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SYNTHESIS AND CHARACTERISATION OF GRAPHENE OXIDE AS PHOTOANODE FOR DYE SENSITISED SOLAR CELL

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Abstract:

Graphene oxide was prepared from graphite powder using modified Hummer's method. Graphite and graphene oxide were characterised by X- ray diffraction studies, FTIR and UV spectral analysis. When graphite is oxidised to graphene oxide, peak at $2\theta = 25\text{-}30^{o}$ *disappear and a new peak at* 10.78^{o} *appears. The interlayer spacing, d of graphite and graphene oxide were calculated using Bragg's law as as 8.29Å. FTIR spectra confirmed the presence of oxygen containing functional groups on graphene oxide. The UV spectra reveal that graphene oxide has a good absorption in the visible region at 350- 600 nm. Solar cells were fabricated using CdS nanoparticles as counter electrode,* KI/I_3^- *as electrolyte solution, Ruthenium complex as sensitizer and the active electrode was varied as* TiO_2 *-graphene oxide, graphene oxide and* TiO_2*. The DSSC was fabricated to measure the photovoltaic performance.*

Key Words: Graphene Oxide, X- Ray Diffraction, Dye Sensitised Solar Cell & Photovoltaic Performance

1. Introduction:

Graphene oxide, a graphene based material was first prepared in 1840, but got prominence only in 2004. Graphene oxide has layered structure similar to that of graphite with various functional groups, epoxy,carbonyl, carboxylic acid and lactol group covalently bonded to its basal plane and edges [1-3] that allows it to expand the interlayer distance and makes it, a complex, inhomogenous system consisting of a hybrid sp^2/sp^3 system [4]. The interlayer spacing in graphene oxide is twice compared to graphene due to the presence of these functional groups. This also accounts for the tunable optical, chemical and electronic properties of graphene oxide [5,6,7].

Graphene oxide is not a naturally occurring compound. The history of graphene oxide research can be dated back to over one hundred and fifty years ago, when it was first made by chemical treatments of graphite with potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3), by British chemists Brodie and Staudenmaier and named it graphitic acid or graphite oxide, which was later termed as graphene oxide [6]. Almost 60 years after Staudenmaier's methodology, chemists Hummers and Offeman in Mellon Institution of Industrial Research developed a different synthetic route for making graphene oxide. A water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate was prepared and maintained below 45 °C for graphite oxidation for two hours that formed the final product with higher degree of oxidation than Staudenmaier's product [7]. In this paper, graphene oxide was prepared using modified Hummer's method [8], which replaced sodium nitrate used in conventional Hummer's method, with increased quantity of potassium permanganate and 9:1 mixture of H_2SO_4: H_3PO_4.

The concept of Dye Sensitised Solar Cell (DSSC) is believed to reduce the production costs and energy payback time significantly compared to standard silicon cells or other thin film cells [9]. DSSC works on the principle that photons are converted into an electric current by charge injection of excited dye molecules into a wide energy gap semiconductor. In DSSC an electron is traced passing through a complete cycle of excitation, injection into active electrode, diffusion into the same, iodine reduction at the counter electrode, diffusion in the I^-/I_3^- electrolyte and regeneration of the oxidised dye [10]. The dye is metalloorganic Ruthenium complex and gets excited upon absorption of photon. The life time of excited state is in the nanosecond range. At high iodine concentration, reductive quenching might deactivate the excited state [11]. In the fabricated dye sensitised solar cell, upon exposure to light, the dye present at the photoanode gets excited and such photo induced electrons from the dye is transferred to the conduction band of the photoanode, which is accompanied with the oxidation of redox species present in the electrolyte (iodide/iodine), and reduction reaction takes place at the counter electrode by accepting electrons [12.,13,14,15].

In this paper, the synthesis, characterisation and the application of graphene oxide in the fabrication of Dye sensitized solar cell were discussed. Two different solar cells were fabricated. Graphene oxide and graphene oxide mixed with TiO_2 were used as separate active electrode. CdS nanoparticles were used to form the counter electrode in both cases.

