



Fabrication of ZnO/ZnO @ carbon dot as photo anode and Natural dye as photosensitizer for dye sensitized solar cell application

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Abstract

ZnO/ZnO @ carbon dot was hydrothermally synthesized and deposited on indium tin oxide coated glass substrate by doctor blade method for application as working electrode in dye sensitized solar cell. Environment friendly natural dye extracted from Lawsonia inermis leaves was used as photosensitizer to fabricate DSSC. Structural and optical properties of the synthesized nanoparticles were studied by X-Ray, UV-Vis, FT-IR and PL spectroscopy. The photovoltaic properties of the cell have been studied and the best solar energy conversion efficiency was obtained.

Keywords: Zinc Oxide; Carbon Dot; Lawsonia Inermis; Sensitizer; Solar Cell

1. Introduction

Dye sensitized solar cells (DSSC) are emerging photovoltaic device which fascinated the attention of researchers due to its eco-friendly approach to convert solar radiation into electricity to meet the growing energy demands [1]. New technologies have been developing to minimize the cost of DSSC by modifying the materials, dyes, electrolyte and engineering [2]. These issues have urged us to synthesize large surface area and low cost nanomaterials for DSSC applications. The aspects which affect the efficiency of DSSC are dye, electrolyte, semiconductor material and fast electron transport. To overcome the above aspects and to enhance the efficiency of DSSC our research group focused on synthesizing natural dye and nano semiconductor material for cathode and anode of DSSC.

Among the various nanomaterials, ZnO wide band gap semiconductor has been preferred as significant material to replace the TiO₂ or silicon based Photovoltaic materials [3]. Due to its unique properties, ZnO nanomaterials have been recognized as potential photovoltaic material for dye sensitized solar cell applications.

Natural dyes are considered to be cost-effective, non-toxic, easy availability and completely biodegradable compared to the expensive synthetic dyes [4]. Natural dye extracts contains phytochemicals which play a significant role in the conversion efficiency of DSSC [5]. In the present work, we have chosen the natural dye Lawsonia inermis leaf aqueous extract due to its vital functional group (hydroxy and naphthaquinone) which anchors better to the ZnO nanomaterials and bring stronger electronic coupling and transfer reactions.

Graphene has attracted the attention of researchers due to its high transparency, good electrochemical activity, and superior conductivity [6]. Concurring to the literature reports, graphene has been considered as a remarkable material for counter electrode of

DSSC. In this study, graphene was synthesized from agrowaste and used as counter electrode in DSSC.

In the current research, the nanoparticles of ZnO, ZnO@carbon dot and graphene were prepared and coated on ITO glass by doctor blade process for photoelectrode and counter electrode in dye-sensitized solar cells (DSSCs). The single layered of ZnO and ZnO@carbon dot in photoelectrode and the high surface area of graphene nanoparticles in counter electrode was investigated for increasing of redox reaction due to the increasing of active surface area.

2. Experimental

2.1. Materials

All chemicals were purchased and used without further purification. Zinc Chloride (99.9%), ammonia (98%), L-Cystiene (99%) and anhydrous Ferric Chloride were purchased from Qualigens (India). Throughout the procedures, double distilled water was used.

2.2. Extraction of dye

A ten gram of Lawsonia inermis leaves was soaked in 100 mL water and grinded at room temperature. Then the solution was filtered using Whatman No. 1 filter paper to remove solid residue. Finally, the concentrated dye solution was shielded from exposure to direct light and stored in dark bottles.

2.3. Synthesis of ZnO nanoparticle

In order to synthesize L-cysteine capped ZnO nanoparticles, 1M zinc Chloride ($ZnCl_2$) solution was prepared. To the solution, ammonium hydroxide (NH_4OH) was added under continuous stirring to get the pH 13. After 1 hour stirring, 5ml of 1M L-cysteine solutions (1M) was introduced into the solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave and hydrothermal growth was carried out at $120^\circ C$ for 20 h and $180^\circ C$ for 2hr. After the treatment, the autoclaves was allowed to cool down and the precipitates was collected and centrifuged at $40,000 \times g$ for 10 min and supernatant was discarded. Thus the L-cysteine capped ZnO nanopowders was obtained by drying the precipitate at $60^\circ C$ for 24 h after washing it three times with ethanol and distilled water in order to remove impurities.

2.4. Synthesis of ZnO @ CDs

The preparation of ZnO @ CDs is as follows:

In a typical procedure 5 g of Neem leaves were chopped very finely and added to 40 mL of distilled water. To the solution already prepared 1M zinc Chloride ($ZnCl_2$) solution and ammonium hydroxide (NH_4OH) was added. Then the solution was transferred to Teflon-lined stainless steel autoclave and given hydrothermal treatment for 4 h at $240^\circ C$. Solution was allowed to cool naturally and large particles were removed by filtration through Whatmann filter paper to remove black insoluble carbonaceous particles. Finally, the solution volume was adjusted with water to obtain ZnO @ CDs for further characterization and use.

