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## Investigation on mild condition preparation and structural, optical and thermal properties of PVP capped CdS nanoparticles

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### ABSTRACT

*Polyvinylpyrrolidone (PVP) capped cadmium sulphide (CdS) nanoparticles are synthesized using a simple hydrothermal method. The powder X-ray diffraction (XRD) result indicates that the nanoparticles are crystallized in hexagonal phase. The optical properties are characterized by Ultraviolet-Visible (UV-Vis) absorption and Photoluminescence (PL) spectra. The transmission electron microscope (TEM) reveals that the nanoparticles of CdS possess well defined morphology and high crystallinity. The d-spacing measured from well resolved lattice fringes of HRTEM ascertains the structure of CdS nanocrystals. The morphology and composition of CdS nanoparticles are investigated using Scanning electron microscope (SEM) and Energy dispersive x-ray analysis (EDAX) respectively. The thermal behavior of the as prepared nanopowder has been studied by Thermo gravimetric analysis (TGA).*

**Keywords:** Nanostructure; Chemical synthesis; Electron microscopy; Powder diffraction; Optical properties;

### INTRODUCTION

Recently, the synthesis of inorganic nanocrystals has attracted much interest due to their strong size dependent, special optical, electronic properties and potential applications in solar cells, light emitting diode, nonlinear optical materials, optoelectronic and electronic devices, biological labelling, thermoelectric coolers, thermo-electronic and optical recording materials, etc. [1, 2]. These properties and the applications are largely dependent on the size, shape and the impurities of the nanomaterials.

As a typical semiconductor material of the II-VI group, cadmium sulphide (CdS) nanocrystals have been widely investigated [3, 4]. CdS is a direct band gap semiconductor with the band gap of 2.4 eV for bulk hexagonal (Wurtzite) structure and 2.38 eV for bulk cubic (zinc blend) structure [5, 6]. CdS nanoparticles are considered to be one of the model systems for investigating the unique optical and electronic properties of quantum confined semiconductors. However, the lack of adequate synthetic methods for producing the desired high quality nanoparticles is currently a bottleneck in this field. Over the past two decades, numerous colloidal chemistry (or solution chemistry) methods have been developed for the preparation of cadmium sulfide nanocrystals [7]. The solution chemistry synthesis of CdS nanocrystals utilizes the organic stabilizers to cap surface atoms of nanoparticles in order to control the growth process. The kind of stabilizers is of great importance, since, it affects the chemical as well as the physical properties of the semiconductor nanocrystals, from stability to solubility to light emission. Modifying the surfaces of nanoparticles with various organic, inorganic, species is projected to remove their surface defects and subsequently, influence their property. Organic capping of nanoparticles with surfactants

would give rise to a barrier to aggregation and electronic passivation of the particles. The ability to segregate between the zinc blend (metastable phase) and wurtzite structures is considered as the main key.

In aqueous phase synthesis of CdS nanoparticles, the conventionally homogeneous phase arrested precipitation with the use of phosphates, various thiols or hydrophilic polymer as capping reagents are usually adopted [8]. Among the various traditional synthesis approaches of the nanomaterials, the solvothermal/hydrothermal methods have been widely applied to improve the crystallinity of nanosized particles. Solvothermal synthesis is one of the most efficient methods used to synthesize CdS with different morphologies. It is simple, convenient and inexpensive. Some polymers such as PEG, PAA, PAN, PVP and PVA have been used to modify the surface chemistry of the crystals and the concentration of soluble species for crystal growing [9-12]. The complexing agent (PVP), can cap the particle surface to prevent the colloidal particle from agglomeration and play an important role in the formation of the nanoparticles. The adsorption of PVP onto the nanoparticles can solubilise the formed nanostructure into water. This may be attributed to the hydrophilicity of the PVP molecules and the repulsion between positively charged PVP molecules adsorbed onto separated nanoparticles. Competitive reaction kinetics between the growth of CdS and termination of growth by capping the surface is considered to induce the growth of CdS nanoparticles [13].

