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## STUDY OF ELECTROCHEMICAL PHOTOVOLTAIC SYSTEMS OF CADMIUM SELENIDE NANOTUBES

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**Abstract:** - In this paper we study electrochemical photovoltaic systems of CdSe nanotubes with a length of approximately 700 nm have been successfully grown by one-step electrochemical technique into anodic alumina membranes. Cyclovoltammetric method has been performed using porous anodic alumina as template electrode and an electrochemical bath containing  $\text{Cd}^{2+}$  ions and  $\text{SeO}_2$ . The as prepared nanotubes have been identified as face-centered-cubic CdSe by XRO, while micro-Raman analysis reveals the typical peaks of nanostructure CdSe. The stoichiometric deposition of CdSe nanotubes formation is suggested by EDX analysis, with an average atomic percentage of Cd:Se of approximately 0.93. Photoelectrochemical measurements reveal that CdSe nanotubes are photoactive materials with direct band gap of 1.75 eV.

**Keywords:** Electros deposition, stoichiometric deposition, photo electrochemical, cyclovoltammetric, PACS:- 78.67 Ch



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## 1. INTRODUCTION

At present, there are only a few papers reporting on the preparation and properties of CdSe nanotubes [1,2] and, as far as we know, there are no works on the electrochemical fabrication of hollow interior CdSe nanostructures.

In this work we tried to employ the cyclic voltammetric method recently proposed in [3] to prepare stoichiometric CdSe films for the fabrication of cadmium selenide nanotubes. At this aim, a porous alumina membrane with uniform pore size is employed as template. Once grown, the nanotubes were characterized by x-ray diffraction and Raman spectroscopy. Photo-electrochemical experiments were performed in order to estimate the band gap of the deposited materials.

## 2. EXPERIMENTAL:

Anodic alumina membranes with one side covered by a sputtered porous Au layer were used as electrodes for electrodeposition of CdSe nanotubes. During electrodeposition, Ti or Au foils were used as backing electrode at the bottom of Anodic alumina membrane template in order to guarantee a uniform electric current. A classic three electrode cell was employed, with a Pt wire used as counter electrode and a saturated Ag/AgCl as reference electrode.

The electrodeposition bath consisted of  $5 \times 10^{-3}$  M CdCl<sub>2</sub>,  $10^{-3}$  M SeO<sub>2</sub>, 0.5 M Na<sub>2</sub>SO<sub>4</sub>. We selected to keep Cd/Se ratio of 5/1 in order to allow a stoichiometric deposition of CdSe that can be favoured by an excess of Cd ions with respect to selenium [3]. The pH value was adjusted to 3 by adding 0.5M H<sub>2</sub>SO<sub>4</sub>. The polarization was performed by scanning the working electrode potential at 50mV/s in the cathodic direction between 0 and -1.2V (Ag/AgCl).

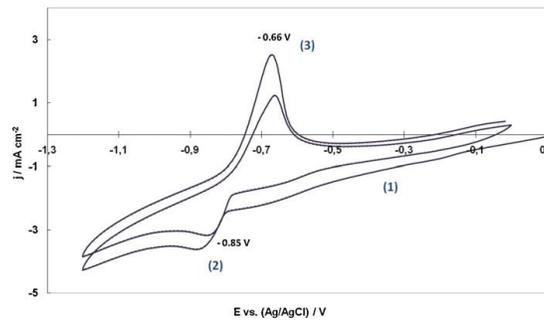
Morphology and quality of the nanotubes were investigated by using Scanning Electron Microscope coupled with EDX equipment. The Anodic alumina membranes/nanotubes electrodes have been sometimes chemically etched in 0.1 M NaOH for 8h in order to remove the alumina host, and successively washed in H<sub>2</sub>O and filtered, producing numerous pieces of random broken NTs arrays on the stub. XRD analysis was realized by a Philips X-Ray Generator and a PW goniometry. Micro Raman analysis were performed through a Renishaw in Via Raman Microscope spectrometer equipped with a microprobe and a CCD detector with a Nd : YAG laser of 532 nm.

