Nanocomposites of reduced graphen oxideand cadimium sulfide(rGO/CdS) as affective photoanode for dye sentisized solar cells(DSSCs) by doctor blade deposition technique

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The synthesis and characterization of reduced graphene oxide/cadmium sulfide (rGO/CdS) are the primary topics covered in this paper. The construction of a photoanode in dye-sensitized solar cells (DSSCs) using synthetic materials is subsequently proposed. Here, graphene oxide (GO) was synthesized using the Hummer's method, and green tea leaves were employed to reduce GO. The rGO/CdS nanocomposites were prepared using a hydrothermal method. A photoanode was fabricated from the as-prepared rGO/CdS nanocomposite paste using doctor blade deposition techniques.
The performance of the fabricated DSSCs was evaluated using current density-voltage (J-V) curves. Transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) spectroscopy were employed to confirm the characterization of the CdS nanoparticles and rGO/CdS nanocomposites. The characterization results revealed that the hydrothermal method produced well-defined, spherical CdS nanoparticles with an average diameter of 45 nm, which were successfully decorated on the rGO sheets.
To construct dye-sensitized solar cells (DSSCs), Congo red dye and natural dye from roselle flowers were used as photosensitizers. The photovoltaic performance of the DSSCs was assessed under a 55 W HID Xenon light source. The sensitized solar cell (RCR) made with the roselle (Hibiscus sabdariffa) extract achieved short-circuit current densities (Jsc) of 3.377 mA/cm², open-circuit voltages (Voc) of 735 mV, fill factors (FF) of 0.169, and total solar energy conversion efficiencies (η) of 0.645%.
In comparison, the Congo red dye-sensitized cell (RCC) produced Jsc values of 1.789 mA/cm², Voc values of 250 mV, FF values of 0.202, and a conversion efficiency of 0.0362%. The roselle extract-sensitized cell demonstrated superior sensitization, consistent with the extract's broad spectrum of absorption on the rGO/CdS surface.

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*Keywords:*DSSC, Hibiscus sabdariffa, Cadmium sulfide, Graphene oxide, Congo red

1. Introduction

The amount of solar energy that reaches the Earth is astounding. The sun, a typical star, is a fusion reactor that has been operating like an oven. It produces enough energy in a minute to meet the requirements of the entire planet for a full year. It delivers more energy in a single day than the present population would need in 27 years. In fact, "the energy stored in all fossil energy sources is comparable to the solar radiation impacting the planet over three days." Despite being a free and limitless resource, harnessing solar energy remains a relatively new concept. Significant progress has been made, considering that "the first effective solar cells were created less than 30 years ago.

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With the persistence of professional solar firms developing tailored solar power systems for individual residences, there is no longer a justification for not considering solar electricity for homes. The invention of the transistor and related semiconductor technologies has led to the most significant increases in efficiency. Photovoltaic solar energy is "one of the most promising renewable energy sources in the world," owing to its many advantages. It is non-polluting, has a lifespan of 20–30 years with minimal operating expenses, lacks moving components that could break down, and requires little maintenance and monitoring. Additionally, solar power systems do not require substantial installations, making them highly adaptable. Remote locations can quickly establish their own electrical supply by building systems as small or large as needed. Solar power generators are also distributed to homes [1].

This system works by creating an electric potential between two electrodes connected to a solid or liquid system when illuminated. A PN-junction in a semiconductor, where the photovoltage is generated and enhanced, is present in almost all photovoltaic devices. These photovoltaic components are commonly referred to as solar cells. The light-absorbing component of the semiconductor is particularly crucial. The semiconductor material must absorb a significant portion of the solar spectrum.

The amount of light absorbed near the surface directly relates to the material's absorption properties. When light is absorbed, electron-hole pairs are created and move to the junction, where they are separated by an electric field. It is also important that the semiconductors are as close to the surface as possible, as most carriers are generated there, even in materials like silicon, which have moderate absorption [2]. Multiple crystalline silicon (Si) cells are connected in series using a layer of thin-film material, or solar cells are grouped into modules for practical applications.

