Synthesis and Design of Carbon Quantum Dots/CdS/ZnS Photoanode Thin-Film Solar Cells with CoNi-C Counter Electrode for Eco-Friendly and Economically Viable Photovoltaics

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Abstract

This study reports the synthesis, characterization, and fabrication of carbon quantum dots (CQDs)/CdS/ZnS photoanode thin-film solar cells using a CoNi-C counter electrode for environmentally friendly and cost-effective photovoltaic applications. CQDs were prepared via hydrothermal synthesis, while CdS and ZnS layers were deposited using the successive ionic layer adsorption and reaction (SILAR) method. The CoNi-C counter electrode exhibited moderate visible-light absorption (1.49–1.80 a.u.) and favorable electrical properties, including low resistivity (3.201 × 10^{-2} Ω·cm), high conductivity (3.124 × 10^{1} S/cm), and a Hall coefficient of 1.906 cm^3/C. The assembled FTO/d-TiO_2/m-TiO_2/CQD/CdS/ZnS/CoNi-C solar cell achieved an open-circuit voltage (Voc) of 0.345 V, a short-circuit current density (Jsc) of 16.20 μA, and a power conversion efficiency (PCE) of 0.85%. These results demonstrate the potential of CQDs and CoNi-C as sustainable alternatives for cost-effective solar energy technologies with positive implications for green energy and economic development.

1.0 Introduction

The transition to renewable energy sources has become an urgent global priority due to the environmental and economic challenges posed by fossil fuels. Solar energy, in particular, offers a sustainable and abundant energy source, and photovoltaic (PV) devices have emerged as a central technology for harnessing this potential. Among various PV technologies, thin-film solar cells have attracted considerable attention because of their low material consumption, flexibility, lightweight nature, and compatibility with large-area fabrication. Despite these advantages, conventional thin-film solar cells often face limitations in terms of efficiency, stability, and cost-effectiveness, which constrain their widespread commercialization (Kumar, Dua, Kaur, Kumar, & Bhatt, 2022).

The expanding global focus on sustainability and environmental conservation has brought green synthesis of nanomaterials into the forefront as a crucial method in modern nanotechnology (Alavi, et all, 2023) Among renewable energy sources, solar energy is particularly promising due to its abundance consequently giving about 120,000 terawatts of electricity to Earth's surface, which is 6,000 times the world's current energy consumption (Gratzel, et all, 2009). Significant advancements have been made recently in solar cells, a technology that uses the photovoltaic (PV) effect to turn sunlight into power (Dixit et al,2023). The creation of several types of solar cells, including perovskite solar cells (Rossi et all, 2024), organic/polymer solar cells(Marlow et all, 2022)[quantum dot solar cells (Jiang et all 2022)], flexible solar cells (Teixeira et all, 2023) tandem solar cells (Zheng et all, 2024), and numerous other designs, is one example of these developments.These advanced PV technologies offer diverse applications like foldable chargers, wearable devices and transparent curtains which addressing the need for adaptable and innovative energy solutions. One of such advances in recent time is carbon qauntum dots (CQDs).

Carbon quantum dots (CQDs) are tiny, carbon-based nanoparticles typically less than 10 nanometers in size (Mansuriya et all, 2021), Strong fluorescence, biocompatibility, and low toxicity are just a few of the special qualities that make these nanomaterials ideal for a wide range of uses, including medication administration, bioimaging, sensing, and energy devices like solar cells (Zahra et all, 2024). Compared to traditional semiconductor quantum dots (SQDs), which often contain hazardous elements like lead (Pb) and cadmium (Cd), carbon quantum dots (CQDs) have emerged as a more ecologically friendly alternative (Dhariwal et all, 2024) . CQDs are

particularly regarded for their capacity to effectively avoid electron-hole pair recombination in solar cells due to their excellent charge transfer capabilities, broad absorption spectra, large two-photon absorption cross-section, and outstanding photostability (Saputra et al, 2024)