Recently, a wide range of cadmium sulfide (CdS) 3D polycrystalline walnut-like nanocrystals were prepared by solvothermal method with polyvinylpyrrolidone (PVP) as stabilizer [14]. The large surface area-to-volume ratio, along with the ability to tune the band gap makes the semiconductor nanoparticles like CdS to be used as sensitizers and catalysts in photochemical reaction being universally accepted.

In spite of the concentrated efforts to develop high quality CdS nanoparticles, there are still challenges to further simplify the synthesis procedures so as to encourage the mass production and the use of hydrothermal synthesis route is one of the best options to move towards this goal. Further, the use of water as a solvent offers several advantages, compared with non-aqueous synthesis, aqueous is more reproducible, low cost, environment friendly and the "as-prepared" samples are more water soluble and bio-compatible [8]. In-situ surface modification under hydrothermal conditions helps significantly in preparing nanocrystals with a highly controlled size, shape and dispersibility. This article deals with the preparation of CdS nanoparticles by a simple hydrothermal method and the influence of water soluble polymeric capping agent like polyvinylpyrrolidone (PVP) on the crystalline quality, morphology, size and crystalline phase is investigated. The sample was systematically characterized by powder XRD, UV-Vis absorption and photoluminescence spectroscopy, SEM and TEM, and thermal analysis.

## MATERIALS AND METHODS

### 2. Experimental

#### 2.1. Materials

Cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) Merck and thiourea ( $\text{H}_2\text{NCSNH}_2$ ) are used as the starting materials. All chemical are of high purity and no further purification is done. Polyvinylpyrrolidone (PVP) is the capping ligand.

#### 2.2. Synthesis of CdS nanoparticles modified with polyvinylpyrrolidone

The stoichiometric ratio of the starting materials ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{NCSNH}_2$ ) was kept as 1:3. Polyvinylpyrrolidone (PVP) is a water soluble polymer used here as the capping ligand. Initially, 2 g of PVP was taken and dissolved in 20 ml of water and then cadmium nitrate solution was added and mixed thoroughly in 75 ml of water. In a similar way thiourea was dissolved in 75 ml of water and stirred magnetically. These two solutions were mixed together for about 1 h. Ammonia was directly added in the solution until the pH of the solution reaches 12. The final solution was transferred into a 200 ml Teflon coated autoclave. The autoclave was placed in an electrical oven and maintained at 180 °C for 6 hours. After that the autoclave is removed from the oven and naturally allowed to cool down to room temperature. The yellow precipitate was washed continuously with water and ethanol several times so as to remove the excessive thiourea and other by products. The as prepared powder is grounded in a mortar and dried with a temperature of 80 °C nearly for 4 hours.

#### 2.3. Characterization

The room temperature powder XRD pattern for the as prepared sample was done using RICH SEIFER with monochromatic nickel filtered  $\text{CuK}_\alpha$  ( $\lambda=1.5461 \text{ \AA}$ ) radiation. The UV-Vis absorption spectral studies were carried out using VARIAN CARY 5E UV-Vis-NIR SPECTROPHOTOMETER in the spectral region of 200 and 800 nm. The photoluminescence spectra of the samples were recorded with a VARIAN CARY 5E UV-Vis-NIR

SPECTROPHOTOMETER. Particles size and distribution analyses were carried out with TEM model JEOL JEM 3010 at an accelerating voltage of 200 kV. For the TEM observations, the sample was dispersed in ethanol and ultrasonicated for 30 minutes and then it was kept on a carbon coated grids. Scanning electron microscope (SEM) was employed for morphological study using JEOL JSM 6310 operated at 10 kV with Energy Dispersive X-ray analyzer (EDX). Thermogravimetric (TG) and Differential thermo gravimetric analysis (DTG) for the air dried sample was performed on a SDT Q600 with a heating rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ .

