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GROWTH AND CHARACTERIZATION OF TRANSITION METAL DOPED CDS NANOSTRUCTURES FOR BLUE, CYAN AND GREEN LIGHT EMISSION

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ABSTRACT

The nanostructures of CdS have been prepared by Green Chemical Synthesis method by using Starch as a green capping agent. Transition metal Copper was doped for emission of visible wavelengths of light for Light Emitting Diode device realization. The structural properties of the doped and un-doped samples were explained by XRD and HRTEM analysis. Energy band gap was calculated by employing UV-Vis spectra. The luminescence properties of the metal doped samples were well explained by PL analysis.

Key Words: *Green Chemical Synthesis, CdS, Starch, Visible Light Emission, LED.*

I. INTRODUCTION

The optical properties of the materials are changed dramatically when the grain size is reduced to the order of Bohr radius limit. Semiconductor nanostructures are recently studied for their excellent optical properties due to the quantum confinement effect. A strong confinement can occur if the grain size could be further reduced below exciton Bohr radius of the material which can enhance the quantum confinement effect to a higher order. This size dependent character is probably the most attractive property of semiconductor used for optoelectronic devices. The high surface to volume ratio of small nanostructure suggests that the surface properties should have significant effects on their structural and optical properties [1-3]. Chemical bath deposition is one of the best solution phase method useful for preparation of compound semiconductor from aqueous solutions. It is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled precipitation of the compounds from the solution. The recent literature also highlights the control of surface stabilization and agglomeration on the nanomaterial for tailoring their optical properties. Much effort has been made to seek the best capping agent to passivate the nanostructure surface. Thus simple and novel method of semiconductor nanostructure synthesis is a new great area of interest. The green synthetic strategy requires the related materials to be environmentally benign, non-toxic and renewable. One of such green capping agent is starch. It is a renewable polymer and it adopts right handed helical conformation in aqueous solution [4,5]. Nanostructures of metal doped CdS become the most extensively investigated material because of their size dependent luminescence properties tunable across the visible spectrum. The superior light emitting properties of Cu doped CdS give rise to promising applications in LED fabrication., Although a of various synthesis techniques have been developed to prepare these cadmium chalcogenide nanostructures but a very few experimental works are devoted to green synthesis route; especially using starch as capping agent [6-8]. The role of bio capping agent in determination of quantum confinement is of considerable interest in recent years. It has the excellent capability in tailoring the newer luminescence properties for application point of view.

II. EXPERIMENTAL

Thin films of nanostructures were deposited on glass substrates by Green Chemical Route. The depositions were carried out in starch solution. The matrix solutions were prepared separately by an aqueous solution (3% by volume) of Starch with constant stirring at a constant temperature 80^0 C maintained for 2 hours. Cadmium acetate solution was prepared at 0.1M concentration for Starch matrix solutions in presence of ammonia solution (pH maintained at 9.5). These solutions were separately added to Sodium Sulfide (Na_2S) solution under constant stirring for another 1 hours. The copper is considered as promising dopant atom as it has the potential to modulate optical as well as electrical properties at large. Thus to understand the effect an impurity ion on the structural and optical properties of nanostructures, the doping of Cu ion was carried out into starch capped CdS nanostructures. Cu doping was done by adding cupric acetate solution into the prepared CdS (0.1 M concentration) nanostructure under constant magnetic stirring at room temperature. The structural and optical properties of doped nanostructures were well studied so that the new properties may be applied for device fabrication. The percentages of copper doping are 3wt% (S 6), 5wt% (S 7) and 7wt% (S 8) in nitrogen environment at room temperature. Sample S 5 is assigned as 0wt% doped for reference un-doped sample. The pH is maintained at 9.5 for all of the samples prepared at room temperature.

III. RESULTS AND DISCUSSIONS

The XRD pattern of CdS nanostructure exhibits cubic zinc blende structure. The grain size of S5, S6, S7, S8 are 5.28 nm, 5.34 nm, 5.41 nm, 5.49 nm respectively. The grain sizes of the particles are increasing with increasing the doping percentage of the metal particles.

The representative X- ray diffraction patterns for the samples are shown in Fig.1

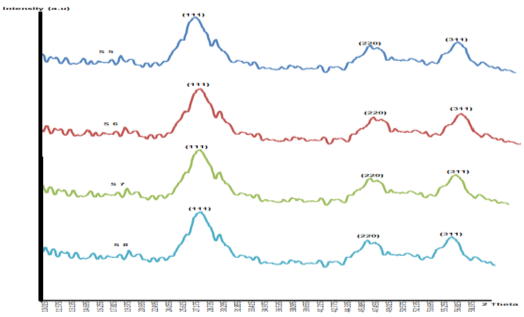

Fig .1: XRD pattern of S 5, S 6, S 7 and S 8

The summary of the obtained results are presented in Table 3.4.

