

Optoelectronic Study on Starch Capped Cadmium Sulfide Nanoparticles

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Green synthesis method using soluble starch as a stabilizing agent in an aqueous medium is used to prepare CdS nanoparticles. It has an advantage over the conventional method involving toxic reagents. Here in, a study on the optical properties of CdS nanoparticles prepared by green synthesis method with different pH values is being reported. The samples were prepared by chemical route and characterized by scanning electron microscopy, UV-Vis absorption spectroscopy, Fourier transform infrared spectroscopy, and photoluminescence spectroscopy. The experimental results showed a blue shift in absorption wavelength with respect to bulk CdS that indicates small size formation of particles and quantum confinement effect with increase in the effective energy band gap. The size was estimated by the Brus equation and empirical Yu model. Photoluminescence spectra show band edge emission and deep trap states emission. The CIE coordinates verify the emission of CdS in visible region. The blue shift in band edge emission and red shift in trap state emission are observed with lower pH values. The existence of functional groups was identified by Fourier transform infrared spectroscopy, it confirms the presence of starch as a stabilizing agent. Variation in pH modifies the optical properties and reduction in the size of cadmium sulfide nanoparticles.

Keywords: Soluble Starch, Cadmium sulfide, UV-Vis Absorption, Photoluminescence, FTIR spectroscopy.

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1. INTRODUCTION

Semiconductor nanomaterials have received considerable attention due to their distinct photophysical properties and wide range of application in biology, biosensing and optoelectronic fields. Tunable band gap and narrow band width emission make them versatile materials. They have been extensively used as fluorescent bio labeling, biological assay, photo catalytic, sensors, LEDs, biological imaging and many more applications [1-3]. Semiconductor nanoparticles have been synthesized by variety of ways like chemical precipitation method, ion exchange reaction, organometallic precursor, sol-gel method [4]. With the wide and diversified applications, the synthesis of semiconductor nanoparticles is drawing attention on an issue of environment safety and eco-friendly. There have been different capping agents like thiols groups, phosphines organic, mercapto acetate, etc. used to synthesize semiconductor nanoparticles [4, 5]. In which thiol group (R-SH) coordinates with functional group and provides good surface stability of the nanoparticles. Nanoparticles prepared with toxic reagents by various methods are not environment-friendly and not applicable in medical or biological purpose. In order to remove or reduce toxicity, the green synthesis of nanomaterials is an alternative method, which can be helpful for various applications and is more reliable and environmentally benign.

Environmentally benign synthetic route has become important aspect of fundamental research. Use of nontoxic chemicals, environmentally benign solvent and renewable stabilizing agent is an approach towards green synthesis. Green capping agents like starch, leaf extract, enzyme, biopolymers etc. are used to stabilize the surface of nanoparticles [1, 6-8]. In 1718, Helcher applied natural starch to stabilize gold nanoparticles. Later, Raveendran et al. have shown that hydroxyl group of starch acts as passivation centers for stabilization of metal nanoparti-

cles [9]. Nowadays, synthetic polymers are commonly used to stabilize different types of nanoparticles. In which the steric force keeps the nucleated legends separated from each other. The soluble starch ($C_6H_{10}O_5$)_n is a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysaccharide is produced by most green plants as energy storage. It is a mixture of amylopectin and amylose; amylose is soluble and known as soluble starch. It has been used as a capping agent or stabilizer in the synthesis of semiconductor or metal nanoparticles. Several reports are available on starch capped metal or semiconductor nanoparticles and used for different optical or biological applications [1, 6, 10]. Among all semiconductors, CdS has been subject of great interest due to its importance in various applications. It is an *n*-type direct band gap semiconductor having band gap of 2.42 eV at 300 K with exciton Bohr radius of 2.7 nm. This corresponds to visible radiation with a wavelength of 512 nm. Moreover, great interest has focused on synthesized CdS nanoparticles due to the wide band gap, good optoelectronic properties and thermal stability. Various parameters like reaction time, pH, temperature, concentration of the capping agent, molar ratio etc. are controlling the reaction and show a considerable effect on the size, shape, morphology and optical properties [3-5]. pH has a great importance in green synthesis route; it has a strong effect on the formation of metal as well semiconductor nanoparticles. pH affects the distribution of starch hydroxyl groups and the hydrolysis and condensation processes of solution during gelatinization, therefore it influences the shape, size, growth mechanism and morphology of the crystals. Uchil et al. have studied the effect of pH on the size of the CdS nanoparticles synthesized in chicken egg membrane by diffusion method. They observed that size of nanoparticles and yield strongly depend on pH in alkaline medium [11]. Sergiel results have presented stable light emission

