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I. Introduction

Now-a-days, nanostructured materials are extensively explored due to their superior physico-chemical properties in various applications, including photovoltaic, electro-optical, and sensor devices [1-4]. Nanotechnology becomes advantageous to make inexpensive and efficient solar cells on a large scale. To this end, nanostructured layers in thin film solar cells offer three significant advantages. First, due to multiple reflections, the actual optical path for absorption is much larger than the definite film thickness [5]. Second, light generated electrons and holes need to travel over a much shorter path, so, the recombination losses are greatly reduced. As a result, the absorber layer thickness in nano-structured solar cells is very thin in few nanometers (nm) instead of several micrometers in the traditional thin-film solar cells (TFSCs) [6]. Third, the energy band gap of different layers of TFSCs can be improved to the preferred design value by simply varying the size of nano-particles [7]. The altered energy band gap energies allows for more design flexibility in the absorber and window layers in the solar cells. In particular, nano-structured cadmium sulfide (CdS), zinc oxide (ZnO), cadmium telluride (CdTe), Cu_2ZnSnS_4, Cu_2FeSnS_4, etc. are of great interest as window and absorber layers in thin film solar cells [8-11].

Among various semiconductors, CdS is one of the most vital semiconductor compounds which is used widely as a photo-electrochemical (PEC) solar cell element due to its optimum band gap energy [12]. Also, to PEC solar cell, CdS has also been exploited in diode lasers, gas sensors, and catalytic applications [13, 14]. Meanwhile, the specific properties of CdS have been correlated with growth conditions and methods. In this direction, CdS have been prepared via a number of physical and chemical techniques. Out of various techniques, chemical bath deposition (CBD) is one of the simplistic and easy methods to prepare CdS thin films with a variety of surface morphologies [15, 16].

In the present paper, attempts were made to engineer the morphology of the CdS thin films by using ionic surfactant; hexamethylenetetramine (HMTA). In this direction, thin films of CdS in assistance with HMTA were prepared at 90°C by using simplistic CBD method. The surface morphological study revealed the interconnected nanoplate-like structure of as synthesized CdS thin films. Further, these interconnected nanowalls of CdS thin films were characterized for their structural, and optical studies through the techniques including X-ray diffraction (XRD), and optical absorption spectroscopy. Finally, the photoelectrochemical (PEC) performance such as J-V characteristics in dark and under illumination, ideality factor of prepared CdS films was studied.

II. Experimental Details

All chemical were purchased from S. D. fine-chemicals and used without any further purification. The cadmium sulfate ($CdSO_4{\cdot}H_2O$) were used as cadmium (Cd) source and thiourea ($H_2N{\cdot}CS{\cdot}NH_2$) as sulfur (S) source. HMTA and liquor ammonia (NH_3) were used as an organic surfactant and a complexing agent, respectively. The experimental parameters like the precursor's concentration, operating temperature, pH, and deposition time were varied to produce a good quality CdS thin films. Initially, the matrix solution was prepared by adding aqueous solution (1 wt %) of an organic surfactants (HMTA) to 1.25 M $CdSO_4$. Then, to

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maintain 11 pH of the solution, the aqueous ammonia (NH_4OH) added to the solution. The initial turbid solution becomes transparent by adding the excess ammonia. Finally, 1.1 M thiourea was added into above solution with constant stirring. The CdS films were deposited by dipping the soda lime glass into the above solution at 90 C for 10 min. Finally, the synthesized CdS thin films were rinsed in distilled water and kept for drying at room temperature overnight.

The X-ray diffractometer (Philips, PW 3710, Almelo, Holland Make) operated at 25 kV, 20 mA with CuKα radiation (1.5407 Å) was used for study of the structural properties of the CdS thin films. Optical absorbance was measured using a UV–vis spectrophotometer (UV1800, Shimadzu, Japan). The surface morphology of the films was examined by SEM (Model JEOL-JSM-6360, Japan), operated at 20 kV. Meanwhile, the thickness of the resulting CdS films was measured using a surface profiler (Ambios XP-1). The J-V characteristics were measured using Semiconductor Characterization System (SCS-4200, Keithley, Germany) using two electrode configurations.

