rGO Sheets / ZnFe_2O_4 Nanocomposites as an Efficient Electro Catalyst Material for I_3^- / I^- Reaction for High Performance DSSCs

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Abstract

In this paper, Reduced Graphene Oxide (rGO) / ZnFe_2O_4 (rZnF) nanocomposite is synthesized by a simple hydrothermal method and employed as a counter electrode (CE) material for tri-iodide redox reactions in Dye sensitized solar cells (DSSC) to replace the traditional high cost platinum (Pt) CE. X-ray diffraction analysis (XRD) and High resolution Transmission electron microscopy (HR-TEM), clearly indicated the formation of rZnF nanocomposite and also amorphous rGO sheets were smoothly distributed on the surface of ZnFe_2O_4 (ZnF) nanostructure. The rZnF-50 CE shows excellent electro catalytic activity toward I_3^- reduction, which has simultaneously been confirmed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. A DSSC developed by rZnF-50 CE ($\eta = 8.71\%$) obtained quite higher than the Pt ($\eta = 8.53\%$) based CE under the same condition. The superior performances of rZnF-50 CE due to addition of graphene in to Spinel (ZnF) nanostructure results in creation of highly active electrochemical sites, fast electron transport linkage between CE and electrolyte. Thus it's a promising low cost CE material for DSSCs.

1. Introduction

In recent years, fossil fuels becoming increasingly scarce and global warming gained momentum from rising carbon dioxide emission that imply the need to go for alternates which can replace the fossil fuel and mitigate the pace of global warming. Natural resources such as solar energy, wind energy, hydroelectric energy, geothermal and thermal energy can be harnessed as alternate energy reserves [1,2]. The incident radiation or light energy of the sun is converted to electrical energy or electricity. The Photo Voltaic systems are employed for this conversion process. Dye Sensitized Solar Cells (DSSC) are identified as significant options due to low manufacturing cost, environmental friendly, non-pollution and high energy conversion under low light conditions [3,4]. The major components of DSSC are photo anode, dye, electrolyte and catalytic Counter Electrode (CE). CE is an indispensable key component in the working of a DSSC to improve conversion efficiency, act as a catalyst for the tri-iodide reduction and also collects the electron from the external circuit and injecting it to the electrolyte. Traditionally Platinum (Pt) is widely used as standard CE material for the DSSC due to its good conductivity, catalytic capacity, low charge transfer resistance and higher activity in visible and infrared regions. However Pt it's costlier, possesses highly corrosive nature in the liquid electrolyte which may lead to serious drawbacks in the large scale production [5]. Therefore, developing materials which reduce the use of Pt in DSSC is the need of the hour. So far, other alternative materials like carbon allotropes (activated carbon, CNTs and graphene), conducting polymers (CP) and transition metals have also been introduced to substitute Pt CEs. However the conversion efficiency of those electrodes is still low compared to Pt as a result of low electron conductivity and poor catalytic activity. Recently, it's reported that graphene-based nanocomposites designed to own high chemical stability, significant electro catalytic activity towards iodine triiodide electrolyte, large surface area and more activated electrochemical functionalized sites. Also, there are reports on spinel type rGO based hybrid materials (MFe_2O_4 and MCo_2O_4 ($\text{M}=\text{Ni}, \text{Co}, \text{Zn}, \text{Mg}$)) examined as a CE material for DSSCs owing to their chemical properties, low cost, high stability

against corrosion, interactions between metal ions via chemical bonds and multi metal composition provide more active sites improving the electrochemical activity[6,7]. In this case, a novel spinel type (MFe_2O_4) nanocomposites consisting of reduced graphene oxide (rGO) are suitable with excellent electro catalytic activity [8,9]. Moreover, graphene possesses π - π conjugation structure, which endowed them with excellent electrical property and superior chemical stability in electrochemical environment. properties. In this favor, we have prepared rGO/ ZnFe_2O_4 nanocomposites by facile one-pot hydrothermal method with a different weight ratio of GO sheets. The influence of structural and electrochemical performances of the nanocomposites is investigated. Finally, Dye Synthesized Solar Cells are made employing as synthesized CEs and the results are compared to that of the cells fabricated with Pt CE.

