

Morphologically controlled CdS microstructures using dc electrochemical template synthesis

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DC electrochemical template synthesis technique has been used to fabricate the CdS microstructures (microwires/tubules) using polycarbonate membrane in an aqueous medium containing $S_2O_3^{2-}$ and Cd^{2+} at 40^o- 45^o celsius. Morphology of the microstructures has been controlled by controlling various parameters like constant stirring, temperature, pH, and activation of the pore walls, during the electrochemical deposition. X-ray diffraction studies have been carried out for structural analysis of the fabricated structures. The results of scanning electron microscopy (SEM) showed the bulk deposition, cauliflower morphology, and uniform deposition of wires as well as tubules, depending upon the fabrication conditions. The diameter of the microstructures depends on the pore diameter and the length depends on the thickness of the template used. Room temperature photoluminescence of the microwires was measured and the spectrum showed a broad band centered at ~ 508 nm.

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1. Introduction

Band gap energy in the visible region and an easy synthetic method makes CdS, one of the most extensively studied semiconductors. CdS (direct band gap of 2.42 eV at room temperature) is one of the most important group II-VI semiconductors, having vital optoelectronic applications such as nonlinear optics, flat panel displays, light emitting diodes, lasers, and thin film transistors [1].

Special attention has been paid to one-dimensional structures, such as nanotubes and nanowires, owing to their interesting properties [2]. They can play an important role both as interconnect and functional units in fabricating electronic, optoelectronic, electrochemical and electromechanical devices with nanoscale dimensions.

The template synthesis is a simple and versatile method for preparing nanostructural materials (metals, semiconductors, polymers, metal-semiconductor junctions), which entails synthesizing the desired material within the pores of the membrane. The electrochemical synthesis in templates has been taken as one of the most efficient methods in controlling the growth of micro/nano structures (heterogeneous-including multilayered, short, squat fibrils, long needle-like fibrils, tubules, tapered conical-single or double cones), because the growth is controllable almost exclusively in the direction normal to the surface [3, 4]. Moreover, the nanostructures obtained by this technique can be assembled into a variety of architectures [5]. Protruding, bristle like crop of the fabricated nanostructures can be obtained on dissolving the membrane, or they can remain inside the pores of the membrane, or they can be freed from the membrane and can be collected as an ensemble of free nanostructures.

Numerous researchers have used anodic alumina membrane for the electrochemical template synthesis [6-7]. But it has been observed that, this template is very brittle, therefore it has to be handled carefully as compared to the polycarbonate membranes, used in the present work, which are flexible and can be cut according to the requirement.

Here, we report the fabrication of structurally ordered arrays of CdS microwires and tubules using electrochemical template synthesis technique. We have also synthesized fractal-like cauliflower morphology [8-10] of CdS microstructures and studied their optical properties. In this work, we have not used any capping/stabilizing agent or surfactants for synthesizing the microstructures.

2. Experiment

2.1. Cell fabrication and synthesis

Nuclepore polycarbonate membranes having pore size of 800 nm, pore density of 10⁸ cm⁻² and 11 μm thickness have been used as templates for the synthesis of cadmium sulphide microstructures through electrochemical deposition. A simple but versatile electrochemical template synthesis cell has been used for the synthesis of the microstructures. Using this teflon made cell, various parameters like temperature, exposed area of the template to the electrolyte, stirring rate, distance between anode and cathode have been controlled. Fig. 1 shows the block diagram of the fabricated electrochemical template synthesis cell to carry out the dc electrochemical deposition using template synthesis technique.

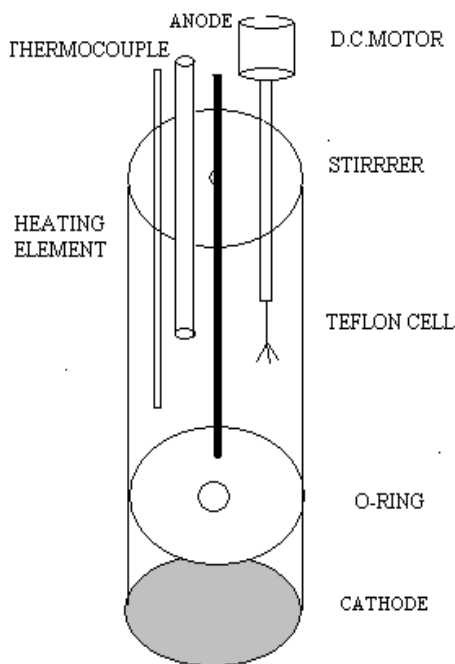


Fig. 1. Block diagram of the electrochemical template synthesis cell used for the fabrication of the CdS microstructures.

