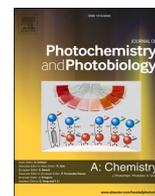




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Metal-free azo dyes anchored on CdS nanowires: Subtle solar cell exploration through experimental and DFT studies

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ABSTRACT

Herein, as-synthesized azo dye (E)-2-isopropyl-5-methyl-4-((4-(4-nitrophenyl) thiazol-2-yl) diazenyl) phenol (D2) has been anchored on a high surface area one dimensional CdS nanowires (NWs) in thin film form. CdS nanowires have been grown through Cd(OH)₂ template formation followed by conversion to CdS by ion-exchange route. The light-electricity conversion efficiency of the CdS-Azo dye-based solar cell has shown about 5-fold remarkable surge (0.159%) compared to the bare CdS (0.03%) with I₃⁻/I₃⁺ redox mediator under standard AM 1.5 illumination (100 mW cm⁻²). Albeit, the DFT studies revealed a higher band gap for pristine D2, alluringly it has depicted higher light-electricity conversion efficiency among the fabricated thin film solar cells after sensitization. The relative increase in sensitivity after sensitization is attributable to facile dye regeneration. Furthermore, after the co-sensitization of CdS thin film with equimolar cocktails of as-synthesized dyes and a natural dye Betanin (Bn), less efficiency was depicted ascribable to plausible dye aggregation upon blending.

1. Introduction

Energy is among the ubiquitous issues that the world will face in the next 50 years. For reducing the use of depleting fossil fuels, study into solar energy harvesting is becoming more and more crucial [1]. In this regard, one of the most significant advancements is a photovoltaic device that efficiently converts solar energy into electricity, and a variety of solar cell types, including dye-sensitized solar cells (DSSCs), which are on the verge of commercialization [2]. Although ruthenium-based dye-sensitized materials are the most effective among other known sensitizers, their widespread usage is constrained by their extremely high cost, the restricted availability of ruthenium in natural reserves, and environmental concerns [3]. The metal-free organic sensitizers DSSCs, have therefore arisen as an emerging class of materials that present various potential advantages to overcome the issues with metal-based dye-sensitized cells [4]. The conjugated donor-linker-acceptor (D-

π -A) structure of organic dyes has a positive effect on the dependability and effectiveness of the DSSCs [5]. Literature reported hitherto revealed that azo dyes are excellent chromophores, strongly absorbing light over the whole visible spectrum [6]. DSSCs have recently seen a renaissance as the ideal technology for a variety of specialized applications due to their unique mix of qualities such as low cost, non-toxic construction, color, transparency, and exceptional performance in low light [7]. Numerous natural dyes, including tannin, betalain, cubebin chlorophyll, anthocyanin, carotene, and natural pyrrole macrocycles have been thoroughly studied as sensitizers in DSSCs [8,9].

In the field of dye-sensitized solar cells, the n-type materials play a crucial role which serves as an important attribute in DSSCs device study. CdS is a n-type semiconducting material with wide band gap (~2.42 eV) which is more suitable for coating the low bandgap materials to harvest more light for the efficient solar cell device. The CdS thin film with nanowires structure has many more advantages for DSSCs

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application [10]. The nanowire structure has one directional conducting path and also provides a high surface area, which allows for more dye absorption and therefore increased light harvesting ability of the photoanode [11]. Also, the nanowire structure can help trap light within the solar cell for longer durations, enhancing light absorption and subsequent energy conversion. Apart from the porosity, CdS thin films are regarded as one alluring option for the development of reliable solar cells that are inexpensive. High surface area and beneficial porosity in a thin film with a large optical energy band gap and a 1-D structure result in excellent potential for charge carrier separation and transportation. Finding suitable narrow band gap semiconducting material, however, remains a significant obstacle towards the creation of heterostructures with 1-D CdS NWs for photoelectrochemical (PEC) solar cell applications [12]. CdS nanowires are relatively easy to synthesize and integrate into the structure of dye-sensitized solar cells. It can be tailored to ensemble-specific requirements, making them compatible with various fabrication techniques. Inspired by these advantages, we have utilized the CdS nanowires as a photoanode for this work.