from sugar stabilized CdS quantum dots, in which amylopectin and meto-dextrin were used as capping agents with starch. [12]. Previously reported study on starch capped CdS nanoparticles was different in terms of reaction time, temperature, concentration, capping agent and reagents [11-13]. The work is focused on investigating the effect of pH and on the size, optical and morphological properties of CdS nanoparticles, using soluble starch as a stabilizing agent. The result of UV-Vis absorption, Fourier transform infrared (FTIR) and photoluminescence (PL) spectroscopy are presented and discussed.

2. EXPERIMENTAL DATA

All the chemicals were analytical grade and were used without further purification. The CdS nanoparticles were prepared by a chemical precipitation method. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 2\text{H}_2\text{O}$ flakes from Merck were used as reagents, non-toxic soluble starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_n from CDH chemicals was used as a stabilizing agent. Dilute aqueous solution of 1M NaOH was taken to adjust pH of the solution within 8-12. In the typical synthesis process, 0.1 M CdCl_2 aqueous solution was mixed with soluble starch (taken as 0.05 wt. %). The initial solution was kept at 80 °C for 30 min and adjusted the pH level of the solutions 8, 10 and 12 with NaOH, thereafter 0.1 M Na_2S aqueous solution was slowly added to the resulting solution with constant stirring. The resulting solution was further stirred for 3 h at room temperature. The final yellow precipitate was obtained. The final precipitate was washed several times with acetone and distilled water alternatively, thereafter centrifuged and dried at 40 °C to get CdS in powder form. Three different samples were obtained for pH 8, 10 and 12 leveled as CdS1, CdS2 and CdS3 respectively.

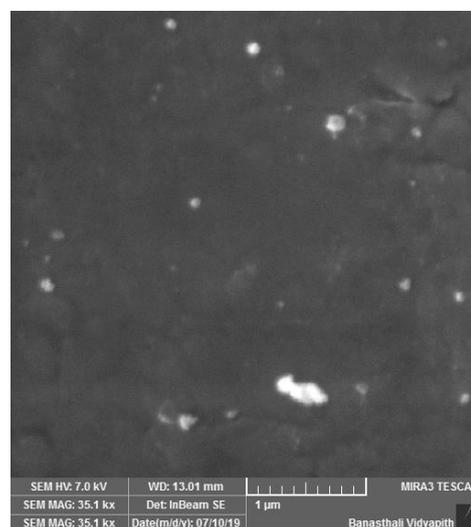
Starch is a carbohydrate polymer insoluble in water. Heat treatment is required to expand the starch granules and accelerate the reduction process. Addition of NaOH to starch promotes rapid swelling, and swelling starch has the ability to act as a stabilizing agent. During the preparation, high swelling of starch granules creates more Starch-O-Na, the starch hydroxyl might coordinate with Cd^{2+} metal ions from salt solution and prevent them from agglomeration [14]. In alkaline solution, Cd^{2+} makes complex ions $\text{Cd}(\text{OH})_2$ and $\text{Cd}(\text{OH})_4$ that dissociate into Cd^{2+} and OH^{2-} with raising temperature.

