CdS Nanoparticles: Glucose/Starch Synthesis Method and Non Linear Electrical Properties Disperse in Polypyrrole Matrix

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Development of environmentally benign methods for the synthesis of nanoparticles is an evolving important branch of nanotechnology. Inorganic-organic hybrid nanocomposites are synthesized by dispersing nanosized CdS in the conducting polypyrrole (PPY) matrix. The samples are characterized by X-ray diffraction, transmission and scanning electron microscopes and UV-VIS spectrophotometer. The wavelength of optical absorption peak of CdS nanoparticle increases from 430 nm to 470 nm with the decrease of polypyrrole concentration. Studies on dc electrical conductivity as a function of temperature suggest that three dimensional Mott's hopping process occurs in CdS-Polypyrrole nanocomposites. The incorporation of CdS nanoparticles enhances the barrier height. The barrier height increases with the content of CdS. The observed nonlinear current-voltage characteristics are satisfactorily explained using the Schottky type barriers. [DOI: 10.1380/ejsnt.2018.14]

Keywords: Glucose/starch synthesis; CdS nanoparticles; Nanocomposites; Optical, non-linear electrical properties

I. INTRODUCTION

Nanotechnology and Nanoparticles based products and their applications are increased now a days due to there use in various research field. This relatively new field is focused on the creation and use of materials at the nanometre size scale for advanced biotechnology. Both equilibrium and dynamic properties of nanomaterials can be very different from those of their corresponding bulk material or isolated atoms and molecules [1]. Their properties are often strongly dependent on the particle size, shape, and surface properties. Metal chalcogenides like sulfides, tellurides and selenides are of great importance because they are potential materials for optoelectronics applications. Nanoparticles have excellent electrical properties over bulk material and are thus being used in various electronic device. Cadmium Sulfide, one of the most studied material among the II-VI compounds and is a wide energy gap semiconductor has emerged as an important material due to its applications in photovoltaic cell as window layers [2], optical fibers and multilayered light emitting diodes [3], detectors [4], thin film field effect transistors [5], gas sensors and transparent conducting semiconductor for optoelectronic devices [6]. CdS is naturally an *n* type material with an optical band gap of 2.4 eV [7]. There are many methods for the formation of Cadmium Sulfide nanoparticles: Successive ionic layer adsorption and reaction (SILAR) [8, 9], Sonochemistry method [10, 11], microwave radiation [12], sol-gel [13, 14], processing of polymer films containing cadmium atoms or ions with a vapor of hydrogen sulfide and others.

The shape plays an important role in determining the electronic properties of nanomaterials. CdS nanoparticles adopt different geometrical shapes like triangular [15] hexagon and pyramid [16], rod [17] and wire. CdS nanocrystals are dispersed in the polymer matrix to design organic-inorganic hybrid nanocomposites. The host polymer assists the assemble of CdS nanoparticles to form a new material with a deviation of spherical shape. Zhan *et al.* [18] successfully fabricated long CdS

nanowires utilizing polyacrylamide. Wire like assemblies of CdS nanoparticles are fabricated within core-shell cylindrical polymer brushes [19]. Composites of CdS nanoparticles incorporated in polyurea [20] and sulfonated polystyrene [21] have been prepared. Conducting polymer [22] are founding a growing number of application in various electronic devices such as in chemical sensors, light emitting diodes, electrochromic display devices etc. among these polymer polyaniline(PANI) and polypyrrole (PPY) has been studied most extensively in recent years due to following reasons: (i) these can be synthesized easily (ii) these are comparatively stable in air (iii) these are relatively cheaper and (iv) these shows number of interesting properties such as chemical sensitivity etc. [23].

Conducting polymer composites (CPC) have drawn considerable interest in recent years because of their electrical and electronic devices. In most of these applications the main objectives is to obtain a sufficient level of conductivity in the material. Lately, it has been found that these composites can exhibits some novel properties such as positive temperature co-efficient(PTC) of resistance, photosensitivity etc. [24–26]. Electrical properties of conducting polymers primarily depend on the preparation condition. The presence of inorganic nanoparticle strongly influences the electronic properties of polymer. Moreover, the integrating properties of inorganic material and polymer give rise to composites with different physical property. Also, it is known that some conducting polymers exhibit piezosensitivity. This paper proposes to couple CdS nanoparticles with conducting polymer composites exhibiting novel properties.