Table 1: XRD Experimental Data of transition metal doped samples

Samples	**Observed Value Of 2θ**	**Plane (h k l)**	**Spacing (d) A^o**	**Lattice Parameter (a) A^o**	**Grain Sizes (D) nm**
CdS/Starch S 5 0% Cu doped	26.36^0, 44.52^0, 52.68^0	(111), (220), (311)	3.37834 2.03347 1.73609	5.85145	5.28
CdS/Starch S 6 3% Cu doped	26.38^0, 44.53^0, 52.76^0	(111), (220), (311)	3.37582 2.03303 1.73365	5.84710	5.34
CdS/Starch S 7 5% Cu doped	26.44^0, 44.55^0, 52.84^0	(111), (220), (311)	3.36830 2.03217 1.73121	5.83407	5.41
CdS/Starch S 8 7% Cu doped	26.48^0, 44.58^0, 52.89^0	(111), (220), (311)	3.36330 2.03087 1.72969	5.82541	5.49

Particle sizes are also investigated by HRTEM analysis. The HRTEM images in Fig 2, Fig 3, Fig 4 and Fig 5 are representing average particle sizes of samples S5, S6, S7 and S8 as 5-6 nm, 5-7 nm, 5-8 nm and 5-8 nm respectively. Similar results are obtained from XRD and HRTEM analyzed data. The particle sizes are increasing with percentage of Cu doping into CdS nanostructures.