2. Materials and Methods:

2.1 Synthesis of Graphene Oxide:

Graphite powder was purchased from Loba chemie Pvt ltd. All chemicals used were of analytical grade and were used without further purification. Graphene oxide was prepared according to the modified Hummer's method [8]. 1g of graphite powder was taken to which excess of potassium permanganate and a mixture of 9:1 ratio of H_2SO_4 and H_3PO_4 were added and stirred for 20 hours. 2ml of H_2O_2 was added by keeping in an ice bath and stirred in ice bath for an hour. The reaction product was washed with water , filtered and dried.

2.2 Fabrication of Dye Sensitised Solar Cell:

2.2.1 Preparation of Active Electrode:

Two different active electrodes were prepared using synthesized graphene oxide and TiO_2. The synthesised graphene oxide was taken and mixed with deionised water- acetone solution (water:acetone 2:1 v/v). The paste so formed was coated on Fluorine doped Tin Oxide (FTO) plates and dried in air for 30 minutes. The coated plates were then heated at 120^oC for 2 hours. The dried graphene oxide film was then coated with Ruthenium dye (0.1M) and then heated at 120^oC for four hours. Two photoanode were prepared by taking graphene oxide and TiO_2 and TiO_2 in the ratio 2:1, and the same procedure was repeated.

2.2.2 Preparation of Counter Electrode:

The counter electrode was prepared by using CdS nanoparticles. CdS nanoparticles were synthesised by coprecipitation method [16] from cadmium acetate and sodium sulphide. CdS nanoparticles were made into a paste with a mixture of deionised water and acetone in the ratio 2:1. The smooth paste was coated on FTO glass plates and dried in air for 30 minutes. It was then heated at 120^oC for 2 hours initially. After this, the heating was continued for another 4 hours.

2.2.3 Cell Assembly:

Active and counter electrode were bound together with coated sides facing each other. Few drops of the electrolyte solution (containing 0.05 M iodine and 0.5 M potassium iodide in water free ethylene glycol) were introduced between the electrodes and it was drawn inside due to capillary action. The three cells were made with the same electrolytic solution with different combination of electrodes. They were

- ✓ Active electrode :graphene oxide, counter electrode: CdS
- ✓ Active electrode: graphene oxide and TiO_2 in the ratio 2:1, counter electrode: CdS.
- ✓ Active electrode: TiO_2 , counter electrode: CdS

The solar cells so prepared were then subjected to J-V studies using sourcemeter. From the plot, different photovoltaic parameters were calculated.

2.3 Instrumentation:

The synthesised graphene oxide was characterised by using X ray diffractometer (MAC Science MO3XHF22) with Cu(K_α) radiation (λ= 1.5405 Å) in the 2θ range of 10- 80°. Optical absorption spectra of graphene oxide was recorded using Jasco UV-vis 2700 spectrometer. Fourier Transform Infrared spectral analysis was carried out between 4000 and 400 cm^{-1} with Shimadzu FTIR Spectrometer using KBr pellets. The current- voltage measurement of solar cell was characterised by GS610 YOGOKAWA source measurement unit.

3. Results and Discussion:

3.1 X- Ray Diffraction Analysis:

X- ray dfiffraction analysis was used to determine the average crystallite size of graphene oxide. The prepared graphene oxide showed a strong peak at 2θ value 10.78° which is in good agreement to exhibit a honeycomb like lattice structure [17,18]. The average crystallite size was calculated using Scherer's formula [18].

$$D = K\lambda / \beta \cos \theta$$

Where D is the crystallite size, λ is the wavelength of X rays(1.5404A°), β is full width half maximum in radian and θ is the Bragg's diffraction angle obtained from 2θ value corresponding to the maximum intensity peak in XRD pattern. Using the Scherer's formuls the crystallite grain size was calculated to be 5.6 nm.