For many optical technologies, including solar cells, CdS has become a crucial component [3]. It is well understood that various physical characteristics of CdS influence its photocatalytic yield. Properties such as crystalline phase, structural defects, specific surface area, particle size, and shape are key factors. Controlling the size and shape of CdS particles is essential for creating an active photocatalyst [4]. Consequently, several novel methods have been developed for creating the building blocks of CdS. Bao et al. [5,6] synthesized nanoporous CdS nanostructures with higher hydrogen yield under visible light through self-templated synthesis.

Other methods, such as biogenic synthesis [7], chemical bath deposition [8–11], hydrothermal processes [12–13], and thermal evaporation [15], have also been successfully employed to produce CdS nanostructures. Among these, hydrothermal synthesis has been particularly effective in producing nanostructures at low temperatures [4].

Graphene, a flexible, atom-thin 2D carbon material, has emerged as a rising star due to its exceptional properties, such as a theoretical surface area of 2630 m^2/g for a single layer of graphene, remarkable electrical and thermal conductivity [17, 18], exceptional mechanical strength [19], and outstanding biocompatibility [20]. Its unique characteristics have driven the development of graphene and its derivatives in diverse fields, including nanoelectronics, high-frequency electronics, energy conversion and storage, biomedical devices, and sensors.

Graphene-based electrochemical studies have garnered significant interest due to graphene's critical role in enhancing electron transport and its advantages of high carrier mobility and outstanding electrical conductivity. These studies offer new opportunities for developing high-performance electrochemical sensors.

Reduced graphene oxide (rGO) is widely used in graphene-based electrochemical sensors instead of graphene oxide (GO) due to its superior properties: (i) it has numerous structural defects that enhance its electrochemical activity; (ii) the chemical moieties on the rGO surface make it flexible for various surface functionalizations that improve sensing performance; and (iii) it exhibits excellent tunable properties [21].

2. Experimental part

2.1. Preparation of GO and rGo

Graphene oxide (GO) was produced from graphite powder using a modified version of Hummer's method. A mixture of 0.2 g of graphite powder and 1 g of sodium nitrate was combined with 47 mL of concentrated H_2SO_4 and stirred continuously for three hours. A total of 6 g of $KMnO_4$ was slowly and intermittently added to the reaction mixture while maintaining continuous stirring at 0–4 °C. Subsequently, 60 mL of deionized water was gently added to the stirring apparatus. The mixture was stirred for an additional 12 hours until the solution turned dark brown. The suspension was then diluted with 190 mL of double-distilled water, turning the entire mixture dark yellow. To terminate the reaction, 10 mL of 30% H_2O_2 was added. The mixture was centrifuged for five minutes at 5000 rpm. The resulting pellet underwent two to three cycles of washing with diluted HCl, deionized water, and ethanol. Finally, the generated GO was dried at 60 °C for 24 hours.

Reduced graphene oxide (rGO) was synthesized by reacting 0.2 g of graphene oxide with 2.5 g of ascorbic acid and 100 mL of deionized water in 100 mL of green tea extract for 12 hours. The solution was repeatedly washed with distilled water and ethanol before being dried [22].

2.2. Preparation of Cadmium sulfide nanoparticles

Aqueous cadmium sulfate ($3CdSO_4.8H2O$) was mixed with thiourea $(NH_2)_2CS$) at concentrations of 0.02 M and 0.05 M, respectively, to produce cadmium sulfide. Until the solution is homogeneous and starts to become yellow, it is continuously stirred. 1.5 hours are spent stirring continuously with increasing the temperature up to 70 º C. Following the cessation of stirring, the mixture is heated for three hours at 70 º C before the precipitate is cleaned and dried [23].