III. Result and Discussion

X-ray diffraction (XRD) patterns of CdS thin films were used for its structural characterization and the assessment of stoichiometry. Fig. 1 shows XRD pattern of HMTA mediated CdS interconnected nanowalls network on soda lime glass substrate. The films deposited were stoichiometric and did not show peaks related to elemental cadmium or sulfur or carbon. CdS peaks in XRD pattern are (111), (200), (220), (311), (222), (400) and (331) appears at 2θ = 26.45, 31.71, 44.13, 51.87, 54.97, 62.67 and 70.23 degree, respectively. The formation of CdS phase was confirmed by comparing the observed XRD pattern with the standard JCPDS data (80-0019). In addition, the standard JCPDS data suggest the cubic crystal structure of as-synthesized CdS thin films. The lattice parameter 'a' is calculated using the following Eq. (1),

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (1)$$

The mean values of 'a' observed in our study (5.810 Å) is in good agreement with the reported value a=5.811Å.

Further, using the breadth of (111) peak, the average crystallite size was estimated using Scherrer's formula given below Eq. (2)

$$D_{(111)} = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where k is the dimensionless constant (0.95), λ is wavelength having value 1.5406Å and, β is the broadening of the diffraction line at half of its maximum intensity (taken in radians by multiplying a factor of $\pi/360$). The D the diameter of crystallite and θ is diffraction angle. The calculated crystallite size is found to be 20 nm for (111) plane. Meanwhile, the broadened peaks indicate the nanocrystalline nature of the films [17].

Due to the nanocrystalline thin films, UV-Vis spectroscopy has become an effective tool in determining the size and optical properties. Fig. 2 shows the room temperature optical absorption spectrum of the CdS thin film recorded in the range of 450–750 nm without taking into account scattering and reflection losses. The optical absorption peak appeared at ~ 522 nm gives band gap energy value of about 2.44 eV. This band gap energy is suitable for the light energy capturing and its conversion to electrical energy [18]. The present UV-visible spectrum reveals as-synthesized CdS thin film has a high absorbance of light in the visible region, indicating applicability as a captivating material in solar cell applications.

The surface morphology of as-synthesized HMT assisted CdS thin films were examined by SEM technique and presented in Fig. 3. The low magnification SEM image as shown in Fig. 3(a) reveals the porous surface structure and the formation of CdS interconnected nanoplates-like assembly over the complete substrate. Also, no overgrowth, pinholes, voids or cracks on the substrate was seen. In addition, the nano-plates like structure covers over the entire substrate. Fig. 3(b) shows the high magnification SEM image of CdS thin films. The high magnification images clearly show the nanoplates connected with each other forming nanoconduits. Such plates having ~70 nm thickness are seen in the SEM image Fig. 3(b). Due to these interconnected nanowalls, the HMT mediated CdS thin film sample provides noticeable surface area. The higher surface area is beneficial for the enhancement of surface activities such as effective permeability of electrolytes into the inner structure of the film, and light absorption [19]. Also, the peculiar interconnected nanoplate-like structure scatters the light internally, which may lead to improvement in the effective light absorption [20]. The light absorption path length of photons can be increased as it is trapped in the nanoconduits. These mechanisms boost the PEC performance of CdS electrode.