## RESULTS AND DISCUSSION

### 3.1 Powder XRD analysis

Fig. 1 shows typical XRD pattern of obtained CdS nanocrystals with Millipore water as a solvent and polyvinylpyrrolidone (PVP) as capping reagent. All the diffraction peaks are conveniently indexed to hexagonal structure. Compared with the standard card (JCPDS card (PDF No.80-0006), the (0 0 2) diffraction peak, the second strongest peak in bulk hexagonal CdS, were unusually strong and narrow, which may be ascribed to the preferential growth along [0 0 1] hexagonal CdS crystallites. The relatively broad peaks probably resulted from the smaller dimensions of the other surfaces [15]. The corresponding lattice constants are  $a = b = 4.121\text{ \AA}$  and  $c = 6.682\text{ \AA}$ . There are reports on the role of different dosages of PVP on the resulting structure and orientation growth [15]. In the present study, the preparation carried out with 2 g of PVP/(20 ml) resulted in good quality nanoparticles with best orientation growth.

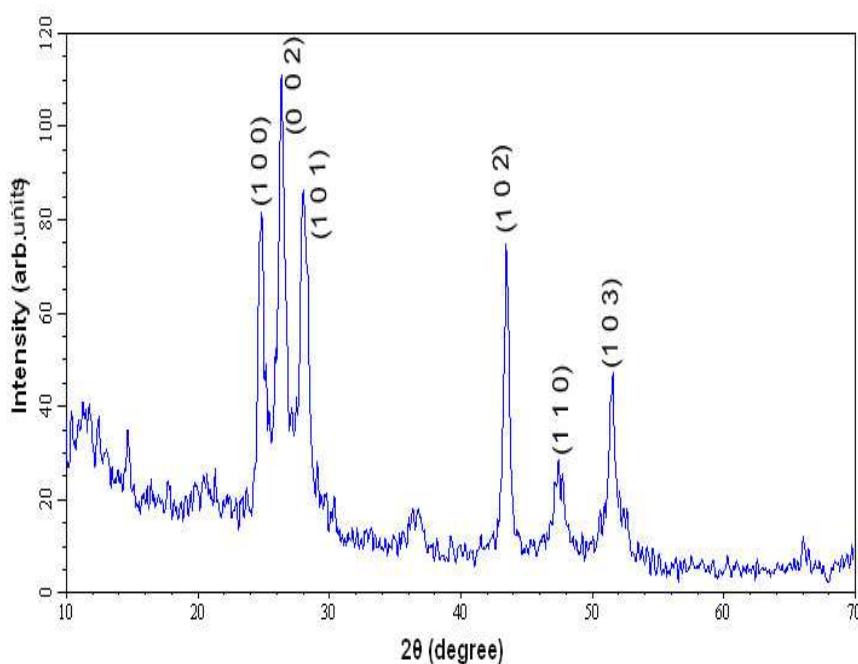


Fig.1. Powder XRD pattern of PVP capped CdS nanoparticles

### 3.2 Energy dispersive X-ray analysis (EDAX)

EDAX is an important technique to analyze the composition of elements quantitatively and solve the chemical identity of any nanomaterial. It is inferred from the result of the EDAX spectrum (Fig. 2) obtained for nanoparticles prepared using PVP, that the sample is composed of only Cd and S which are exactly CdS nanoparticles and no trace of other elements is observed. From the Fig. 2 it is clear that the sample is generally cadmium rich even though a relatively higher concentration of sulphur was used than the cadmium to synthesize CdS nanoparticles. The should be mainly composed of cadmium atoms. From the EDAX and XRD analyses, it is clear that the obtained product is pure cadmium sulphide in wurtzite phase.