The samples were characterized by field emission scanning electron microscopy (FE-SEM) with Tescan MIRA 3 LMU FEG to study size and surface morphology of CdS samples. The optical absorption of the samples was recorded by UV-2450 UV-Vis spectrometer over the wavelength 300-700 nm with step size 2 nm. Samples were characterized by RF-5301 fluorescence spectrometer in the wavelength range 300 nm to 700 nm with step size 1 nm and excitation wavelength 390 nm for PL study. Samples were placed in quartz cuvettes (1 cm path length) for absorption and PL study. FTIR Bruker (ALPHA-T) spectrometer was used to study FTIR spectrum.

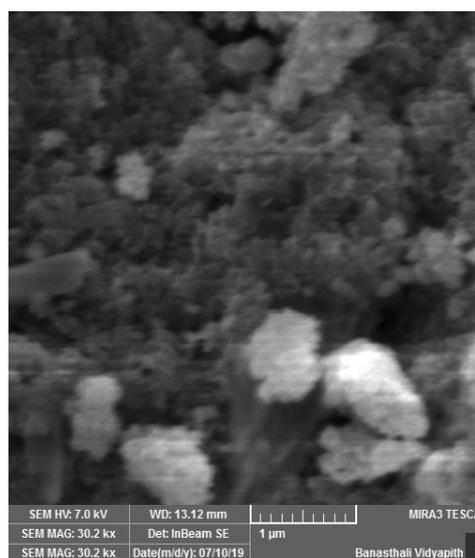
3. RESULTS AND DISCUSSION

3.1 Field Emission Scanning Electron Microscopy

FE-SEM images of CdS nanoparticles for pH 10 and pH 12 are displayed in Fig. 1. It shows that the CdS nanoparticles were well distributed in the starch matrix. From Fig. 1 it can be seen that CdS nanoparticles are spherical in shape and these nanoparticles tend to agglomerate owing to high surface energy and form clusters. The average diameters ranging from 30 to 50 nm were obtained.



a



b

Fig. 1 – FE-SEM image of CdS II nanoparticles (a), FE-SEM image of CdS III nanoparticles (b)

3.2 Absorption Study

Fig. 2 shows the UV-Vis absorption spectra for CdS nanoparticles samples. An increase in absorbance below 500 nm with a broad shoulder around 450 nm was observed. The absorption shoulder presented in the spectrum can be assigned to the first excitonic state transition [15]. A spectrum with a broad shoulder and absence of the excitonic peak is indicative of a broad size distribution [11]. The blue shift in absorption onset with respect to the band edge of bulk CdS (512 nm) indicates

the increase in effective band gap by quantum confinement effect. The energy band gap (E_g) was calculated by assuming direct transition between valence band and conduction band using the Tauc plot $(\alpha h\nu)^2$ versus $h\nu$, and extrapolating the straight line on the energy axis.

Fig. 3 represents the Tauc plot for CdS nanoparticles samples, and the calculated values of optical band gap from the plot are listed in Table 1. They were found to be larger than those for bulk CdS (2.42 eV). The widening of band gap is indicative of quantum confinement. By assuming the spherical shape of nanocrystallites and coulomb interaction, the average size of nanoparticles can be estimated by Brus equation using effective mass approximation mode reported in literature [5]. According to this model, the confined band gap energy is given by

$$E_{gn} = E_{gb} + \frac{\hbar^2 \pi^2}{2r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] + \frac{1.786e^2}{4\pi\epsilon_0\epsilon_r r} \quad (1)$$

where E_{gn} is the band gap of nanocrystals, E_{gb} is the band gap of bulk material, r is the radius of cluster, m_e^* and m_h^* are the effective masses of electrons and holes respectively for CdS ($m_e^* = 0.19m_0$, $m_h^* = 0.80m_0$) and ϵ is the dielectric constant for CdS. The estimated particle size is shown in Table 1. In literature, various models related to quantum confinement effect were reported. Yu et al. [16] has provided an empirical relation to calculate the diameter of particle from excitonic absorption wavelength

