

Fabrication of Graphene based counter-electrode for Dye Sensitized Solar Cell (DSSC) by using Bitumen precursor

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Abstract. Conventional Dye Sensitized Solar Cell (DSSC) comprises the dye sensitized semiconductor photo-working electrode, the redox (reduction and oxidation) electrolyte and the electron transfer catalytic counter-electrode. Graphene is the suitable electron transfer catalyst for the DSSC because it's higher active surface area, higher electron mobility, physically and chemically stabilization in the redox electrolyte of DSSC. Although it can be synthesized in different ways, the laborious steps and state of the art technology are needed and can result the higher cost of production. Hence, it is desirable to develop an eco-friendly simple technique to synthesize graphene. Graphene can be sensitized simply by the chemical vapor deposition (CVD) technique through the use of Bitumen product, Asphalt as the carbon precursor. A graphene layer was formed on the heated conductive glass substrate (ca.650°C) by the chemical vapor deposition (CVD) of the carbon fumes from the thermal decomposition of Bitumen carbon precursor to get the graphene based counter-electrode. The formation of graphene layer was confirmed by X-ray Diffraction (XRD) and its surface morphology was examined by Scanning Electron Microscopy (SEM). Thermo-gravimetric Analysis (TGA) was carried out to inform the stages of graphene synthesized reaction and the transition temperature of graphene formation. The effect of graphene electrode on the photovoltaic efficiency of DSSC was investigated by evaluating the current-voltage (I-V) measurement of DSSCs with and without graphene layer under the standard regional annual mean insolation (incoming solar radiation), 240Wm⁻².

Keywords: Graphene, Bitumen product, Asphalt, Chemical Vapor Deposition(CVD), conductive glass substrate (FTO),Dye Sensitized Solar Cell (DSSC), counter-electrode, X-ray Diffraction (XRD), Scanning Electron Microscopy(SEM),Thermo-Gravimetric Analysis (TGA), current-voltage (I-V) measurement of DSSCs and the photovoltaic efficiency of DSSC.

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INTRODUCTION

Dye Sensitized Solar Cell (DSSC) is one of the promising candidates for Photovoltaic Technology to overcome the energy crisis of our century due to its cheap production cost. Conventional DSSC comprises the dye sensitized semiconductor photo-working electrode, the redox electrolyte and the electron transfer catalytic counter-electrode. The function of the catalytic counter electrode is to transfer electrons from the external circuit to the oxidized electrolyte to regenerate the electrolyte. The role of the catalyst is to enhance the electron transfer kinetics of DSSC. The conventional catalyst of DSSC is platinum, Pt but it is very expensive and so the carbon powder, C is used as the alternative catalyst to reduce the cost of manufacturing. Although the price of C is lower than that of Pt, the electron transfer kinetic efficiency of C based counter electrode is lower than that of Pt counter electrode. It is therefore needed to fabricate the new kind of counter electrode which must be low-cost and has relatively higher electron transfer efficiency. The ideal counter electrode must have less electrical resistance, higher electron transfer efficiency and be

stable chemically and physically in the redox electrolyte of DSSC.

In order to agree those requirements, Graphene based counter electrode was fabricated in this research. Graphene is the new generation of carbon material which is two-dimensional single-atom carbon sheet with conjugated honeycomb lattice structure. [1] Since the graphene has large active surface area, good chemical stabilization, high thermal stability and higher electron mobility, it is a suitable catalyst for DSSC. [2] Although the graphene can be synthesized in different ways, the laborious steps and post synthesis cleaning are needed. They can cause the barrier to reduce the cost of production. Thus, it is desirable to develop eco-friendly simple technique to synthesize the graphene. Recent researches show that the graphene can be synthesized from the cheap diverse carbon sources such as sugar, food, organic waste, insect and bio-gas by using the chemical vapor deposition (CVD) method. [3]

This research introduces a simple technique in which the Bitumen product, Asphalt, is used as the carbon precursor for the synthesis of graphene. A graphene layer is formed on the heated conductive glass substrate, (ca.650°C) by the CVD of carbon fumes