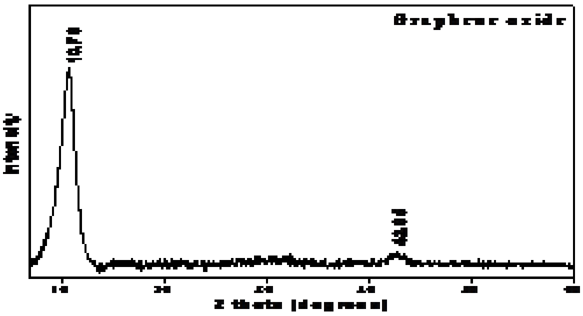

Figure 1: XRD pattern of graphene oxide

3.2 FTIR Analysis:

Fourier Transform Infrared spectrum was recorded between 4000 and 400 cm^{-1} with Shimadzu FTIR Spectrometer using KBr pellets. FTIR spectra was used to confirm the presence of oxygen containing functional groups on graphene oxide .The broad peak around 3500 cm^{-1} for graphene oxide corresponds to O-H bond stretching vibration, suggesting the presence of hydroxyl group. The shoulder peak around 1736 cm^{-1} may be due to C=O stretching. The peak at 1626 cm^{-1} may be due to C=C stretching and the peaks at 1221 cm^{-1},1046 cm^{-1} for graphene oxide could be due to the oxygen containing groups, C-O-C and C-OH respectively.

Table 1: IR peaks depicting the stretching frequencies of different functional groups

Wave no in cm^{-1}	Assignment
3500	-OH stretching

1736	C=O
1626	C=C
1221	C- O- C
1046	C-OH

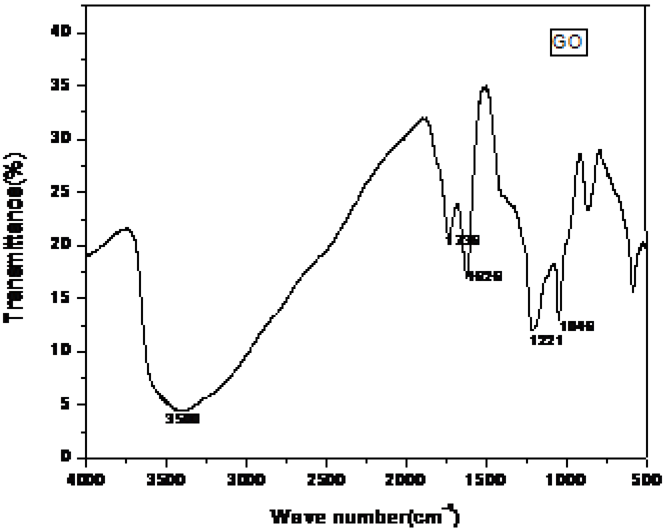

Figure 2: FTIR spectra of graphene oxide

3.3 Optical absorption:

The UV- vis spectra (Fig 3) reveals a strong peak around 350- 600 nm suggesting that it has a good photoresponse in the visible region which is suitable for fabricating solar cell. UV-vis spectrum of graphene oxide has featured peak around 233 nm due to $\pi \rightarrow \pi^*$ transition of C=C bonds, and broad shoulder between 290- 300 nm assigned as $n \rightarrow \pi^*$ transition of C=O bonds.