2.3. Preparation of Binary Composite (rGO/ CdS nanocomposite)

100 mL of deionized water and 0.4 g of rGO were combined to create the composite, which was then put in an ultrasonic device for an hour. Thiourea $(NH_2)_2CS$ solution and cadmium sulfate $3CdSO_4.8H_2O$ solution were produced as in the preceding sentence and added progressively to the rGO solution. Drops of ammonium hydroxide were added until the pH reached 10 and a precipitate formed in the solution.

The solution is continuously stirred until it becomes homogenous and becomes yellow. After two hours of heating at 70 °C with continuous stirring, the heating is stopped and the temperature is maintained at 70 °C for another three hours. The precipitate that forms is then cleaned and dried.

2.4. Hibiscus flower extract

Using a mortar, 10 g of hibiscus flower petals were broken into small pieces and crushed .After that, 200 mL of distillation water was added to the crushed petals, They were thereafter kept at ambient temperature for around six hours. After another hour of stirring at room temperature, 10 ml of ethanol and 10 ml of diluted acetic acid were added to the mixture.

2.5. Fabrication of DSSCs

The FTO (Fluorine Doped Tin Oxide) plates were used to construct the solar cell using the doctor blade technique. The rGO/ CdS nanocomposite was used to prepare the active electrodes. After being coated, the plates were immersed in Congo Red and Hibiscus extract dye and sintered at 120°C for 2 hours.

The conductive side of the glass plate was prepared for the graphite-coated slide by lightly sweeping carbon onto the surface using a graphite stick pencil. The carbon-coated side of the glass plate was then painted black by holding it over a candle flame.

The glass plate with carbon coating was then heated on a hot plate for 15 minutes at 150°C before being allowed to cool to room temperature. Iodide/iodine was utilized as an electrolyte solution and positioned between the FTO plates in [24].

3. Results and discussion

3.1. Field-Emission Scanning Electron Microscopy of ternary composite

For the binary composite rGO–CdS, cadmium sulfide molecules are uniformly distributed on the surface of reduced graphene oxide sheets, as observed in the FE-SEM image (Fig. 1). The composite's structure facilitates electron transmission and reduces the recombination process (i.e., the recombination of the electron-hole pairs). Notably, the particles are uniformly and spherically dispersed.

To determine the ratio of components in the composite, EDX atomic analysis coupled with SEM was utilized. The results confirm the presence of carbon, oxygen, sulfur, and cadmium elements in the sample (Fig. 2).

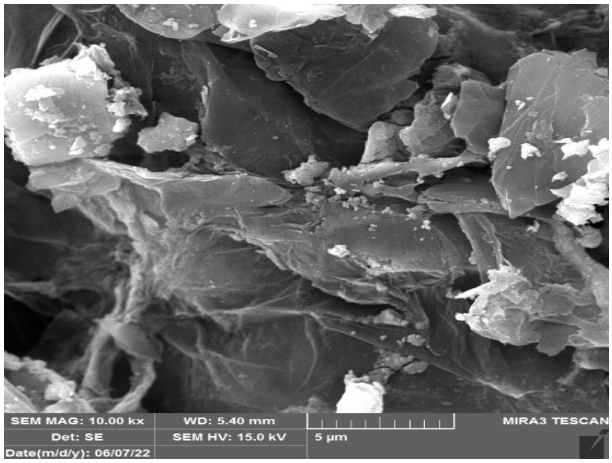

Fig. 1. FE-SEM for the binary composite.