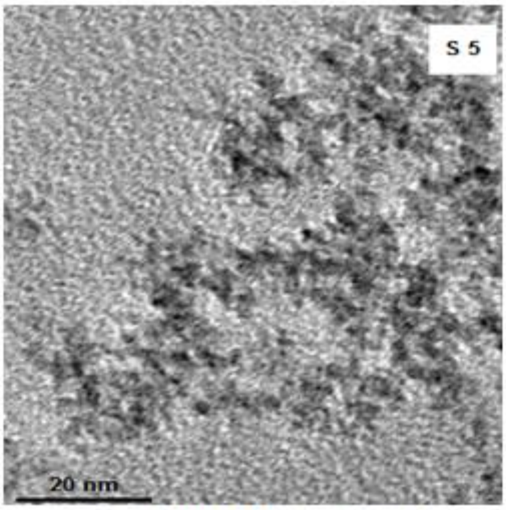

Fig 2: HRTEM image of S 5

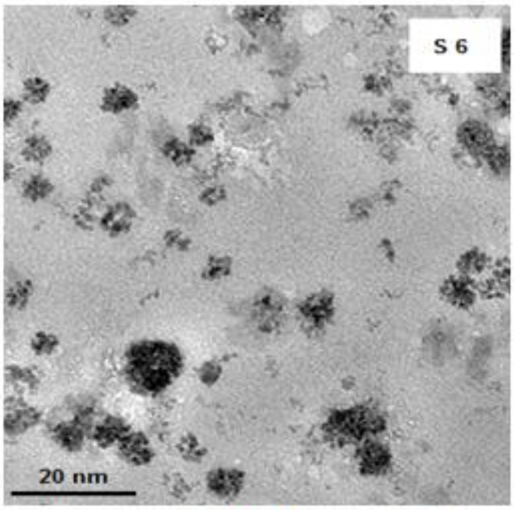

Fig 3: HRTEM image of S 6

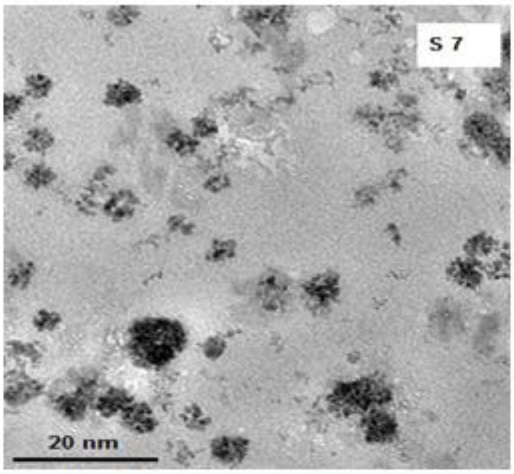

Fig 4: HRTEM image of S 7

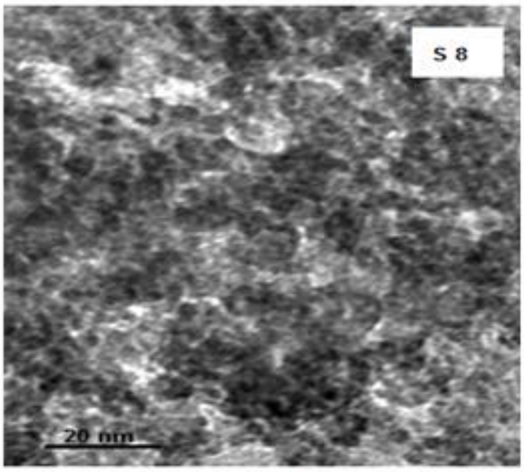

Fig 5: HRTEM image of S 8

The chemical reaction directly affects the time evolution of the number of nuclei and it determines both nucleation and growth process. Growth will be strongly influenced by the nuclei number already formed at a given time. A great number of nucleation favours a fast autocatalytic growth and giving rise to a large number of small particles. Chemical reaction controls this kind of growth, being the autocatalytic growth faster as chemical reaction is faster. In the formation of nanostructure, there is another contribution to the growth molecule on the surface of small particle as they will tend to diffuse through solution and add to the surface of larger particle growth by Ostwald repining. A slow chemical reaction favors continuous nuclei, keeping always a certain number of nuclei in the system. This fact clearly explains the bigger particle size obtained from a slow reaction. It may be conclude that a slow chemical reaction rate is associated with a more important repining contribution to the growth. A high number of nuclei are still forming at this stage if the reaction is slow. Therefore in case of slow reaction, nucleation and growth takes place simultaneously. This overlapping of nucleation and growth process in a slower chemical reaction is leading to larger sizes of nanoparticles. Rate of reaction depends on the type of the reactant and also on the doping percentage of the dopants solution. As the smaller size of CdS nanostructure are obtained at lower doping concentration in the present case, therefore the rate of reaction may become faster for undoped sample and become slower with increase of doping percentage level of Cu atom. The contribution of repining force may be minimized by lowering the doping percentage.

The UV-visible absorption spectroscopy is an efficient technique to monitor the optical properties of nano sized particles. Fig 6 shows the room temperature UV-Vis absorption spectrum of sample S5 to S8. The spectrum exhibits well defined absorption feature peaks at 332.8 nm, 388.9 nm and 397.8 nm for sample S6, S7 and S8 which are considerably red shifted relative to the absorption peak of sample S5 (326.8 nm). Thus the quantum confinements are decreasing due to metal doping. The calculated values of energy band gaps for S5, S6, S7 and S8 are 3.79 eV, 3.72 eV, 3.19 eV and 3.12 eV. The decreasing of energy band gap with percentage of Cu in the sample is also recorded.