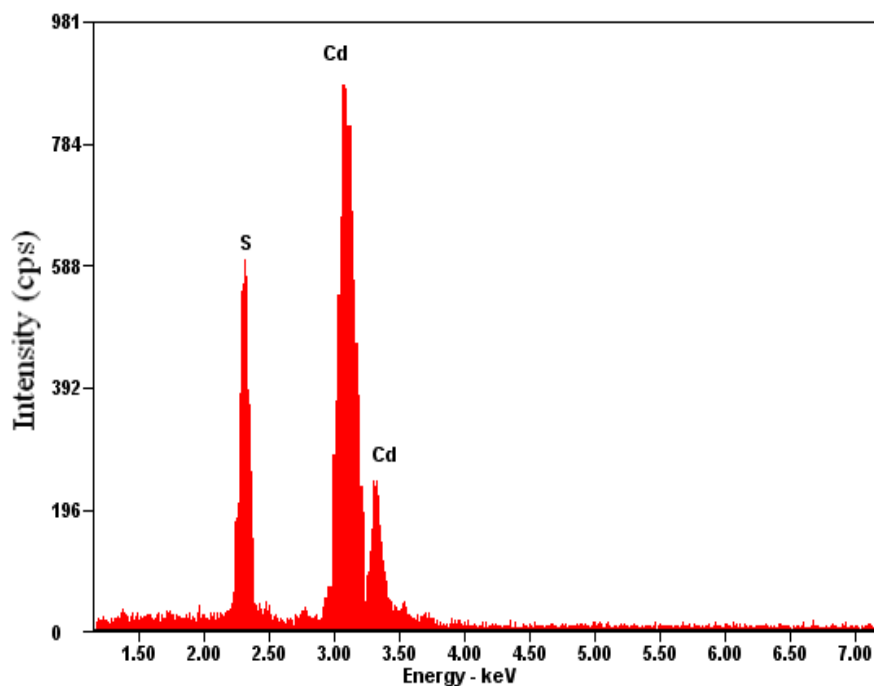


Fig.2. EDAX pattern of CdS nanoparticles modified with PVP capping ligand

### 3.3 UV-Vis absorption spectroscopy

The controlling and tuning of band edge emission and surface traps state emission of CdS nanocrystals are obviously very important to realize the tunable optical properties and laser emission [16]. The UV-Vis spectral analysis was carried out between 200 nm and 800 nm. Fig. 3 shows the absorption spectrum of CdS nanoparticles prepared with surfactant PVP. The absorption band edge was shifted to 490 nm and the corresponding band gap is 2.53 eV which is higher compared to bulk CdS band gap (2.4 eV). Thus it is clear from the optical absorption study that the capping of CdS with PVP modifies the band gap of the CdS nanoparticles and the sample is blue shifted when compared with the bulk CdS (512 nm).

