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ABSORPTION AND PHOTOLUMINESCENCE PROPERTIES OF CdS:Mn^{2+}: Cu^{+} NANOSTRUCTURES

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A layer of doped CdS nanocrystals was deposited on the surfaces of nanopores of polyethyleneterephtalate (PET) membranes. Optical absorption measurements were used to determine the bandgaps of the nanocrystals; CdS:Mn^{2+} and CdS:Mn^{2+}:Cu^{+} show a blue and red shift, respectively, relative to the band gap of nanostructurated CdS. Photoluminescence spectra of the doped and undoped CdS samples exhibit wide bands covering the visible spectrum range.

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1. Introduction

The increasing interest in nanotechnology in the last decade is given by the extraordinary wide field of possible applications starting from electronics and communications including computer technologies and ranging to life sciences and biotechnology. Nanostructurated semiconductors show properties different from the bulk ones, properties induced by their size and their large surface bulk ratio. The exploitation of these size induced properties opens up new fields for applications and promises a revolution in the fields of electronics, optoelectronics and spintronics [1].

From another point of view the doping of semiconductor materials with various transitional elements such as Mn or Co became a hot topic in the last few years due to numerous possible applications of these magnetic diluted semiconductors, thus, becoming one of the most important research directions of the field of spintronics [2, 3].

The template method which was employed in the present work was successfully used previously in the preparation of metallic [4], semimetallic [5] and semiconductor nanostructures [6,7].

In this paper we present a study of the optical properties of doped CdS nanostructures chemically prepared into nanopores of PET membranes.

2. Experimental

Polymer foils (PET, 19 μm thick) were irradiated with swift heavy ions (e.g. Au with 11.4 MeV/nucleon specific energy). Each ion passing through the polymer foil produces a change in the physical and chemical properties along its trajectory, forming a cilindrical latent ion track. By employing a suitable etchant the latent ion track can be selectively etched and thus nanopores can be obtained. The shape and size of the pores depend on the etching bath composition and temperature. For the present study cylindrical pores with different diameters were prepared. The etching solution was 2M NaOH at a temperature of 50 °C.

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The porous membranes used for the nanocrystals synthesis had pore diameters of 160 nm and 320 nm and a density of pores (given by the heavy ion fluence) of 10^8 cm^{-2}. The membranes were inserted between the two chambers of a deposition device which allows their simultaneous exposure to the two components of the synthesis solution: from one side the sulphur source and from the other the metallic ions source.

The synthesis solutions have the following compositions:

- the sulphur source: 0.1M sodium citrate and 14g/l thioacetamide
- the metal ions sources:

a) CdS crystallites: 0.03M $CdCl_2{\cdot}2H_2O$, 0.1M sodium citrate , PH 8.5

b) $CdS:Mn^{2+}$ crystallites: 0.03M $CdCl_2{\cdot}$ $2H_2O$, 0.005M $MnCl_2$ $\cdot42H_2O$, 0.1M sodium citrate, PH 8.5

c) $CdS:Mn^{2+}:Cu^{+}$ crystallites: 0.03M $CdCl_2$ $2H_2O$, 0.005M $MnCl_2$ $\cdot42H_2O$, 0.001M CuCl, 0.006% triethanolamine, 0.1M sodium citrate , PH 8.

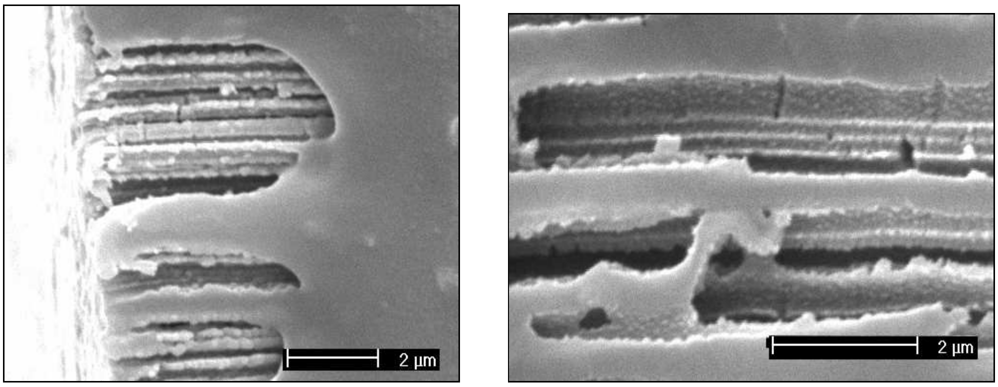
The membranes were left in the synthesis cell for 30 minutes then washed with distilled water and dried at 30°C.

