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Biological resemblance of cadmium sulphide seaweeds coral honeycomb nanostructures by a chemical bath deposition technique

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ABSTRACT

Nanostructures of cadmium sulphide (CdS) have been attracting considerable research interests in electronic device fabrication due to their unique wide band gap (~2.4 eV) and high photosensitivity. Thin-films of CdS nanostructure have huge potential for solar cells, flat-panel displays and light-emitting-diodes. However, lack of a simple and convenient preparation method impedes their wide-spread device development. Here, a facile, efficient and scalable chemical bath deposition technique based preparation of thin films of CdS nanostructure is reported. Utilization of various complexing agents in the reaction mixture provided a unique surface topography to the CdS nanostructures similar to biological objects such as seaweed, coral-reef, and honeycomb. For the first time nanocrystalline, optical absorbance and morphology of three different CdS nanostructures derived from CBD are discussed.

1. Introduction

One dimensional (1D) semiconductor nanostructures have become promising recently due to their potential applications in the field of opto-electronics, photovoltaic, LED, logic gates, etc. [1,2]. Cadmium sulphide (CdS) is one of the important II–VI semiconducting materials with wide band gap (~2.4 eV) and very high photo-sensitivity values, which make it a valuable material for the photovoltaic applications [3,4]. ZnO was the most popular 1D nanostructure, but in recent years there are a number of new varieties of 1D nanostructure which have being developed, among which CdS nanostructures have the close fundamental physical properties with ZnO, including lattice constant, crystal structure and so on [5]. Although CdS is a well-known studied material over the last few decades, deposition of 1D CdS nanostructure on the solid glass substrate has recently emerged owing to its potential application in opto-electronic devices. In general, CdS nanostructures can be synthesized using different preparation techniques such as CVD [6], MOCVD [7], thermal evaporation [8], laser assisted catalytic growth [9,10], hydrothermal [11] and electrochemical deposition [12]. Most of these techniques require high temperature working conditions, expensive equipments and often need time consuming process. Chemical bath deposition (CBD) is a low cost, environmental friendly, and large area deposition technique, which can be carried out even at room temperature (RT). Hence in this paper we report the fabrication of novel CdS thin films using a simple but versatile CBD technique. Surface topography of as-obtained thin films of CdS nanostructures resembles the biological objects such as 'coral-reef', 'seaweed' and 'honeycomb'. A possible mechanism attributed to such distinct surface morphology is derived by the use of different compositions of complexing agents in the reaction mixture. These CdS nanostructures are efficient for applications in the field of solar PV cell and optoelectronic devices.

2. Experimental

Soda lime glass substrate was used as the solid support for deposition of CdS thin films. Prior to the deposition process, the glass plates were sequentially cleaned using soap solution in acetone, alcohol and deionized water (DI) with aid of ultrasonic bath for 5 min. These substrates were further dried using dry nitrogen gas flow. The chemical bath consists of 1 mM $3CdSO_4 \cdot 8H_2O$ and 1 mM thiourea and the total volume of the reactants was kept as 40 ml. This is a proven fact that the cadmium ions are released much faster than the sulphide ions [3]. Hence for stochiometric formation of the CdS, a complexing agent is required. In this study, we used three types of complexing agents: (A) triethylamine (B) mixture of triethylamine and ammonia and (C) triethylamine, ammonia and tin chloride (0.01 mM, 1 ml). Hereafter the three respective CdS samples are named as A, B and C. The glass substrate was placed vertically in the reaction mixture with one of the surface facing the glass beaker. The mouth of the glass beaker containing the reaction mixture was covered with paraffin wax. There were some holes provided on the paraffin

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wax cover, in order to avoid the development of the excess pressure inside the beaker. Then the reaction vessel placed in the water bath has been kept at RT. The deposition time was fixed at 40 min. After the deposition process, the film formed on the glass substrate was taken out from the solution and washed in DI water, followed by annealing in hot air oven temperature at 60 °C for 20 min. As-obtained films were further subjected to morphological and optical characterizations. Optical absorption measurements were carried out using UV–vis spectrophotometer (Shimadzu UV 3100). Surface morphology of the samples was studied using field emission scanning electron microscopy (FE-SEM, JEOL-JSM7500F) and transmission electron microscopy (TEM, JEOL 300 kV). The structural properties of the films were studied by an X-ray diffraction (XRD) system with a Cu Kα radiation 2θ angles varies from 15° to 60°.

3. Results and discussions

The XRD analysis of the three samples was carried out and the diffraction patterns of all the samples are depicted in Fig. 1. Sample A shows almost a cubic-crystal structure. In addition a strong cadmium hydroxide $Cd(OH)_2$ peak can be observed around 17.5°. Since the samples are prepared at RT from a chemical bath, the presence of Cd $(OH)_2$ is unavoidable. Sample B showed (102), (110), (103) and (202) hexagonal planes along with (220) cubic CdS plane. The peak observed around 23.5° can be attributed to $Cd(OH)_2$ phase. The peaks at 40° and 49.5° are yet to be identified. On the other hand, sample C showed a mixture of hexagonal cubic and orthorhombic structures, as well as that of $Cd(OH)_2$. Further there are two unidentified peaks observed around 32.5° and 35.7°. These unidentified peaks observed from sample C and sample B show a resemblance to the cadmium sulphide-hydrated [$CdS \cdot xH_2O$] phase.