2.5. Synthesis of Graphene

Graphene was synthesized from coconut shell waste.

To the 3g of coconut shell powder, 50 ml of $ZnCl_2(9g)$ and 3 M ferric trichloride ($FeCl_3$) solution was added and heated at $800^\circ C$ for 2 h with continuous stirring. Thus the carbon precursor is obtained by drying the above mixture at $1000^\circ C$ in a conventional oven. The obtained precursor was heated in a tubular furnace under a N_2 atmosphere by heating the sample at a rate of $50^\circ C$ per min up to $12000^\circ C$ for 1 h.

2.6. Fabrication of Electrodes

Indium doped tin oxide on glass (ITO glass) was used as a substrate. The ITO glass were coated with ZnO, ZnO@Carbondots and graphene paste by doctor blade process using propanol solution and annealed at $100^\circ C$ for 10 min. Then the plates are immersed in a concentrated dye solution for 10 min at room temperature [7].

2.7. Preparation of electrolyte solution

The liquid I3/I2- electrolyte was a mixture of 0.05 M iodide (I_2), 0.5 M sodium iodide (KI).

2.8. DSSC assembly

The DSSC was assembled using ZnO and ZnO@ carbon dot coated Lawsonia inermis leaves dye sensitizer film as the working electrode and Graphene as the counter electrode. These two electrodes were assembled using a semi-closed DSSC method. The electrolyte was filled into the cells. The Schematic diagram of DSSC is shown in the Fig.1

2.9. Characterization

UV-Vis spectroscopy was used to analyze the formation of ZnO and ZnO@CDs using a Hitachi Double beam spectrophotometer model U2800 with a scanning wavelength between 200 and 900

nm. The obtained powder and colloid was centrifuged, dried and analyzed by FT-IR (FT-IR spectrometer- ThermoNicolate Company Avatar 330) and Powder X-ray diffraction ($Cu K\alpha$, PANalytical). Photoluminescence spectroscopy was used to measure the optical emissions from 350 nm to 700 nm wavelength range. The photocurrent-voltage of DSSC cells was measured.

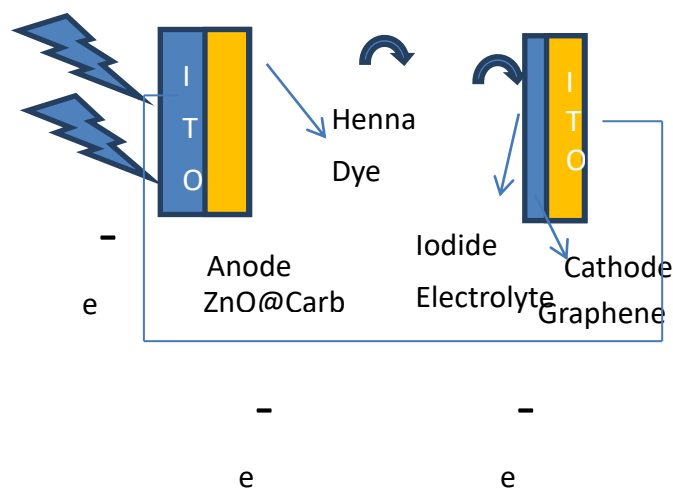


Fig.1.Schematic diagram of DSSC

3. Results and Discussion

In this current research L-cysteine capped ZnO and ZnO@CD was synthesized hydrothermally as photo anode materials to increase the adsorption of Dye.

In order to evaluate the UV-Vis absorption property of nanoparticles, the UV spectrum of L-cysteine capped ZnO nanoparticle was recorded. The result was shown in Figure.2. the UV-Vis absorption spectrum shows a strong absorption peak at 335 nm which confirms the formation of ZnO [8]. Figure.3 represents the X-ray diffraction pattern of L-cysteine capped ZnO nanoparticle. The diffraction peaks have been keenly indexed as hexagonal wurtzite phase of ZnO [9]. (JCPDS NO: 79-2205)