The photoelectrochemical experiments were performed in 0.1 M ammonium baborate or 0.1M NaOH electrolyte using platinum wire as counter electrode and saturated Ag/AgCl as reference electrode.

### 3. RESULTS AND DISCUSSION

#### 3.1 Electrochemical Growth

In Fig. 1 we report the cyclic voltammograms (CV) relating to the electro deposition of CdSe nanotubes in to AAM template in Cd<sup>2+</sup> and Se<sup>2-</sup> containing solution. The CV curves were recorded by scanning the electrode potential at 50mV/s from the open circuit value to -1.2V Vs Ag Agcl (forward) and then from -1.2 to 0V Vs Ag Agcl (reverse). During the forward negative-going scan a gradual increase in cathodic current was recorded up to -0.78V, revealing the occurrence of a cathodic process at the electrode. Afterward, a rapid increase occurs and a reduction peak at -0.85V appears. In the reverse positive-going scan, the presence of a main peak at -0.66 V Vs Ag/Agcl is revealed, followed by a very low current until 0V.

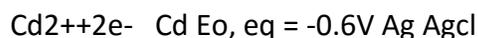


**Fig. 1 : CV curve relating to CdSe nanotubes electrodeposited into AAM from 5×10<sup>-3</sup> M CdCl<sub>2</sub>, 10<sup>-3</sup> M SeO<sub>2</sub>, 0.5M Na<sub>2</sub>SO<sub>4</sub> at pH=3, temperatures 25oC and potential scan of 50 m V/s**

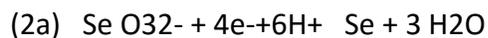
In order to understand the possible processes occurring during the CV, the possible reactions will be discussed through the analysis of the thermodynamic potentials calculated at 25oC and pH3 and 5×10<sup>-3</sup> M Cd<sup>2+</sup> and 10<sup>-3</sup> Se O<sub>2</sub> concentrations.

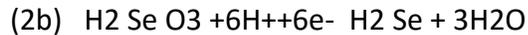
In the exploited potential window, in acidic solution where SeO<sub>2</sub>, is hydrolyzed to H<sub>2</sub> Se O<sub>3</sub>, and in presence of Cd<sup>2+</sup> ions, the following reactions can occur at the cathode.

Metallic Cd formation :

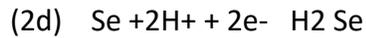


Se and H<sub>2</sub> Se formation :





$E_0, eq = 0\text{V Ag/AgCl}$  (assuming  $10^{-6}\text{MH}_2\text{Se}$ )

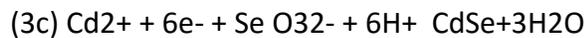
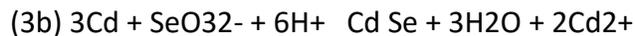
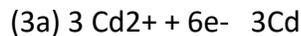


$E_0, eq = -0.95\text{ Ag/AgCl}$  (assuming  $10^{-6}\text{MH}_2\text{Se}$ )

Cd Se electrodeposition:

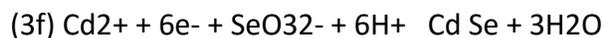
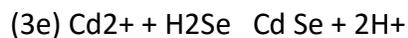
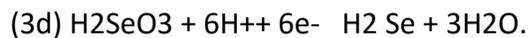
#### Mechanism I:

One of the most accepted mechanism for Cd Se cathodic formation was proposed by Tomkiewicz and involves a first step where  $\text{Cd}^{2+}$  ions were reduced to Cd metal followed by a second step where direct CdSe electrodeposition occurs through  $\text{SeO}_3^{2-}/\text{Se}^{2-}$  reduction process :



#### Mechanism II:

Another possible mechanism reported in the literature [4] involves the partial reduction of  $\text{SeO}_3^{2-}$  to  $\text{H}_2\text{Se}$  and subsequent chemical reaction to form Cd Se according to :



The formed  $\text{H}_2\text{Se}$  can be involved into two competitive reactions, one giving selenium (O) (2C) and the other the desired product, i.e. Cd Se (3e).