Scanning electron microscopy was employed for imaging the structures. A cross section of the membranes was obtained by cutting the foils parallel with the direction of the pores.

UV-vis transmission spectroscopy and photoluminescence measurements were performed on the polymer foils containing the nanocrystals. A Perkin Elmer UV-vis spectrometer model Lambda 25 and a home build photoluminescence setup were employed for the optical measurements. The electron paramagnetic resonance spectra were recorded with a MiniScope spectrograph.

3. Results and discussion

In Fig.1 images of nanostructures obtained in porous membranes by chemical deposition are presented. A layer of pure or doped Cds nanocrystals grow on the nanopores surface.



(a) (b)

Fig.1. CdS (a) and $CdS:Mn^{2+}$ (b) nanostructures deposited on the walls of PET porous membranes with pore diameter of 320 nm.

The influence of the pore size on the structures bandgap was explored by measuring the absorption spectra of CdS structures deposited inside membranes with pore size 160 and 320 nm respectively. The absorption spectra are presented in Fig.2.

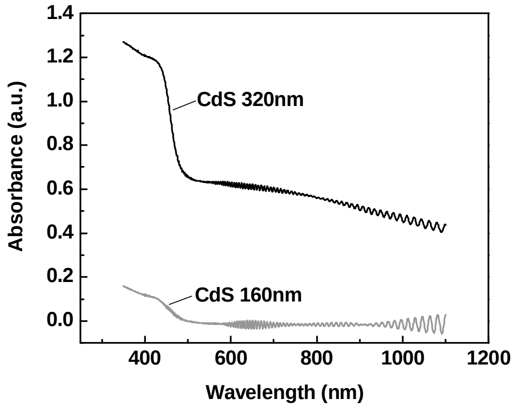


Fig. 2. Absorption spectra of CdS prepared inside of membranes with different pore diameters.

In Fig.3 the absorption spectra of pure and doped CdS structures obtained in membranes with pore diameters of 320 nm are presented.

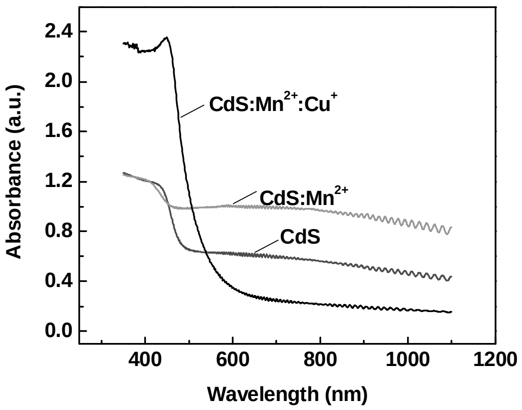


Fig. 3. Absorption spectra of PET membranes containing CdS and doped CdS nanostructures obtained in 320 nm diameter pores.

The absorption spectra allowed us to determine the bandgap of CdS, CdS:Mn^{2+} and CdS:Mn^{2+}:Cu^{+} (Table 1) using the relation $\alpha h\nu \sim (h\nu - E_g)^{1/2}$, where α is the absorption coefficient, E_g is the width of the bandgap and ν is the absorbed light frequency.

Table 1. The bandgap value for pure and doped CdS nanocrystals determined from the absorption spectra

Material	Pore diameter (nm)	E_g (eV)
CdS	160	2.62
CdS	320	2.57
CdS:Mn^{2+}	320	2.61
CdS:Mn^{2+}:Cu^{+}	320	2.48

One can see from Table 1 that the bandgap of CdS and doped CdS nanostructures is shifted towards blue when compared with a bulk CdS crystal (E_g=2.42 eV). We consider that nanocrystals dimension is responsible for this shift. Based on data presented in literature [8, 9] we estimate the size of the crystallites at about 10 nm. One can also observe that for smaller pore diameters a stronger shift is produced, meaning smaller crystallites. We think that there are several mechanisms through which the pore diameter can influence the particles dimension: the curvature radius of the pore inner surface and the reactants diffusion into the pore.

Doping with Mn ions induced a small additional blue shift, also observed in bulk crystals [10] while doping with Cu ions causes a red shift, with respect to nanostructurated pure CdS.