In photovoltaic systems, CQDs can also serve as light absorbers, electron donors/acceptors, and interlayer spacing components that match energy levels across different functional layers (Kumar et all, 2023). CQDs have demonstrated significant promise in improving device performance while maintaining environmental safety when integrated into different layers of solar cells, including electron-transporting layers (ETL), active absorbing layers, hole-transporting layers (HTL), and energy level alignment interlayers (Litvin et all, 2020). CQDs are more attractive for scalable and ecologically friendly manufacture than cadmium sulfide (CdS) and zinc sulfide (ZnS) QDs, which offer robust electron transport characteristics and stability.Due to its potential applications in optoelectronics and biomedicine (Magesh et all, 2022), the bottom-up hydrothermal synthesis of carbon quantum dots (CQDs) from citric acid and ammonia (or nitrogen sources) has attracted a lot of attention. Numerous studies have demonstrated the efficiency of citric acid as a carbon precursor and the role that nitrogen doping plays in improving the properties of CQDs (Jorns et al, 2022). Other synthetic methods that have been used to create CQDs include green synthesis (Manikandan et al, 2022), pyrolysis technique (Wang et al, 2022), microwave assisted electrochemical, carbonization laser ablation, and chemical oxidation (Tan et al, 2019). Recent advances in nanomaterials have opened new avenues for overcoming these challenges. Carbon quantum dots (CQDs) are a class of nanomaterials with exceptional photoluminescence, tunable bandgap, high electron mobility, and excellent chemical stability. These properties make CQDs ideal candidates for enhancing light absorption, facilitating charge separation, and improving electron transport in photoanodes. When combined with semiconductor materials such as cadmium sulfide (CdS) and zinc sulfide (ZnS), CQDs can form heterostructures that optimize photogenerated electron transfer and reduce charge recombination, ultimately increasing photocurrent density and solar cell efficiency. The integration of CQDs into photoanodes represents a significant advancement in the design of high-performance, cost-effective thin-film solar cells.

On the other hand, thin films of CdS and ZnS are binary semiconductors with special qualities that make them appropriate for use in solar cells and other optoelectronic devices. With a straight

bandgap of roughly 2.4 eV, cadmium sulfide (CdS) thin film is ideal for optoelectronic applications (Moa et al, 2024). Because it can transmit light efficiently and form a heterojunction with other materials like copper indium gallium selenide or cadmium telluride, it is commonly used as a window layer in thin-film solar cells and exhibits excellent light absorption properties in the visible spectrum (Faremi et al, 2022). The total performance of solar cells is enhanced by these heterojunctions, which make effective charge separation and collection possible. The bandgap of zinc sulfide (ZnS), a wide-bandgap material, is roughly 3.65 eV.making it transparent to visible light and suitable for applications requiring high optical transparency and luminescence . In solar cells, ZnS is valued for its non-toxic nature compared to alternatives like cadmium sulfide. CdS/ZnS heterojunction thin films combine the advantageous properties of both binary semiconductors, forming a junction that exhibits excellent properties for solar cell application (Hernández et al, 2017)]. ZnS is frequently used as a buffer or window layer in tandem with materials or other thin film technologies. Its role is to enhance light transmission and serve as an electron transport layer, contributing to the efficiency and stability of the device (Mude et al 2022).

Recent works (Liu, 2022; Kumar et al., 2023; Dhariwal et al., 2024) highlight that CQD-based sensitizers improve photon absorption and reduce recombination losses due to quantum confinement and surface functionalization. However, efficiency remains limited (<2%) due to interfacial defects and carrier trapping.Similarly, studies on bimetallic counter electrodes such as CoNi-C and CuS-C (Rocco et al., 2023; Fang et al., 2024) show improved electrocatalytic activity and mechanical stability compared to Pt, offering a viable green alternative. Despite these advances, integration of CQDs/CdS/ZnS photoanodes with CoNi-C electrodes remains underexplored, which motivates the present study.