For the PEC characterization of the HMT mediated CdS thin film sample (CdS), the measurements were performed in an electrolyte of 1 M polysulfide (Na_2S-NaOH-S) in a two-electrode arrangement of the following configuration:

Glass/FTO/CdS/Na_2S-NaOH-S/G

In the photo-electrochemical cell, poly-sulfide solution acts as an electrolyte and the CdS thin film deposited on the FTO acts as a working electrode. The

graphite (G) acts as a counter electrode. The active area of working and counter electrode was about 1 cm^2. The J-V characteristics were measured by a SCS-4200 unit in the dark and under light illumination at 30 mW/cm^2. Fig. 4 suggest that, the J-V characteristics is like diode characteristics for the PEC cells fabricated with CdS thin film samples. Under illumination, shifting of the J–V curve in the fourth quadrant of the graph suggests that the electrons are the majority carriers, confirming the n-type conductivity of CdS thin films [21]. The CdS cell shows the photo-electric conversion efficiency (η) of 0.34 % with (J_{SC}) =1.25 mA/cm^2, open-circuit voltage (V_{OC}) =435 mV and fill factor (FF) =0.31.

The ideality factor 'n_d ' of CdS films is determined under forwarding bias by using following equation (Eq. (3)) as,

$$I = I_O\,(e^{qV/ndkT}) - 1 \qquad (3)$$

Where Io is the reverse saturation current, V is forward bias voltage, k is Boltzmann's constant, and T is ambient temperature. Usually, the value of 'n_d' is found to be in between 1 to 2. This value depends on the relation between diffusion current and recombination current. When diffusion current is more, then, ideality factor becomes 1 and, it becomes 2 when the diffusion current is less than recombination current. The ideality factor in our CdS film was found to be 1.6. The value of 'n_d' is a suitable parameter that describes how closely the diode's behavior matches the behavior predicted by theory.

IV. Conclusion

In summary, CdS composed of a uniform interconnected nanoplate-like network have been successfully prepared via a non-ionic surfactant-assisted chemical bath deposition at ambient atmosphere. The as-deposited CdS film showed a cubical crystal structure. The well-covered porous structure with the interconnected nanoplates network morphology leads to a high surface area which is observed by SEM studies. Further, this structure is a good prospective way for PEC solar cell application.