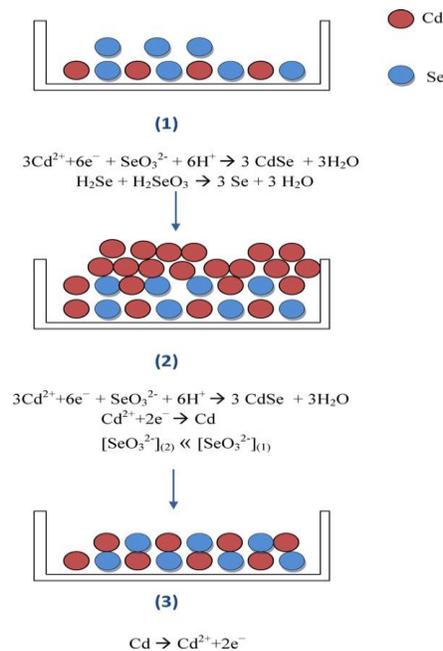
This initial look to possible reactions and equilibrium potentials evidences two common problems that typically characterize cathodic electrochemical deposition of Cd Se :

A great excess in Se (o) content, i.e. non-stoichiometric CdSe formation and

**Co-deposition of metallic cadmium.**

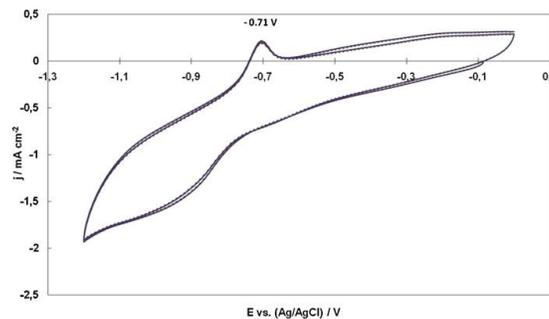
According to equilibrium potentials the reduction of Se(IV) directly to selenium [Eqn. (2a)] is strongly favoured, having Cd and Se extremely different standard electrode potentials. According to mechanism II, the excess of selenium in the deposit attributed to chemical reaction of H<sub>2</sub>Se with H<sub>2</sub>SeO<sub>3</sub> (2c) occurs in competition with the desposition of CdSe through reaction (3e). Thus, at low concentration of Se (IV), reaction (2c) is expected to be suppressed.

The use of cyclovoltammetric technique contributes to solve the problem of bulk cadmium and selenium formation in CdSe deposit, because allows to deposit sequential layers of CdSe by sweeping the potential of the substrate continuously in a solution containing Cd<sup>2+</sup> ions and SeO<sub>3</sub><sup>2-</sup>. Using a low Se/Cd atomic ratio (1/5) in the bulk of the electrolyte, only sub-monolayer of Se were formed by reduction of SeO<sub>2</sub> per cycle. During negative-going scan, the first formed species are Se and H<sub>2</sub>Se [reactions (2a) and (2b)] which will react with the excess of Cadmium to form CdSe, having CdSe a large negative free energy of formation [Fig.2, Scheme 1]. The great excess of cadmium deposited at the same time [Fig.2, Scheme 2] is subsequently stripped during the anodic scan [Fig. 2, Scheme 3]. By continuously cycling the working electrode potential, the deposition of stoichiometric 1:1 CdSe semiconductor becomes possible.



