Synthesis and EPR study of manganese-doped CdS nanoparticles

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Introduction

Mainstream - search for new methods of nanoparticles fabrication for combined electro-optical and spintronics applications

Focus - CdS-based nano-composites

Goal - testing of the new fabrication method of light-emitting nano-composite doped with magnetic ions

Composite - CdSMn/polyvinyl alcohol

Nano-CdS

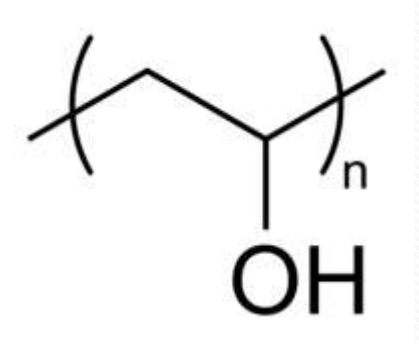
- light emission in the visible range;
- size-dependent color.

Prospective applications:

- light-emitting devices;
- luminescent med- and bio-markers.

PVA $(C_2H_4O)_x$

- cheap;
- flexible;
- transparent;
- biodegradable.



Applications:

- from textile and metallurgical industries to medicine and food industry.

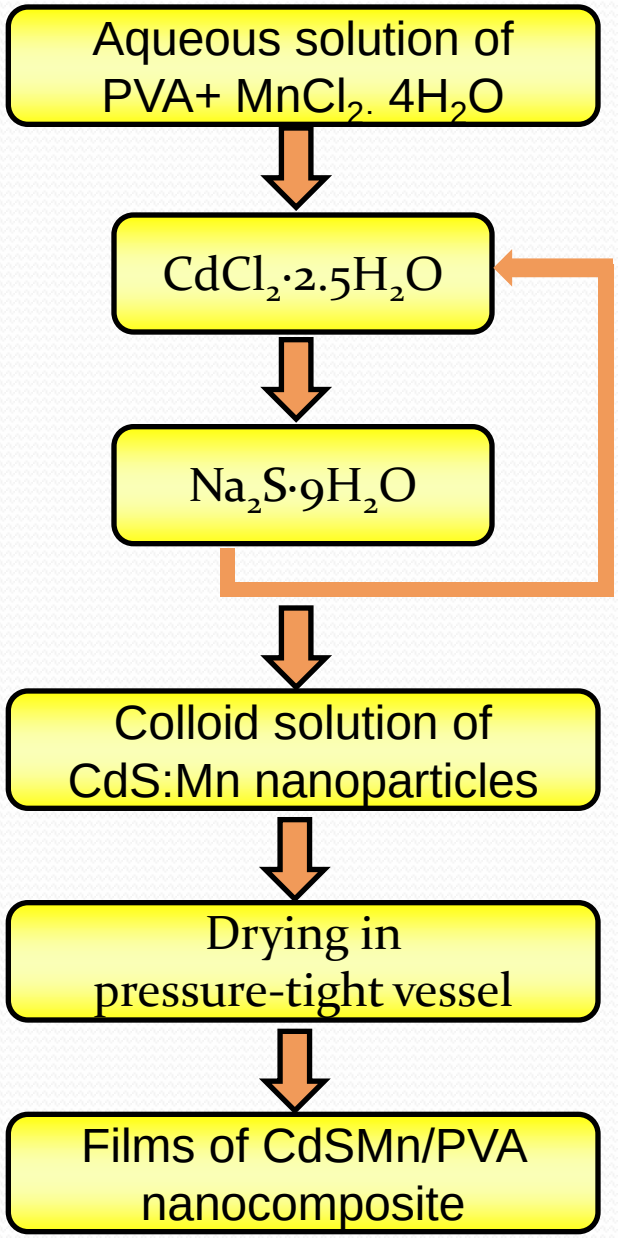
Mn

- adds magnetic properties;
- changes light emission.

Prospective applications:

- combined light-emitting and spintronic devices.