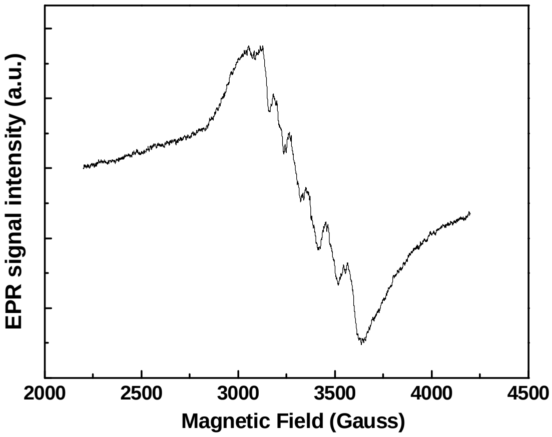


Fig. 4. EPR spectra of CdS: Mn^{2+}:Cu^{+} nanocrystallites.

Electron paramagnetic resonance measurements were also employed to characterize the doped compound CdS:Mn^{2+}:Cu^{+} (Fig.4).
In the case of Mn^{2+} ions the results are interpreted using the spin Hamiltonian:

$$\mathrm{H}_s = g\mu_B \vec{H}\vec{s} + A\vec{I}\vec{s} + D[s_z{}^2 - \frac{1}{3}s(s+1)]$$

where g is the Lande factor, μ_B is the Bohr magneton, $\vec{H}$ is the applied magnetic field, s is the electronic spin component, I is the nuclear spin component, A is the hyperfine split constant and D is the crystal field split parameter.

The spectrum obtained for the CdS:Mn^{2+} contains a series of sharp lines superimposed on a wide band. The wide band is centered at g=2 and presents a band width of 590G. The six superimposed lines represent the hyperfine structure specific to Mn^{2+} with a splitting constant of A=91G. The splitting parameter in crystalline field was evaluated at D=120G. The lines in the hyperfine structure contain a shoulder which is consequence of the existence of a forbidden transition relaxed by the disorder in the case of Mn^{2+} complexes. Comparing our results with literature data [11, 12] we found a Mn-Mn distance to be about 4Å.

Fundamental absorption is given by the width of the bandgap. In the domain where the material is transparent the Mn^{2+} complexes present absorption bands with the position determined by the type of symmetry and the degree of covalence. The absorption specific to the Mn^{2+} dopant, due to the transition from the fundamental level $^6A_1$ on the excited states is very weak being forbidden by the spin selection rule. In this case we used the photoluminescence excitation spectrum which presents the emitted light intensity as a function of the wavelength of the exciting light. The excitation spectrum for CdS:Mn^{2+} is plotted in Fig.5 and the observed excitation bands are employed for calculating of the corresponding Mn energy levels in CdS nanocrystals.

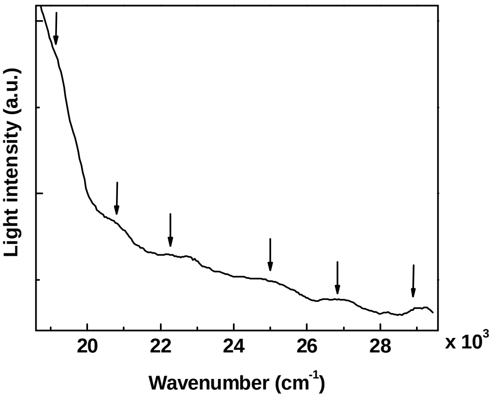


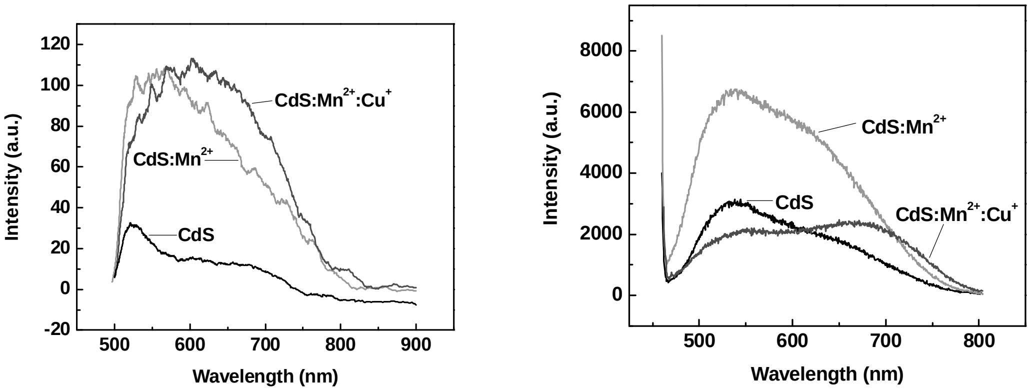
Fig. 5. Excitation spectra for CdS:Mn^{2+}:Cu^{+} obtained for the emission band at 580 nm; Arrows denote the position of the Mn energy levels

