a thermal evaporation method [27]. They observed that the substrate temperature has significant role to obtain different morphology. Figure 4 shows the CdS nanostructures that were grown on Si substrates that have been

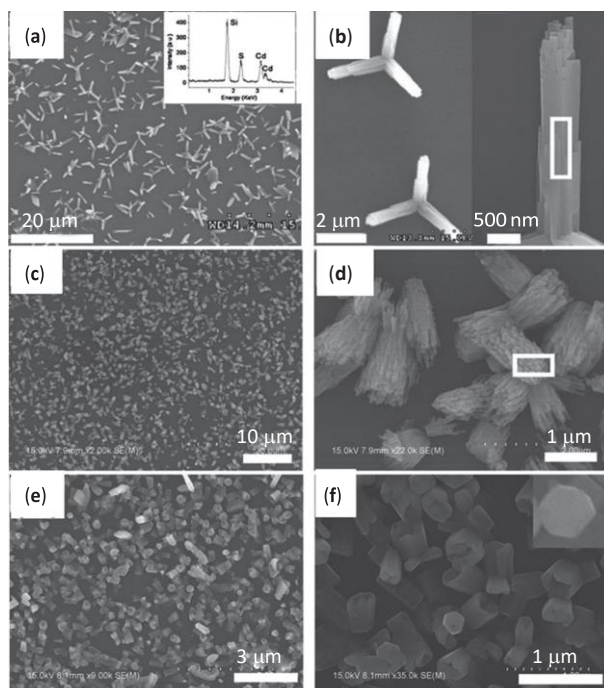


Figure 4 (a) SEM image of CdS multipede formed in zone I and EDS spectrum of tripods (inset) corresponding to rectangular area in the inset of (b); (b) high-

magnification SEM images of the tripods. (c and d) SEM images of CdS nanobrushes formed in zone II. (e and f) SEM images of CdS nanocups formed in zone III.

placed in three temperature zones (I: high temperature, II: mid temperature, and III: low temperature). In addition, optical properties of the CdS nanostructures have been affected by substrate temperature. Figure 9.6 reveals CL spectra of these nanostructures. It can be seen that the samples that were grown at the lower-temperature zone show better optical properties than those grown at the higher-temperature zones. We also observed the effect of substrate temperature on morphology and optical properties of ZnO nanostructures that were grown by using a thermal evaporation method [28–30]. However, the effect of substrate temperature on physical properties of the nanostructures, which are grown by thermal evaporation method, is one of the open questions that have not been answered yet. In addition, thermal evaporation method can be used to dope CdS nanostructures. For example, Ji *et al.* applied thermal evaporation method to grow Mn-doped CdS nanobelts that were grown via VLS process. They used Au as metal catalyst to grow CdS nanobelts. Figure 5(a) and (b) shows the FESEM images of the undoped and Mn-doped CdS nanobelts, respectively [31]. It can be seen, the Au droplets at the tips of the nanobelts in figure 5(b). Yan *et al.* also doped CdS nanowires with Mn using a thermal evaporation method without using any metal as catalyst. They used different amount of Mn in CdS structure and studied the effect of Mn concentration on morphology of the nanowires. They observed that increasing Mn concentration could change cross section of the nanowires from hexagonal to triangular. Figure 6 shows SEM images of this type of the nanowires [32].

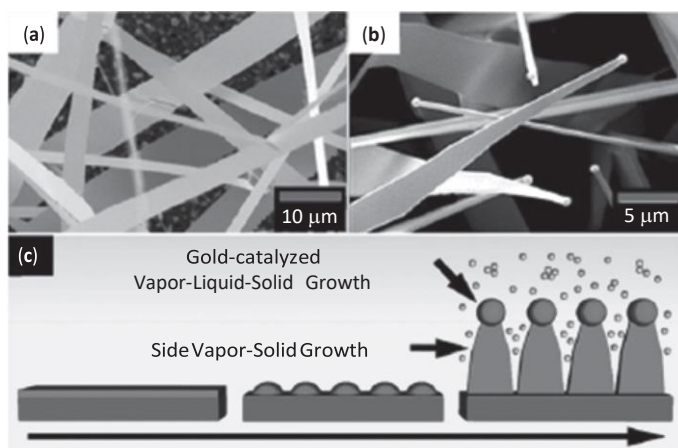


Figure 5 FESEM images of (a) the pure CdS nanobelts and (b) the nanobelts with variational width and with Au particles on their tips. The growth time and temperature are 3 h and 925°C, respectively. (c) Schematic illustration of the gold-catalyzed VLS combined with the side VS growth of the CdS nanobelts.

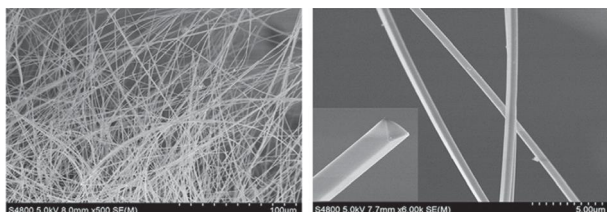


Figure 6 SEM images of the triangular Mn-doped CdS NWs. (a) Low-magnification image and (b) high-magnification image, the inset image shows a single representative triangular facet nanowire.

4.CONCLUSIONS

Fundamental properties and different growth methods of Cd-chalcogenide (CdE, E=S, Se, and Te) nanostructures were presented. It was observed that thermal evaporation method was the simplest method to obtain different morphology with high quality of the Cd-chalcogenide nanostructures. In addition, the Cd-chalcogenide nanostructures were grown with high quality by PLD method as an advanced and complex method. The CBD method used to grow Cd-chalcogenide thin films. Electrodeposition method was a controllable method to grow Cd-chalcogenide nanostructures. It was observed Cd-chalcogenide hierarchical nanostructures with more branches were better solar energy harvesting due to add more material to absorb incident light. It was observed that if these materials jointed with a high window properties material for visible solar energy, then efficiency of the solar cells was improved. As a future study, the other metal chalcogenide nanostructures such as PbE, ZnE, and In_2E_3 can be considered as converter energy.

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