II. EXPERIMENTAL

All the chemicals used were of analytical grade. Pyrrole and ammonium peroxydisulphate (APS) ((NH₄)₂S₂O₈) were obtained from E. Merck (India). Pyrrole (AR grade) was purified and stored at –15°C in a refrigerator prior to use. APS oxidant was used as received.

A simple chemical co-precipitation method was followed for the synthesis of CdS nanoparticles. We utilized cadmium nitrate (Cd (NO₃)₂) as a source of cadmium ion and

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TABLE I. Weight percentage of pyrrole (x), room temperature dc conductivity ($\sigma(\text{RT})$), σ_0 , T_0 as indicated in Eq. (2) in the text, density of states $N(E_F)$, hopping length R_{hop} , and activation energy W_{hop} .

Sample	x	$\sigma(\text{RT})(10^{-3})$ (S/cm)	$\sigma_0(10^3)$ (S/cm)	$T_0(10^7)$ (K)	$N(E_F)(10^{21})$ ($\text{eV}^{-1}\text{cm}^{-3}$)	R_{hop} (Å)	W_{hop} (meV)
S1	75	7.51	7.41	1.02	2.02	15	87
S2	68	5.29	12.08	1.38	1.49	17	94
S3	52	3.15	30.94	2.02	1.02	21	104
S4	35	1.95	230.50	3.44	0.6	25	120

sodium sulfide (Na_2S) as a source of sulfide ion and glucose/starch is used as a capping agent. Cadmium nitrate (2.36 g) is dissolved in 100 ml distilled water, sodium sulfide (0.78 g) was dissolved in 100 ml of water, then sodium sulfide solution was added drop wise to cadmium nitrate solution and stirred continuously, an orange colour solution is obtained. The solution is stirred on magnetic stirrer for 16 hours at 500 rpm. Add 1.8 g glucose/9 g starch is taken and mix it to 100 ml water. Divide the orange solution in three equal parts and 10 ml glucose/starch in each solution drop wise. The sample is then heated and then put it to oven for 7 hours at 100°C . Filter the precipitates and dried in oven for 70°C for 6 hours.

The required quantity of CdS nanoparticle was ultrasonically dispersed in 40 ml deionized water. Pyrrole monomer of known volume was slowly added into the dispersion under sonication at room temperature. Then the aqueous solution of APS maintaining a pyrrole: APS mole ratio of 1:1.25 was added drop wise into the previous solution. After few hours the resulting solution was turned into black color which indicates the formation of polypyrrole. The solution was then kept under sonication for about 6 hours to ensure complete polymerization. Finally the resulting black dispersion were centrifuged. The resulting nanocomposites were washed thoroughly with distilled water for several times. Different compositions of nanocomposite samples by varying the weight percentage of pyrrole(polypyrrole) were prepared as shown in Table I.

The samples were characterized by x-ray powder diffraction patterns employing a scanning rate of 0.020° per 2 sec in 2θ range from 20 to 70 using a Philips PW1710 x-ray diffractometer equipped with monochromatized Cu-K α radiations. The nanocrystallite powder was pressed inside the sample holder and X-ray data were collected in step scan mode. Morphological studies were performed with JEOL JSM6700F Scanning electron microscope. Transmission electron micrograph (TEM) was taken from JEOL JEM 2010 with acceleration voltage of 200 kV. A drop of aqueous solution of CdS-PPY nanoparticles was placed on a carbon coated copper grid and dried before putting it onto the TEM sample chamber. FTIR spectrometer were recorded as KBr disc on Perkin-Elmer Spectrum-2000, FTIR spectrophotometer between 500 and 4000 cm^{-1} . UV-visible spectra of the diluted nanocomposite dispersions in the 200-1000 nm range was obtained using Perkins-Elmer instrument. The temperature dependent dc conductivity was measured by the standard four-probe method using Keithley digital multimeter (Keithley 2000 programmable multimeter). The room temperature current-voltage (I - V) characteristics were measured by Keithley 220 programmable current source meter. Dry powdered sample were made into pel-

FIG. 1. X-ray diffraction pattern of CdS-PPY nanocomposites sample S4.

lets using a steel die of 1 cm diameter in a hydraulic press under a pressure of 7 ton. The thickness of the samples varies from 0.08 cm to 0.12 cm. For electrical measurements the electrical contacts were made by silver paint.