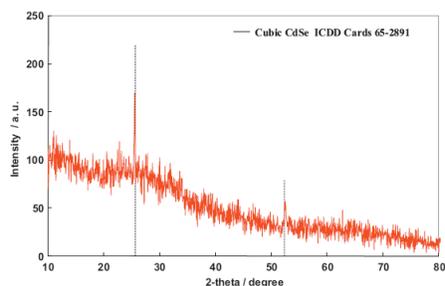
**Fig. 2. Scheme of the formation mechanism of CdSe into AAM pore through potential scan illustrated in Fig.1**

As reported in the literature [7], Cd Se can be deposited in a wide range of potentials [from – 0.7 to -0.9V Ag/AgCl] depending on substrate and electrolyte composition. Thus, the cathodic peak at -0.85 V Ag/AgCl it is expected to be associated to both the formation of Cd metal and Cd Se [Fig. 2 scheme 2]. XRD analysis confirms this assertion [Fig. 4.] Any Se and/or H<sub>2</sub>Se formed before will react with the excess of cadmium to form CdSe, having CdSe phase a large negative free energy of formation. At this stage the high depletion of SeO<sub>3</sub><sup>2-</sup> ions inhibits further selenium formation. By reversing the potential in the positive direction, the oxidative peak at -0.63 V Vs Ag/AgCl corresponds to excess Cd metal stripping, which leaves behind small quantity of

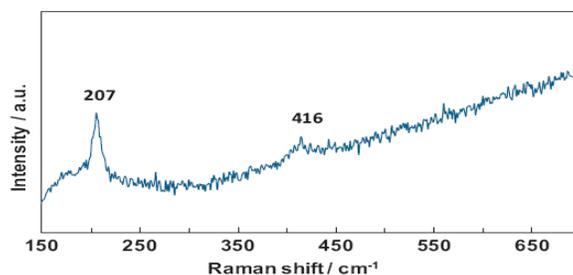


**Fig. 3. CV curve relating to Cd nanotubes electrodeposited into AAM from 5×10<sup>-3</sup> M CdCl<sub>2</sub>, , and 0.5M Na<sub>2</sub>SO<sub>4</sub> at pH=3, temperatures 25oC and potential scan of 50 m V/s**

Cd Se [Fig. 2, Scheme 3]. This is supported by the fact that such peak is similar to that obtained from a pure solution of Cd Cl<sub>2</sub> at the same concentration [Fig. 3]. In such figure it can be also noted that the cathodic peak related to Cd<sup>2+</sup> reduction is less pronounced than the one related to CdSe formation. By comparing the two CV curves [Figs. 1 and 3] it also appears that in Cd<sup>2+</sup> and SeO<sub>3</sub><sup>2-</sup> containing electrolytes the cathodic peak shifts towards more positive potentials by increasing the number of scans. This can be explained by a decrease in the energy required for cadmium reduction and CdSe formation on existing Cd/CdSe deposit in comparison to gold particles exposed to the solution at the beginning of electrodeposition. All these findings indicate that CdSe nanotubes can be successfully deposited scan by scan, i.e. layer by layer, as confirmed by XRD and Raman identification.



**Fig. 4. X-ray diffraction patterns of AAM/CdSe nanotubes electrodeposited  $5 \times 10^{-3}$  M CdCl<sub>2</sub>,  $10^{-3}$  M SeO<sub>2</sub>, 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH=3, temperature 25oC and potential scan of 50mV/s.**



**Fig. 5. Micro-Raman analysis performed on CdSe nanotubes after AAM template removal prepared by electrodeposition in  $5 \times 10^{-3}$  M CdCl<sub>2</sub>,  $10^{-3}$  M SeO<sub>2</sub>, 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH=3, temperature 25oC and potential scan of 50mV/s.**

## 3.2. STRUCTURAL CHARACTERIZATION

### 3.2.1 XRD ANALYSIS:

X-ray diffractometry was employed to evaluate the phase structure and crystal orientation of the cadmium selenide nanodeposits inside alumina membranes. In Fig. 4 we report typical X-ray diffraction pattern of CdSe nanotubes embedded in AAM template. The two main X-ray diffraction peaks recorded in the diffractogram can be indexed as fcc CdSe with peak positions that agree very well with those of fcc structure.