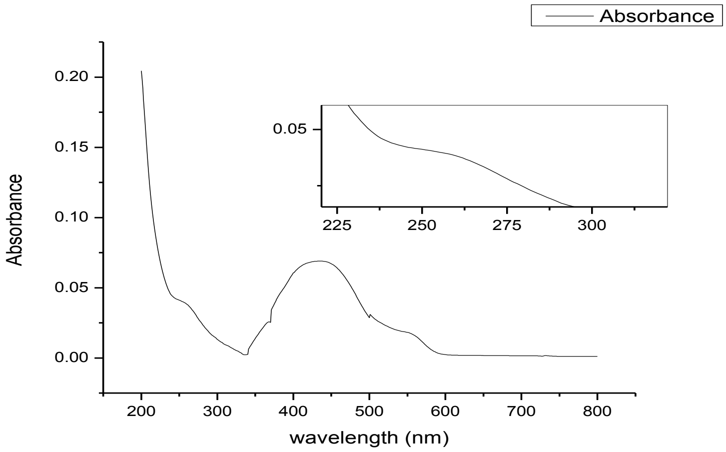

Figure 3: UV Vis spectra of graphene oxide

3.4 Photovoltaic Performance:

In dye sensitized solar cells, the organic dye captures photons from the light source which is injected into the conduction band of the oxide, which serves as the photoanode or the active electrode. At the counter electrode, reduction takes place. Iodide / iodine couple serves as the electrolyte. Fig 4 shows the J-V plot of the DSSC with graphene oxide and TiO_2 forming the active electrode and CdS served as the counter electrode. The photovoltaic parameters, short circuit current (Jsc), open circuit voltage (Voc), fill factor (FF) and power conversion efficiency (Ƞ) were calculated from these curves and are given in Table 2. The average short- circuit current (Jsc) for the cells is higher in the DSSC where graphene oxide is the active electrode. The higher Jsc in graphene oxide solar cell is due to it's greater light harvesting capacity as indicated by the absorption spectra. Meanwhile the absorbance ratios among different sensitised photocathode are consistent with the corresponding Jsc values. Beside the enhancement of Jsc, a distinct improvement in the open circuit voltage (Voc) has been observed.

The efficiency of a solar cell is defined as the output power density divided by the input power density. If the incoming light has a power density (Pin), the efficiency will be

$$\eta = \frac{Voc\ Isc\ FF}{Pin} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The fill factor ,FF is defined as the ratio of the product of the maximum power output (Pm) to the product of short circuit photo current and open circuit voltage

$$FF = \frac{Imp \times Vmp}{Isc \times Voc} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where Imp and Vmp represent the photocurrent and photovoltage corresponding to the maximum power . The four parameters Jsc, Voc, FF and ƞ are used to characterize the performance of a solar cell which is given in Table 2

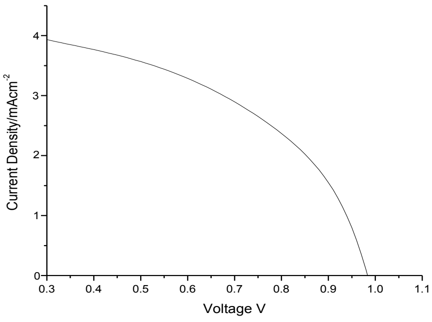

Figure 4

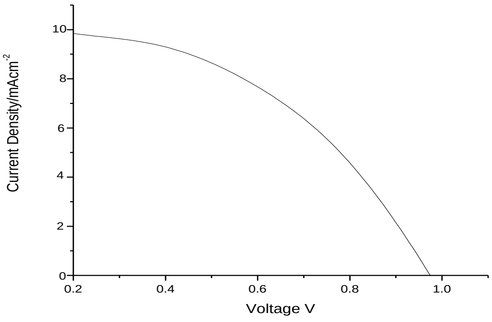

Figure 5

Figure 4 Current – voltage (J-V) curve of the DSSC with graphene oxide and TiO2 as active electrode & Figure 5 Current voltages (J-V) curve of the DSSC with graphene oxide as active electrode

Table 2: Photovoltaic parameters of the graphene oxide based DSSCs

Parameters	GO	GO + TiO_2	TiO_2 [19]
Voc [V]	0.97	0.96	0.35
Jsc [mA]	9.8	3.8	4.3
FF [%]	0.4566	0.5128	0.48
ƞ [%]	7.7	3.4	2.2

4. Conclusion:

Graphene oxide was synthesised using modified Hummer's method and characterised by XRD, IR and UV spectral analysis. The crystallite size was calculated to be 5.6 nm from XRD pattern. The IR spectra showed peaks corresponding to the various functional groups present in graphene oxide. Graphene oxide and graphene oxide with TiO_2 were used to fabricate dye sensitised solar cell. The hybrid DSSCs using synthesised nano CdS as photocathode, graphene oxide and graphene oxide mixed with TiO_2 were used as separate active electrodes, ruthenium dye as sensitizer, I^-/I_3^- as electrolyte were fabricated and the maximum quantum conversion efficiency was calculated. The J- V plot and the photovoltaic parameters suggest that graphene oxide has higher light harvesting capacity and shows an efficiency of 7.7 %

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