Photo-Current Enhancement at $Cu/p\text{-}Cu_2O/rGO$-Electrolyte Interface

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Abstract

A considerable photocurrent enhancement was found at the $Cu/p\text{-}Cu_2O/rGO$-electrolyte interface in a photo-electrochemical cell with compared to that of $Cu/p\text{-}Cu_2O$-electrolyte interface. The reason for the photocurrent enhancement may be due to the efficient charge separation process provided at $Cu/p\text{-}Cu_2O/rGO$-electrolyte interface. Here rGO (reduced graphene oxide) acts as an electron acceptor for the photo-generated charge carriersas it readily accept electrons from the conduction band of $p\text{-}Cu_2O$. rGO was synthesized using electro-phoretic deposition (EPD) technique. Fabricated samples were characterized using diffuse reflectance spectra, photocurrent action spectra and the time development of the photocurrent of photo-electrochemical cells.

Keywords: Photo-current, Electrolyte Interface, Photo Electrochemical Cell

1. Introduction

With the crisis of the non-renewable energy sources, many researches are focusing on renewable energy sources. Among these, solar energy has been considered as an ideal alternative, since it is the most powerful and richest renewable and sustainable source of energy. It can be directly converted into electric energy by photovoltaic effects [1].

Since recent years considerable research has been devoted on graphene based materials, because of their excellent electrical, mechanical and thermal properties and their possibilities for applications as transparent conductive film in composite materials and others. Reduced Graphene Oxide (rGO) has already been composited with semiconductor, acts as good electron acceptor that help to enhance charge separation within the semiconductor [2]. The electrophoretic deposition (EPD) technique is used to apply rGO layer among various deposition methods such as membrane filtration, dip coating, and spray coating. This method has many advantages such as high deposition rate, good thickness controllability, good uniformity, and simplicity of scale upcoating [3].

In this study rGO layer is fabricated on p-type cuprous oxide ($p\text{-}Cu_2O$) layer. $p\text{-}Cu_2O$ is a non-toxic and low cost semiconductor material which has a direct band gap around 2.0eV [4]. There are several methods to fabricate $p\text{-}Cu_2O$ such as thermal oxidation, electrochemical oxidation, chemical bath deposition and chemical vapor deposition [5,6]. For this study thermal oxidation has been used to fabricate $p\text{-}Cu_2O$ layer, at a constant temperature of 300^0C for 30 minutes obtained by maintaining a heating rate of 100^0C min^{-1} starting from room temperature in a furnace [7]. The diffuse reflectance spectra, photocurrent action spectra, FTIR spectra and time development of the photocurrent measurements are presented to explain the photocurrent enhancement and the remarkable stability at $Cu/p\text{-}Cu_2O/rGO$- electrolyte interface.

2. Experimental

2.1. Preparation of $p\text{-}Cu_2O$ Layer

Well cleaned Cu plates (3 cm×1 cm) were inserted into the furnace maintaining a normal air atmosphere during the oxidation process. A rate of 100^0C min^{-1} was provided inside the furnace starting from room temperature. After reaching 300 ^{0}C it was furthermore kept constantly in 300 ^{0}C for 30 minutes and then cooled down again to the room temperature. Finally brownish red colored Cu_2O layer was appeared on the Cu surface.

2.2. Preparation of rGO Layer

The Graphene Oxide (GO) used in this study was synthesized from purified natural graphite by the

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modified Hummers method [8]. Then GO was dispersed in distilled water and a solution of pH of 4 was made. Figure 01 shows the diagram of the EPD cell experiment. When 10V DC voltage was applied between Pt plate and Cu plate, the GO platelets migrated towards the Cu plate (positive electrode). After deposition, samples were dried [3].

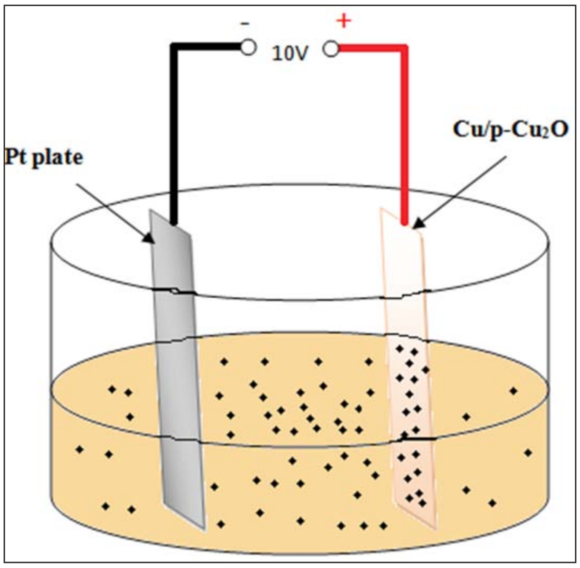

Fig. 1: **Experimental Setup of the EPD Technique (rGO Solution at pH=4).**

2.3. Characterization Techniques

Diffuse reflectance spectra were obtained by using SHIMADZU 1800 UV spectrophotometer. The photocurrent measurements were done using Hokuto Denko HA-131 potentiostat. Shimadzu IRA Affinity -1S FTIR spectro-photometer was used to measure the IRspectra.

Here a Pt plate (2cmx2cm) was used as the counter electrode, an Ag/AgCl electrode was used as the reference electrode with three electrode configuration. (10^{-2}M) Fe^{2+}/Fe^{3+}(10^{-2}M) solution was used as the electrolyte.

