Gradation of Nanoparticle Size by Stokes' Law: A New Approach for Synthesis of CdS Nanoparticles

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Abstract: The synthesis technique and its allied process parameters have a specific effect on the nucleation, growth-dominated microstructure and properties of nanostructure materials. The properties of semiconductor nanoparticles strongly depend on its size, shape, composition, crystallinity and structure. Recently, semiconductor nanoparticles have been extensively investigated and gained much interest due to their unique properties and applications in diverse areas of science and technology. A new controlled technique for synthesis of CdS nanopartlicles by means of kinetic approach using well-known Stokes' law for free body falling in quiescent and viscous fluid has been employed. Nanoparticles of cadmium sulfide (CdS) have been synthesized by simple controlled chemical method using IR radiation heating without using any capping agent and stirring. The desired concentration of aqueous solutions of cadmium chloride ($CdCl_2.2H_2O$) and thioacetamide (CH_3CSNH_2) were reacted in a controlled manner by IR radiation heating at the reaction area (top layer of reactants solution) of solution results the formation of CdS nanoparticles following Stokes' law. The as-synthesized nanoparticles were characterized by XRD, optical spectroscopy and SEM with EDX analysis.

Keywords: Stokes' law, Cadmium sulfide, Nanoparticles, IR radiation, Optical spectroscopy, XRD, SEM.

1. INTRODUCTION

The innovation of new processes and phenomena at the nanoscale provides a new prospect for the development of innovative nanostructure materials. In the synthesis of nanostructure materials, the exposure of exact size, shape and orientation controlled synthesis is becoming a great challenge for the nanotechnologists. Consequently, a specific emphasis has been focused on the control of size, shape and orientation of nanocrystals to obtain prerequisite properties of the materials. Generally, the nanoparticles with diameters in the range of 1-20 nm, promise to play a significant role in developing technologies [1]. Semiconductor nanocrystals have attracted great deal of attention in both theoretical research and technological applications [2] owing to their size dependent optical, electronic, magnetic, electrical and chemical properties, which are different from those of bulk materials [3, 4].

The Bottom up approach is more accepted in synthesis of nanoparticles owing to fewer defects, more homogenous chemical composition and better ordering. This is because that bottom up approach is driven mainly by the reduction of Gibbs free energy. Thermodynamic equilibrium and kinetic methods are the main strategies of nanoparticles synthesis in bottom up approach. The thermodynamic equilibrium is most widely and commonly used approach in which the synthesis process occur in two steps: first, the formation of small nuclei (nucleation) at critical supersaturation and second, the subsequent growth of crystal. These two steps need to be separated for producing uniform nanoparticles. In kinetic approach, the formation of nanoparticles is achieved by either limiting the amount of precursors available for the growth or confining the process in a restricted space. The kinetic approach is more challenging and need more attention in the controlled synthesis of semiconductor nanoparticles. The semiconductor nanoparticles have been the focus of much research recently due to their unique properties and applications in diverse areas of science and technology.

An entirely new method for the synthesis of nanopartlicles by means of kinetic approach using well-known Stokes' law for free body falling in quiescent fluid has been employed in nanoparticles synthesis laboratory investigation. Although, recently, Carney R.P. *et al.* [5] have devised a technique for determination of nanoparticle size distribution together with density or molecular weight by 2D analytical ultracentrifugation based on Stokes' law. The Stokes' law describing the motion of a sphere in a viscous fluid with description of the force required to move a sphere through a quiescent, viscous fluid at specific velocity.

Stokes' law is written as,

$$F_d = 6\pi\mu Vd$$

where F_d is the drag force (Stokes' drag) of the fluid on a sphere, μ is the fluid viscosity, V is the velocity of the sphere relative to the fluid, and d is the diameter of the

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sphere. Using above equation, along with other well-known principles of Physics, the rate at which the sphere falls through a quiescent and viscous fluid has been described. To describe the motion of a sphere dropping through a column of liquid, all of the internal and external forces acting on the sphere should be recognized. Three forces; namely the buoyancy (F_b), drag force (F_d) and gravity (mg) are acting on the sphere dropping through a column of quiescent and viscous liquid. The first two forces arise from the buoyancy effect and acting in upwards direction as buoyancy tends to float the sphere and drag force resisting the acceleration of gravity and the summing forces in the vertical direction can be written as,

$$F_b + F_d = mg$$

We have designed an laboratory experiment in accordance to above for the synthesis of nanoparticles inspired by Stokes' law and primarily the gradation of nanoparticle size has been confirmed in the synthesis of CdS nanoparticles.