III. RESULTS AND DISCUSSION

To confirm the formation of CdS nanoparticles and its crystallographic phase, a wide angle diffractogram (XRD) was recorded for the dried precipitate of CdS nanoparticles. It can be attributed to a very small grain size of the particles. Figure 1 displays the powder X-ray diffraction (XRD) of the sample S4. The characteristic peaks at angles (2θ) of 26.5, 30.8, 43.7, 51.9, 54.9 are indexed to the reflections from 111, 200, 220, 311 and 222 planes of nanocrystalline CdS which are reported in many research paper [27, 28]. It is well known that CdS exists in two crystalline phases, cubic zinc blende and hexagonal wurtzite. The present XRD pattern matches well with the reported cubic phase of CdS [Joint Committee on Powder Diffraction Standards (JCPDS) No. 42-1411]. The peaks are fairly broad suggesting the nanostructure of CdS.

The scanning electron micrograph (SEM) of the nanocomposite sample S4 is shown in Fig. 2. The CdS nanoparticles are aggregated in the presence of conducting polymer and are of spherical in shape with uniform diameter lying in the range from 25-35 nm. Larger particle size may be due to the aggregation of smaller particles in the presence of polymer matrix.

Figure 3 shows the TEM micrograph of the CdS-PPY nanocomposite S4 sample. In this micrographs nearly spherical crystallites are observed. The mean particle size

FIG. 2. Scanning Electron Micrograph (SEM) of nanocomposite sample S4.

FIG. 3. Transmission Electron Micrograph (TEM) of nanocomposite sample S4.

of pure CdS is in the range of 10 nm which is good agreement with XRD result (Not shown in this manuscripts). Larger particle size due to the aggregation of smaller particles in the presence of polymer matrix having particle size in the range 20-30 nm.

A typical FTIR spectrum of the nanocomposite sample S4 is illustrated in Fig. 4. It is reported [29–32] that the absorption peak at 3427 cm^{-1} in the figure is assigned to water molecule. The band at 1556 cm^{-1} and 1469 cm^{-1}

FIG. 4. Fourier Transform Infrared (FTIR) spectra of sample S4.

FIG. 5. UV-VIS absorption spectra of the nanocomposite samples.

corresponds to $\text{C}=\text{C}$ stretching and peaks at 922 cm^{-1} and 799 cm^{-1} due to $=\text{CH}$ out of plane vibration. The characteristic bands at 1310 cm^{-1} is due to $\text{N}-\text{C}$ bonding and band at 1190 cm^{-1} is due to $\text{N}-\text{C}$ stretch bending. 1050 cm^{-1} is related to $\text{C}-\text{H}$ in plane vibration and 664 cm^{-1} is due to ring deformation. The characteristics bands of bare PPY are 1551 cm^{-1} , 1440 cm^{-1} , 921 cm^{-1} , 788 cm^{-1} , corresponding to pyrrole rings, in and out of plane $=\text{CH}$ vibrations. Almost all the bands reveal blue shift in the nanocomposites which indicates that there is a strong interaction between polypyrrole and CdS nanoparticles.