To determine the crystalline field parameter, D_q, energy diagrams can be calculated with a set of parameters B and C, choosing the value closest to experimental data (absorption maxima or zero phonon line). The calculation of the energy levels was performed in the strong field approximation (Tanabe-Sugano) by resolving the order 3 determinants for T levels and second order determinants for E levels. The results of the calculations are presented in Table 2.

Table 2. Observed and calculated data for the Mn energy levels (cm^{-1}) in CdS nanocrystals

Material	Ref.	$^4T_1{}^1$	$^4T_2{}^1$	$^4E^aA$	$^4T_2{}^2$	$^4E^b$	$^4T_1{}^2$
CdS nanocrystals	Observed	19 000	20 800	22 200	25 000	26 900	28 800
	Calculated	18 674	20 835	21 725	25 150	26 205	28 574

Photoluminescence spectra were obtained exciting the material in two modes: at λ=436 nm by using a monochromator and at λ=457.9 nm by using an Ar laser. The spectral distribution of the emitted light is presented in Fig.6.



(a) (b)

Fig. 6. Photoluminescence spectra of CdS and doped CdS nanostructures: (a) excitation with λ=436 nm light using a xenon lamp and monochromator and (b) excitation with λ=457.9 nm using an Ar laser.

Light emission observed in the two excitation modes is similar in shape in the spectral range 500 to 800 nm and presents wide features with the intensity ratio depending on doping. In the case of pure CdS the observed green emission centered at 525 nm is due to near band-to-band transition, a wide red band with a maximum at 650 nm due to defect related emission being also observed. For the nanostructures of CdS:Mn^{2+} the emission shows an intensity increase in the range of wavelengths centered at 580 nm; this emission is superimposed on the emission spectrum of the pure material [13, 14]. The introduction of the second dopant, the Cu^{+} ion produces a supplementary emission band centered at 680 nm. In the case of laser excited luminescence one can notice an overall intensity decrease of the emission when compared with the one obtained in the experiment with the monochromator which can be attributed to the width $\Delta\lambda$ of the exciting radiation. In this experiment the monochromator allows a bandwidth of $\Delta\lambda$=10nm which excites carriers to both the levels of the host material and of dopants. In the case of laser excitation the number of excited levels is reduced and a resonant transfer occurs, partially quenching the emission of the green region of the spectrum.

The analysis of the emission spectra can individualize the contribution of the host lattice and of the dopants. In the case of the pure CdS nanostructures, the emission centered at 525 nm is attributed to near band to band transitions (excitonic levels) and has a large bandwidth (of about 500 cm^{-1}). The wide emission peak centered at 650 nm is attributed to transitions from levels situated in the bandgap related to surface and bulk defects. For the case of doped CdS nanostructures the emission at 580 nm is due to the Mn^{2+} ions and from the last excited level $^4T_1{}^1$ on the fundamental level $^6A_1$. The excitation is produced indirectly on the excitonic band and the emission takes place by recombination on the Mn^{2+} centers. The 680 nm component of the emission spectra is related to self trapped excitons resulting from Cu^{+} ions excitation. A possible energetic transfer from the CdS levels onto Cu^{+} levels is relevant in the laser excitation experiment where a decrease in the green emission was observed coupled with an increase in intensity for the red band centered at 680 nm.

4. Conclusions

Using a special experimental arrangement a layer of pure and doped CdS nanocrystals were prepared inside the pores of PET ion track membranes.

Optical absorption data for these nanostructures showed a variation of the bandgap value as a function of both the pore size and doping. In all nanostructures a blue shift was observed when compared with the data for bulk materials. When compared to pure CdS structures the doping with Mn^{2+} ions causes a blue shift while doping with Cu^{+} induces a red shift in the absorption of the doped CdS.

Photoluminescence data showed that the CdS structures present a near band-to-band excitonic luminescence and a defect related band with longer wavelength. Doping influences strongly the position and intensity of the luminescence bands.

The excitation spectrum of Mn doped samples were used for determining the energy levels structure for this impurity.

Electron paramagnetic resonance measurements showed also the specific values for manganese, the existence of a disorder in the case of Mn^{2+} complexes being noticed.

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