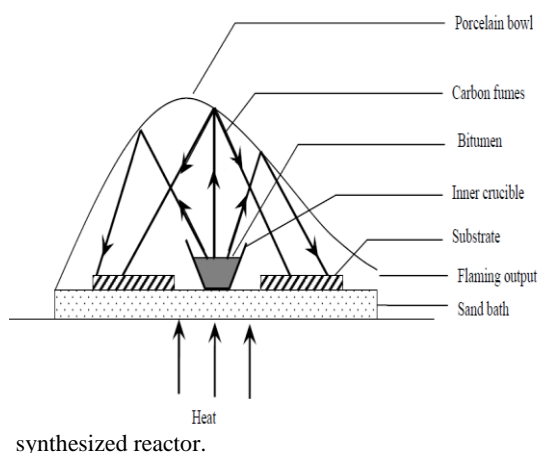
from the thermal decomposition of the bitumen carbon precursor.

EXPERIMENT

Fabrication of Graphene Based Counter-electrode:

Graphene based counter electrode of DSSC was fabricated by using CVD technique. The experimental setup of graphene synthesized reactor is shown in **Fig.1**. Firstly, sand bath with thickness 1cm was placed on the cooking surface of halogen lamp stove to sustain temperature and avoid carbon-staining on the surface of oven and then Fluorine-doped Tin Oxide (FTO) transparent conducting glass substrates were heated on the sand bath at 100°C for 15min to dehydrate the surface of the substrates. The crucible with the carbon precursor Bitumen product, Asphalt (6.4g) and organic dehydrogenating agent sulfur (3.6g) was put on the sand bath accompanying with the substrates and covered them with the porcelain mortar bowl. The graphene synthesized reaction was initiated by applying heat externally to the reactor through it's under the surface of oven. The annealing stages were performed as follows: annealing at 100 °C for 10min, 500 °C for 10min, 800 °C for 30min and 1200 °C for 10min and then cool-down stage slowly for 30min. Finally, the graphene layer was formed on the glass substrates by the chemical vapor deposition (CVD) of carbon fumes from the thermo-decomposition of carbon precursor; Bitumen product, Asphalt. The resultant graphene electrode was soaked in Toluene for 10min to remove the remaining sulfur particle without combustion and the remaining ordinary carbon from the surface of graphene electrode before the surface analysis.

FIGURE 1. Experimental set-up of the Graphene



Construction of Dye Sensitized Solar Cell (DSSC):

A dye sensitized solar cell (DSSC) was constructed by using the dye sensitized semiconductor photo-electrode, the graphene-based counter electrode and the iodine redox electrolyte. The electrolyte was sandwiched between two electrodes of solar cell. The schematic representation of the DSSC is shown in **Fig. 2**. The photo-electrode was made up of a wide band gap semiconductor, TiO_2 , which is modified with the mercurochrome dye (organomercuric disodium salt compound) on the transparent conducting glass (FTO). The redox electrolyte was prepared by mixing 0.5M potassium iodide and 0.05M iodine in water free ethylene glycol. [4]

Material-Characterization:

The formation of graphene layer was confirmed by X-ray diffraction (XRD). The morphology of the graphene layer was investigated by the scanning electron microscopy (SEM). Thermal analysis of graphene synthesized reaction by (SHIMADZU) DTG 60H Simultaneous TGA-DTA was made on 3.6mg of carbon precursor, Bitumen product (Asphalt), and 6.4mg of dehydrogenating agent Sulfur. Thermo gravimetric analysis (TGA) was carried out under Nitrogen (N_2) atmosphere with the flow rate of 50ml/min and the annealed temperature ranging from the ambient temperature to the final temperature 1000 °C with the temperature scanning rate of 20°C/min. TGA analysis provided the information concerning the reaction stages of grapheme synthesizing reaction and the transition temperature of graphene phase.