CdS is an important and chemically stable group II–VI semiconductor. It has a bulk band gap energy of 2.42 eV [6-8] at room temperature which corresponds to the visible region of e-m spectrum of radiation and exciton Bohr radius 5.8 nm [9]. CdS nanoparticles have gained great concern due to their unique size-dependent chemical and physical properties. Extensive research has paying attention on the synthesis of various shape and size of CdS nanostructures owing to its great potential for uses in photochemical catalysis [10], solar cells [11-14], nonlinear optical materials and various luminescence devices [15, 16]. Different synthesis techniques such as co-precipitation [17], micro-emulsion [18], solvothermal [19] and thermolysis of single-source precursors [20-22] have been used by various researchers to synthesize CdS nanoparticles. Among these techniques, nanoparticles of CdS have been synthesized by using different surfactants, capping agents with thermal treatment and vigorous stirring. In this research work, we have successfully synthesized CdS nanopaticles by a simple controlled chemical method using IR radiation heating by means of kinetic approach using well-known Stokes' law for free body falling in quiescent and viscous fluid without using any capping agent and stirring.

2. EXPERIMENTAL DETAILS

In the present research work, an experiment has been designed in accordance to the Stokes' law for the gradation of nanoparticle size of CdS. This is mainly consists of a long beaker (~30 cm), infra-red (IR) radiation source for heating the upper surface of the solution, and micro burette to add the anion solution to the cation solution in a controlled manner. All the chemicals are of analytic grade and used without further purification. Nanoparticles of CdS was made by controlled chemical precipitation method using aqueous solution of cadmium chloride ($CdCl_2.2H_2O$) and thioacetamide (CH_3CSNH_2) followed by Stokes' law for free body falling in viscous and quiescent fluid as shown in schematic diagram Figure **1**. The entire process is carried out in distilled water for its inherent benefit of being straightforward and environment friendly. Firstly, the stock aqueous solutions of cadmium chloride ($CdCl_2.2H_2O$) (0.5M) and thioacetamide (CH_3CSNH_2) (0.5M) were made. The stock solution of cadmium chloride and thioacetamide was transferred to a long beaker (~30 cm) and a micro burette separately. Then, the solution of thioacetamide was added in a controlled manner to the solution of cadmium chloride with the help of a micro burette drop-by-drop on beaker wall side in presence of continuous IR lamp heating on the top of beaker as shown in Figure **1**. A controlled precipitation reaction occurs when a cation (cadmium chloride solution) and an anion (thioacetamide solution) of two aqueous solutions react only on the upper surface (top layer) of beaker in presence of IR radiation to form an ionic insoluble solid (CdS) as a precipitate in the solution and consequently, the nanoparticles of CdS go down to the bottom of the long beaker following Stokes' law. The process is continue as particles starts generate at top and moved downward under gravity in a quiescent and viscous solution according to Stokes' law and lastly reach at bottom. The rate of reaction is very slow so the process of formation of nanoparticles takes few days and after completing the process the nanoparticle accumulates in term of precipitate. Finally, the precipitate was decanted and dried to have final product for further characterization.