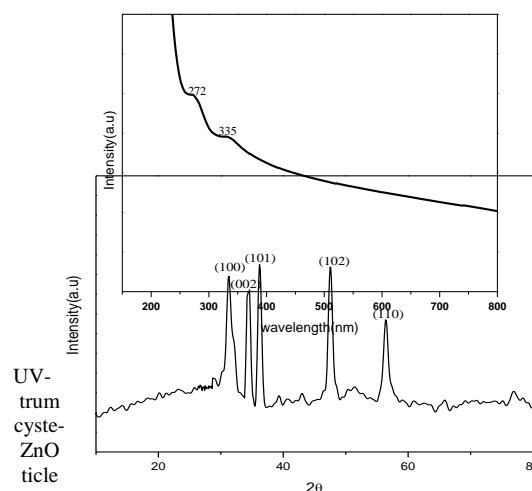


Fig. 2: Vis spec- of L-cysteine capped nanopar-

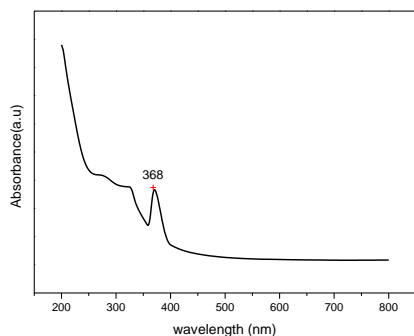


Fig. 4: UV-Vis spectrum of ZnO @CD nanoparticle

Figure.4 shows the UV-Vis spectrum of ZnO@CD. The UV-Vis absorption spectrum shows absorption peak at 368 nm which corresponds to ZnO[10]. Figure. 5.shows the FT-IR spectrum of ZnO@CD nanoparticles. A peak observed at 421 cm^{-1} which is characteristic of the stretching vibration of Zn-O bond [11] which further confirms the formation of ZnO @CD nanoparticle. Room temperature PL spectra for ZnO@CD nanoparticle is shown in Figure.6 which was obtained with an excitation wavelength of 350 nm. A broad green light emission is observed at 550 nm which is commonly referred to a deep level of trap state emission [12].The stronger intensity suggests the presence of higher singly ionized oxygen vacancies in ZnO.

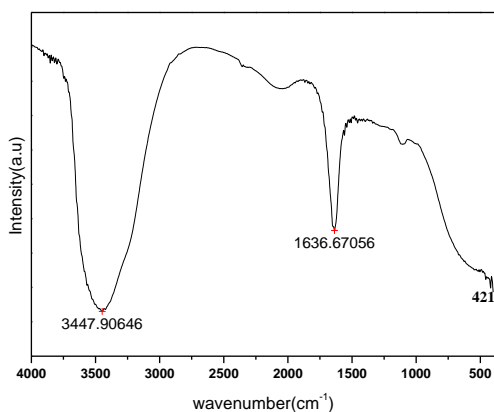


Fig. 5: FT-IR spectrum of ZnO @CD nanoparticle

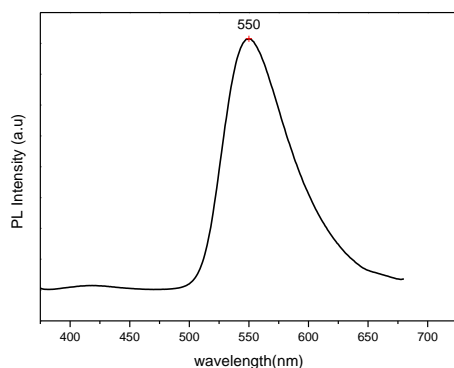
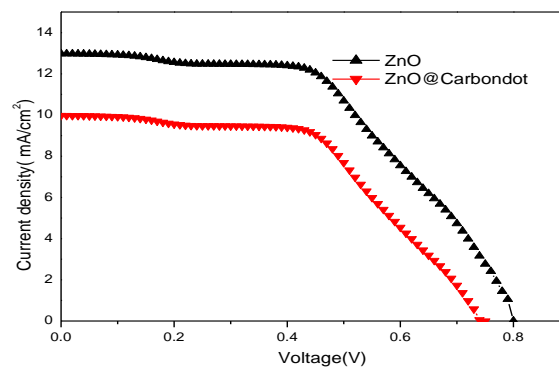


Fig. 6: PL spectrum of ZnO @CD nanoparticle

The photovoltaic performance of the DSSC cells of single layer of ZnO and ZnO@CD was shown in Fig.7. with the measured and calculated values obtained from the I-V curve shown below. From the figure.6 L-cysteine capped ZnO nanoparticle DSSC cell

showed higher efficiency (8%) compared to ZnO@Carbon dot DSSC cell (7.5%). A higher amount of dye was adsorbed on L-cysteine capped ZnO nanoparticle than on ZnO@CD due to its larger surface area which enriches the photon absorption and carrier generation. This results confirms that efficiency of the DSSC cell depends on the electrode surface area [13]. As per the literature reports increase in surface area enhances the dye adsorption which results in higher conversion efficiency [14].



	J_{sc} (mA/cm^2)	V_{oc} (V)	η %
SLZnO	13	0.80	8
SLZnO@CD	10	0.74	7.0

Fig. 7: J-V characteristics of L-Cysteine capped ZnO and ZnO @CD nanoparticle

4. Conclusion

In this study, we proposed L-cysteine capped ZnO nanoparticle by hydrothermal method which is simple, easy for use as photo anodes in DSSC. Moreover, the results reveal that DSSC containing L-cysteine capped ZnO exhibit higher photovoltaic performance than DSSC containing ZnO@CD. Compared to ZnO@CD, L-cysteine capped ZnO possess larger surface area, which aids efficient dye loading and light harvesting and faster electron transport. These improvements enhances the power conversion efficiencies of DSSC.

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