Equally critical to the performance of solar cells is the selection of counter electrode materials. Conventional platinum-based counter electrodes, while highly efficient, are expensive and scarce, limiting their scalability. Transition metal alloys, particularly cobalt-nickel (CoNi) composites, have emerged as promising alternatives due to their high electrocatalytic activity, chemical stability, and abundance. The use of CoNi-C counter electrodes not only reduces material costs but also contributes to environmentally friendly fabrication processes, aligning with the broader goal of sustainable photovoltaics.

The combination of CQD/CdS/ZnS photoanodes with CoNi-C counter electrodes offers a synergistic approach to developing efficient, eco-friendly, and economically viable thin-film solar cells. By enhancing light absorption, charge separation, and electron transport, while simultaneously employing low-cost and stable counter electrodes, this strategy addresses the critical challenges of modern photovoltaics.

We used carbon quantum dots (CQDs)/CdS/ZnS trilayer thin films with CoNi-C counter electrodes to develop eco-friendly and efficient solar cells. ZnS lowers environmental risks related to cadmium, while CQDs, which are non-toxic and cost-effective, improve light absorption and sustainability. The CoNi-C counter electrode provides a low-cost, scalable alternative to rare materials, increasing the commercial viability of the cells. This study explores CQDs/CdS/ZnS trilayer thin-film solar cells with CoNi-C counter electrodes, offering a low-cost, environmentally sustainable approach to solar energy that improves both device performance and economic viability.

1.1 Research Objectives and Questions

Research Objectives

1. To synthesize carbon quantum dots (CQDs) via a hydrothermal green synthesis route using citric acid and ammonia.

2. To fabricate CQDs/CdS/ZnS photoanode thin films and integrate them into a solar cell using a CoNi-C counter electrode.

3. To characterize the optical and electrical properties of the developed materials and evaluate the device performance.

4. To assess the economic and environmental implications of employing CoNi-C and CQDs as sustainable photovoltaic materials.

Research Questions

How does the incorporation of CQDs affect the light absorption and charge transport properties of CdS/ZnS photoanode thin films?

Can CoNi-C counter electrodes provide comparable conductivity and efficiency to conventional noble metal electrodes at lower cost?

Hypothesis

Incorporating CQDs and CoNi-C into CdS/ZnS-based solar cells will enhance photovoltaic efficiency and promote environmentally sustainable, cost-effective solar technology.

2.0 Experimental Details

Ti-Nanoxide D/SP (Solaronix), Titanium (IV) isopropoxide (Aldrich), Zr-Nanoxide Z/SP (Solaronix), Elcocarb B/SP (Solaronix), Methanol (Aldrich), Distilled water, Flourine doped Tin Oxide transparent conducting glass TCO30-8 (Solaronix), Acetylacetone (MERCK), Titanium (IV) chloride (MERCK), dimethyl sulfoxide (JHD), N,N-Dimethylformamide (JHD), Methylammonium Iodide (MA) (Solaronix), and Lead Iodide (Searle) are among the additional materials and reagents used in the production of the solar cell.

2.1 Solar cell Fabrication

Before the solar cell was manufactured, the FTO substrates were cleaned using a sequence of procedures that included rinsing with distilled water, washing in a detergent solution, washing with isopropanol one last time, and drying with a spin coater (Labscience model 800) set to 3000 RPM. To make a 4 x 8 mm cell, the cleaned FTO was masked.

2.1.1 Deposition of densed TiO_2 thin film layer

Electrostatic spray pyrolysis was used to deposit a thin layer of TiO2. 400°C was the substrate temperature, 0.1 ml/min was the precursor flow rate, 8 kv was the atomizing voltage, and 20 mm separated the substrate from the nozzle. The amount of precursor sprayed was 0.3 ml. 0.15M titanium (IV) isopropoxide, 0.30M acetylacetone, and methanol were the constituents of the precursor composition.