The crystallinity and particle size of as-prepared CdS nanoparticles were examined by X-ray powder diffraction (XRD) using a Bruker, D8 Advance X-ray diffractometer with CuK$_\alpha$ radiation (1.5406 Å) over the 2θ range 20–80°. The morphology of the synthesized powder was investigated by Scanning electron microscopy (SEM) with EDX analysis to investigate the details of their composition. The instrument UV-VIS Spectrophotometer (Hitachi U-3400) was used to measure the absorption spectra of sample. Absorption
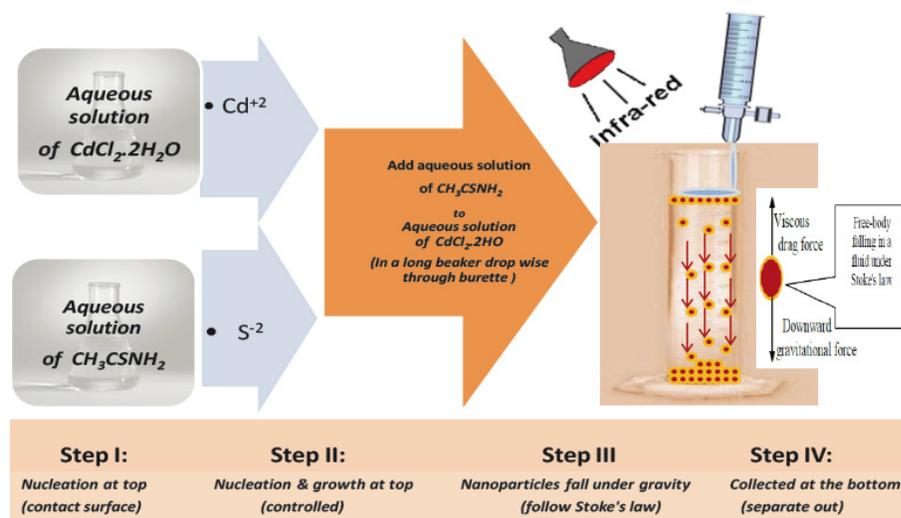
Figure 1: Schematic illustration of controlled chemical precipitation method using well-known Stokes' law for free body falling in quiescent and viscous fluid for IR radiation assisted synthesis of CdS nanoparticles.

measurements were performed to study the optical behavior of the CdS nanoparticles.

3. RESULTS & DISCUSSIONS

3.1. X-ray Diffraction (XRD) Studies

X-ray diffraction pattern of as-prepared CdS nanoparticles with 2θ ranging from 20° to 80° is shown in Figure **2.** As an initial outcome, the presence of intense peaks with good peak broadening clearly indicative of the formation of CdS nanoparticles. CdS can crystallize mainly in two different crystalline structures, namely hexagonal (wurtzite) and cubic (zinc blende). However, among these two structures, the hexagonal (wurtzite) is common and most stable [23]. Figure **2** shows that the as-prepared CdS nanoparticles had high intensity peaks at 2θ value about 26.52°, 43.73° and 51.97° corresponds to the hexagonal (002), (110) and (200) planes respectively. From the XRD patterns, it is cleared that the CdS nanoparticles was polycrystalline in nature having hexagonal structure.
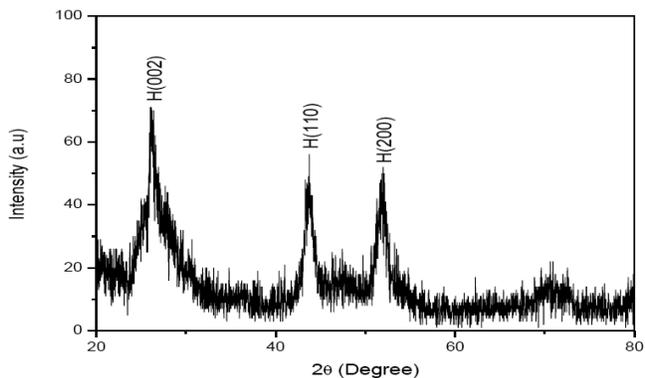
Figure 2: X-ray diffraction (XRD) pattern of as-prepared CdS nanoparticles.

The crystallite size (D) was calculated from Scherrer formula [24]:

$$D = \frac{K\lambda}{B\cos\theta}$$

where B is the full width half maximum (FWHM) of a particular diffraction peak (according to Gaussian profile) in radians, θ is the Bragg angle and K is a constant equal to 0.9, λ is the wavelength used (λ=1.54 Å). The peak broadening at lower angle is more meaningful for the calculation of particle size; therefore the size of CdS nanoparticles was calculated using high intensity peak (002) at 2θ value 26.52°. The calculated size is found to be 4.11 nm.