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times)\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29, \quad (2)$$

where D is the diameter, λ is the excitonic absorption wavelength. By putting the value of excitonic absorption wavelength, size was estimated and given in Table 1. The estimated sizes for all the samples are larger than the exciton Bohr radius, indicating a weak quantum confinement regime. The increase in particle size with higher pH value is consistent with coordination of Cd^{2+} [14]. According to literature reports, in more alkaline medium, the availability of S^{2-} ions is because of more OH ions are available for hydrolysis of Na_2S thus, increased S_2 concentration leads to the formation of larger CdS nanoparticles [11]. The results are in agreement with previous reports [8, 13]. Moreover, it is found that relative absorbance for pH 8 was lower than pH 10 and pH 12; it is an indicator of the quantity of the CdS formed or the yield. The decreased solubility with an increase in pH is benefit for nucleation and growth of nanoparticles and therefore more nanoparticles are generated. These results are consistent with the earlier reports [11, 13]. The optical transmittance of CdS samples is more than 50 % in the 600-800 nm wavelength range, which is sufficient for optical and solar cell applications.

3.3 Photoluminescence Study

The PL spectra of starch capped CdS nanoparticles are shown in Fig. 4. PL spectra show the two emission bands: a high energy band around 471 nm in the blue region and a low energy band at 612 nm in the red region. The blue emission around 460 nm is due to radiative recombination of an exciton which is bound to

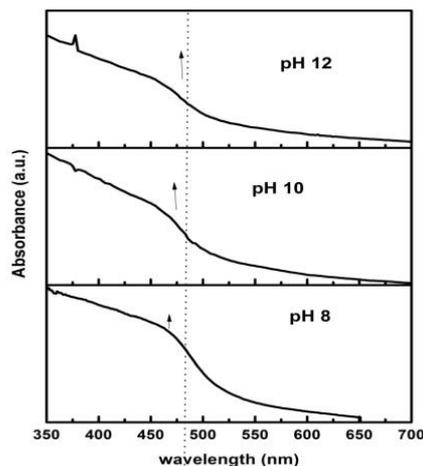


Fig. 2 – UV-Vis absorption spectra of CdS nanoparticles with different pH value

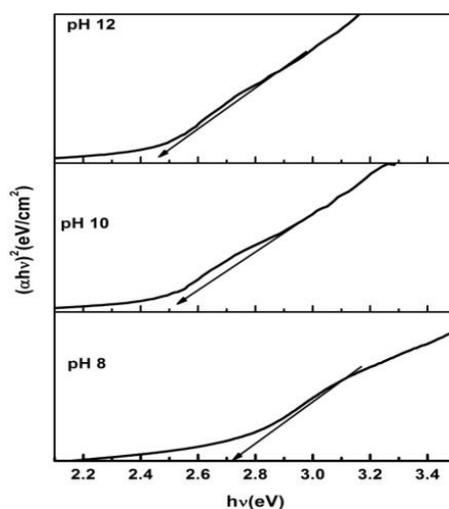


Fig. 3 – Tauc plot of CdS nanoparticles with different pH

Table 1 – Average size and band gap of CdS nanoparticles for different pH values

Sample	pH value	Absorption		Band gap E_g (eV)	Size estimated by	
		Onset (nm)	Shoulder (nm)		Brus Eq.	Yu model
CdS1	8	470	460	2.7	6.1 nm	5.8 nm
CdS2	10	490	467	2.52	8.6 nm	7.8 nm
CdS3	12	500	475	2.48	11 nm	8.6 nm

the neutral acceptor and donor in delocalized states in CdS nanocrystals [15], which is slightly blue shifted with lower pH value. It is found that intensity of the blue emission is increased and peak becomes broadened with pH 8. The broadening of the excitonic emission shows inhomogeneous broad size distribution due to size dispersion. Small stoke's shift has been observed between excitonic absorption wavelength and PL emission. Nandkumar et al. observed relatively large stokes shifts in band edge PL emission, and excitonic absorption band indicates strong coupling between electrons and phonons, which may lead to reduced PL intensity by thermal quenching and small Stoke's shift indicating weak coupling results in high PL emission band intensity [17]. Therefore, electron phonon coupling of CdS is an important factor. The increased

oscillator strength and weak electron phonon coupling enhanced the excitonic band emission. The strength of coupling increases with larger particle size.