In the present work, porous one dimensional (1-D) CdS NWs thin films anchored with thymol-based azo dyes to serve as a photoelectrode to fabricate DSSCs. CdS NWs were fabricated through a simple and cost-effective chemical route [13]. The porous structure offers high surface area, distinctive optoelectronic capabilities, linked porosity, and periodic distributions of pores, which are all well-known facts. Also, the sensitization of CdS with a cocktail of the thymol-based azo dyes with betanin (Bn) (Beetroot Red) has been aptly explored. Furthermore, investigations based on the crystalline structure, optical and electrical properties of the manufactured electrode have been performed along with solar cell performance through photo-electrochemical investigations under dark and standard illumination conditions.

2. Experimental

The experiment employed a fluorine-doped tin oxide (FTO) coated glass substrate (thickness 2 mm, transparency 84 %, sheet resistance $8 \Omega \cdot \text{cm}^{-2}$); pre-treated with dilute HCl for 7 s, then washed with soap solution, rinsed in double-distilled water (DDW), subjected to ultrasonication for 30 min, and lastly allowed to dry at ambient temperature (27 °C). All the used chemicals namely thymol, 2-Amino-4-(4-bromophenyl)thiazole, sodium nitrite, sulfuric acid, etc were procured from Sigma Aldrich, India, and used without purification.

2.1. CdS-Compact and CdS-NWs film preparation

Both thin films were prepared as per the procedure reported in the earlier literature [14,15]. In this concern, the deposited CdS-compact layer was used to prevent direct contact between the FTO and platinum coated FTO through liquid electrolyte to avoid shortening of the device as liquid electrolyte can penetrate easily through nanoporous CdS network. Aqueous equimolar solutions of precursors such as thiourea ($\text{CH}_4\text{N}_2\text{S}$) and cadmium chloride (CdCl_2) complexed by aqueous ammonia (NH_4OH) with resultant pH ~ 12 were mixed and stirred for 15 min at 100 rpm to produce the CdS-compact layer.

In order to grow CdS NWs, a bundle of cadmium hydroxide [$\text{Cd}(\text{OH})_2$] NWs was deposited on top of the CdS-compact layer thin sheet. In this instance, NH_4OH solution was used to complex a 1 M CdCl_2 solution, producing a transparent solution with a pH of 12 at 27 °C. After moving the prepared CdCl_2 solution into a different beaker and adding the pre-deposited CdS-compact film for 9 h, the $\text{Cd}(\text{OH})_2$ NWs film, which is white, was developed over the CdS-compact film. DDW was used for rinsing to get rid of excess loosely linked $\text{Cd}(\text{OH})_2$ NWs. The deposited $\text{Cd}(\text{OH})_2$ NWs sheets were then immersed in a solution of Na_2S [20 mM] for 50 min to convert the $\text{Cd}(\text{OH})_2$ NWs into CdS NWs.

Here, because CdS has a lower negative Gibbs free energy than Cd ($\text{OH})_2$, there has been an interchange of hydroxyl ions with sulfur ions, which has left a yellow film on the substrate surface. In order to improve

crystallinity and reduce the hydroxyl content from the prepared film, the final film was air-annealed at 250 °C for 1 h.

2.2. Syntheses of azo dyes (R)

The azo dyes (E)-2-isopropyl-5-methyl-4-((4-phenylthiazol-2-yl) diazenyl) phenol (D1) and (E)-2-isopropyl-5-methyl-4-((4-(4-nitrophenyl) thiazol-2-yl) diazenyl) phenol (D2) were synthesized as per the literature reported [16] method (Fig. 1). In 6.6 g of concentrated H_2SO_4 and 6.6 g of ice-cold water, a solution of the used substituted 2-amino-4-aryl thiazole moieties [15 mmol, 2.64 g and 3.31 g] was swirled progressively for around 30 min in an ice bath. After 30 min, an ice-cold solution of 2-amino-4-aryl thiazole was added slowly, dropwise, for 45–50 min, while being constantly stirred, to a solution of 1.04 g of NaNO_2 (0.0152 mol) and 9 g of concentrated H_2SO_4 . The solutions temperature was kept below 0 °C during the addition using an ice- CaCl_2 bath.