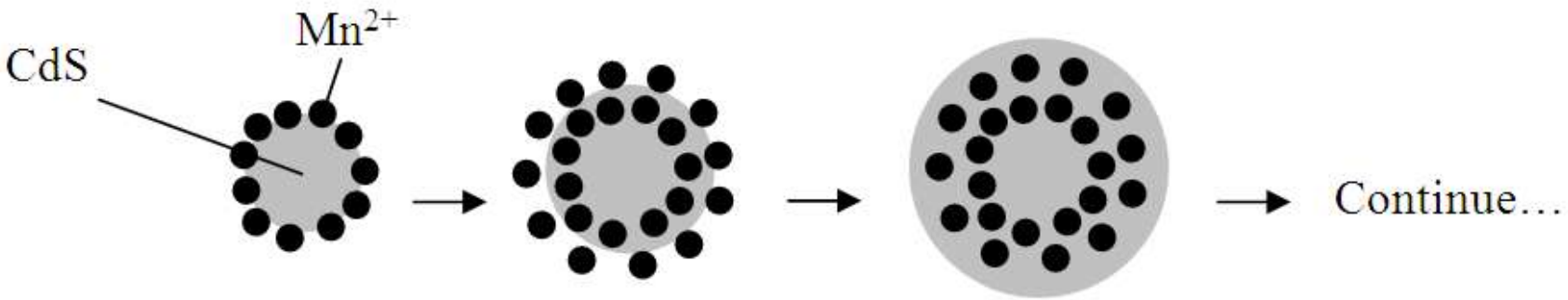
Details of nanocomposite fabrication



- aqueous solution
- ambient conditions
- capping agent - polyvinyl alcohol (PVA)
- precursors - $CdCl_2$, $MnCl_2$, Na_2S.
- Mn^{2+} precursor 10^{-3} – 10^{-1} mol/l

NPs sizes - 5-25 nm

Scheme of paramagnetic impurity incorporation into nanoparticles by adsorption



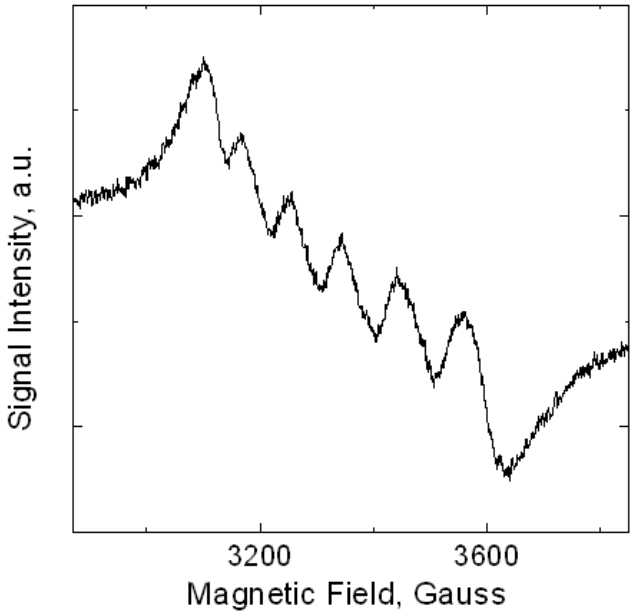
Incorporation of paramagnetic impurity into nanoparticles was done by adsorptive doping method in order to avoid dopant exclusion from a seed that has been previously suggested to be a general phenomenon [e.g.,1,2]

[1] N.S. Norberg et al. J.Am. Chem. Soc. 128 (2006) 13195 .
[2] J.D.Bryan et al. J.Nanosci. Nanotechnol. 5 (2005)1472.

EPR results

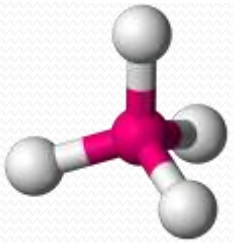
1 Six characteristic Mn lines - due to hyperfine interactions.

(These lines are attributed to $\Delta M_I = 0$ and $\Delta M_s = +/-1$ allowed transitions of the Mn^{2+} ions with I=5/2).