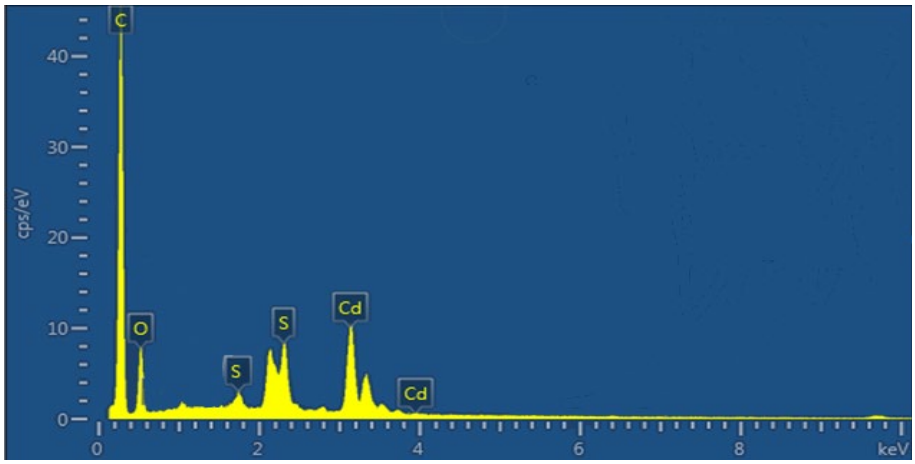

Fig. 2. EDX of rGO-CdS Nanocomposite.

3.2. XRD studies of rGO–CdSnanocomposite

For the rGO–CdS nanocomposite, the X-ray diffraction spectrum shows prominent peaks at diffraction angles of 64.45° and 53.22°, attributed to the planar hexagonal crystals of CdS. Additionally, a clear peak observed at 26.38° corresponds to the characteristic structure of graphene oxide (Fig. 3).

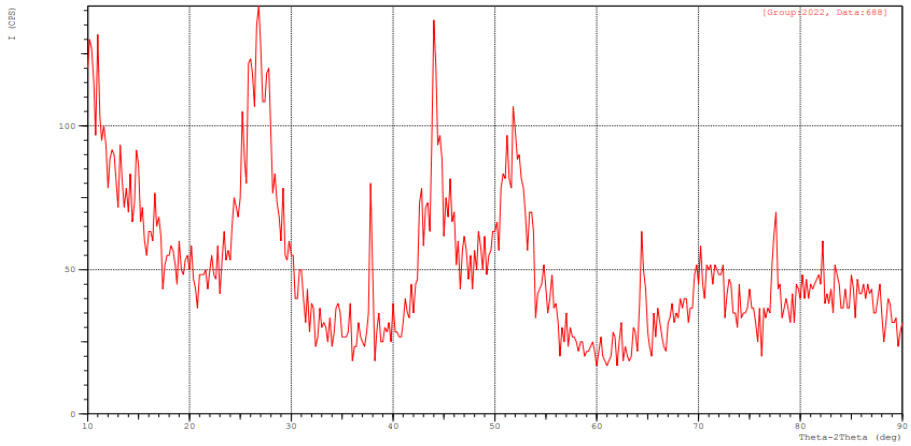

Fig.3. X-ray diffraction spectrum of rGO/CdS Nanocomposite.

3.3. DRS spectra for the RGO–CdS Nanocomposites

The UV-visible absorption spectra (Fig. 4) provide insights into the optical properties and the energy gap (Eg) of the produced composites. It is evident that rGO significantly enhances visible light absorption in the 500 nm range. The energy gap of the rGO–CdS composite is lower than that of pure CdS, due to the apparent bathochromic shift of the rGO–CdS binary composite towards higher wavelengths. Consequently, the energy gaps of pure CdS and the rGO–CdS binary composite are approximately 2.42 eV and 2.07 eV, respectively.