Following the completion of the diazotization procedure, the solution containing the diazonium salt was gently added to the ice-cooled thymol solution [15 mmol, 2.25 g], and the mixture was then continuously stirred for about an hour while being dissolved in 15 mmol of an aqueous 10 % sodium hydroxide solution. A development solvent, hexane: ethyl acetate (8.5:1.5 v/v) was employed to monitor the progress of the diazonium coupling process using thin layer chromatography (TLC). The reaction was completed, and the end product was separated into crystals. These crystals were filtered via the suction pump and washed with more water. Then, utilizing column chromatography with the solvent system used with TLC and silica gel (70–230 mesh) the crude product was purified [16].

2.3. Preparation of a DSSCs photoanode

The 15 ppm solution of the dye molecule has been prepared in the chloroform (CHCl_3) solvent with continuous stirring at 400 RPM for 15 min. Only betanin (Bn) dye solution was prepared in water taking into account its solubility. Then thin film consisting of CdS NWs has been dipped for overnight (16 h) in dye molecules and cocktails dye molecules with a concentration of 15 ppm in the dark at room temperature (27 °C) for overnight for the chemically attachment of the dye molecules. Dye-loaded CdS NWs films were thoroughly rinsed in CHCl_3 to eliminate un-anchored dye molecules and aggregation of dyes on the surface of the CdS NWs, if any. The dye molecules were chemically attach onto the surface of the CdS NWs after the dipping procedure, and the dye molecules were considered to have “sensitized” for individual dyes and “co-sensitized” for the equimolar mixture of dyes and betanin on the CdS NWs films. Fig. 2 shows photoimage of bare CdS and CdS anchored bare dyes and cocktails.

2.4. DSSCs fabrication

The CdS nanowires films anohred with dye molecules were termed as photoanodes. A sandwich-type device was assembled by utilizing photoanode and a platinum coated FTO as a counter electrode. The liquid electrolyte was prepared by a mixture of 0.50 M tetra-n-propylammonium iodide ($(\text{C}_3\text{H}_7\text{CH}_2)_4\text{NI}$) and 0.10 M iodide (I_2) in an ethylene carbonate and acetonitrile mixed solvent (20:80 by volume) and injected via capillary action. The device was fabricated with a structure of FTO/CdS/dye (bare or cocktail)/Pt and polyiodide as redox electrolyte.

3. Instrumentations

X-ray diffraction (XRD) measurements were conducted with the ‘Ultima IV, Rigaku Corporation, Japan diffractometer having CuK_α incident beam with $\lambda = 1.5406 \text{ \AA}$ in 2θ range from 20° to 70°. A surface profiler (Dektak 150) was utilized to measure the surface thickness. The

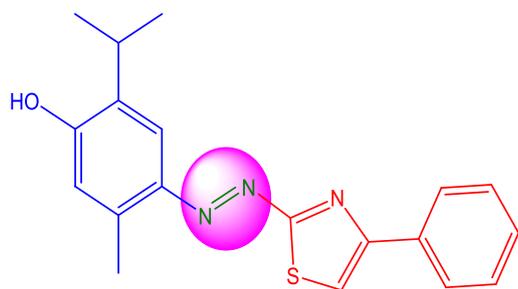
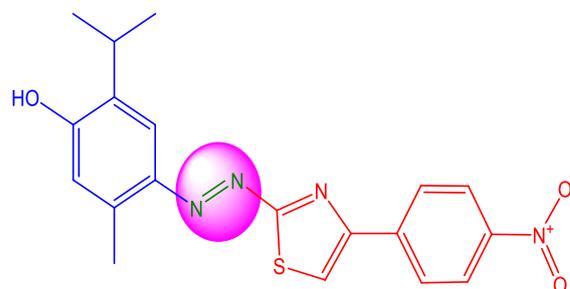
(E)-2-isopropyl-5-methyl-4-((4-phenylthiazol-2-yl) diazenyl) phenol (**D1**)(E)-2-isopropyl-5-methyl-4-((4-(4-nitrophenyl) thiazol-2-yl) diazenyl) phenol (**D2**)

Fig. 1. Chemical structures of the prepared Dye (D1) and Dye (D2) molecules.