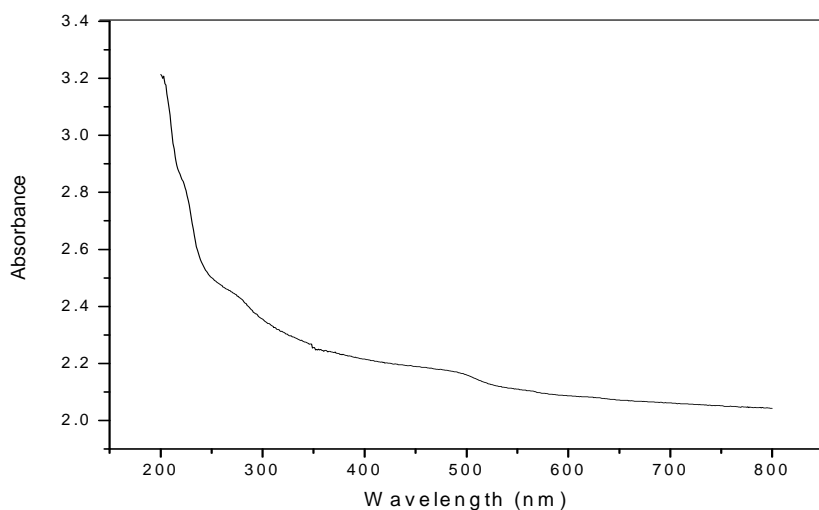


Fig.3. UV-Vis absorption spectrum of PVP capped CdS nanoparticles

### 3.4 Photoluminescence (PL) study

One of the interesting aspects of the photo-physical properties is the photoluminescence (PL) of CdS nanocrystallites. The PL studies on CdS nanocrystallites have been investigated by various research groups [17]. In general, the reported emission spectrum consists of two broad bands in the range 400-520 nm and then 520-800 nm. Usually, the peaking is observed at around 480 and 650 nm respectively [18]. Recently, Li et al investigated the room temperature luminescence of CdS nanostructured materials prepared with various sulphur sources and studied the influence of S sources on the green and red emission spectra of the nanopowder [19]. The PL property is influenced by the structure, composition, particle size and morphology of the CdS nanoparticles. In addition, the method of preparation has marked influence. Fig. 4 shows the PL spectrum of CdS nanoparticles prepared with PVP. It is evident from the PL spectra that the emission peak at 505 nm for the sample can be assigned to the surface trap induced fluorescence which involved the recombination of electrons trapped inside a sulphur vacancy with the hole in the valence band of CdS nanoparticle. The emission peak observed at 505 nm for CdS synthesized by PVP assisted solvothermal method goes well with the earlier report [15].

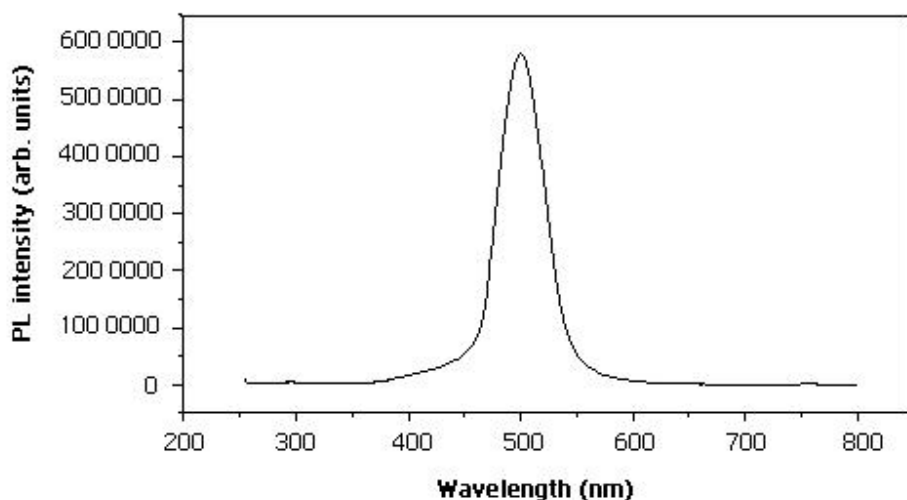


Fig.4. PL spectrum of PVP capped CdS nanoparticles

### 3.5 SEM analysis

The SEM image of CdS nanocrystals with water as a solvent and polyvinylpyrrolidone as capping reagent is shown in Fig. 5. The solvothermal temperature along with the capping agent can influence the nanoparticle size. At the lower temperature around 80°C only irregular nanospheres of large diameter are usually formed. A close observation of the SEM image of the present case suggests that the surfaces of the nanospheres are relatively smooth and there are few prolated spheres as well and this could be attributed to the relatively high reaction temperature employed. It reveals that PVP played an important role in controlling the size and mono-dispersion of the CdS nanocrystals in this process. The absence of agglomerates is attributed to the role played by PVP. In the formation process of the shape evolution of CdS architectural structure, the capping agent PVP is adsorbed onto the different planes of the incipient CdS nuclei and it not only prevents the particles from agglomeration, but also influences the growth of these planes [14].