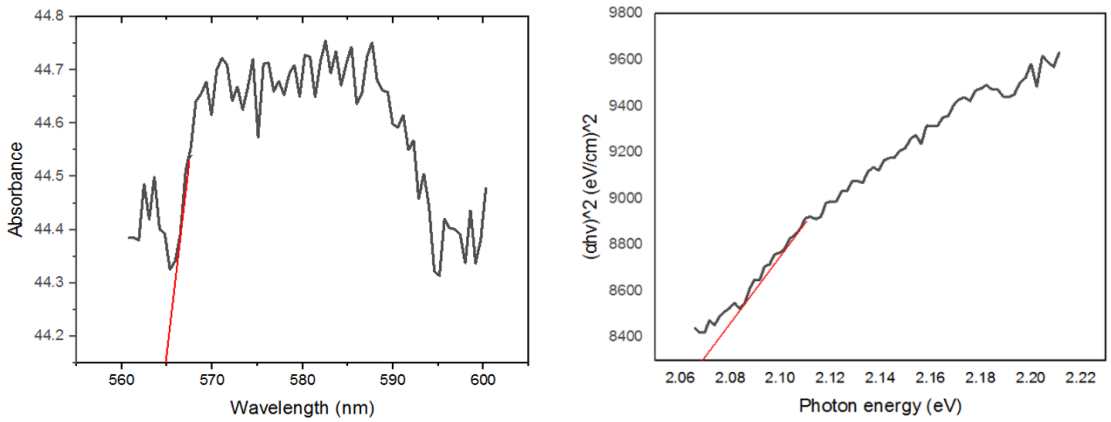

Fig. 4. DRS of the binary composite.

3.4. Surface area analysis studies of rGO–CdS nanocomposite

The BET isotherms for nitrogen adsorption and desorption on the surface of the binary composite are illustrated in Figure 5, providing insights into the pore size distribution of the composite surface. The binary composite's isotherms (adsorption–desorption) are classified as type IV, according to IUPAC standards. Hysteresis loops of type H3, observed in the relative pressure range of $0.3 < P/Po < 0.9$, indicate multilayer adsorption. This suggests that the surface pores have a non-solid, plate-like assembly structure.

Using the BJH method, the surface properties of the binary composite were determined, revealing a pore size of 0.3030 cm^3/g, a surface area of 15.431 m^2/g, and an average pore diameter of 22.422 nm.

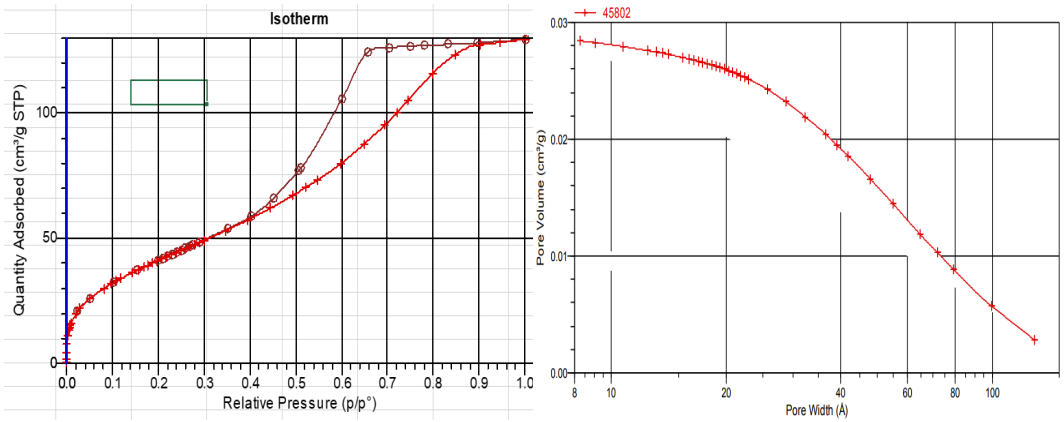

Fig.5. BET –BJH of Binary Nanocomposite.

3.5. Solar Cell Analysis

The J-V measurements of the DSSCs sensitized with extracts of *Hibiscus sabdariffa* and Congo Red dyes are illustrated in Figs. 6 and 7. These values were measured under illumination from a 55 W HID Xenon lamp.

The conversion efficiency of a DSSC can be calculated using Equation (1) below:

$$\eta = \frac{FF * V_{oc} * J_{sc}}{P_{in}} x100\% \quad (1)$$

To evaluate DSSC performance, the short-circuit current density Jsc, open-circuit voltage Voc, maximum power point, fill factor (FF), and conversion efficiency η must be determined. The short-circuit current density and open-circuit voltage are derived from the J-V curve intersections with the y-axis and x-axis, respectively. The output power of the DSSC can be calculated using P=J.V . The maximum power point can then be determined from the output power data. Input power, fill factor, and conversion efficiency can also be derived using standard methods [25].