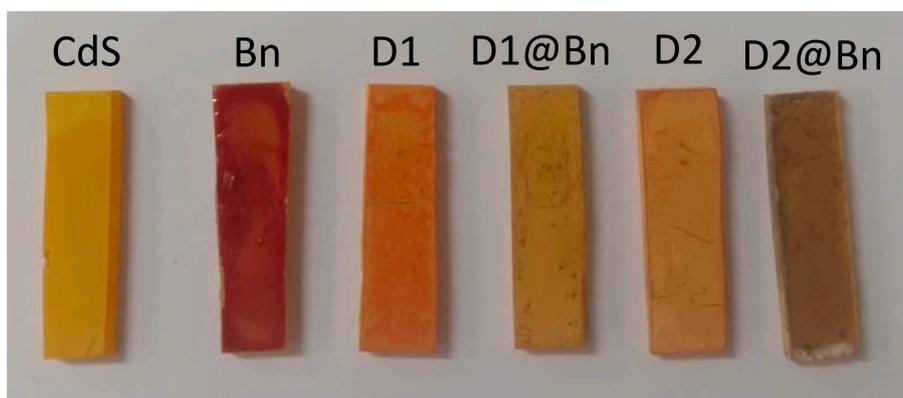


Fig. 2. Bare CdS NWs and bare dyes and cocktail anchored on CdS NWs.

UV-Vis (Shimadzu, UV-1700PharmaSpec) spectrophotometer was used to record the spectra in the wavelength range between 300 and 700 nm in order to measure the optical absorption curve. Keithley source meter was used to measure the current density–voltage (J-V) characteristics under both dark and light conditions (High current source unit, Model-2611A). At ambient temperature, 100 mW/cm² of simulated sunlight from a solar simulator (Sciencetech AAA, Model-SS150) at AM 1.5 conditions was employed. For all devices, a 0.2 cm² exposed area was fixed by using a black-painted mask. Morphology and elemental mapping were revealed with Field Emission Scanning Electron Microscope with Energy Dispersive Spectroscopy (EDS) (HITACHI, Japan, SU8010 Series).

4. Results and discussion

4.1. Structural and surface morphological studies

Fig. 3 shows the X-ray diffraction (XRD) patterns of CdS NWs thin films deposited over CdS-compact coated FTO substrate. The revealed FTO peaks are denoted by the symbol '#' whereas the peaks of CdS-compact and CdS NWs are denoted by '\$' and '*' symbols, respectively. The revealed values of the diffractogram are in harmony with the literature-reported values and the standard JCPDS cards. In the present work, the peaks of CdS-compact are matched with JCPDS cards (File No. 42-1411) and (File No. 80-0019), while the peaks of CdS NWs are matched with the JCPDS card (File No. 41-1049) [17–19]. CdS showed the formation of mixed cubic and hexagonal phases.

Fig. 4a & b depicts FE-SEM images of CdS NWs and CdS-compact. Fig. 4 revealed morphology like the clusters of CdS NWs. The developed interconnected NWs clusters are grown in all possible directions and possess a high surface area. It is an established fact that NWs are highly effective for the adsorption of dye molecules, due to their high

