



Spin Active Excitonic States in Mn Doped CdSe Nanolayers

Satchidananda Rath*, O. Halder, D K Swain

Department of Chemistry, Indian Institute of Technology Bhubaneswar, Odisha, India

ABSTRACT

Insertion of spin degrees of freedom in the semiconductor by doping of transition metal, activates a long range magnetic ordering suitable for spin-photonics and carrier-induced magnetism applications. The spin dominated optical properties in manganese doped cadmium selenide ultra-thin (thickness~1.5 nm) layered nanosheets are demonstrated. Our studies reveal the presence of magnetic ordering up to 48 K and co-existence of the multivalency Mn based local structures corroborated to the x-ray absorption near-edge structure and Raman scattering measurements. The room temperature based optical absorption and Photoluminescence (PL) measurements affirm the emissions corresponding the band edge and dopant level mediated transitions. The circularly polarized magneto-PL studies at cryogenic temperatures demonstrate the spin allowed radiative transitions confirming the presence of spin-active excitonic states leads to white light emission.

Keywords: Magnetism; Spin-photonics; Raman scattering; Polarized magneto-PL

INTRODUCTION

The two-dimensional (2D) semiconductors and doping effect in its layered structures are an active domain of research to offer advanced optical, conductive and magnetic properties as a prospect of new generation device applications. Simultaneously, no effective methods of enhancing the sensitivity of these materials with reference to the external field has been established so far. Skillful doping of transition metal ions in nanostructures alter their spin degrees of freedom with promising giant zeeman splitting, magneto-optical and fast spin-lattice dynamics. For instance, it activates a long range magnetic ordering crucial for spin-photonics, spintronics and carrier-induced magnetism [1]. Moreover, the reports on doping Manganese (Mn) ions are currently establishing the coexistence of Mn²⁺/Mn³⁺ states leading to various interactions and spin-allowed transitions. In particular to Mn doped bulk Cadmium Selenide ((Cd, Mn) Se),

antiferromagnetism is stereotype due to the short range d-d interactions. However, the calculations predict hole-induced long range Ferromagnetism (FM) from nanocluster state or co-doping. Besides this, M. Sawicki et al., G. L. Gutsev et al. and J. Yang expressed intriguing magnetic states and related spin-active optical properties depending upon the concentration and ionic co-ordinations of the dopant. Similarly, the optical studies of a very low Mn doped CdSe/ZnSe core-shell quantum dots predicts insignificant role of an individual Mn²⁺ on the properties of host lattice [2]. Nevertheless, studies on different quantum structures report on quenching and shifting of optical properties with the Mn²⁺ state. Despite of the low solubility, several groups have initiated the Mn doping in various structure and composition regardless of the ordinary properties. However, the concerns over doping stabilization in multilayered nanostructures and its correlated properties originating from intra-layer and inter-layer connected electronic states are yet to be explored [3].

Received:	29-July-2020	Manuscript No:	IPNNR-24-5501
Editor assigned:	03-August-2020	PreQC No:	IPNNR-24-5501 (PQ)
Reviewed:	17-August-2020	QC No:	IPNNR-24-5501
Revised:	02-September-2024	Manuscript No:	IPNNR-24-5501
Published:	30-September-2024	DOI:	10.12769/IPNNR.24.8.21

Correspondence author: Satchidananda Rath, Department of Chemistry, Indian Institute of Technology Bhubaneswar, Odisha, India; E-mail: s.rath444@gmail.com

Citation: Rath S, Halder O, Swain DK (2024) Spin Active Excitonic States in Mn Doped CdSe Nanolayers. J Nanosci Nanotechnol Res. 8:21.

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In this work, we report on (i) the successful doping of Mn into the Cadmium Selenide (CdSe) multilayered nanosheets (LNSs) lattice using a solvothermal route, (ii) strain induced stabilization and co-existence of $\text{Mn}^{2+}/\text{Mn}^{3+}$ states leading to multi-phase magnetic ordering with sharp ferromagnetic ordering at temperature ~ 48 K, (iii) spin-polarized excitonic properties and (iv) fast spin permitted electronic transitions covering the visible realm at room temperature [4].

LITERATURE REVIEW

Synthesis method

Mn doped CdSe LNSs were synthesized *via* surfactant assisted solvothermal growth technique using Cadmium Chloride (CdCl_2), Selenium (Se) powder and Manganese Chloride (MnCl_2) as the source materials and octylamine as a surfactant. For the synthesis of (Cd, Mn) Se LNSs, the typical parameters comprising a 0.2750 g of CdCl_2 and 0.0013 g of MnCl_2 were mixed in a glass container containing 10 ml of octylamine under continuous stirring followed by the constant heating at 393 K for 2 hrs to achieve the Cd-Mn-octylamine complex. Similarly, a 0.0513 g of Selenium (Se) powder was added to the 10 ml of octylamine under vigorous stirring followed by the addition of CdMn-octylamine complex at constant temperature, 423 K for 24 hrs aiming the growth of the (Cd, Mn) Se LNSs. Then, the (Cd, Mn) Se LNSs were extracted by repeated washing with trioctylphosphine and ethanol [5].