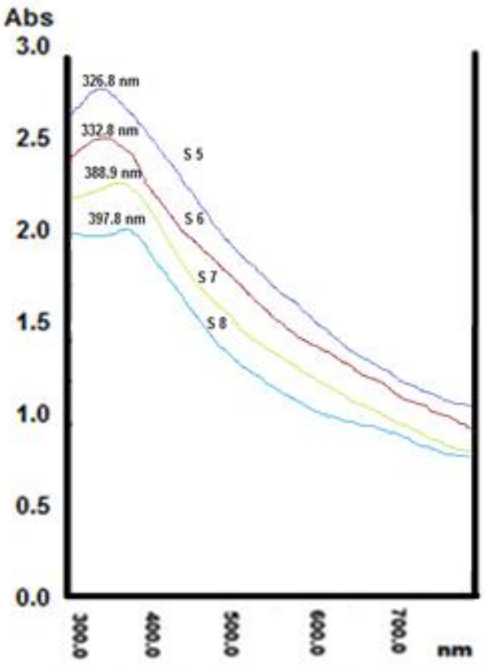

Fig 6: UV-Vis study of S 5, S 6, S 7, S 8

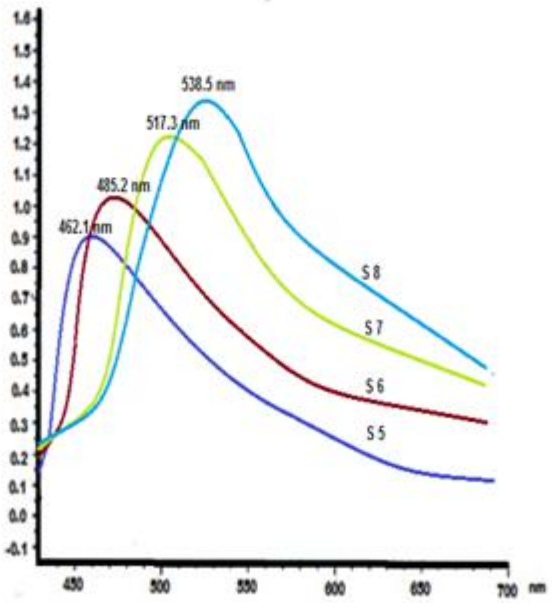

Fig 7: PL images of S 5, S 6, S 7, S 8

The structural and absorption studies exhibit the quality of the grown samples and also reflect the small distinct changes in the quantum size effects those are likely to have an impact on the luminescence properties of the nanostructures. The important effects of Cu-doping on CdS regarding luminescence are shown in Fig 7. A clear signature of red shift on Cu substitution can be seen from the photoluminescence data. The PL spectra of samples S5, S6, S7 and S8 have been measured with an excitation of wavelength at visible wavelength region. The visible light found for these particular wavelengths are 462.1 nm (Blue color), 485.2 nm (Blue color), 517.3 nm (Cyan color) and 538.5 nm (Green color) respectively. The localized energy level of exciton states of Cu^{2+} is different from that of Cd^{2+}, which leads to a shift in the PL peaks of the doped samples than undoped sample S5.

Again the calculated values of Stokes shift are 135.3 nm, 152.4 nm, 128.4 nm and 140.7 nm for the samples. The photoluminescence technique is important to investigate the effect of Cu doping on CdS nanostructure. It may be assumed that during the doping process, Cu atom either can be interstitially located at the crystalline lattice or substituting cadmium atoms. These Cu atoms create donor energy level near the CdS valance band which may modify the band gap energy of CdS. For Cu doped samples S6 (485.2 nm), S7 (517.3 nm) and S8 (538.5 nm) the luminescence peaks are located near 500 nm. These peaks are corresponding to a band to band radiative recombination emission and can be associated with the energy band gap of the doped samples, which is in good agreement with the absorbance spectra. In some Cu doped CdS samples, a broad peak may be obtained around 700 nm, which is associated with a red band related to sulfur vacancies. But in the present case no such peaks are observed. PL intensities are also found to increase with the doping concentration of copper. The observed emission peaks are not symmetrical which indicate that besides band to band recombination, there exist additional recombinations at surface defect states. It could be due to cadmium vacancies at the surface of the samples S6, S7 and S8. The surface states due to Cd vacancies can act as hole trap states. Hence, these emissions are assigned to relaxation of carriers from the excitonic to the surface trap states. The PL spectra show red shift on doping. The red shift of emission spectra peak may be due to the indirect recombination of free electrons moving from trap level formed by Cu atoms to the holes in valence band. These trap level are in energy gap and shift towards the valence band on doping. Therefore these prepared samples of transition metal Cu doped CdS nanostructures are useful for LED fabrication for the emission of blue, cyan and green light as found in photoluminescence spectra.

IV. CONCLUSIONS

The synthesis of CdS nanostructures were carried out by chemical synthesis method. Starch matrix was used as capping agent for doped and un-doped samples. The doping transition metal Cu was done for visible light emission from the prepared samples. The optical properties of CdS nanostructures were modulated by varying the percentage of copper doping were 3wt%, 5wt% and 7wt% respectively in nitrogen environment at room temperature. One sample was kept as un-doped CdS for carried out the comparative study with the doped samples. The formation of cubic zinc blend structure was confirmed by XRD analysis. The d-spacing, plane orientation, lattice parameter and grain sizes were calculated from XRD spectra. Particle sizes were also investigated by HRTEM analysis. The particle sizes were increase with percentage of Cu doping into CdS nanostructures. The rate of reaction may be responsible for this reduction of sizes of the nanostructures. Rate of reaction always depends on the type of reactant and the doping percentage of metal atom. The rate of reaction is faster for un-doped and it is generally become slower with higher doping percentage level of metal atom. The UV-Vis and PL spectra were used to explain the optical properties of the nanomaterials. The energy band gaps were calculated for all the samples by using UV spectroscopy. The decreasing of energy band gap was observed with higher percentage of Cu doping. From the luminescence spectra, it was confirmed that the emission of different visible light wavelength are possible by changing the doping percentage of transition metal atom. The visible light found for these particular wave lengths were blue color for un-doped sample at 462.1 nm, again blue color found for 3wt% Cu doped sample at 485.2 nm, cyan color for 5wt% Cu doped sample at 517.3 nm and green color for 7wt% Cu doped sample at 538.5 nm respectively. The doping of copper atoms had created its presence in interstitial position by substituting Cadmium atom. For metal doped samples, the luminescence peaks were corresponding to a band to band radiative recombination emission. Since the observed emission peaks were not symmetrical, therefore besides of band to band recombination there may be an additional recombination at surface defect states. These Cu metal doped CdS nanostructures can be utilized for the fabrication of LED for blue, cyan and green color emission from it.

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