The electrolyte solution consisted of 0.1539g/100ml $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (98%) and 1.2604g/100ml Na_2SO_3 (99.9%) in the double-distilled de-ionized water [10]. The pH of the electrolyte was adjusted in-between 1.65 and 1.80 using concentrated sulphuric acid. It was observed that the electrolyte once made should be used within 10-15 hours, as no desired electrochemical reaction occurs after its aging. It is advisable to prepare fresh electrolyte for every experiment.

The wetting of the membrane was done by dipping it in the electrolyte for a while. Proper wetting of the membrane was found to be an essential condition for the simultaneous growth of the structures in all the pores of the membrane [9]. In case of fabrication of microtubules, the membrane was dipped in 50 ml of 0.01M SnCl_2 solution, to which 4-5 drops of concentrated HCl had been added. This was done to activate the pore walls of the membrane so that, the deposition starts at the walls of the membrane. While adhering the membrane to the cathode (the copper tape), extra electrolyte was wiped off from the membrane. This is to prevent the formation of a layer of electrolyte between the copper tape and the membrane, which will hinder the contact between the two. Subsequently, the membrane was fixed in the electrochemical cell with the pores exposed to the growth solution and the deposition reaction was carried out. The deposition process was performed at temperatures between 40° and 45° celsius. The applied voltage was kept low to avoid side reactions such as hydrogen evolution. It was observed that the current decreased slowly throughout the pore filling process and after the deposition inside the pores is completed, it becomes nearly constant for a couple

of minutes and then increased. After the electrodeposition process the polymer membrane was dissolved in dichloromethane.

2.2. Characterization

The cleaned and dried samples were coated with a layer of gold-palladium alloy in Jeol, Fine Sputter JFC 1100 sputter and subsequently mounted on aluminium stubs using double-sided adhesive tape. The samples thus mounted were then viewed under Jeol, JSM 6100 scanning electron microscope at an accelerating voltage of 20kV. In order to confirm the crystalline quality of the deposits, the membrane containing the microstructures was peeled-off from the copper strip and X-ray diffraction of the deposited microstructures was carried out using D/Max Rint 2000 Rigaku (Tokyo) X-ray diffraction machine using the copper characteristic wavelength of 1.5418 \AA . UV-Visible absorption spectra were recorded by dispersing the microwires in spectroscopic grade ethanol using a spectrophotometer (Hitachi U 3410). Photoluminescence (PL) measurements were carried out at room temperature with a luminescence spectrometer (Hitachi, FL 2500) using 400 nm as the excitation wavelength.

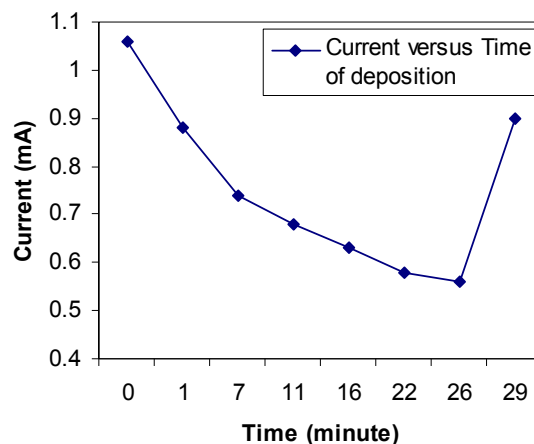


Fig. 2. Current-time plot for the deposition of CdS inside the pores of the membrane.

3. Results and discussions

3.1. XRD analysis

Fig. 3 shows the XRD pattern of the deposited CdS microwires in the polycarbonate membrane at room temperature. The spectrum shows various diffraction peaks at 2θ values of 26.8° , 44.1° and 52.0° . The peaks were identified to originate from (100), (220) and (311) planes of the cubic phase of CdS respectively (compared with JSPDS, 10-454).