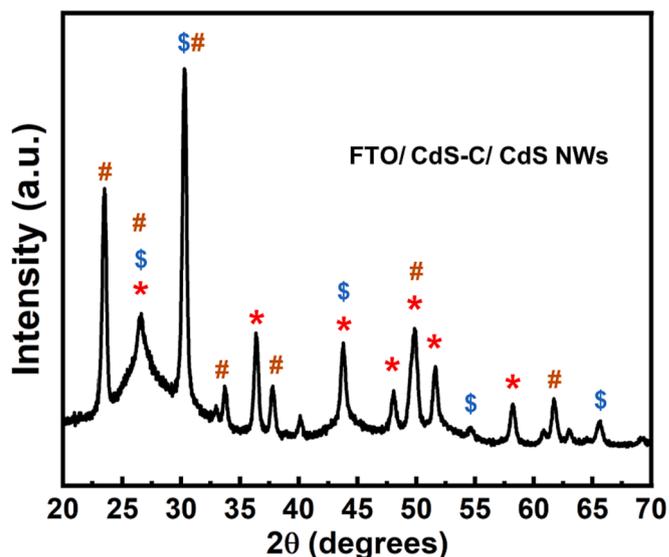


Fig. 3. X-ray diffractogram for CdS NWs grown on CdS-compact thin films.

surface area to volume ratio. The higher surface area of NWs with higher concentrations of active sites allows the adsorption of higher number of dye molecules, and as a consequence, improved efficiency can be observed in DSSCs and optoelectronic applications [20]. Fig. 4c & d depicts EDS image and elemental mapping of CdS NWs. The spread of the constituent elements in the specimen is shown by elemental mapping.