### 3.6 Transmission electron microscopy (TEM)

The transmission electron microscopic analysis allows one to visualize particles at nanosize regime with high degree of accuracy, it offers better understanding about growth aspects and helps to analyze the actual size of the particles, shape and growth pattern.

The TEM micrograph of the PVP capped CdS nanopowder is shown in Fig. 6, which suggests the formation of spherical as well as short rods of nanoparticles. Further, the side faces of the product are not smooth and the particles and the level of agglomeration are slightly on the higher side and the short rods are not clearly visible. In the present case, the aspect ratio of the nanorods formed is only 3-4 and this is possibly due to the short duration of the reaction time employed. In the HRTEM image, a representative nanorod of width 6 nm and 25 nm length is

clearly visible. There are reports on the capping mechanism of PVP in growth process of CdS nanoparticles and also the influence of PVP dosage in tailoring the shape and size of the CdS nanostructures. The best dosage of PVP for the orientation growth of CdS nanocrystal was optimized as 0.8 g for 50 ml by Qingqing et al [15]. The HRTEM image shows the presence of few short nanorods which are seen crosslinked due to agglomeration, in spite of this, we notice in Fig. 6 (iv), the formation of well arranged lattice fringes in a single nanorods. Thus the problem of agglomeration and improving the aspect of the nanorods are the issues yet to be addressed. The SAED pattern of the CdS nanoparticles is presented which confirms the hexagonal (Wurtzite) phase of CdS. The pattern consists of diffraction rings corresponding to particle size and morphology.