Experimental

The samples were characterized by Transmission Electron Microscopy (TEM) using FEI, TF30 set up operated at 300 kV equipped with a GATAN orius CCD camera and Energy Dispersive X-Ray (EDX) facility as an attachment was used for the TEM analysis of the samples. For the TEM studies, samples were collected on the carbon coated copper grid. The X-ray Absorption Near Edge Structures (XANES) measurements at manganese K-edge were carried out at BL-9, scanning EXAFS beamline of INDUS-2, RRCAT Indore, India [6]. The measurements were done in a fluorescence mode using Vortex energy dispersive detector. The beamline consists of Rh/Pt coated meridional cylindrical mirror for collimation and a Si (111) Double Crystal Monochromator (DCM) to select excitation energy of Mn K-edge (6539 eV). The second crystal of the DCM is a sagittal cylinder which provides beam focused in horizontal direction. The inferences in the energy range -20 eV below to +20 eV above the Mn K-edge were obtained by utilizing the Linear Combination Fitting (LCF) protocol [7]. The vibrational properties of the samples were analyzed using HORIBA-T64000 micro-Raman spectrometer coupled with peltier cooled CCD detector having spectral resolution as 0.8 cm^{-1} in presence of a laser excitation of wavelength, 488 nm and power, 20 mW from argon-ion source focused to a 5 μm circular spot. The Raman spectra were collected in a back-scattering geometry.

The magnetic measurements of the (Cd, Mn) Se LNSs powdered sample were carried out using quantum design make Physical Properties Measurement System (PPMS). Room temperature based optical absorption measurements were done by dispersed in a chloroform using a UV-1800 UV-Vis Shimadzu spectrophotometer [8]. The background corrections were made using chloroform as the reference sample. For the Magneto-Photoluminescence (M-PL) spectroscopy, experimental conditions are the following: The M-PL is excited with a continuous wave 405 nm (3.06 eV) laser. The diameter of the laser spot on the sample surface is 0.1 mm and the excitation power density is of around 5 W/cm^2 . The sample is immersed in superfluid helium at temperature of ~ 2 K. The PL measurements are performed in the Faraday configuration ($\mathbf{B} \parallel \mathbf{k}$) in a cryostat equipped with a superconducting coil. The coil provides a magnetic field of up to 10 T. A peltier-cooled CCD camera coupled to a grating (1200 grooves/mm) monochromator serves as a detector (overall spectral resolution of the setup 0.12 meV). A long wavelength pass filter placed at the entrance of the monochromator cuts off the stray light of the laser. The X-Ray Powder Diffraction (XRD) measurements were carried out using the Bruker D8 Advance instrument [9]. The Electron Paramagnetic Resonance (EPR) studies were performed using Bruker EMX plus (ER 073), EPR instrument at low temperature regulated by continuous flow of liquid nitrogen. Here, the instrument optimization has been achieved at magnetic field, 3 tesla and frequency, 9.47 GHz. The time resolved photoluminescence was achieved using a Horiba Scientific system coupled with MCP-Hamamatsu photomultiplier detector, having time resolution 5 ps. An excitation laser source of wavelength, 379 nm and pulse rate ~ 200 ps was used for the measurements.

DISCUSSION

In order to understand the doping and nanolayer structure formation, the samples were characterized by the TEM and EDX measurements. The average gap between two consecutive nanolayers is found to be 1.28 nm. The lattice distance is estimated to be 3.3 Å corresponding to the hexagonal phase of the CdSe. From the EDX spectral analysis, the atomic percentage of the Cd, Se and Mn in the LNSs are estimated to be 45.23%, 49.35% and 5.40% respectively referring to the composition of $\text{Cd}_{0.9}\text{Mn}_{0.1}\text{Se}$. The additional Copper (Cu) and carbon line observed in the EDX may be from the carbon coated Cu grid as a substrate [10].

The crystallinity of the samples was verified using the XRD measurements. The XRD spectrum consists of crystallographic planes peaking at 2θ (in degree) as 23.80, 24.60, 25.29, 26.16, 32.14, 40.07 respectively. Comparing with standard data (JCPDS file # 77-2307), the 2θ peaks at 23.80 and 25.29 may be attributed to the hexagonal phase (100) and (002) plane of the CdSe. Moreover, as reported by R. Sharma et al., the 2θ peaks at 24.9 and 26.7 denote to the (100) and (002) plane of the hexagonal MnSe; and the peak at 32.5 originating from (200) plane represents the cubic (Cd, Mn) Se like phase [11].

Therefore, in our case, the diffraction 2θ peaks appearing at 24.60 and 26.17 and 32.14 may be the hexagonal and cubic phase of the MnSe respectively. The diffraction line appearing at 40.07 may be attributed to the MnSe₂ like phase. The lattice parameters, “a” (=b) and “c” of hexagonal phase MnSe present in our sample, have been estimated as 4.172 Å and 6.799 Å respectively. Interestingly, the c/a ratio is found to be 1.63 which is higher in comparison to the bulk MnSe (1.61). This eliminates the probability of acquiring individual Mn at the surface as a separate alloy like phase. Rather, it endorses the substitutional nature of the Mn ion along the c-axis of the hexagonal CdSe lattice [12].

CONCLUSION

Notably, the above crystallographic planes are observed to be broaden and shifted towards lower 2θ . This could be due to the lattice strain referred to quantum structures and doping effect. To infer the valence state of the Mn dopant, the XANES has been carried out. It shows the Mn K-edge XANES spectra of (Cd, Mn)Se LNSs along with the Mn²⁺ and Mn³⁺ as standard references represented by blue, black and red spectrum respectively. Using the Linear Combination Fitting (LCF) from athena software in the energy range 6540-6555 eV, the experimental curve is fitted. The Mn K-edge analysis reveals the coexistence of Mn²⁺ and Mn³⁺ states in the sample. Even though the Mn^{3+/2+} states are witnessed in Mn doped semiconductors, Mn²⁺ state is frequently reported (Mn ion substituting Cd and having Se neighbors) for Mn doped CdSe. Therefore, the observation of Mn³⁺ state in our case is exceptionally possible due to the favourable site specific Mn ion substitution by single or double or mixed Cd and Se neighbors interacting within the ultrathin 2D lattice.

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