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Figure Captions

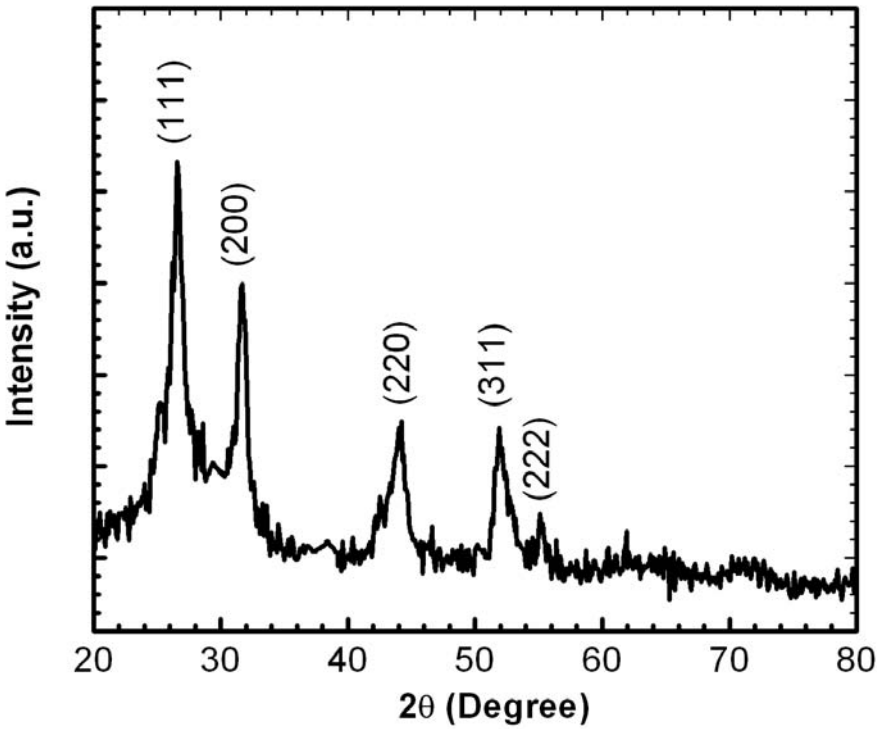

Fig. 1: X ray diffraction pattern of HMTA mediated CdS thin film

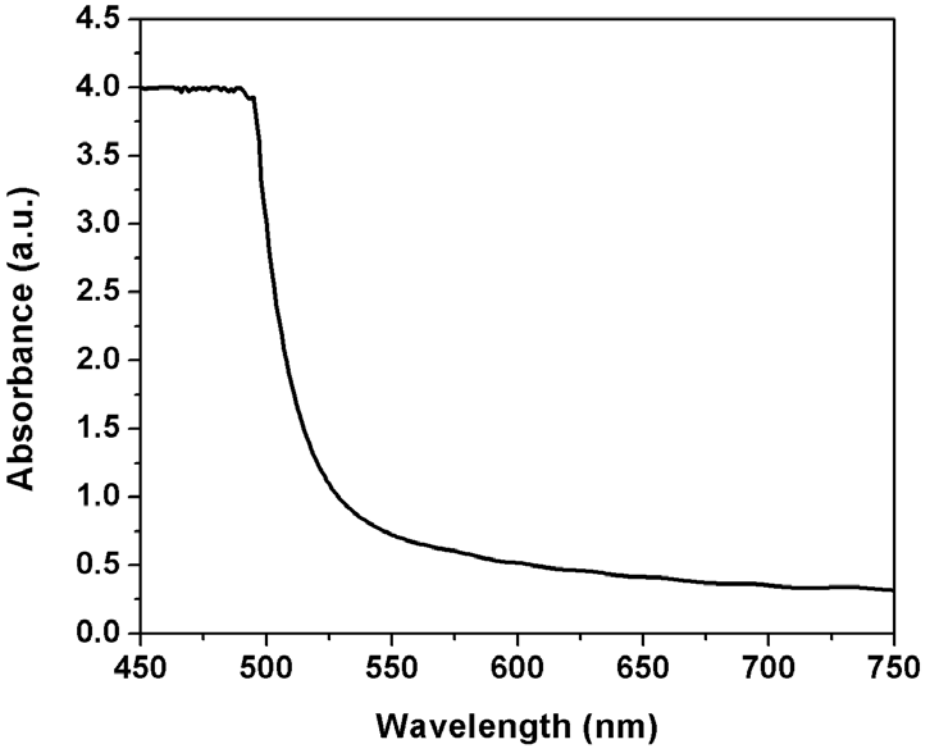

Fig. 2: Optical absorption spectrum of HMTA mediated CdS thin film

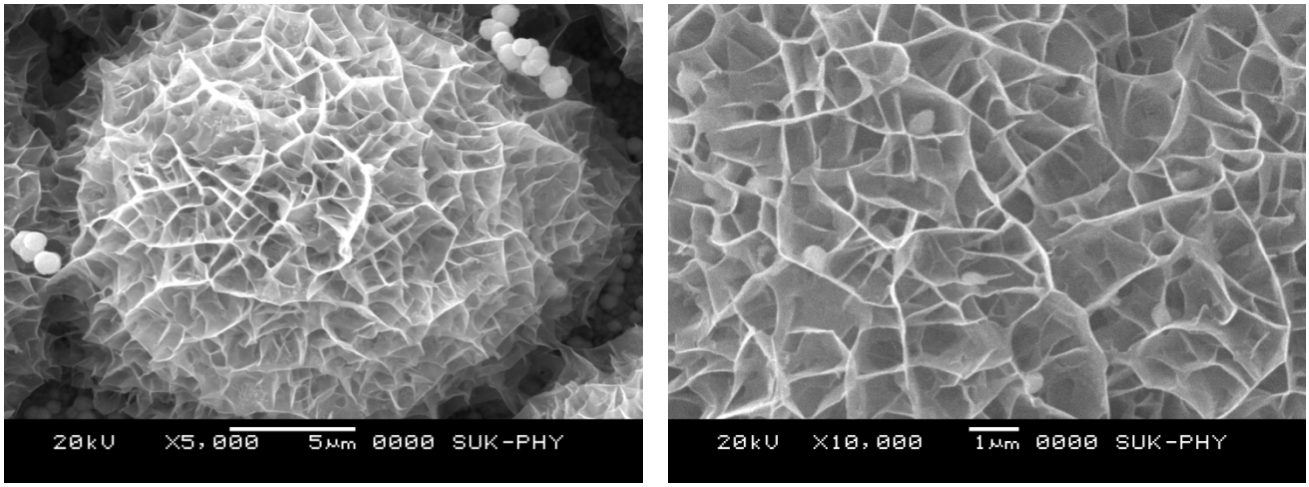