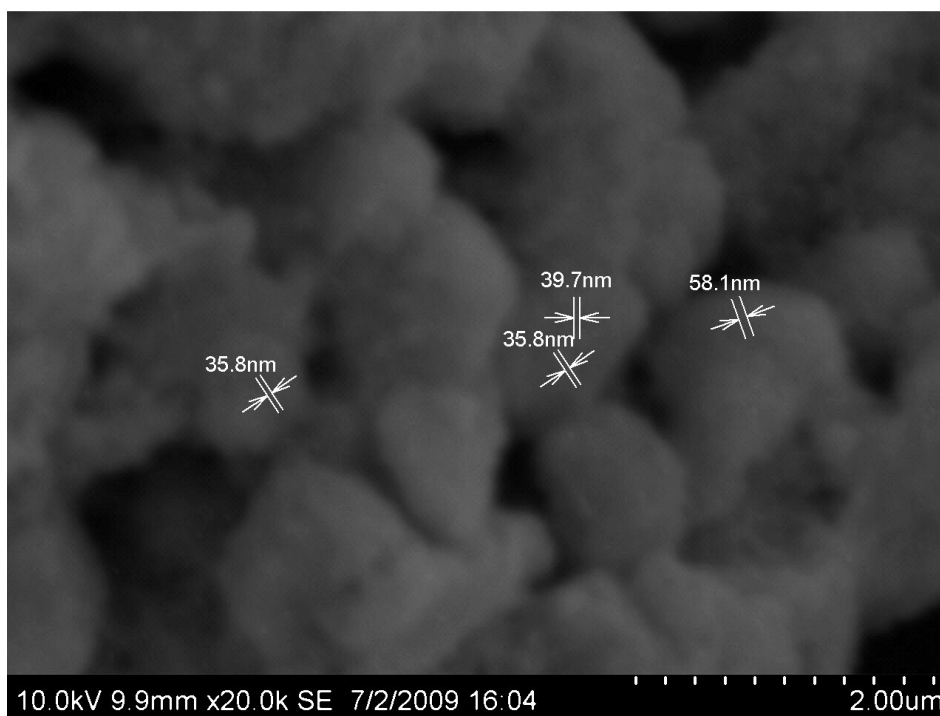


Fig.5. SEM image of PVP capped CdS nanoparticles

### 3.7 Thermal analysis

The thermal behavior of the semiconductor nanoparticles of CdS was studied by employing TG/DTA analysis. Since the temperature plays an important role in the formation of nanostructured materials, temperature induced phase changes are important for the utility of these nanoparticles for various applications. The TG analysis of the sample CdS obtained with PVP was done at the heating rate of 20°C/min. The TGA graph (Fig. 7) of the sample synthesized using PVP as capping agent shows the sharp weight loss of about 3.277 % at 525 °C. A gradual weight loss of about 1.246 % was obtained between 525 °C and 840 °C.

### CONCLUSION

Semiconductor nanoparticles of CdS are successfully prepared under solvothermal/hydrothermal conditions in surfactant assisted synthesis. The powder XRD result shows that particles are purely crystallized in hexagonal phase with the broadening of diffraction peaks is attributed to nanoscale size of the particles. From the optical absorption spectra, the blue shift of 490 nm as compared to bulk counterpart is due to the quantum confinement effect. The broad emission band observed in the PL spectrum for PVP capped CdS nanoparticles is assigned to the surface trap induced fluorescence which involved the recombination of electrons trapped inside a sulphur vacancy with the hole in the valence band of CdS nanoparticle. From TEM, it is evident that the nanoparticles of CdS exhibit well defined morphology and high crystallinity. The HRTEM result reveals the well resolved lattice fringes of CdS nanoparticles. Thus, the present study demonstrates that the hydrothermal synthesis method with capping ligand is one of the successful routes for obtaining good quality CdS nanoparticles.