2.1.2 Deposition of Mesoporous TiO_2 thin film layer

Mesoporous TiO2 (m-TiO2) was prepared by screen printing Ti-nanoxide and then annealing it for 30 minutes at 500°C. After 30 minutes of treatment with a 70 mM solution of TiCl4 at 70°C, the resulting m-TiO2 film was washed with water and annealed for 30 minutes at 100°C.

2.1.3 Synthesis of Carbon Quantum Dots

To synthesized carbon quantum dots, hydrothermal method of synthesis was adopted. Citric acid mixed with amonia and distilled water was used as reagemts. Firstly, 3.0 grams of citric acid was mixed with 12 mL of ammonia solution. The mixture was stirred for 20 minutes to have a homogenous mixture. 100 mL of distilled water was added gradually to the mixture under continous stirring for another 10 miutes. The final solution was heated at 200 ℃ for 3 hours in a hydrothermal chamber. Formation of carbon quantum dot is confirmed by the brownish black coluor observed. The CQD is dried and grinded. CQD is mixed with a solvent called methanol by centrifugation The CQD solution is stored in a test tube.

2.1.4 SILAR synthesis of CdS and ZnS thin films layers

Cadmium sulphide (CdS) and zinc sulphide (ZnS) thin films were synthesized using successive ionic layer adsorption reaction (SILAR). These were achieved using aqueous solutions of 0.10 M of cadmium chloride and 0. cadmium sulphide (CdS) 0.1M and 0.10 M of zinc acetate as precursors of Cd and Zn ions respectively. Sodium Sulfide was used as a source of S^{2-} ions. The pH of metal ions were adjusted to 8.0 using few drops of concentration NH_4OH solution. Four steps SILAR cycle approach similar to the steps used by [72-74].

2.1.5 Synthesis of CoNi-C Counter Electrode Thin Film

CoNi-C layer was deposited using an electrolytic cell at 3.5V. Carbon (graphite rod) and silver plate were used as anode and cathode electrodes respectively. This was done for two hours to form Cu-CuS which is conductive. To form Cu-CuS layer was formed using H_2SO_4 (54g / 1.5 l), $CuSO_4$-(55g / 1.5 l) and sodium sulphide of 0.5 mol was soaked with copper, the reaction forms copper sulphide.

2.1.6 Assembly of Carbon Quantum Dot Sensitized Solar

The CQDSSC is assembled by sandwiching these layers as shown in figure 1. The counter electrode is then attached with a glue and the electrolyte filled through a hole drilled on the counter electrode. The CQDSSC architecture is madeup of FTO/d-TiO_2/m-TiO_2/CQD/CdS/ZnS/CoNi-C as shown in figure 1(a). The prototype design is shown in figure 1(b). The syntheszied solar cell is made of 6 thin film layers of CdS and 2 of ZnS. The developed CQDSSC was characterized to determine the cell parameters such as power conversion efficiency (η), open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factors and others.