Fig. 3: (a) Low magnification SEM images of HMTA mediated CdS thin films sample

(b) SEM images show the formation of interconnected nanowall network of HMTA mediated CdS over the substrate

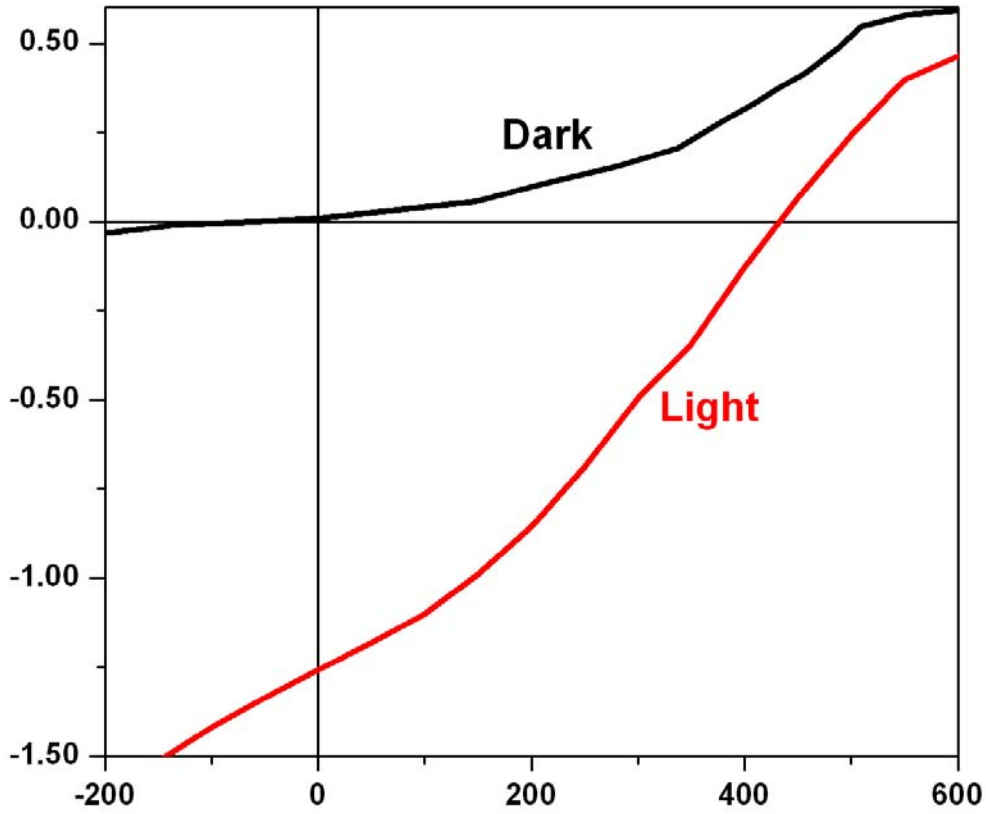

Fig. 4: The J-V characteristics of interconnected nanowall network of HMTA mediated CdS thin film sample