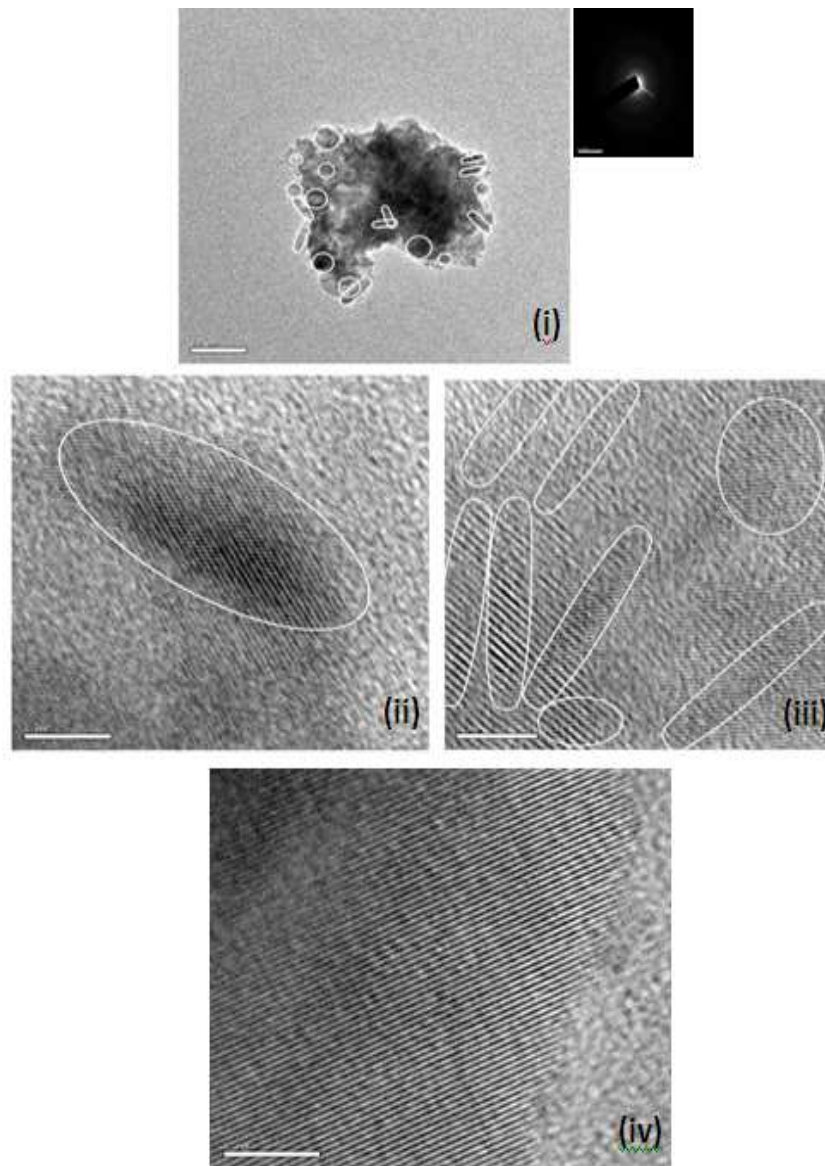


Fig.6. TEM and HRTEM images of CdS nanoparticles capped with polyvinylpyrrolidone (PVP). (i) Nanoclusters with small CdS nanoparticles (Inset SAED pattern), (ii, iii and iv) HRTEM images of one dimensional CdS with lattices fringe

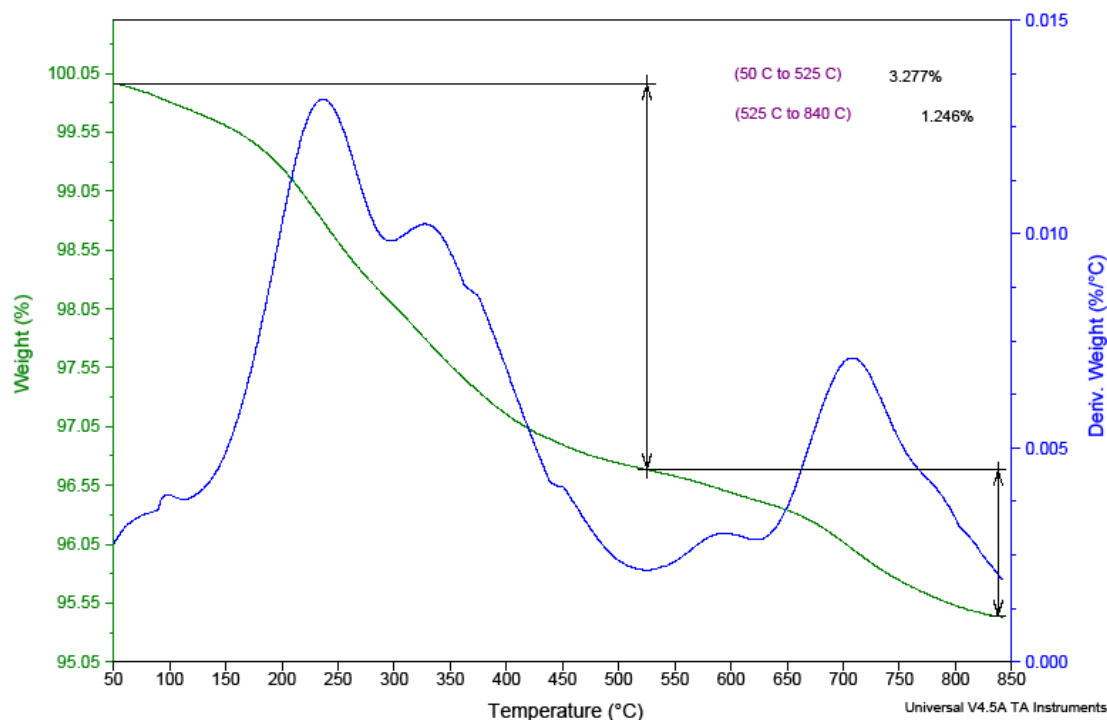


Fig.7. TG/DTA traces of PVP capped CdS nanoparticles

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