2. Experimental

2.1 synthesis of rZnF nanocomposites

The Preparation of graphene and reduced graphene oxide (rGO) procedure were followed as reported by Muthu et al (2017) [13]. For rGO/ ZnFe_2O_4 nanocomposites, 25 mg of GO were dispersed in 40ml of DI water by ultrasonication for 30 minutes, on the side 1:2 ratio of Zinc (III) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$) and iron III nitrate nonohydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were mixed 40ml of DI water mixed by stirring. Then 5M of NaOH solution added until the pH value exceeds above 10. The above solution mixture was slowly added to as previously prepare GO suspension. Then the solution was taken in autoclave and heated at 180°C for 12 Hrs. After that the precipitate was collected by centrifuge several times and dried at 80°C for 12 Hrs. The obtained sample named as rZnF-25. For rZnF-50 prepare by adapting the same procedure additionally double amount of adding GO. For comparison pure ZnFe_2O_4 (ZnF) also prepared by without adding GO.

2.2 Fabrication of DSSCs

The CEs paste is prepared by 100mg as prepared sample was ground well in mortar, then adding (N, N-dimethylformamidel solution) NMP and PVDF to form a slurry sticky paste, Then the slurry was coated in FTO subtract by using doctor blade method with a contact area of 1.5 cm^2 and sintered 500°C for 30 minutes. The Pt CE was prepared by drop coating method using H_2PtCl_6 solution with a contact area of 1.5 cm^2 and sintered 500°C for 30 minutes. After natural cooling to room temperature all prepared CE was ready for both electrochemical and photovoltaic studies. simultaneously, the same procedure followed by the preparation of photo anode using commercially available TiO_2 paste. Then the prepared photo anode soaked into 0.5M of N719 dye solution for 12 hours and dried at 60°C . Liquid electrolyte ($\text{I}_3^- / \text{I}^-$) mediator prepared by 0.5 M of KI and 0.05 M of I were dissolved in acetonitrile solution. The gap between photo anode and CEs were filled with the above electrolyte solution.

The Photo conversion Efficiency and Fill Factor were calculated by the following equations

$$\text{Efficiency (\%)} = \frac{J_{sc} * V_{oc} * FF}{P_{in}}$$

$$\text{Fill Factor} = \frac{J_{mp} * V_{mp}}{J_{sc} * V_{oc}}$$

Where the J_{mp} and V_{mp} are the current density and voltage at the maximum power point

2.3 Characterization measurements

Electrocatalytic activities of the CEs, Cyclic Voltammetry (CV) were examined 0.5 M of KI and 0.05 M of I₂ iodine/triiodide electrolyte in the potential range 0.1 to 0.6V at the Scan rate of 50mVs⁻¹. Tafel polarization curves of the symmetrical cells composing of two identical electrodes in the same electrolyte were recorded between (0.1 to 0.6 V) on the same workstation. Electrochemical impedance spectroscopy (EIS) of the symmetric cells were recorded at zero bias potential and 10 mV amplitude over 0.01≈10⁵ Hz. The photovoltaic (J-V) measurements of the device were at room temperature using a Keithley 2400 high current source power meter under the light illumination of 500 W Xenon lamp (AM1.5G).

3. Results And Discussions

3.1 X-Ray Diffraction

XRD pattern of GO, rGO, ZnF, rZnF-25and rZnF-50 are Shown in Fig.1 (a,b). Graphene oxide characteristic peak at 9.8° following to the plane (001) indicates the successful preparation of graphene oxide from graphite power. For rGO, small broad peak observed at 24.4° corresponds to (002) plane has confirmed the conversion of rGO from GO. The peaks at 29.78°(220), 35.15°(311), 37.90°(222), 42.73°(400) 53.28°(422), 56.71°(511) and 62.36°(440) confirm the formation of high crystallinity cubic spinel structure of ZnF, which were very well synchronized with the JCPDS (card No.01-077-0011).For nanocomposites, there is no disordered graphene oxide peaks were seen, which is due to the considerable amount of adding graphene in the composites and also the diffraction of disordered graphene planes is weak as compare to fine crystalline ZnF planes [14]. This confirms the graphene oxide is successfully dispersed on the surface of ZnF nanoparticles and does not make any structural changes in the planes. The average particle size is calculated using Scherer's equations and the value is found to be 26.1, 17.8 and 15.3 nm for ZnF, rZnF-25 and rZnF-50 respectively. Also In this study, addition of graphene plays a key factor for adjusting the size of the particles. Lattice parameter of cubic crystal lattice (a=b=c) was calculated using the formula, the obtained lattice parameter is listed in Table 1.