3.2. Optical Properties

The optical absorption spectroscopic technique is used to study the electronic band structure of semiconductors for determination of their optical properties. The absorption spectra of as-prepared CdS nanoparticles was recorded at room temperature using Hitachi spectrophotometer Model U- 3400 as shown in Figure **3** in the visible range of e-m radiation. The as-prepared CdS nano powder has been suspended in glycerol using magnetic stirrer and optical absorption spectra has been recorded by using glycerol as a reference during measurements. The most remarkable property of the optical absorption spectrum is its sensitivity to the size of the nano regime. Figure **3** shows the optical absorption coefficient increases sharply as moves towards the lower wavelength. which signify the narrower size distribution of the

nanoparticles. CdS is a direct band gap materials with absorption edge for the bulk hexagonal CdS is at 511 nm which has the band gap energy 2.42 eV. The absorption spectra show a blue shift (absorption edge at about 450 nm) from the corresponding absorption data for CdS bulk material due to quantum confinement in nanocrystalline range. The optical band gap of as-prepared CdS nanoparticles was determined using absorption spectra by the well-known following Tauc relation [25]:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where α is the absorption coefficient, $h\nu$ is photon energy, A is a constant, E_g is the optical energy band gap of the material and exponent n depends on the nature of optical transition and $n = \frac{1}{2}$ for allowed direct transition. The various types of transitions give rise to different frequency dependencies absorption coefficient near the fundamental absorption edge. The optical band gap was obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot as in inset shown in Figure **3** and comes out 2.87 eV. The higher value of optical band gap than bulk band gap 2.42 eV [6-8] was obtained which attributed due to the nanocrystalline nature of CdS particles.
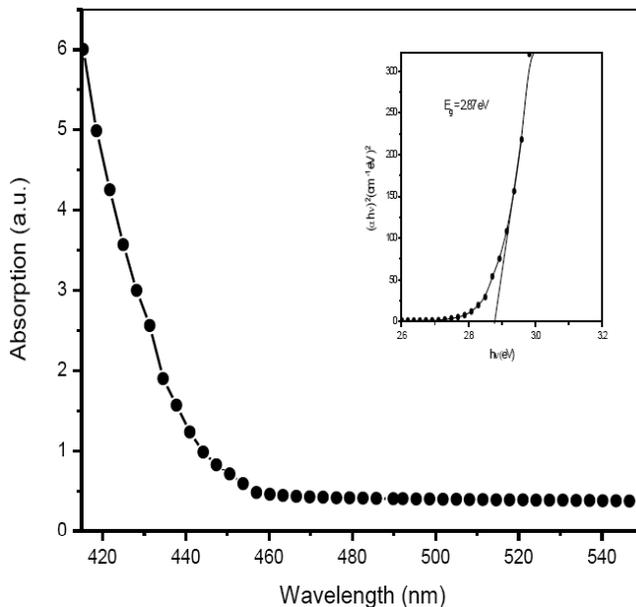
Figure 3: Absorption spectra of as-prepared CdS nanoparticles. Inset shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for determination of optical band gap of nanoparticles.

The value of E_g of as-prepared CdS nanoparticles was used to calculate the value of 'n' (nature of band gap) from the slope of plot of $\ln((\alpha h\nu)$ vs $\ln(h\nu - E_g)$ as shown in Figure **4**. The slope of linear fit of this plot