Electronic UV-Vis absorption spectra of nanocomposites samples with the variation of polymer fraction are shown in Fig. 5. The fundamental absorption which corresponds to the transition from valance band to the conduction band, can be determine the band gap of the material. The absorption spectra consist of three absorption bands in the entire wavelength range. Out of these three absorption peaks, one prominent broad peak is observed around 430-470 nm and two broad peaks at 400-1000 nm. Different spectroscopic techniques [33] and theoretical energy band calculation [34] indicate that the absorption band at 400-500 nm is assigned to $\pi-\pi^*$ transition of polypyrrole. Upon doping PPY exhibits an unusual electronic structure due to electron-phonon coupling. Polaron and bipolarons states appear within the band gap which give rise to the broad band at wavelength 600-1000 nm. The absorption peaks of PPY in the nanocomposites are less pronounced as the strong absorption of CdS overlaps with that of PPY. The absorption peak associated with CdS are found in the wavelength range 470-430 nm as shown in Table II. The excitonic peaks for all the samples are well shifted from absorption peak at 530 nm for bulk CdS. The reduction of size in semiconductor reveals a blue shift due to quantum size effect. The dramatic modifications of electronic absorption bands of individual CdS and PPY suggest that nanosized CdS are incorporated into polypyrrole matrix.

CdS is n -type direct band gap (2.42 eV) semiconductor. Electronic energy band structures of cubic and hexagonal phases of CdS are very similar [35]. $4d$ states of Cd and $3p$ states of S play crucial role in the determination of optical band gap. Photoemission experimental results of

TABLE II. Absorption wavelength on CdS-PPY solution, Saturation current density J_0 , Ideality factor n and Barrier height β as indicated in Eqs. (6) and (8) in the text, respectively.

Sample	λ_{peak} (nm)	$J_0(10^{-7})$ (A-cm $^{-2}$)	n	β
S1	470 ^a	22.45	14.95	4.75
S2	458 ^a	13.45	20.90	3.45
S3	444 ^a	8.40	24.25	2.34
S4	430 ^a	6.45	32.25	1.75

^a CdS band.

FIG. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for nanocomposite sample S4 to determine the optical band gap for sample S4.

nanostructured CdS provided the distinct changes of d and p states [36, 37]. The optical band gap E_g is related to the absorption coefficient α by the relation [38]

$$\alpha = \frac{B(h\nu - E_g)^{1/2}}{h\nu} \quad (1)$$

where B is the absorption constant for a direct transition. For allowed direct transition one can plot $(\alpha h\nu)^2$ vs. $h\nu$ and extrapolate the linear portion of it to $\alpha = 0$ value to obtain the corresponding band gap. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ for S4 sample is presented in Fig. 6. The calculated band gaps are 2.61 eV, 2.69 eV, 2.75 eV and 2.82 eV for S1, S2, S3 and S4 respectively. The higher band gaps compared to the bulk energy gap (2.42 eV) are consistent with the quantum confinement effects of CdS nanoparticles.

The variation of room temperature conductivity $\sigma(RT)$ with the weight percentage of PPY are shown in Table I. The conductivity increases with the increasing content of PPY. The enhancement of $\sigma(RT)$ is about one order of magnitude for the highest fraction of PPY. The conductivity of pure PPY is 6.67×10^{-2} S-cm $^{-1}$ and the conductivity of nanosized CdS at room temperature is of the order of 10^{-9} S-cm $^{-1}$ [39, 40]. Much higher room temperature conductivity of the nanocomposites indicates that electrical conduction is dominated by the PPY. Percolating behavior is commonly observed by dispersing conductive particulate in the insulating matrix. The conductive fillers form a conductive path in a three dimensional network which gives rise to a sharp increase of electrical conductivity at certain volume fraction of filler. In

FIG. 7. Temperature variation of dc conductivity of the nanocomposite samples S1-S4. The solid lines are fits to Eq. (2).

the present system, insulating CdS nanoparticles are dispersed in the conducting PPY matrix. The specific volume of PPY is much higher than the percolation threshold. Hence, the plot of conductivity with the content of PPY does not exhibit percolation like behavior. The temperature dependence of conductivity for all samples are shown in Fig. 7. Chemically induced disorder of conducting PPY plays an important role in the electrical transport. Hence the temperature dependence of conductivity $\sigma(T)$ is interpreted by three dimensional Mott's variable range hopping (VRH) model [41],

$$\sigma(T) = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right) \quad (2)$$

where σ_0 is the high temperature limit of conductivity and T_0 is Mott's characteristic temperature associated with the degree of localization of the electronic wave function. The values of Mott's characteristic temperature T_0 and the pre exponential factor σ_0 are obtained from the slopes and intercepts of Fig. 7 and are given in Table I. The values of T_0 and σ_0 decrease with the increase of PPY content.