$$a = d (h^2 + k^2 + l^2)^{1/2} \text{ \AA} \dots\dots\dots (1)$$

Table 1. Obtained parameters from X-Ray Diffraction

Parameter	ZnF	rZnF-25	rZnF-50
Average particle size (D) nm	26.1	17.8	15.3
Lattice parameter($a \pm 0.001$) Å	8.373	8.362	8.357

3.2 HR-TEM

Additionally, Fig 2 (a&b) shows the HR-TEM images of rGO and rZnF-50 samples respectively. The sheet-like rGO sheets are found to exhibit wrinkled morphology with high transparency representing single layer graphene. In Fig 2(b) it can be seen that the amorphous rGO sheets were smoothly distributed on the surface of ZnF nanostructure, which is expected to provide low charge transfer resistance and efficient channel path for conductivity of the material [13]. Fig. 2(c) shows the SAED pattern of rGO, which confirms the amorphous nature of the graphene sheets. In Fig 2(d) SAED pattern of rZnF-50, consist of several concentric diffraction rings and spots and thus indicating high crystallinity nature of the sample. The well-resolved lattice fringes are observed in the magnified HRTEM images Fig 2(e). The fringes with inter planar spacing of 0.25 nm and 0.24 nm correspond to the (002) plane of rGO and (311) plane of ZnF, respectively. From HR-TEM analysis, the particle size is found to be 29.7, 20.2 and 18.8 nm for ZnF, rZnF-25 and rZnF-50 respectively. The decreasing in particle size benefitted the quick spread of electrolyte and fast charge transport. The obtained particle size from TEM results are in good agreement with XRD results.

3.3 FT-Raman

FT-Raman spectra of graphene oxide, rZnF-25 and rZnF-50 nanocomposites are shown in Fig 3. Generally, Ferrite cubic spinel structure which gives rise to 39 normal Raman modes in which $2A_{1g}$, $1E_g$, $3F_{2g}$ are Raman active modes. The Raman spectra of rZnF-25 and rZnF-50 samples reveals four Raman active modes. The band at 648, 371, 297 and 198 cm^{-1} were belonging to the vibration modes of A_{1g} , F_{2g} , E_g and T_{2g} respectively. The vibration mode A_{1g} and F_{2g} represent Fe-O and M-O stretching at the tetrahedral sites, additionally E_g and T_{2g} modes present corresponds to the asymmetric stretching of oxygen atoms with respect to the metal ion at the octahedral site respectively [15]. The corresponding graphene oxide peaks such as 1340 cm^{-1} and 1590 cm^{-1} were represents **D-Band**, breathing point of Phonon A_{1g} symmetry and **G-band**, E_{2g} Phonon of Sp^2 C-atoms respectively. Generally, the value of the intensity ratio of the D band to the G band (I_D/I_G) is used to estimate the degree of disorder and the defects of carbon material. The obtained ratio is 0.98, 1.17 and 1.26 for rGO, rZnF-25 and rZnF-50 respectively. I_D/I_G values were higher than that rGO confirms a low graphitic degree, more defects or edges, and disordered structures were introduced in rZnF-25 and rZnF-50 samples which could be beneficial for triiodide reduction process [8].

3.4 Electrochemical Measurements

Cyclic Voltammetry (CV)

To evaluate the ion diffusivity and electro catalytic activity towards I_3^- reduction were examined by CV measurements and (oxi/red) peaks of CE shown in Fig 3a. The pair of negative and positive peaks was observed in all the samples were determined the following redox reactions.