gives 'n' value ~ ½, which indicated allowed direct transition in as-prepared CdS nanoparticles.
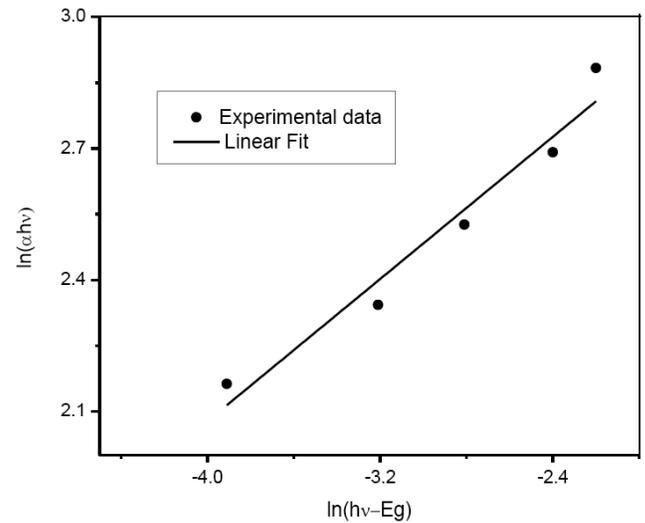
Figure 4: Plot of $\ln(\alpha h\nu)$ vs $\ln(h\nu-E_g)$ of as-prepared CdS nanoparticles. The slope (n) ~0.5, shows the direct type transition.

It is well-known that the UV-VIS spectroscopy is an well-organized technique to examine the different properties of the quantum sized particles. The values of optical band gap (Figure **3**) calculated from absorption spectra (Figure **3**), shows a significant blue-shift comparative to the corresponding optical band gap of bulk CdS (2.42 eV), [6-8]. Such observed shift reveals quantum size effect in the as-prepared CdS nanoparticles. The enhancement in the optical band gap due to quantum confinement is now well established in literature. According to "effective mass approximation" (EMA) for spherical clusters [26] and consecutive development made by Brus [27] by introducing coulomb interaction term, the quantum confinement equation is given as:

$$E_g^{nano} - E_g^{bulk} = \Delta E = \frac{h^2}{8r^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right] - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_o r} - 0.248E_{RY}^*$$

where, E_g^{nano} and E_g^{bulk} are the optical band gap energy for nanoparticles (with spherical geometry) and bulk material respectively. ΔE represents the difference (enhancement) in the same, r is the radius of nanoparticle, m_e^* and m_h^* are the effective masses of electron and hole in units of free electron mass (m_o), e is the electronic charge, ε is the dielectric constant, ε_o is the permittivity of free space and E_{RY}^* is the effective Rydberg energy. The second and third term are much smaller than the first confinement term [28] due to relatively high value of dielectric constant for

semiconducting materials, so may be omitted from the above equation leaving equation as:

$$\Delta E = \frac{h^2}{8r^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right]$$

The values of the effective mass of electron and hole for CdS (in terms of free electron mass) are m_e^* = $0.19m_o$ and m_h^* = 0.8 m_o [29]. Substituting the value of Plank's constant and effective masses for CdS nanostructure materials, the relation between the particle radius (*r*, in nm) and the change in optical band gap (ΔE, in eV) becomes:

$$r(nm) = \frac{1.566}{\sqrt{\Delta E(eV)}}$$

The average particle size of as-prepared nanoparticles was also calculated using above described mathematical model of effective mass approximation and found to be 4.66 nm, which is in good agreement with the particle size calculated by Scherrer formula using XRD parameters.

3.3. Surface Morphology by Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) with Energy dispersive X- ray analysis (EDAX) is a suitable technique to study the microstructure and chemical composition of nanostructure materials. The SEM micrographs (at different magnification) of as-prepared CdS nanoparticles are shown in Figure **5**. From these SEM images, it is noticed that the surface morphologies are in the form of assemblies of nanoparticles are having round shape, and the particles size of few micron ranges to nanometer range.

Elemental composition of as-prepared CdS nanoparticles was verified using energy dispersive X-ray analysis (EDAX) as shown in Figure **6**. Electron beam induced inner-shell ionization and subsequent emission of characteristic fluorescence are analyzed in order to obtain the composition. The subsequent characteristic fluorescence of Cd L-fluorescence (L_α & L_β around 3-4 keV energy range), and S K_α-fluorescence (around 2-3 keV energy range) in EDAX spectrum confirms the presence of Cd and S components in the as-prepared CdS nanoparticles. The At% of constituents are shown in the underneath tables of Figure **6**. The average atomic percentage formation of Cd and S in CdS nanoparticles is 50.20 % and 49.80 % respectively. The underneath table of Figure **6** reveals that the Cd/S atomic percentage ratio of the CdS is relatively consistent with the theoretical Cd/S atomic ratio of 1 for the CdS. These results show that atomic percentage of Cd is slightly more which indicates the cadmium rich formation of CdS nanoparticles.

