# Effect of 8 MeV electron irradiation on the optical properties of PVP capped CdS nanoparticles in PVA matrix

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## Abstract

Results of the studies carried out on the effect of electron irradiation on the optical properties of polyvinyl pyrrolidone (PVP) capped cadmium sulphide (CdS) nanoparticles embedded in polyvinyl alcohol (PVA) matrix are reported. PVP capped CdS nanoparticles are prepared by a non-aqueous chemical method with cadmium nitrate as the cadmium source and hydrogen sulphide as the sulphur source. Synthesized nanoparticles are used for X-ray diffraction (XRD) studies that confirmed the formation of cubic CdS nanoparticles with an average size of $\sim$3–5 nm. The synthesized CdS nanopowder is dispersed in PVA matrix and self-standing flexible (PVP-CdS) PVA films of thickness 0.2 mm are obtained. The nanocomposites are subjected to optical absorption spectroscopy and photoluminescence (PL) studies. The PL emission spectra of the nanocomposites show two peaks, at 502 and 636 nm, which are attributed to the band edge and surface defects of CdS nanoparticles, respectively. The composite films are irradiated with 8 MeV electrons from a Microtron and optical absorption and PL studies are carried out on the irradiated samples. Irradiation of the samples leads to the quenching of surface defect-related emission.
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## 1. Introduction

II–VI group semiconductor nanomaterials are very important in the field of optics due to their strong size-dependent optical properties [1]. The inherently high surface-to-volume ratio of nanocrystals offers the possibility of a significant contribution of the surface states to act as centres for luminescent quenching and photo bleaching [2]. Wu et al. [3] reported the effects of various additives on the photoluminescence (PL) property of cadmium sulphide (CdS) nanoparticles. More effective surface passivation has been an important objective to reduce the detrimental effects of surface states on luminescent properties, which will lead to efficient and photostable luminescence. Inorganically passivated nanocrystals have been developed and shown to have dramatically enhanced luminescence

properties [2,4]. Surface passivation and corresponding increase in luminescence efficiency by ultraviolet (UV) irradiation of ZnS: Mn nanocrystals in polyvinyl alcohol (PVA) is reported [5]. The increase of PL emission was attributed to UV-stimulated increased polymerization and cross linking leading to more complete surface passivation. Josifovska et al. [6] reported the size and structure modification of semiconductor nanocrystals, while maintaining their stoichiometry, by pulsed laser irradiation of CdS nanocrystals. Shim et al. [7] reported that the optical properties of colloidal semiconductor nanoparticles are extremely sensitive to excess electrons and improved surface passivation or electron injection might lead to the fluorescence quenching of semiconductor nanoparticles by the injection of a single electron. Significant enhancement of PL efficiency in CdS nanocrystals has been observed when embedded in polymeric matrices, indicating improved electronic passivation of surface bond. There are reports on the synthesis of highly luminescent CdS

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nanocrystals with tunable band edge emission with oleic acid as the surfactant and incorporated in optically transparent polystyrene [8]. In this article, the results on the effect of 8 MeV electron beam irradiation on the optical absorption and the PL property of polyvinyl pyrrolidone (PVP) capped CdS nanoparticles embedded in PVA matrix are reported.

## 2. Experimental

Solution of cadmium nitrate at a concentration of 0.1 M is prepared in methanol and 0.5 g of PVP is added into it and stirred for ~10 min using a magnetic stirrer. $H_2S$ gas from a KIPP's apparatus is passed through Cd $(NO_3)_2$ solution for ~30 s. After 10 min methanol was removed using a rotary evaporator. PVP capped CdS powder obtained is washed several times with fresh methanol and air dried at room temperature. The PVP capped CdS nanoparticles are dispersed in 2 g wt% PVA solution in dimethyl formamide (DMF) at 70 °C with stirring. The solution is spread over a clean glass plate and air dried to get (PVP-CdS) PVA nanocomposite films of thickness ~0.2 mm.

A set of six samples is prepared by varying the concentration of $Cd^{2+}$ ion from 1.6 to 6.5 mM at a fixed PVP concentration of 0.5 g wt%. X-ray diffraction (XRD) studies were carried out for the PVP-CdS powder samples using BRUKER D8 Advance X-ray diffractometer with CuK$_\alpha$ radiation. The (PVP-CdS) PVA samples are irradiated with 8 MeV electron beam from a Microtron. Optical absorption and PL studies were carried out before and after electron irradiation using SHIMADZU 3101PC UV–vis–NIR spectrophotometer and JASCO-FP-6500 spectraflurometer, respectively.