The highest cathodic reduction peak current density (J_{red}) and the smallest peak to peak (E_{pp}) separation between pair of negative and positive peaks are the important parameter to determine the electricatalytic activity towards I^- regenerations [16] It is observed that rZnF-50 obtained highest J_{red} density and smallest E_{pp} among the other Counter electrodes. Indicates that rZnF-50 CE provide large edge active sites for electro catalytic activity, provide fast electron conducting channel and shorten diffusion sites to the I_3^- reduction reaction which results faster redox reactions. Moreover, graphene could provide large pore channels which enables efficient electrolyte diffusion path and spread quickly into the pores leading to fast reaction kinetics. The J_{red} values are in the following sequences rZnF-50>Pt >rZnF-25>ZnF>rGO. Stability is another significant parameter to determine function and reversibility of the CEs shown in Fig 3b. No significant loss in after 100 CV cycles which indicates rZnF-50 has better reversibility and stability for triiodide reductions

Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were performed to evaluate charge transfer abilities at different CEs interfaces in the presence of I_3^-/I^- redox electrolyte. Fig. 4c shows the nyquist plot of symmetric cells with two identical electrodes (CE/electrolyte/CE). The obtained values were fitted to the equivalent circuit shown in inset Fig.4c. Where (R_s) is series resistance (R_{ct}) is charge transfer resistance (Z_w) is resistance of nernst diffusion [17]. Obtained values in the following sequence rZnF-50> Pt >rZnF-25>ZnF>rGO. rZnF-50 exhibits lower R_s and R_{ct} values than other electrodes due to addition of graphene sheets evenly covers ZnF nanoparticles which offer more channels for electron transfer and also improve electrode electrolyte interface area, as well as their bonding in the subtract benefits fast charge transfer improves electrochemical activity.

Tafel Polarization

To further confirm the electrocatalytic activity abilities of different CEs, Tafel polarization measurements were performed on same potential window as performed in CV measurements (Fig 4d.). In the tafel studies exchange current density J_0 and limiting current density J_{lim} were obtained from anodic and cathodic slopes which are directly related electro catalytic activity of CEs. J_0 and J_{lim} are obtained from the following Equations:

$$J_0 = \frac{RT}{nFR_{ct}} \dots\dots\dots (1)$$

$$D_{eff} = \frac{\delta}{2nFC} J_{lim} \dots\dots\dots (2)$$

A Tafel polarization result confirms that rZnF-50 exhibit higher J_0 values than other electrodes and displays superior electrocatalytic performance of the CE material [10]. This is mainly credited to adding graphene structure into ZnF which gives large number of tiny holes and pores for I_3^- / I^- electrolyte to linkup inside the CE area and accelerates the reduction reaction. As a result, large J_0 and j_{lim} values demonstrate significant electro catalytic performance of rZnF-50 CE material. All the obtained parameters from CV, EIS are in good agreement with Tafel measurements. Additionally ECSA was examined by double layer capacitance (C_{dl}) of each CE material in different scan rates, 1 to 5 mVs⁻¹ [18]. The graph plotted between $\Delta j = (J_{anodic\ current} - J_{cathodic\ current})$ Vs scan rates depicted in Fig. 4e. The linear fit is corresponding to double layer capacitance (C_{dl}) of the CEs. Obtained electrochemical parameters are listed in Table 2.

Table 2. Obtained parameters from electrochemical measurements

CEs	J_{red}	E_{pp} (mA cm ⁻²)	$R_s (\Omega)$	$R_{ct} (\Omega)$	$Z_N (\Omega)$	D_{iff} (cm ² s ⁻¹)	log J_0 (mA cm ⁻²)	log J_{lim} (mA cm ⁻²)	ECSA (cm ²)
rGO	0.70	1.45	8.9	2.1	0.89	2.32*10 ⁻⁶	0.433	0.72	0.44
Pt	4.95	1.24	7.4	1.1	0.32	4.23 *10 ⁻⁶	0.441	0.94	1.62
ZnF	2.76	1.34	9.2	2.3	0.71	2.71 *10 ⁻⁶	0.434	0.84	0.92
rZnF-25	4.8	1.27	7.8	1.4	0.35	3.92 *10 ⁻⁶	0.438	0.90	1.71
rZnF-50	7.36	1.21	7.2	0.7	0.27	4.54 *10 ⁻⁶	0.447	0.98	2.35