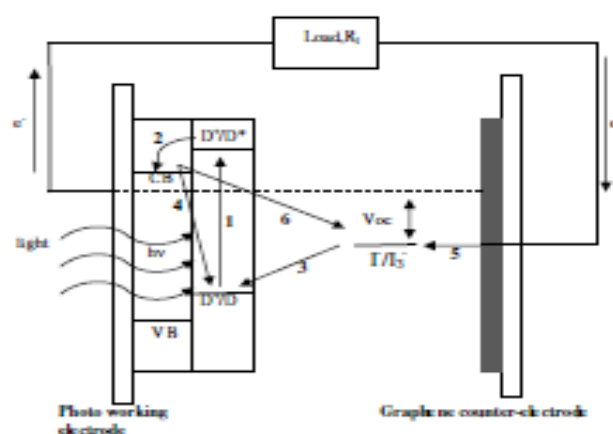


FIGURE 2. The schematic representation of the Dye Sensitized Solar Cell (DSSC).

Device-Characterization:

The photovoltaic performance of DSSC was evaluated from the current-voltage (I-V) measurement under the regional standard annual mean incoming solar radiation, 240Wm^{-2} . [5] The photovoltaic performance of DSSC was investigated by the following equations. [6]

Maximum power, P_{max} :

$$P_{\text{max}} = I_{\text{max}} V_{\text{max}} \quad (1)$$

Current density, J :

$$J = \frac{I}{A} \quad (2)$$

Fill-factor, FF:

$$FF = \frac{J_{\text{max}} V_{\text{max}}}{I_{\text{sc}} V_{\text{oc}}} \quad (3)$$

Efficiency, η :

$$\eta = \frac{J_{\text{max}} V_{\text{max}}}{P_{\text{in}}} \times 100\% \quad (4)$$

Results and Discussion

The XRD-pattern shown in **Fig-3** was observed by using CuK_α as a source ($\lambda = 1.5406 \text{ \AA}$) radiation and secondary mono-chromator in the 2θ range from 0° to 90° . A sharp intensive peak seen at the diffraction angle (2θ) of 24.1° corresponds to an inter-planer distance of 0.42nm , which is the specific crystalline structure of graphene. [7]

Thermo-gravimetric (TGA) analyses were performed on the elemental sulfur, Asphalt and the mixture of Asphalt and sulfur to know the stages of graphene formation and the effective minimum temperature range to form the graphene. The three different TGA

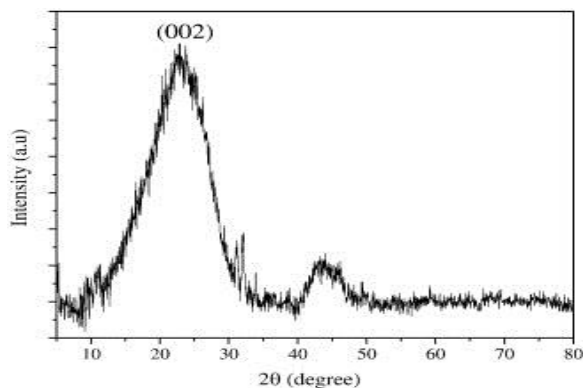


FIGURE 3. XRD-pattern of the resultant Graphene.

curves in Fig-4 show the reaction existence between sulfur and Asphalt. The initial loss of the mass of the mixture of Asphalt occurred between the room temperature and 140°C due to the evaporation of the some constituents of Asphalt. However, the mass of the Asphalt mixture was stabilized between 140°C and 240°C . At 240°C , dehydrogenating reaction of sulfur started and went on until 400°C . The TGA-curve of the mixture of Asphalt was dropped to complete mass loss at 450°C and the remaining non-volatile carbon constituent of Asphalt re-arranged to form the graphene at the temperature about 450°C .

As shown in **Fig-5**, the morphological microscopic study of SEM-analysis describes the layer characteristic of graphene which is coated on the substrate.

Table-1 enlists the values of V_{oc} , I_{sc} , FF and cell efficiency (η) for the cells with different counter electrodes of active area ($1\text{E-}4\text{m}^2$) illuminated by a halogen lamp with incident light of 240Wm^{-2} . Since FF values for both cells with different counter electrodes are almost the same, types of counter electrode used in this work have no effect on FF. The use of graphene counter electrode facilitates the electron transfer process to regenerate the electrolyte in the cell. Consequently it has higher I_{sc} , V_{oc} and η values than the carbon counter electrode. The efficiency of the DSSC could be increased by about 1% with using the graphene counter electrode instead of carbon counter electrode.