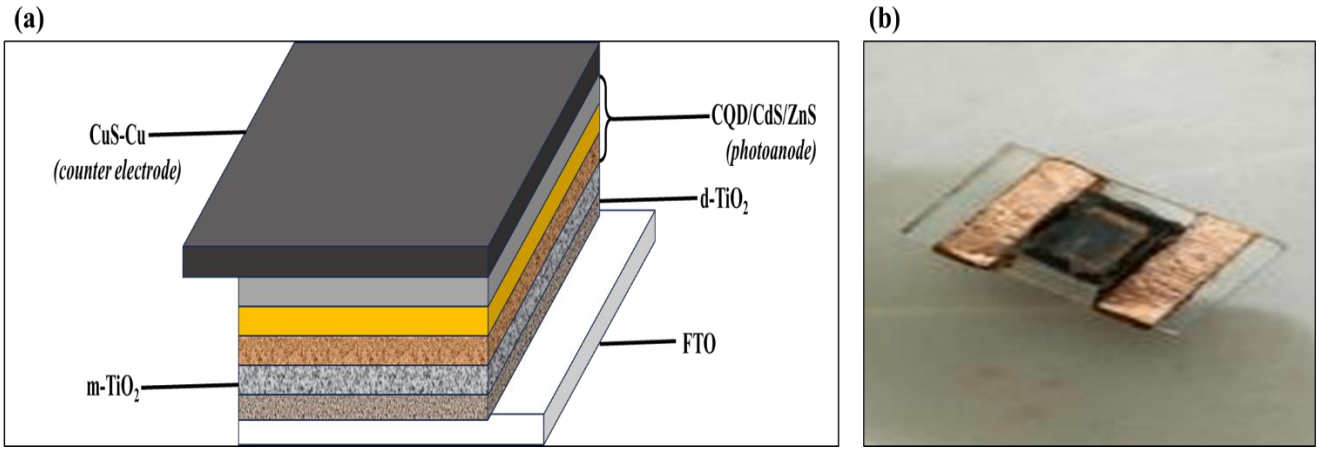


Figure 1: Assembled QDSSC (a) designed structure and (b) prototype

3.0 Results and Discussions

3.1 Solar cell parameters

To determine the properties of the fabricated FTO/d-TiO_2/m-TiO_2/CQD/CdS/ZnS/CoNi-C (6 cycle of CdS and 2 cycle of ZnS) CQDSSC, the current and voltage measurement of the cell was down. I-V curve was obtained under irradiance intensities of 1000 W/m^2 at 25 ºC. For an ideal solar cell, the light-induced current generated (I_{ph}) is closely linked to the incident photon flux on the photodiode by the equation (1) as given by [75]

$$I = I_{ph} - I_d$$

$$I = I_{ph} - I_0\left[e^{\left(\frac{qV}{KT}\right)} - 1\right] \quad 1$$

Where I_d is diode current, K_B is boltzman constant, T is absolute temperature, q is the electron charge, V is voltage at terminals and I_o is saturation current. The short circuit current (J_{SC}) is equal to the light-generated current (I_{ph}). In this case, the open-circuit voltage (V_{OC}) can be calculated using equation (2) as given by [75]

$$V_{oc} = \frac{K_B T}{q} \ln\left(1 - \frac{I_{ph}}{I_0}\right) \quad 2$$

The short-circuit current (I_{SC}) is the current when the voltage across the cell is at its minimum (zero) and the current is at its maximum. The open-circuit voltage (V_{OC}) is the voltage when the cell is not connected to any load. The fill factor (FF) is given in equation (3) by [76-77]

$$FF = \frac{I_{mp} \times V_{mp}}{J_{sc} \times V_{oc}} \quad 3$$

Where I_{mp} is the maximum power current and V_{mp} is the maximum power voltage. The power conversion efficiency of the solar cell is given in equation (4) by [76-77]

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oc} \times J_{sc} \times FF}{incident\ solar\ power\ (P_{in})}$$

The I-V measurement of CoNi-C counter electrode based solar cell was carried out using solar simulation equipment at SHESTCO, Abuja Nigeria. The IV results obtained were plotted and solar parameter determine d from the plot. The area of the solar cell was found to be 32 mm^2. Figure 2 shows the I-V curve of the solar cell while table 1 gives the corresponding solar cell parameters obtained from Figure 2.