4. CONCLUSIONS

In the present study, CdS nanoparticles were successfully synthesized by an entirely new controlled chemical precipitation method by means of kinetic approach using well-known Stokes' law for free body falling in quiescent and viscous fluid. The characterization of as-prepared CdS nanoparticles confirms the nano-scale formation of the product. The XRD pattern confirms the nano size formation and hexagonal phase of as-prepared CdS nanoparticles. These initial results show the worth of new synthesis approach and further work to expose the control of size, shape and orientation of the nanoparticles by optimizing the process parameters is in progress. This
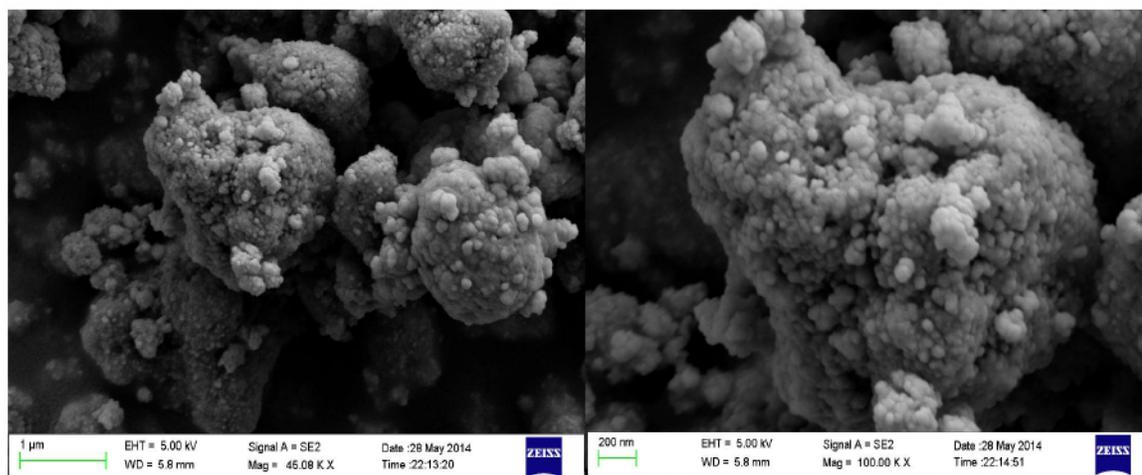
Figure 5: SEM images (at different magnification) of as-prepared CdS nanoparticles.
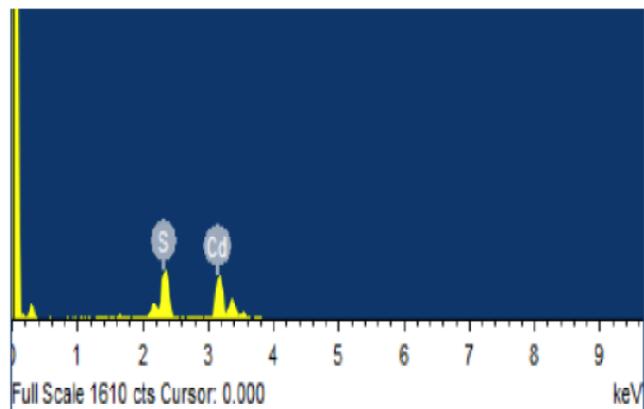
Element	Weight%	Atomic%
S K	22.05	49.80
Cd L	77.95	50.20
Totals	100	100

Figure 6: EDAX spectrum of as-prepared CdS nanoparticles. Underneath is the elemental composition of the product.

new method may be applicable in any chemical precipitation to synthesis nano-scale materials.

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