From the investigation of current-voltage (I-V) characteristic curves of DSSCs as in **Fig-6**, we can depict the maximum power points of DSSCs. The maximum power of DSSC with carbon counter electrode is, $P_{\text{max,C}} = 344.5\mu\text{Wcm}^{-2}$ and that of DSSC with graphene based counter electrode is, $P_{\text{max,G}} = 555\mu\text{Wcm}^{-2}$. The net increment of the maximum power of DSSC with the graphene based counter electrode is ca.60%.

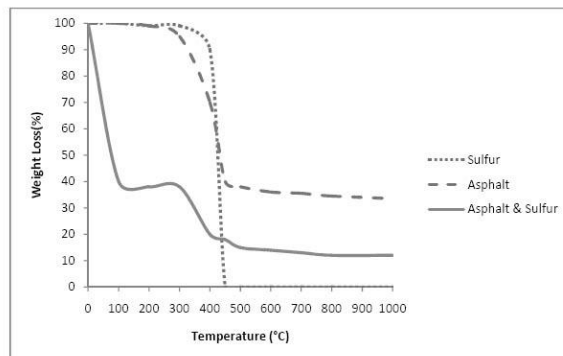


FIGURE-4. Thermo-grams of TGA –analysis

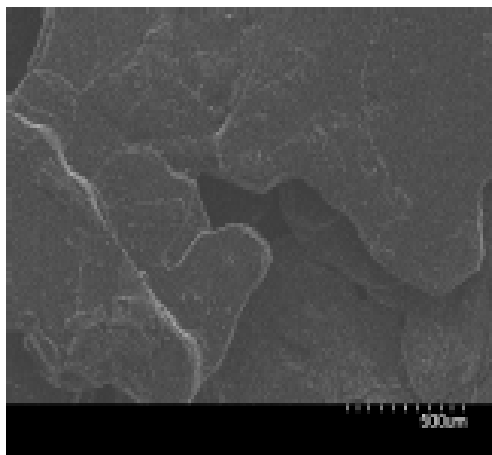


FIGURE -5. SEM micrograph of graphene

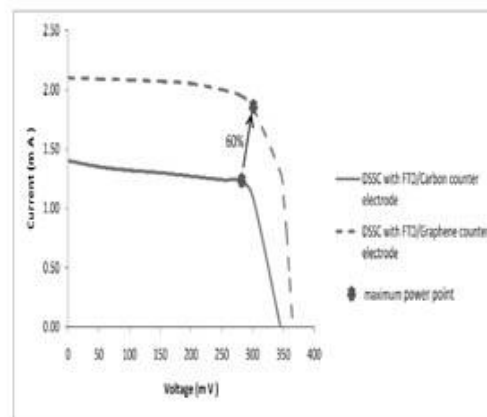


FIGURE-6. Current-Voltage (I-V) characteristic curves of DSSCs

Table1 . Photovoltaic Performance of DSSCs

Fabricated flexible DSSC	$V_{oc}(mV)$	$I_{sc}(mA)$	FF	η	$P_{max}(\mu Wcm^{-2})$
DSSC with FTO/carbon counter electrode	345	1.40	0.71	1.43%	344.5
DSSC with FTO/graphene counter electrode	365	2.10	0.72	2.31%	555

Conclusion

The graphene counter-electrode has been fabricated through the use of Bitumen carbon precursor, Asphalt, by using simple CVD technique. The minimum effective temperature for the formation of graphene is ca.450°C. The attributions of graphene to large active surface area, physical and chemical stabilization, high thermal stability and high electron mobility can enhance the short circuit current, I_{sc} by 0.7mA and improve the photovoltaic efficiency by ~1% of the DSSC. In addition, the maximum power of DSSC with the graphene based counter electrode is enhanced by ca.60%.

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