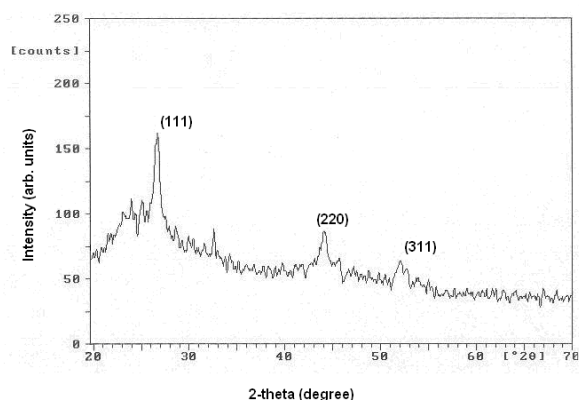


Fig. 3. XRD pattern taken on the microwires embedded in the polycarbonate membrane.

3.2. SEM studies

Fig. 4 shows the bulk deposition of CdS, on the membrane. This has resulted from the unoptimised growth conditions such as longer time duration, high voltage supplied, pH value of the electrolyte and temperature inside the electrochemical cell during the deposition. It was also observed that the stirrer played an important role in the electrochemistry involved in synthesizing CdS electrochemically. Without the stirrer, the color of the electrolyte did not change after the experiment and a grey colored layer of cadmium was deposited on the cathode instead of the yellow colored CdS.

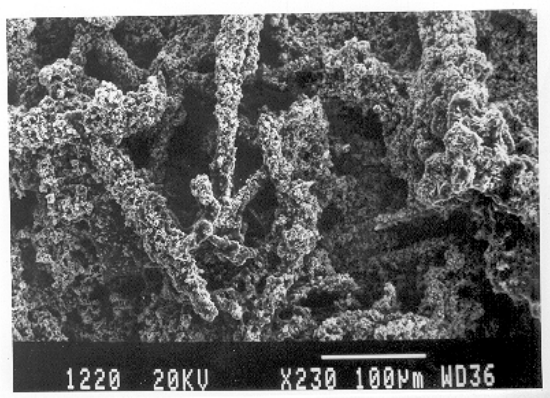
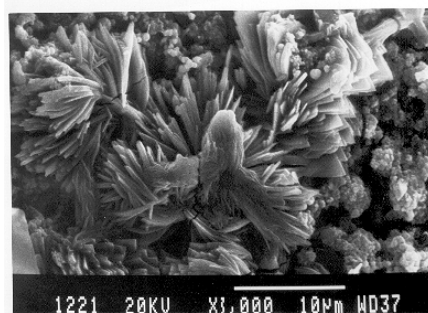


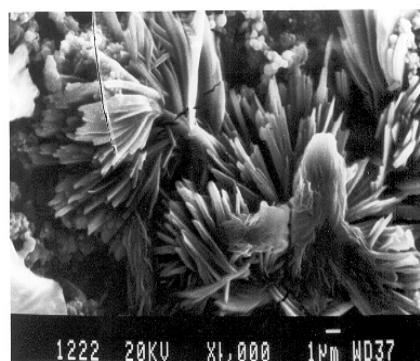
Fig. 4. SEM image showing bulk deposition.

Fig. 5 (a, b) shows the cauliflower morphology of the fabricated microstructures. After the template was removed, the embedded arrays of microwires having high aspect ratio, collapsed into an entangled mass due to the surface tension force exerted on the nanowires. Figure 5(c) shows the uneven deposition due to improper wetting of the polycarbonate membrane. A full grown microwire, as shown in figure 5(c), resulted from the proper adhesion of the membrane with the cathode strip, whereas the other microwires have just begun to grow, as the wetting in this region was not proper. In figure 5(d), a crop of well separated microwires, grown normal to the cathode and having high aspect ratio is obtained. The onset of the

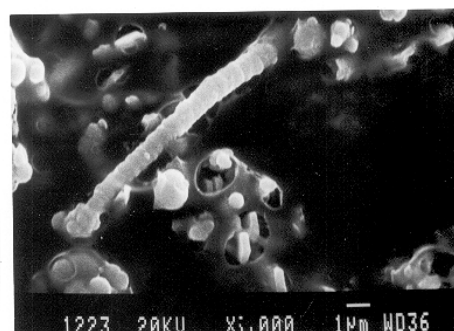
growth of microtubules having outer diameter ~ 720 nm and thickness varying between 125 nm and 185 nm have been shown in figure 5 (e, f). The pore walls of the membrane have been activated using aged SnCl_2 solution, which initialized the pore filling starting from the pore wall inwards rather than starting from the bottom of the pore upwards (refer Fig. 6).