Optical absorption analyses of the samples were carried out in the wavelength range 800–350 nm. The optical absorbance *vs.* wavelengths graphs of all samples are shown in Fig. 2. The optical absorption of the samples showed a minimum for sample A and maximum for sample C. On increasing the incident photon energy beyond the Urbach tail both samples A and C showed a sharp absorption edge, whereas sample B showed a shallow absorption

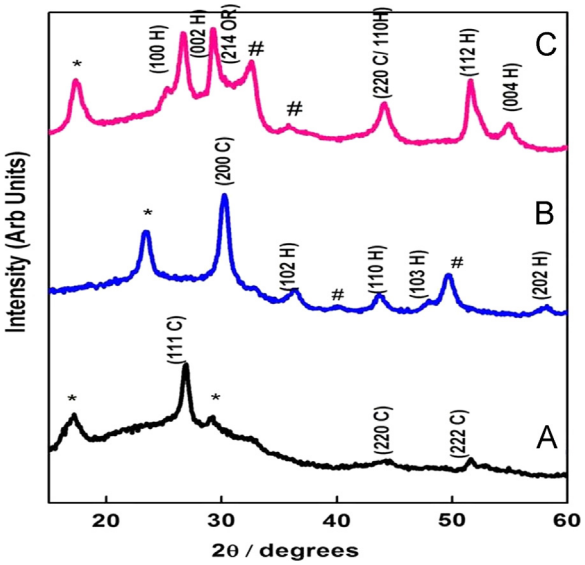

Fig. 1. X-ray diffraction patterns of (A) seaweed-like CdS, (B) coral-reef-like CdS and (C) honeycomb-like CdS samples. Marked crystal planes with indexes C, H and OR indicate the cubic, hexagonal and orthogonal structures, respectively. Peaks with * correspond to cadmium hydroxide and peaks with # are not assigned.

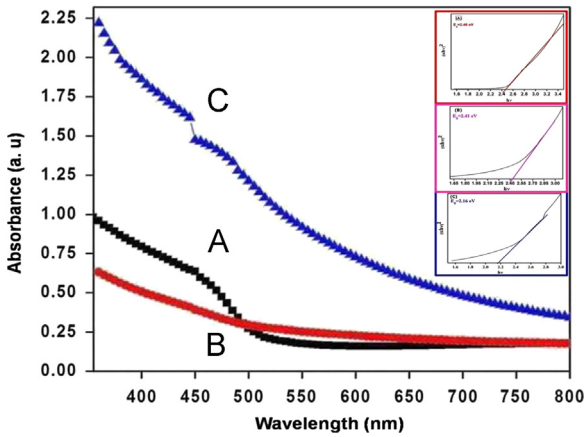

Fig. 2. UV–vis absorbance spectra of (A) seaweed-like CdS nanostructures, (B) coral-reef-like CdS nanostructures and (C) honeycomb-like CdS nanostructures.

edge. The mechanism behind such distinct observation remains elusive. The optical band gap (E_g) of the semiconductors can be found using the relation $(\alpha h\upsilon)^{\gamma} \sim (h\upsilon - E_g)$ where $h\upsilon$ is the incident photon energy and α is the optical absorption coefficient [10,3]. The values of γ are given as 1/2 and 2 for indirect and direct band gap materials respectively. The band gap of the samples was calculated from extrapolation of the vertical edge, above absorption edge (i.e. wavelength values above 500 nm), on $h\upsilon$ *vs.* $(\alpha h\upsilon)^2$ graph, to the *X*-axis [3,13,14]. Sample A and sample B showed band-gap values of 2.46 and 2.41 eV, respectively. On the other hand, sample C showed a small shift in the band gap value, towards the lower wavelength side (2.16 eV). It may be due to the incorporation of CdS in $Cd(OH)_2$ matrix. This result is agreed well with the crystalline pattern detected by XRD.

Surface topographical information of CdS nanostructures obtained from the CBD technique was studied from FE-SEM. As can be seen from Fig. 3A and C, simple variation in the reaction mixture with different compositions of complexing agents has derived a functional change in the surface of CdS with three unique shapes. For instance, sample A prepared in presence of triethylamine shows a resemblance to the 'seaweed' structure, whereas sample B prepared in support with mixture of triethylamine and ammonia produced a 'coral-reef' like structure. On the other hand, sample C produced from a combination of triethylamine, ammonia and tin chloride generated a unique 'honeycomb' like nanowall structure. Utilization of various complexing agents has directly influenced the reaction kinetics and release of ions (Cd^{2+} and S^{2-}) under the chemical bath and its dependence in the deposition of CdS molecules. The detailed morphology and structural analysis of the CdS nanostructures were also investigated from HR-TEM. It can be observed that HR-TEM images (Fig. 3A′ and C′) show a trace of ordered crystalline structures embedded by the non-crystalline phase. It was previously been demonstrated that $Cd(OH)_2$ is known to have an intermediate stage. From the observed results, it can be justified that the CBD derived CdS nanostructures of three distinct morphologies are significantly modified with cadmium sulphide-hydrated or cadmium hydroxide matrices and this result is well correlated with the optical absorbance and XRD analysis.

4. Conclusions

CdS nanostructures were prepared by, cost-effective and low temperature, the CBD technique. Simple alteration of complexing agent's composition in the reaction mixture gives varied surface