3.5 Photovoltaic Measurements

The photocurrent density (J) vs voltage (V) curves of DSSCs based on as prepared different CEs shown in Fig 5. The obtained photovoltaic parameters are summarized in table 3. Generally, High electrocatalytic ability of the CE material leads to fast reduction of I_3^- and generation of I^- ions, which enables to achieve highest short current (J_{sc}) and photo conversion efficiency (PCE). The DSSC fabricated with rZnF-50 CE exhibits higher J_{sc} of ($17.98\text{mA}/\text{cm}^2$), FF of 0.62 value and power conversion efficiency PCE of (8.71%) than the PCE of platinum (Pt) (8.53%) CE. The increase in J_{sc} and FF is achieved by the intrinsic conductivity created by grafting graphene sheets on rZnF-50 CE which results enhanced electrochemical active sites for triiodide reduction I_3^- and generation I^- reactions. It also reduces the diffusion resistance between CE and electrolyte and smooth surface accelerates fast electron transmission pathways. At the same time ZnF and rGO exhibit lower value of J_{sc} and conversion efficiency mainly due to rough surface and low conductivity and electrochemical stability of the CEs.

Table 3. Shows the value obtained from Photovoltaic Measurements

CEs	J_{sc} (mA/cm ²)	V_{oc} (V)	(FF)	η (%)
rGO	13.24	0.645	0.61	5.2
Pt	17.95	0.69	0.69	8.53
ZnF	14.05	0.649	0.59	5.37
rZnF-25	16.92	0.68	0.64	7.46
rZnF-50	17.98	0.707	0.69	8.71

4. Conclusion

rGO has been successfully dispersed on the $ZnFe_2O_4$ nanoparticle by one pot hydrothermal method. The electrochemical performance of the electrode was examined by CV, EIS and Tafel measurements. Dispersion of graphene on ZnF nanoparticle results in faster electron dispersion, rapid reduction of I_3^- ions and act as a functional CE material for DSSC. The presence of graphene increases the adhesion of catalytic layer on FTO subtracts displays low charge Transfer (R_{ct}) resistance and swift transfer of electrons. As a result, rZnF-50 nanocomposite is capable of providing excellent electro catalytic activity and stability towards I_3^-/I^- redox couple. The PCE of 8.71% is obtained for rZNF-50 electrode which is better than existing Pt CE (8.53%). Its implies that to build a low cost, Pt-free fabrication of DSSCs and for its commercialization, rZnF-50 can be an alternate CE material.

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Figures

Figure 1

(a)XRD pattern of GO and rGO, (b) ZnF, rZnF-25 and rZnF-50 nanoparticles

Figure 2

(a,b)HR-TEM image rGO,and rZnF-50 nanoparticles and (c & d) shows the SAED Pattern of rGO and rZNF-50 nanoparticles. (e) Shows the lattice inter planer distance of rZnF-50

Figure 3

FT-Raman spectra of rGO, rZnF-25 and rZnF-50nanocomposities

Figure 4

(a)CV Graphs of I₃⁻ / I⁻ redox electrolyte for various CEs at 50mVs⁻¹, (b) CV graph of rZnF-50 CE at 100 cycles(c) Nyquist plot of GO, rGO, ZnF, rZnF-25 and rZnF-50 CEs, (d) Tafel polarization curve of GO, rGO, ZnF, rZnF-25 and rZnF-50 CEs, (e) ECSA fit of GO, rGO, ZnF, rZnF-25 and rZnF-50 CEs

Figure 5

The photocurrent density (J) vs voltage (V) curves of GO, rGO, ZnF, rZnF-25 and rZnF-50 CEs