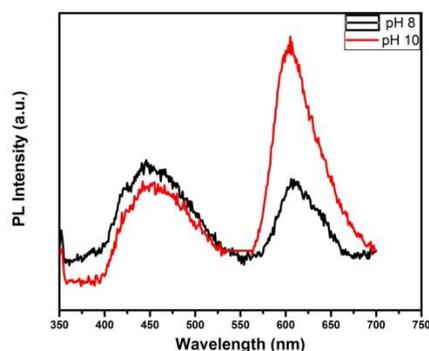


Fig. 4 – PL spectra of CdS nanoparticles

The second weak red emission for pH 8 was ascribed to the transition of a bound electron from Cd vacancy to the valence band [15]. The peak position is slightly red shifted and intensity increases rapidly with pH 10. It is suggested that surface passivation removes the trap states; therefore, density of trap states should be lower with lower pH value due to smaller particle size hence weak trap states emission obtained.

Gonza et al. have reported a single broad emission at energy 2.2 eV in starch capped CdS nanoparticles. The peak was red shifted and became broad and intense with higher pH value [18]. In our case, the defect related emission peak is red shifted and highly intense with pH 10, which is consequence of the dependence of size of nanoparticles, and large Franck-Condon displacement of excited states. It is reported that at lower pH value, the reduction rate is low, therefore more probably oxidation will occur, while at higher pH the reduction rate becomes faster and aggregation of particles more, so that bigger particles are formed [19]. Hence, with increasing pH value, the size of the CdS particles increases causing an upward shift in the valence band edge. This reduces the energy difference between sulfur states and valence band giving rise to a red shift in the peak.

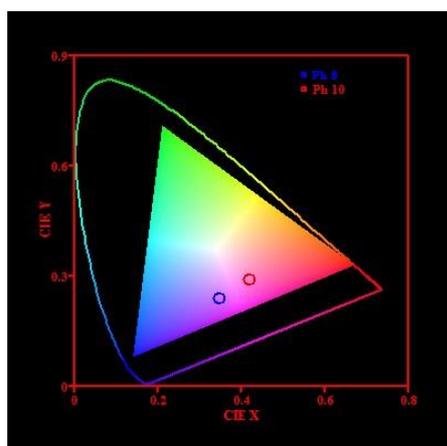


Fig. 5 – CIE plot of CdS nanoparticles

In order to analyze the color of emission, Commission International de l'Éclairage (CIE) system is most commonly used. Fig. 4 demonstrates the CIE 1931 color coordinates of PL of starch capped CdS nanoparticles for

pH 8 and 10 values. The CIE color coordinates of PL emission were found to be 0.35 and 0.24 for pH 8 and 0.42 and 0.29 for pH 10. It is appeared as purple color emission. It is observed that color of emission is changed with changing the pH of the solution.

3.4 FTIR Spectroscopy

The existence of functional groups was identified by FTIR spectroscopy that confirms the formation of CdS with starch. Fig. 5 shows the FTIR spectrum of CdS with pH 8. The presence of characteristic peaks at 1690 cm^{-1} and 1640 cm^{-1} was ascribed to H-O-H stretching and bending modes of the absorbed water on the particle surface respectively, which indicates that CdS tightly bounds with a water molecule presented in starch [6]. The band at 1008 cm^{-1} was attributed to vibration modes of α 1-4 glycosidic linkage (C-O-C) of starch molecules. While the band at 1400 cm^{-1} was attributed to the angular deformation bonding of C-C vibration mode [20]. Signature peaks at 700 cm^{-1} and 854 cm^{-1} were assigned to Cd-S stretching vibration modes [20]. The peak at 2359 cm^{-1} can be assigned to the involvement of triple bond molecule like alkynes and nitriles inorganic mixture. The increase in pH value indicates the alkaline nature of the solution, which increases the hydrolysis of salts of a weak acid in strong base medium, as a result, helpful for the formation of nanoparticles.