Table 1 presents the photoelectrochemical properties of the fabricated DSSCs. The DSSC sensitized with *Hibiscus sabdariffa* extract demonstrated an open-circuit voltage Voc of 735 mV, while the DSSC sensitized with Congo Red dye exhibited a Voc of 250 mV. The short-circuit current densities Jsc were measured as 3.377 mA/cm² for the *Hibiscus sabdariffa*-sensitized DSSC and 1.789 mA/cm² for the Congo Red-sensitized DSSC. The fill factors (FF) were 0.169 for *Hibiscus sabdariffa* and 0.202 for Congo Red dye. Correspondingly, the energy conversion efficiencies (η) were calculated as 0.645% for the *Hibiscus sabdariffa*-sensitized DSSC and 0.036% for the Congo Red-sensitized DSSC.

Table 1. Photoelectrochemical parameters of the fabricated DSSCs.

Cell	Voc(V)	Jsc(mA/cm^2)	Vmax(V)	Imax(A)	FF	Pmax(mW)	PCE%
RCC	250	1.789	110	0.822	0.202	90.420	0.036
RCR	735	3.377	225	1.864	0.169	419.400	0.645

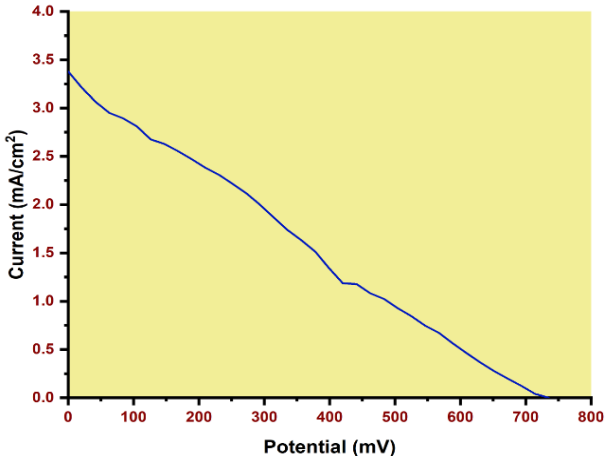

Fig. 6. J-V Graph of rGO/CdSsolar cell sensitized with Hibiscus Sabdariffa(RCR).

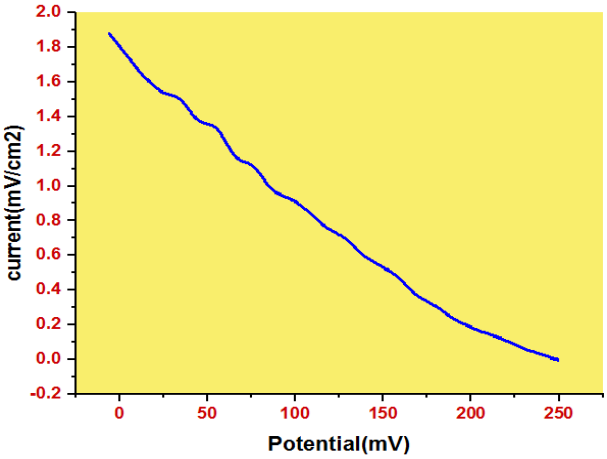

Fig. 7. J-V Graph of rGO/CdS solar cell sensitized with Congo Red (RCC).

4. Conclusions

In this article, DSSCs were constructed using Congo Red dye and a dye made from Hibiscus Sabdariffa flowers. In comparison to the DSSC sensitized with Congo Red dye, the DSSC sensitized with Hibiscus Sabdariffa produced a superior I-V output.

Since both dyes have a maximum wavelength in the 509–520 nm range, the difference in their sensitizer performance may be due to the chemical makeup of the natural extraction, the dye's strong affinity for the composite surface, or a match between the conduction band of the semiconductor and the hole-redox conductor's potential.

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