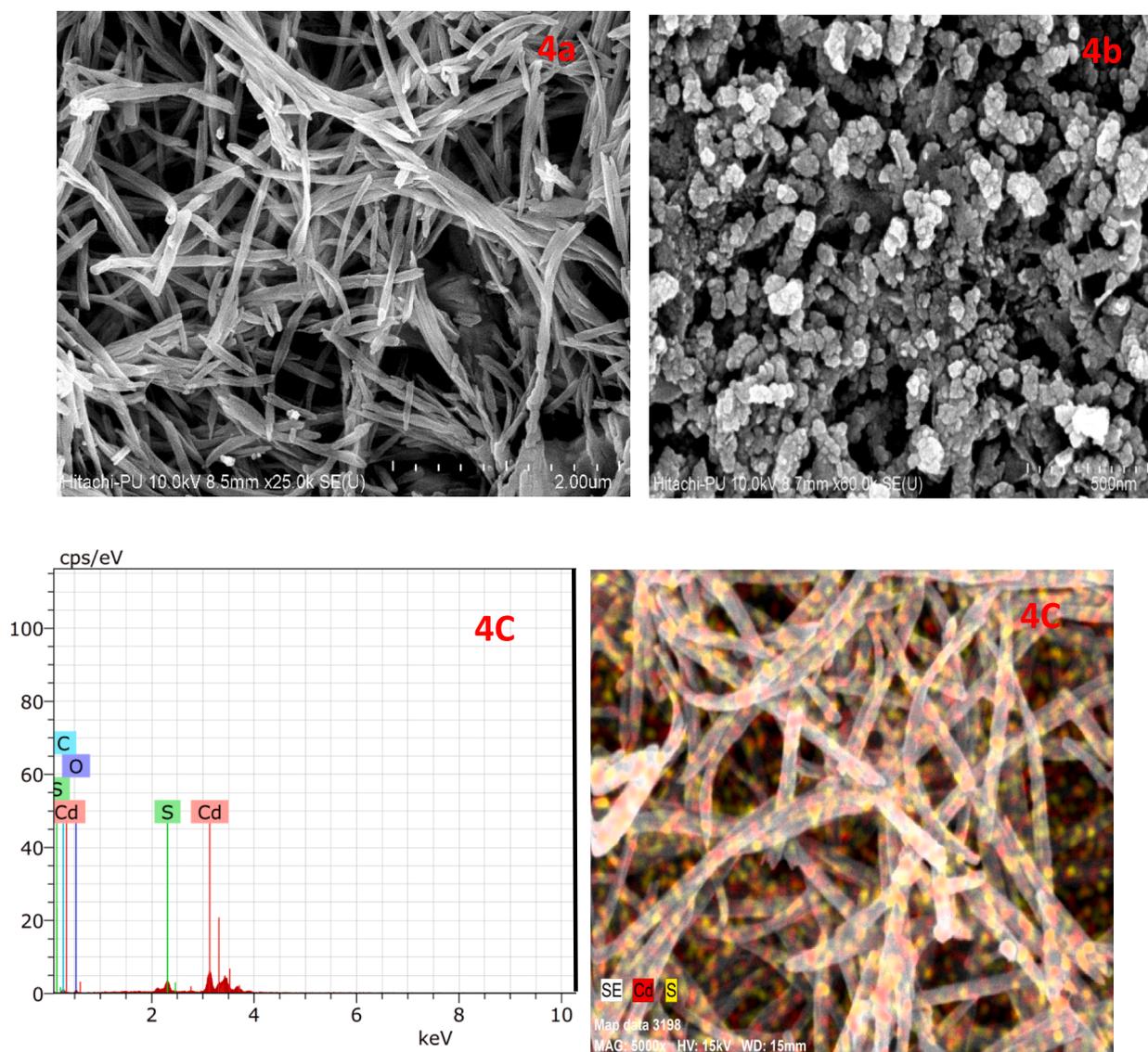


Fig. 4. FESEM images for the CdS NW(a) and CdS-compact (b). Figure(c) and (d) represents EDS and elemental mapping of CdS NWs.

4.2. Exploration of optical studies

Fig. 5 shows the UV–Vis absorption contour for the bare dye molecules and dye molecules loaded over the CdS NWs thin films. The spectral contour revealed the absorption maximum (λ_{\max}) of betanin dye at 530 nm as reported in the literature [21]. Fig. 5a depicts the

quantitative absorption spectra for bare dyes; whereas Fig. 5b shows the absorption spectra for Bn, D2, and D2 + Bn (cocktail) over the CdS NWs to study the impact of absorption contour after dye loading. The findings demonstrate CdS absorption peaks at 518 nm corresponding to the band gap of 2.39 eV, which was ascribed to hexagonal CdS nanowires from the literature [22]. The intrinsic band gap absorption of CdS can be

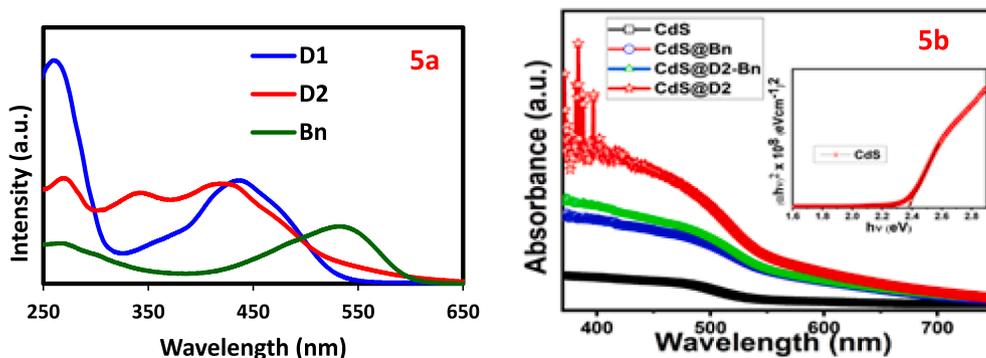


Fig. 5. UV–Vis absorptions spectra for (a) Bare dye molecules D1, D2 & Bn (b) Bn, D2, and cocktail of D2 + Bn over CdS. The inset shows the Tauc's plot for CdS.

attributed to a substantial shift in the absorption at wavelengths shorter than 518 nm for all the fabricated photoanodes (2.39 eV) [23]. The absorption spectra of the dye molecules adsorbed onto the CdS NWs revealed that the alteration in the energy of the Lowest Unoccupied Molecular Orbital (LUMO) due to π - π^* and n - π^* transitions, can be attributed to the redshift in the absorption maximum of the dyes [24–27]. The azo (D2) dyes combined as acceptors to CdS NWs (bulk material) resulting in improved topography and morphology, enhancing charge carrier mobility while suppressing charge carrier recombination, probably can result in enhanced efficiency [28].

4.3. Computational studies of azo dyes D1 and D2

The quantum chemical calculations of the synthesized azo dyes D1 and D2 have been performed using the density functional theory (DFT) and all theoretical computations were made by using the computational Gaussian16 software [29].