HF interaction constant value:

70 G – Mn in bulk of CdS



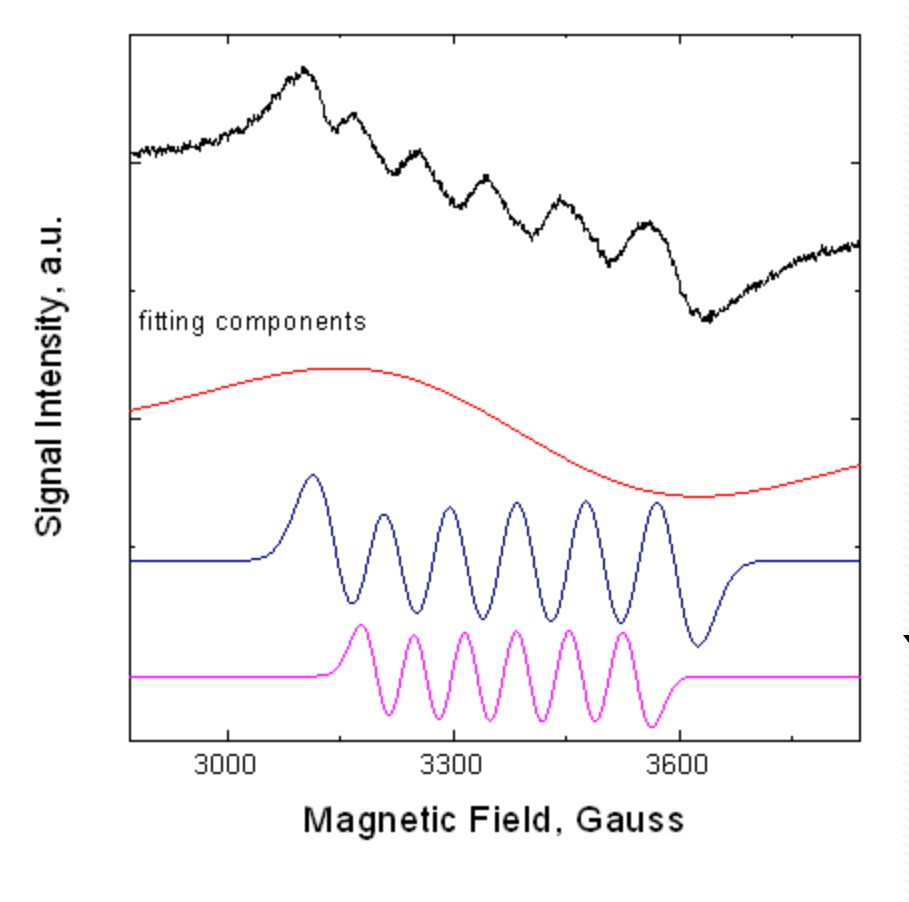
tetrahedral coordination

90 G – for Mn near-surface

octahedral coordination

2 Broad feature related to Mn-Mn interactions

Fitting components

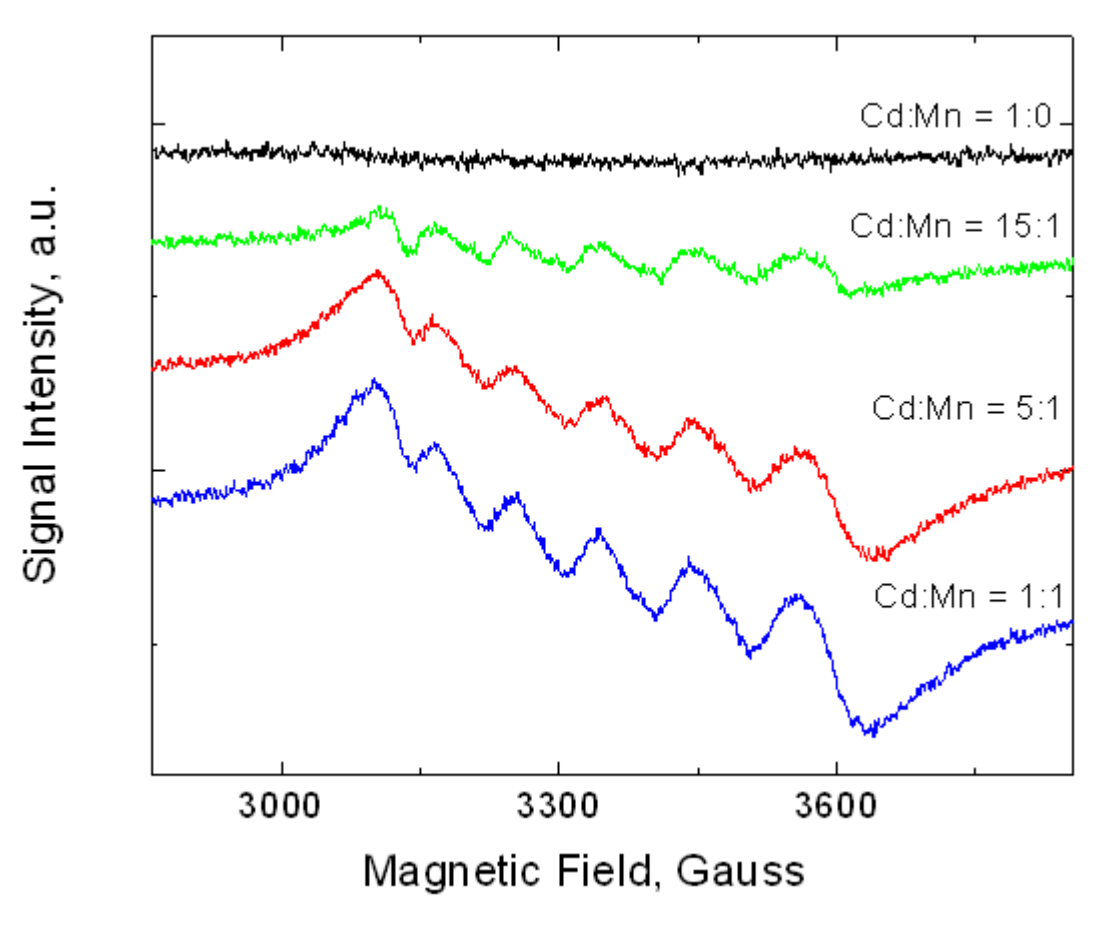


Mn-Mn interaction

Mn^{2+}-ions located in near-surface positions

Mn^{2+}-ions located in a bulk

EPR spectra of CdS:Mn/PVA nanocomposites



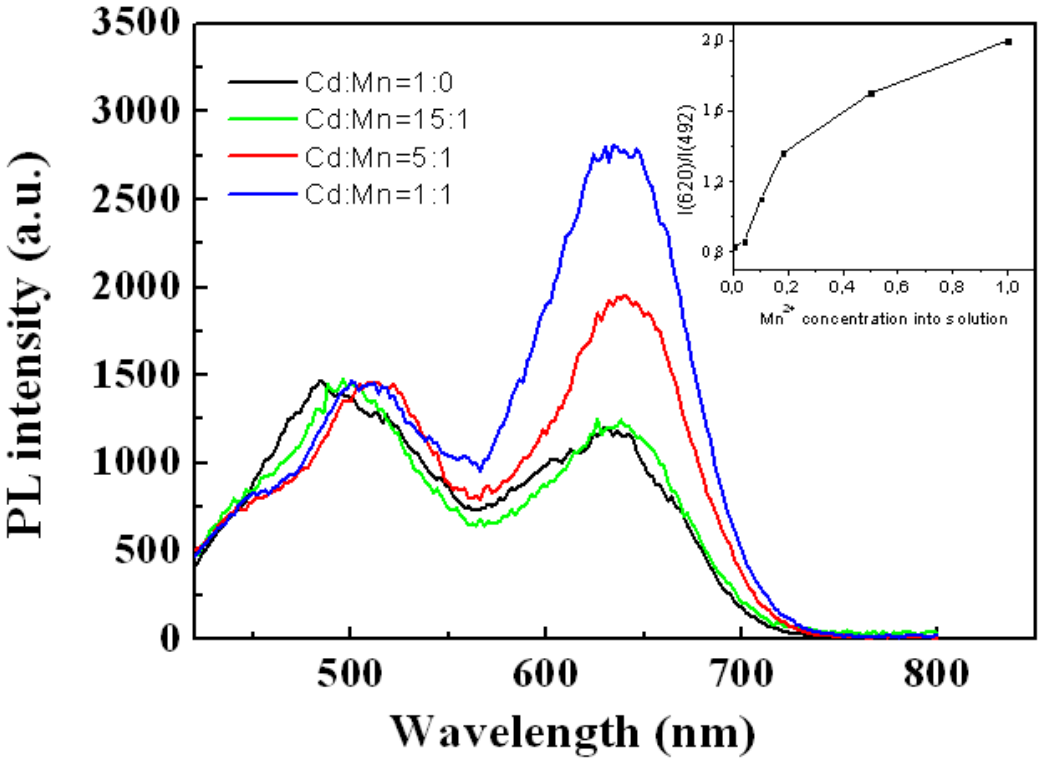
Mn^{2+} concentration increase ➡

- the ratio Mn(bulk)/Mn(near-surface)≈constant
- Mn-Mn interaction increases

EPR shows that both bulk and near-surface Mn^{2+} ions are present in nanocomposite

Photoluminescence spectra of CdSMn/PVA nanocomposites

1) Weak wing at ~ 450 nm - residual emission of the PVA matrix