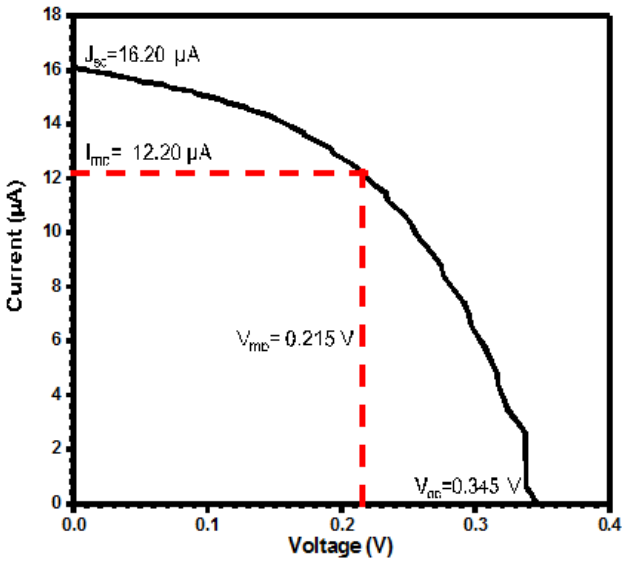


Figure 2: I-V curve of FTO/d-TiO_2/m-TiO_2/CQD/CdS/ZnS/CoNi-C (6 cycle of CdS and 2 cycle of ZnS) CQDSSC

Table 1: Solar cell parameters of FTO/d-TiO_2/m-TiO_2/CQD/CdS/ZnS/CoNi-C (6 cycle of CdS and 2 cycle of ZnS) CQDSSC

Cell name	J_{sc} (μA)	V_{oc} (V)	I_{mp} (μA)	V_{mp}(V)	P_{max} (μW)	P_{in} (W)	FF	η (%)
CoNi-C-ZnSx2	16.20	0.345	12.20	0.215	2.62	0.032	0.469	0.820

Figure 2 shows that this cell achieved a $\mathbf{J_{sc}}$of 16.20 μA, $\mathbf{V_{oc}}$of 0.345V, and an efficiency of 0.820%. The increased number of CdS layers resulted in higher light absorption

Architecture and Composition: Cell 3 builds upon the architecture of Cell 2 by doublingthe number of CdS layers to 10, while keeping the same CoNi-Cu_2S counter electrode.

Performance: The cell achieved a $J_{sc}$of 16.20 μA, $V_{oc}$of 0.345 V, and an efficiency of 0.820%. The increased number of CdS layers resulted in higher light absorption, leading to improved $J_{sc}$and efficiency. The increase in CdS layers significantly improved the cell's performance by enhancing light harvesting. However, the slightly lower V_{oc}suggests that there might be increased recombination or resistance losses associated with the thicker CdS layer. In summary,

I–V measurements under 1000 W/m² at 25°C showed:

Jsc = 16.20 μA

Voc = 0.345 V

FF = 0.469

PCE = 0.82%

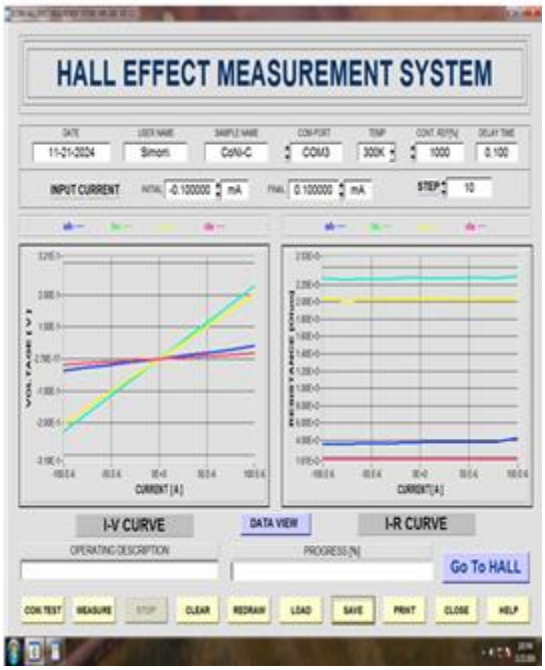
Increasing CdS layers enhanced light absorption, improving Jsc and efficiency, though Voc slightly decreased due to possible recombination or resistance losses.