The isosurfaces (of value 0.035a.u.) for HOMO and LUMO for the Dyes D1 and D2 are displayed in Fig. 6 [30]. The figure indicates that the HOMO of D1 is spread over the benzene ring on the right side while the spread of HOMO in D2 is reduced for the same benzene ring due to NO_2 substitution. The LUMO of both dyes is almost similar. The increase in the band gap of D2 as compared to D1 may be due to the reduced spread of HOMO on the benzene ring to which the NO_2 group is attached in dye D2.

4.4. Photoelectrochemical studies of fabricated solar cells

Fig. 7 displays the current density–voltage (J–V) curves of both CdS NWs and dye-sensitized CdS NWs. Studies were performed on the as-synthesized films that are used to construct devices to confirm the experimental and theoretical data. The photovoltaic parameters computed, including short circuit photocurrent (J_{sc}), open circuit photovoltage (V_{oc}), fill factor (FF), and photovoltaic conversion efficiency (η) are listed in Table 1. Herein, CdS@Bn indicates that the pristine natural dye betanin (Bn) is anchored on CdS NWs. The J–V investigations

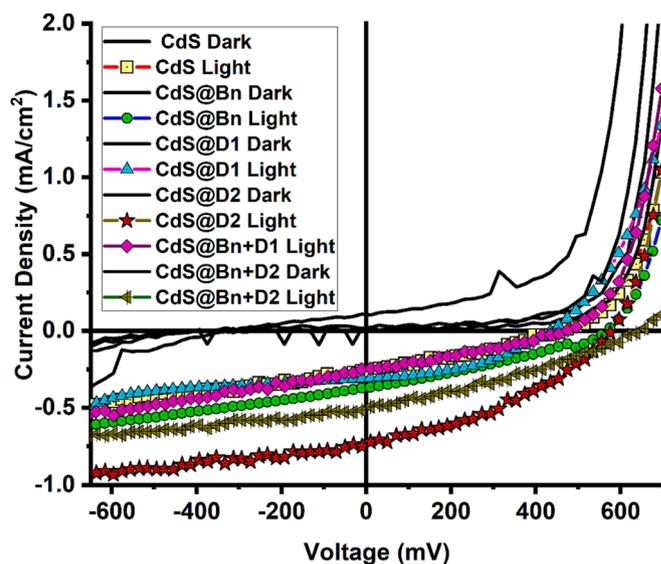


Fig. 7. J–V Curve for CdS NWs, CdS@Bn, CdS@D1, CdS@D2, and cocktails of CdS@D1-Bn and CdS@D2-Bn respectively.

Table 1
Photoelectrochemical performance of fabricated Solar Cells.

Label	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (η)	R_s (Ω)	R_{sh} (K Ω)
CdS NWs	463	0.261	27.21	0.032	330.73	110.09
CdS@Bn	565	0.367	30.07	0.062	258.20	575.40
CdS@D1	435	0.307	33.61	0.044	297.69	301.11
CdS@D2	578	0.738	37.53	0.159	103.43	1131.9
Cds@D1-Bn	471	0.246	47.30	0.054	177.58	500.41
Cds@D2-Bn	643	0.580	31.25	0.116	173.85	755.71