2) The short wavelength band at ~ 510 nm - transitions involving shallow traps
3) Band at ~ 640 nm is a superposition of 2 bands related to surface traps in CdS and Mn-related radiative transitions [3]



Excitation - 375 nm,
T = 4.2 K.

[3] R. Beaulac et al. J. Sol. St. Chem.181 (2008) 1582

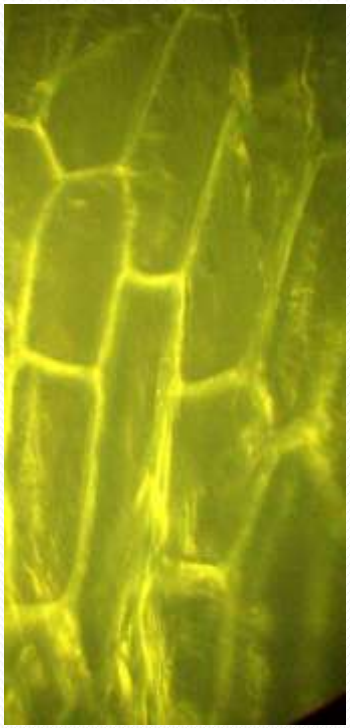
Conclusions

- Nanocomposite consisting of semiconductor $Cd_{1-x}Mn_xS$ nanoparticles embedded in polymer (PVA) matrix is fabricated;
- Introduction of paramagnetic impurity was done by new adsorptive doping method;
- EPR results shows that Mn^{2+} is incorporated both in the bulk nanoparticle and on its surface
-Bright photoluminescence of nanocomposite is observed. The spectra reveal the bands related to the radiation of Mn^{2+} ions in CdS

Thank you for the attention!

Applications in biological studies

The nanoparticles obtained can be used as fluorescent labels for investigations of the shape of certain plant cells.



The example of such application –

the photo of onion cell colored with CdS nanoparticles in fluorescent microscope.

Motivation

CdS nanoparticles –

- show unique chemical and optical properties,
- potential applications in the fields of nonlinear optics, luminescence, electronics, and optoelectronics.

The doping of nanoparticles with magnetic impurities could open new possibilities to combine new optical and magnetic properties;
however, magnetic dopant exclusion from the particles has been supposed to be a general trend

Goal

To elaborate a new method of growth of Mn2+-doped CdS nanocrystals