3.2 Hall effect measurement and I-V curve of counter electrode material

Figure 3 and table 2 show the I-V and hall measurement parameters of CoNi-C. The carrier concentration of 3.274 $\times 10^{19} cm^{-3}$demonstrates a moderate density of free electrons, suitable for efficient charge transport. The mobility of 5.955 $cm^2/V \cdot s$ indicates that the charge carriers experience relativelylow scattering, enhancing their movement under an electric field. The resistivity 3.201 $\times$ $10^{-2}\Omega$·cm is low, highlighting the film's capability to conduct electricity effectively. The Hall coefficient 1.906 $\times$ 10^{-1}cm^3/C) suggests electron-dominated conductivity. Additionally, the surface carrier concentration of 2.292$\times$ $10^{17} cm^{-3}$and conductivity 3.124 $\times 10^1$S/cm further reinforce the material's suitability for electronicapplications.Thesheetresistance4.573 Ω/sqindicatescompatibilitywiththin-film device architectures. These parameters implythat CoNi-C thin films can function as efficient counter electrodes in quantum dot solar cells, facilitating charge transfer at the electrode- electrolyte interface. Their good conductivity, coupled with moderate carrier mobility, ensures minimal energy losses during operation. In summary

,Parameter	Value
Carrier concentration ($n_e \times 10^{19}$ cm^{-3})	3.274
Mobility ($\mu \times 10^2$ cm^2/V·s)	5.955
Resistivity (Ω·cm)	3.201 × 10^{-2}
Hall coefficient (RH × 10^{-1} cm^3/C)	1.906
Surface carrier concentration (ns × 10^{17} cm^{-3})	2.292
Conductivity (σ × 10^1 S/cm)	3.124
Sheet resistance (Rs, Ω/sq)	4.573

These properties indicate excellent conductivity, suitable carrier density, and minimal energy loss during charge transport. The CoNi-C bandgap of ~3.1 eV reduces recombination and enhances carrier separation.



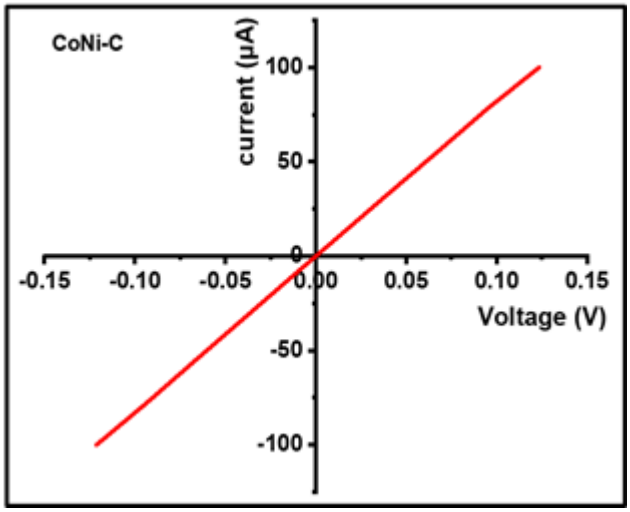


Figure 3(a-b): Hall effect measurement of and I-V curve of CoNi-C counter electrode

Table 2: Hall effect parameters of the deposited CoNi-C thin films

$.n_b \times 10^{19}$ (cm^{-3})	$\boldsymbol{\mu} \times 10^2$ (cm^2/Vs)	$\boldsymbol{\rho} \times 10^{-2}$ **(Ω *cm*)**	$R_H \times 10^{-1}$ **(cm^3/C)**	$n_s \times 10^{17}$ (cm^{-3})	$\boldsymbol{\sigma} \times 10^1$ (S/cm)	R_s (Ω/sq)
3.274	5.955	3.201	1.906	2.292	3.124	4.573