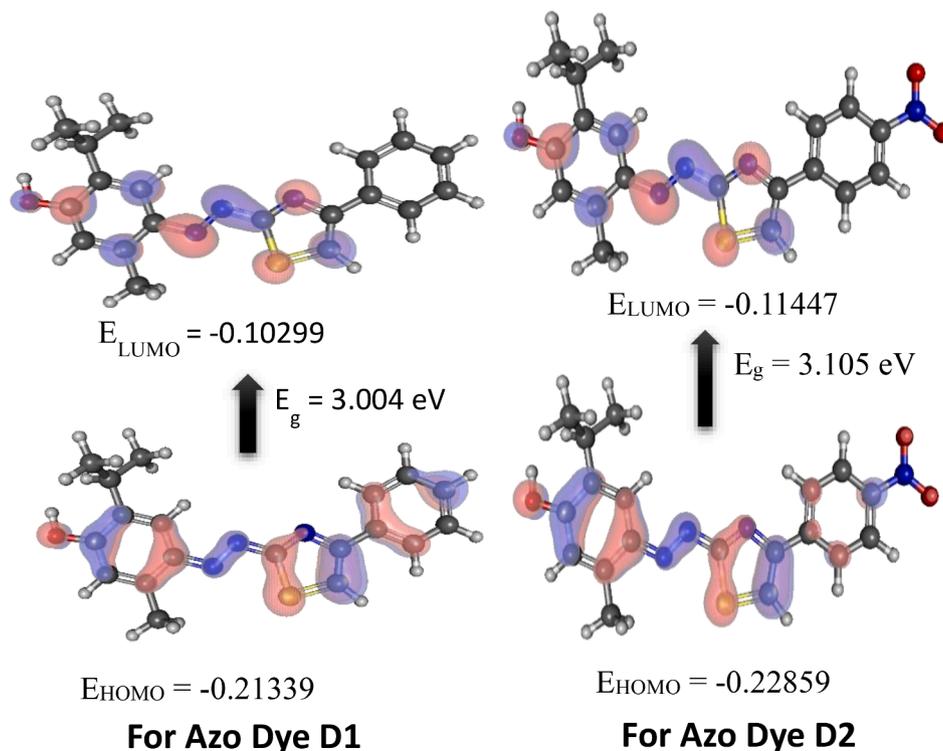


Fig. 6. DFT optimized structures of azo dyes D1 and D2.

of the devices were explored in the -1.0 to $+1.0$ V range of voltage under dark and illuminated conditions. CdS NWs under light had an estimated efficiency of 0.032 %. Interestingly, the efficiency of the device has risen for the CdS NW loaded with the dye molecules to 0.159 %, improving the material's absorption toward redshift as oxidized dye must be thoroughly reduced to its original ground state after electron injection (regeneration). Table 1 compares the device efficacy of dye compositions with CdS to that of bare CdS NWs film. According to the parameters listed in Table 1, CdS@D2 exhibits the greatest efficiency for the manufactured device in polyiodide electrolyte which is nearly five times higher than bare CdS NWs. Intriguingly, when the Bn dye was mixed with both D1 and D2 to prepare the solar cell devices CdS@D1-Bn and CdS@D2-Bn; the observed outcomes are shown reduced solar cell performance, which might be due to the formation of dye aggregates on the mixing of both dye molecules, as it blocks the light reaching to the semiconductor surface and also hinders the electron injection and dye regeneration mechanism.

5. Conclusions

Photoelectrochemical investigations were performed on bare CdS NWs as well as dye-sensitized and co-sensitized over CdS NWs. Due to the presence of compact CdS and CdS NWs, exploration of thin films, X-ray diffractometry showed the mixed cubic and hexagonal phases. Dye D2 has a larger bandgap than azo Dye D2, according to calculations using density functional theory (DFT), but after being sensitized with CdS NWs, azo Dye D2 has demonstrated the greatest efficiency, with an improvement in the efficiency of about five times over that of bare CdS NWs. The cocktails D1-Bn and D2-Bn employed in 1:1 stoichiometry for loading on CdS NWs have shown reduced efficiency after sensitization compared to the pristine dye-sensitized CdS NWs.

CRedit authorship contribution statement

Maheshkumar Jadhav: Methodology, Investigation, Formal analysis. **Avinash Mendhe:** Visualization, Validation, Software, Project administration, Methodology. **Tushar Deshmukh:** Investigation, Formal analysis. **Chandrakant Sarode:** Formal analysis. **Sachin Yeole:** Writing – original draft, Visualization, Software, Data curation. **Gaurav Gupta:** Methodology, Investigation, Conceptualization. **Maroti Sudewad:** Formal analysis. **Prajakta Jadhav:** Formal analysis. **Ankita Suryawanshi:** Formal analysis. **Babasaheb Sankapal:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology. **Kundan Tayade:** Writing – original draft, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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23/2341).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jphotochem.2023.115303>.

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