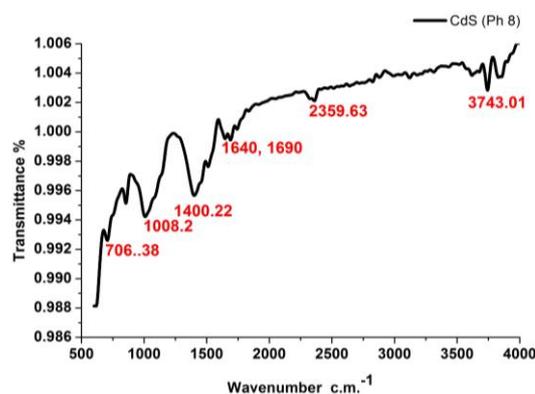


Fig. 6 – FTIR spectrum of CdS I sample

4. CONCLUSIONS

A simple, cost effective, eco-friendly chemical method was used to prepare CdS nanoparticles using soluble starch with different pH value. The samples were characterized by FESEM, UV-Vis absorption spectroscopy, PL and FTIR spectroscopy. It is observed that the steric hindrance of soluble starch protects the CdS from agglomeration with little size dispersion. It is found that size and color of emission are a function of pH value, and in alkaline medium – a lower pH value leading to the formation of smaller particles with large effective band gap. Thus, optical properties of CdS were found to be dependent upon pH of the solution. With increasing pH value, enhanced red shifted defects related emission has been obtained. The study reveals that an optimal value of pH is required for the preparation of smaller nanoparticles. The study may be helpful to find out tunable light emission from CdS nanoparticles for optoelectronic applications.

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Оптоелектронне дослідження наночастинок сульфїду кадмію, покритих крохмалем

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Метод зеленого синтезу з використанням розчинного крохмалю як стабілізуючого агента у водному середовищі використовується для отримання наночастинок CdS. Він має перевагу перед звичайним методом із залученням токсичних реагентів. У статті повідомляється про дослідження оптичних властивостей наночастинок CdS, підготовлених методом зеленого синтезу з різними значеннями рН. Зразки готували хімічним шляхом та досліджували методами скануючої електронної мікроскопії, абсорбційної спектроскопії в УФ та видимому діапазонах, інфрачервої спектроскопії з перетворенням Фур'є та фотолюмінесценційної спектроскопії. Результати експериментів показали синій зсув довжини хвилі поглинання у випадку об'ємного CdS, що вказує на утворення частинок невеликих розмірів та ефект квантового утримання із збільшенням ефективної ширини забороненої зони. Розмір частинок був оцінений за рівнянням Бруса та емпіричною моделлю Ю. Спектри фото-люмінесценції показують випромінювання границі зони та випромінювання станів глибоких пасток. Координати СІЕ перевіряють випромінювання CdS у видимому діапазоні. Синій зсув у випромінюванні границі зони та червоний зсув у випромінюванні станів пасток спостерігаються із меншими значеннями рН. Існування функціональних груп було визначено інфрачервоною спектроскопією з перетворенням Фур'є, це підтверджує наявність крохмалю як стабілізуючого агента. Зміна рН модифікує оптичні властивості та зменшення розміру наночастинок сульфїду кадмію.

Ключові слова: Розчинний крохмаль, Сульфід кадмію, Поглинання в ультрафіолетовому та видимому діапазонах, Фотолюмінесценція, Інфрачервона спектроскопія з перетворенням Фур'є.