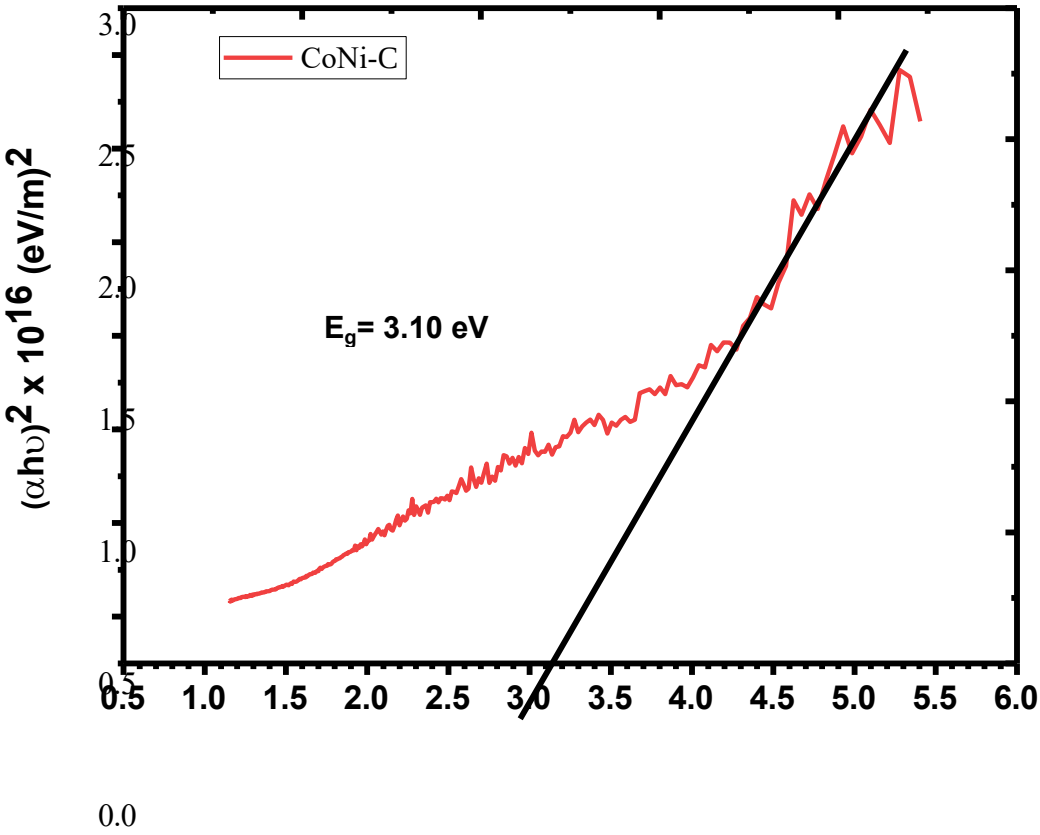


Figure 4: Plot of absorption coefficient $(\alpha hv)^2$ against photonenergy for CoNi-C thin film

Band gap: Band gap of CoNi-C is 3.10 eV, although with band gap at 3.0ev, caused reduced recombination losses, and enhanced charge carrier separation.

4.0 Conclusion

This study successfully fabricated and characterized a carbon quantum dots (CQDs)/CdS/ZnS trilayer thin-film solar cell incorporating a CoNi-C counter electrode. The device achieved a power conversion efficiency (PCE) of 0.80%, a short-circuit current density (Jsc) of 16.20 µA, and an open-circuit voltage (Voc) of 0.345 V under standard test conditions. The CoNi-C counter electrode exhibited excellent electrical characteristics, including a low resistivity (3.20×10^{-2}

Ω·cm), high conductivity (3.12×10^1 S/cm), and moderate Hall coefficient (1.91 cm^3/C), indicating its suitability for efficient charge transport.

These results are consistent with efficiencies reported in similar quantum dot-sensitized solar cells and confirm that green-synthesized CQDs can enhance device sustainability while maintaining comparable performance. Future optimization—particularly in improving CQD coverage and minimizing interfacial resistance—could further enhance cell efficiency. Overall, this work demonstrates the feasibility of eco-friendly and low-cost CQD/CdS/ZnS–based solar cells using CoNi-C as a sustainable alternative to precious metal electrodes, thereby contributing to a greener and more economically viable photovoltaic technology.

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