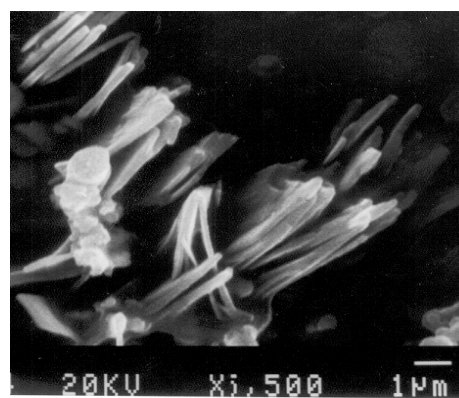
a



b



c



d

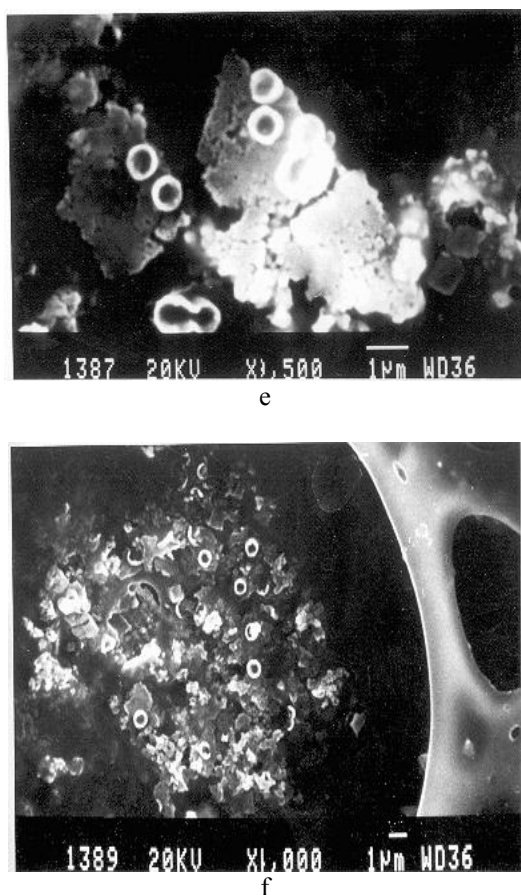


Fig. 5. SEM images of the CdS microstructures (a, b) cauliflower morphology (c) uneven deposition due to improper wetting of the polycarbonate membrane (d) crop of directional microwires (e, f) onset of the formation of microtubules.

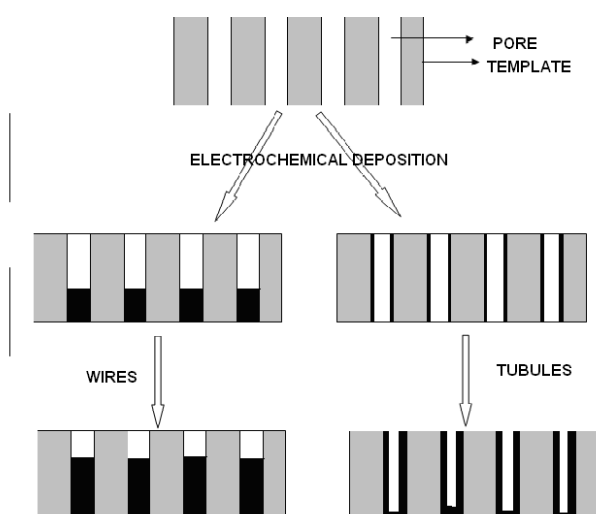


Fig. 6. The block diagram of the electrochemical deposition showing the two different ways of the pore filling.