## 3. Results and discussion

XRD were recorded for the PVP-CdS powder samples, before dispersing it in the PVA matrix. Fig. 1 is a typical XRD of PVP coated CdS nanoparticles prepared at a precursor concentration of 1.6 mM. The diffraction peaks at $2\theta = 27°$, $44°$ and $52°$ correspond to the cubic phase of CdS nanoparticles [9,10]. The mean crystallite size of CdS particles were estimated from the line broadening of the most intense peak for the cubic (1 1 1) reflection at $27°$ using Scherrer formula [11]. The particle size calculated from the X-ray line width is ~3±1 nm that agrees fairly well with the particle size of ~4±1 nm, determined from transmission electron microscopy (TEM) study of the samples prepared under the same conditions [12].

Optical absorption as a function of wavelength for the (PVP-CdS) PVA composite at various precursor concentrations is shown in Fig. 2. The absorption onsets are at shorter wavelengths than that for bulk CdS (520 nm) indicating that the CdS particles in the PVA matrix are in the nanometer regime [13] and this blueshift in the optical absorption edge increased with decrease in precursor
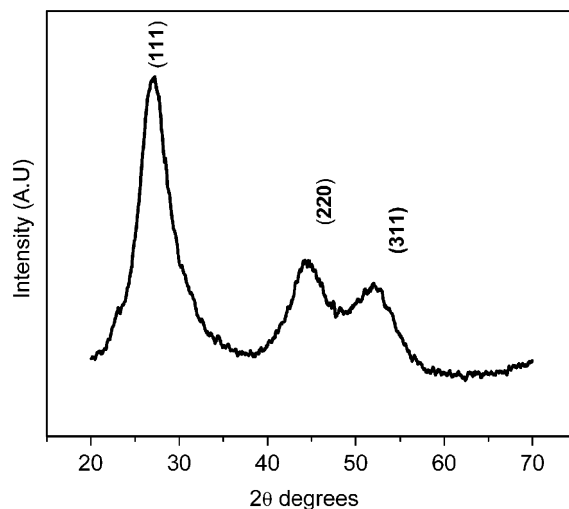


Fig. 1. X-ray diffractogram of PVP capped CdS nanocomposite at a typical Cd $(NO_3)_2$ concentration of 1.6 mM.
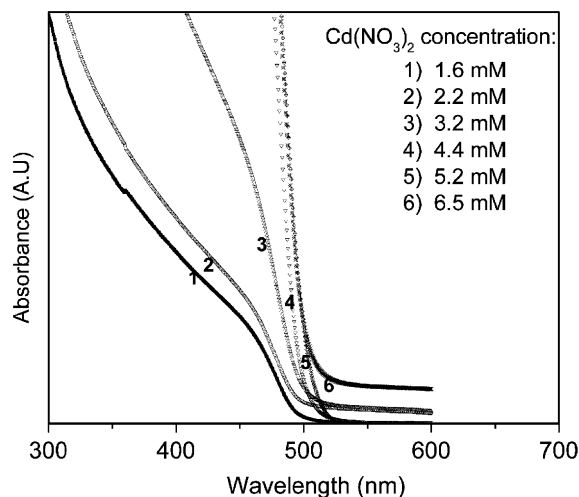


Fig. 2. Optical absorption spectra for (PVP-CdS) PVA composites at various Cd $(NO_3)_2$ concentrations.

concentration as can be seen from the figure. The two slopes in the absorption shoulder observed at lower concentrations can be due to an additional phase [14,15] or due to size inhomogeneity, phonon broadening and the presence of defects [10]. As the XRD showed only one phase, it may be due to the effects suggested by Wang et al. [10]. The band gap values were obtained from the optical absorption spectra by plotting $(h v \alpha)^2$ versus $(h v)$ and by extrapolating the straight-line plot to the energy axis. From the band gap values, the particle sizes were estimated using Brus equation [16]

$$E_{np} = E_g + \frac{\hbar^2 \pi^2}{2r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r r}, \qquad (1)$$

where $E_{np}$ is the band gap of the CdS nanoparticle, $E_g$ is the band gap of bulk CdS (2.42 eV), $m_e^*$ is the effective mass of electron (0.19 $m_e$ in CdS), $m_h^*$ is the effective mass