The characteristic temperature T_0 for three dimensional hopping transport is given by,

$$T_0 = 16/(kL^3N(E_F)), \quad (3)$$

where L is the localization length and $N(E_F)$ is the density of states at the Fermi level. The values of $N(E_F)$ are calculated by considering the charge transport primarily arising from conducting PPY phase and assuming

FIG. 8. I - V characteristics curve for the nanocomposite sample S4.

FIG. 9. Forward bias (J vs. V) of the nanocomposites sample S4.

localization length of the polypyrrole monomer unit about 3 Å [42, 43]. The higher values of density of states at the Fermi level are found with increase of PPY content.

The average hopping distance R_{hop} between two sites and the activation energy W_{hop} are

$$R_{\text{hop}} = (3/8)(T_0/T)^{1/4} L \quad (4)$$

$$W_{\text{hop}} = (1/4)kT(T_0/T)^{1/4} \quad (5)$$

At room temperature the average hopping distance varies from 15 Å to 25 Å for as shown in Table I. This corresponds to about 5-8 monomer units in length. The estimated activation energies for hopping as shown in Table I are in the range of 87-120 meV. In case of *in situ* polymerization of PPY in the presence of CdS nanoparticles, monomer is adsorbed on the surface of nanoparticle. The growth of PPY depends on the concentration of CdS. The increase of CdS amount reduces the conjugation length of polymer. The conductivity of conjugated polymers critically depends on its conjugation length. It is observed that the conductivity decreases with decreasing conjugation length [44]. Moreover CdS is less conducting than PPY. As a results of it, the conductivity of nanocomposites decreases with increasing weight percentage of CdS.

Figure 8 shows the current vs voltage (I - V) characteristics of the sample S4 at room temperature. Current

versus voltage characteristics are asymmetric and nonlinear for forward and reverse directions of applied voltage. This suggests that Schottky barriers are formed in the nanocomposites. The applied forward bias and the current based on thermionic emission current can be written as [45]

$$I_f = I_0(\exp[\frac{qV}{nkT}] - 1) \quad (6)$$

where n is the ideality factor, I_0 is the saturation current and defined by

$$I_0 = AA^*T^2 \exp[-\frac{q\Phi}{kT}] \quad (7)$$

where the quantities A , A^* , T , q , k and Φ are the area, the effective Richardson constant, temperature in Kelvin, the electronic charge, Boltzmann constant and the apparent barrier height. The current density J is obtained from the geometrical area. The variation of current density, J with forward voltage is shown in Fig. 9. The values of saturation current density J_0 and n are determined from the non linear curve fitting to Eq. (6) as shown in Fig. 9. The calculated values of J_0 and n for all the samples S1, S2, S3, S4 are shown in Table II.

The voltage dependence of the reverse current can be written as [45],

$$I_r = I \exp[\frac{\beta V^{1/2}}{kT}] \quad (8)$$

where

$$I = AA^*T^2 \exp[-\frac{\Phi}{kT}] \quad (9)$$

where β is related to the barrier height. The linear behavior in plot of the current density J vs. $V^{1/2}$ as depicted in Fig. 10 indicates that the I - V characteristics are consistent with Eq. (8). The estimated values of β for are shown in Table II. Saturation current density and ideality factor decrease while β increases with increase of PPY amount. The Schottky type energy barrier at the grain boundaries are observed in the nanocomposite samples. Polypyrrole influences the surface states of nanocrystalline CdS which leads to nonlinear behavior in I - V characteristics.

IV. CONCLUSION

The growth and the assemble of CdS nanoparticles in the polymer matrix is a very complicated process. The

FIG. 10. Reverse bias ($\ln J$ vs. $V^{1/2}$) of the sample S4.

incorporation of nanosized CdS strongly affects the electronic structure of polyaniline. The presence of nanocrystalline CdS in the disordered polypyrrole lead to Mott VRH type electric charge conduction. The modification

of surfaces of CdS nanoparticle by polypyrrole and the formation of nanosize grains give rise to diode like current voltage characteristic in nanocomposite.

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