3.3. Optical characterization

Fig. 7 shows the UV-Visible absorption spectra of the samples. The fundamental absorption, which corresponds to the transition from the valence band to the conduction band, can be used to determine the band gap of the material. The absorption coefficient (α) is determined from the absorbance versus wavelength (λ) traces recorded for the microstructures. The optical band gap (E_g) in a semiconductor is determined by assuming the nature of transition (m) and plotting $(\alpha h\nu)^{1/m}$ versus $h\nu$, where m represents the nature of transition. Now, m may have different values respectively $1/2$, 2, $3/2$ or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions [11]. For allowed direct transition $(\alpha h\nu)^2$ versus $h\nu$ has been plotted and the linear portion of it has been extrapolated to $\alpha = 0$ value to obtain the corresponding band gap ($E_g = 2.48$ eV) (inset of figure 7).

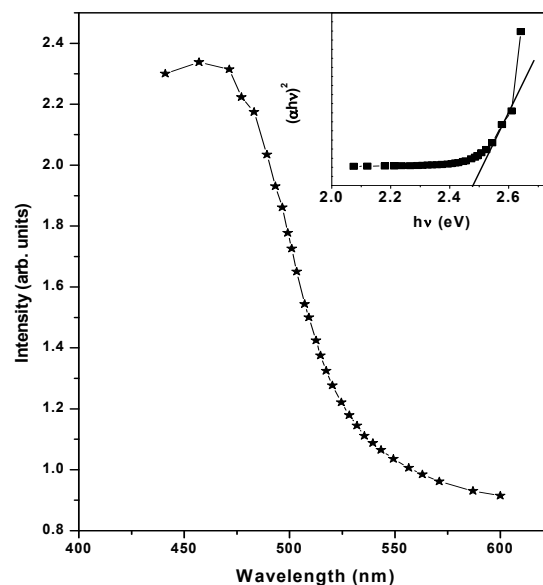


Fig. 7. UV-Visible absorption spectra of the CdS microstructures. Inset shows the plot of $(\alpha h\nu)^2$ versus $h\nu$.

Fig. 8 shows the room temperature photoluminescence (PL) spectra of the CdS microstructures, using an excitation wavelength of 400 nm (3.11 eV), which is well above the band gap (2.42 eV) value of the bulk CdS. The PL spectrum shows a broad band centered at ~ 508 nm (2.45 eV). This green colored, broad peak is attributed to the band-to-band emission [12, 13]. No deep-level defect emissions are observed. The absence of emission from trap states suggests the stoichiometric nature of CdS microstructures, without a surface excess of Cd^{2+} or S^{2-} vacancies [14].

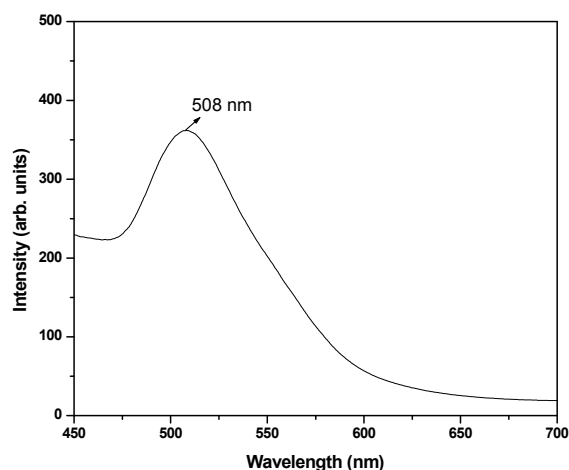


Fig. 8. Room temperature photoluminescence spectra of CdS microstructures using an excitation wavelength of 400 nm.

4. Conclusions

In summary, monodisperse CdS microwires/tubules have been synthesized in polycarbonate membranes using dc electrochemical template synthesis technique by controlling the deposition conditions. This method is cost-effective, simple and versatile, and can be extended to prepare nanowire arrays of many materials (i.e., metals and semiconductors), and preparation of many low-dimensional nanomaterials like, nanorings, nanotubes, nanowires, nanobelts. The PL emission of the CdS microstructures in the visible region (~ 508 nm, green emission) suggests potential applications in the field of light-emitting devices. Further studies on the fabrication of low-dimensional nanowires/tubules and their optical properties are being done.

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