The absence of (103) and (102) peaks of the hexagonal phase at about 48o and 37o gives a further indication of this cubic structure. Furthermore, no peaks of other materials appear in the diffraction pattern, confirming the quality of the formed nanotubes.

### 3.2.2. RAMAN ANALYSIS.

Micro-Raman analysis of CdSe nanotubes after removal of alumina template is reported in Fig. 5. The revealed Raman peaks are commonly reported in the literature for Cd e. The most prominent mode at 207 cm<sup>-1</sup> can be attributed to the first-order CdSe longitudinal optical phonon and the mode at 416 cm<sup>-1</sup> to its overtone mode. The red shift of the longitudinal optical peak from its position for bulk CdSe crystals reported at 210 cm<sup>-1</sup> can be related to spatial confinement of phonons usually reported for CdSe nanocrystals with sizes below 10 nm [5-7]. The value of 207 cm<sup>-1</sup> fits very well with the value of 207.5 cm<sup>-1</sup> reported for CdSe nanotubes prepared through surfactant- assisted synthesis [2]. In such paper the diameter of the nanoparticles has been estimated through the phonon confinement model to be 5.7 nm.

### 3.2.3 PHOTOELECTROCHEMICAL RESULTS:

In order to get information on the band gap of the deposited material a photoelectrochemical characterization of as prepared CdSe nanotubes embedded in the AAM template was performed. The electrodes were immersed soon after the deposition in aqueous solution, more specifically in 0.1M ABE (pH 8.5) and 0.1M NaOH (pH and characterized at the open circuit potential. In Fig. 6. we report the raw photocurrent spectrum relating to CdSe nanotubes embedded in the AAM template, recorded by polarizing the as prepared electrode in 0.1M ABE at 0.0V Vs (Ag/AgCl). The optical band gap of CdSe nanotubes is estimated according to the following equation.

$$(I_{ph}h\nu) (h\nu - E_{gopt})n/2$$

With n = 1 or n=4 for direct and indirect optical transitions respectively. I<sub>ph</sub> is the photocurrent yield, proportional to the light absorption coefficient, hν is the photon energy.

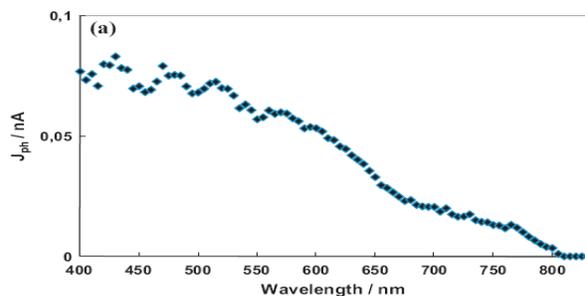


Fig. 6. (a) Raw photocurrent spectrum relating to CdSe nanotubes into AAM/Au electrode recorded at +0.003V (Ag/AgCl) in 0.1 M ABE solution.

#### 4. CONCLUSIONS:

CdSe nanotubes were successfully prepared via a template assisted one-step electrochemical process. The typical difficulties arising during the cathodic deposition of CdSe, such as a great excess of Se content in the material, i.e. non-stoichiometric CdSe formation and Co-deposition of metallic cadmium, were overcome by using a Cd<sup>2+</sup> concentration much higher than that of Se O<sub>2</sub> and by employing a cyclic voltammetric technique.

According to the experimental results coming from Raman spectroscopy and EDX compositional measurements, by scanning the potential between 0 and -1.2V (Ag/AgCl) for 100 cycles, 1/1 stoichiometric and well- aligned Cd Se nanotubes 700 nm in length were easily grown. X-ray diffraction revealed that such nanotubes are crystalline with a cubic structure.

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