3. Results and Discussion

3.1. The Variation of Steady State Photocurrent with rGO Deposition Period on

Cu/p-Cu_2O

Fig.2 shows the variation ofsteady state photo-current for Cu/Cu_2O/rGOphotoelectrodes fabricate with different rGO deposition periods at electrolyte interface. It should be mentioned thatbare Cu/p-Cu_2O electrode produce 0.15 $mAcm^{-2}$steady state photo-current at the electrolyte

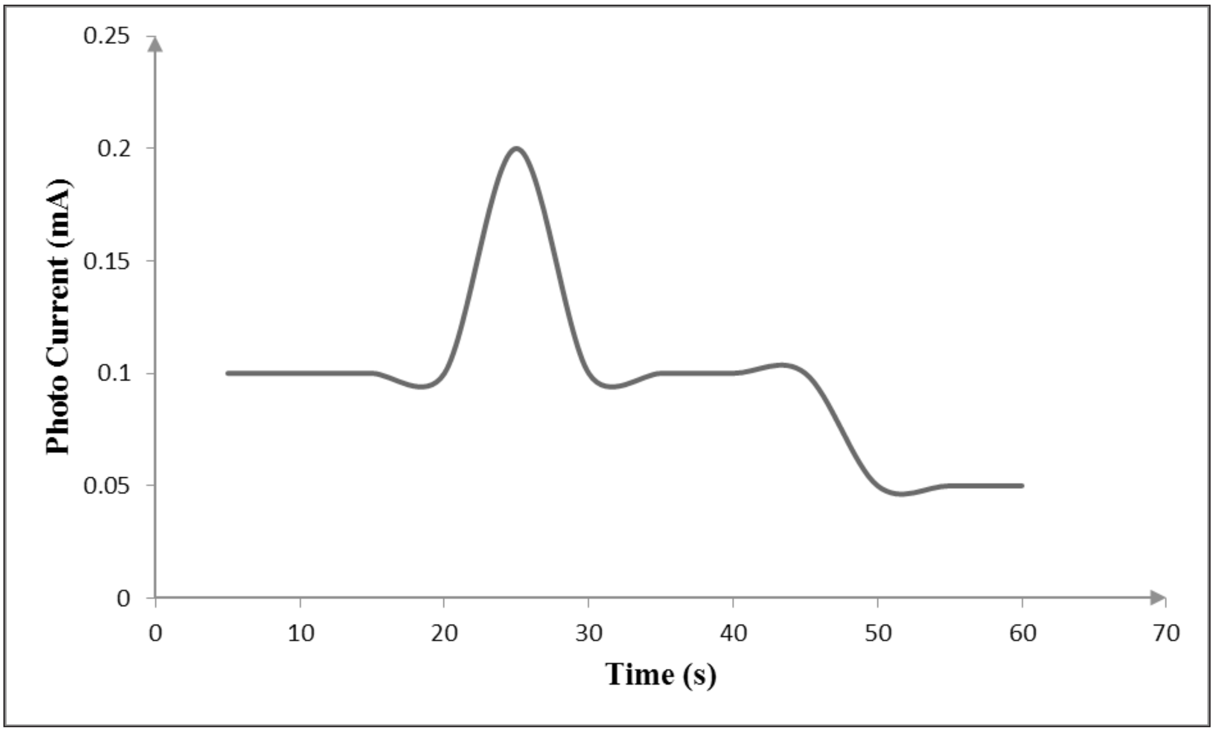

Fig. 2: **The Variation of Photo-Current with rGO Deposition time on Cu/p-Cu_2O Photo-Electrode**

interface. It is seen with the increment of the rGO deposition time steady state photocurrent increases up to 25 seconds deposition period. There after steady state photocurrent decreases continuously with the increase of the rGO deposition period. It is well known that rGO can act as an electron acceptor [2]. During the illumination, photo-generated electrons at p-Cu_2O-electrolyte interface are tunneled into the electrolyte. After depositing rGO layers, photo-generated electrons are readily collected by rGO layers deposited on the surface of the p-Cu_2O suppressing the recombination of the photo-generated electrons with holes inside the thin surface layer of Cu_2O increasing the steady state photocurrent enhancing the charge separation process. The photo-current reduction after 25 seconds deposition period may be due to the light cut off due to heavy deposition of rGO layers on p-Cu_2O.

3.2. Diffuse Reflectance Spectra and the Photocurrent Action Spectra

Fig. 3 shows the diffuse reflectance spectra of Cu/p-Cu_2O and Cu/p-Cu_2O/rGO photo-electrodes. Both spectra shows a unique absorption properties of p-Cu_2O confirming that the photocurrent generation process in the photo-electrochemical cells is due to only light absorption of p-Cu_2O layers, reporting absorption edges 625nm (band gap ≈ 2.0eV) and 635nm (band gap ≈ 1.9eV) for Cu/p-Cu_2O and Cu/p-Cu_2O/rGO respectively. In the photocurrent action spectra as shown in Fig. 4 shows a photocurrent maximum at the absorption edge observed in the diffuse reflectance spectra confirming that the photocurrent generation is due to the light absorption of p-Cu_2O semiconductor at electrolyte interface. For higher energy photons incident after absorption edge a photocurrent decrease can be observed. The highest photocurrent enhancement is clearly observed as observed in the Fig. 2 with rGO 25 seconds deposition period on p-Cu_2O at electrolyte interface.

4. Time Development of the Photocurrent

Fig. 5 shows the variation of the steady state photocurrent with time. It should be mentioned that remarkable stability of the photocurrent can be observed for the Cu/p-Cu_2O/rGO photo-electrochemical cell with compared to that

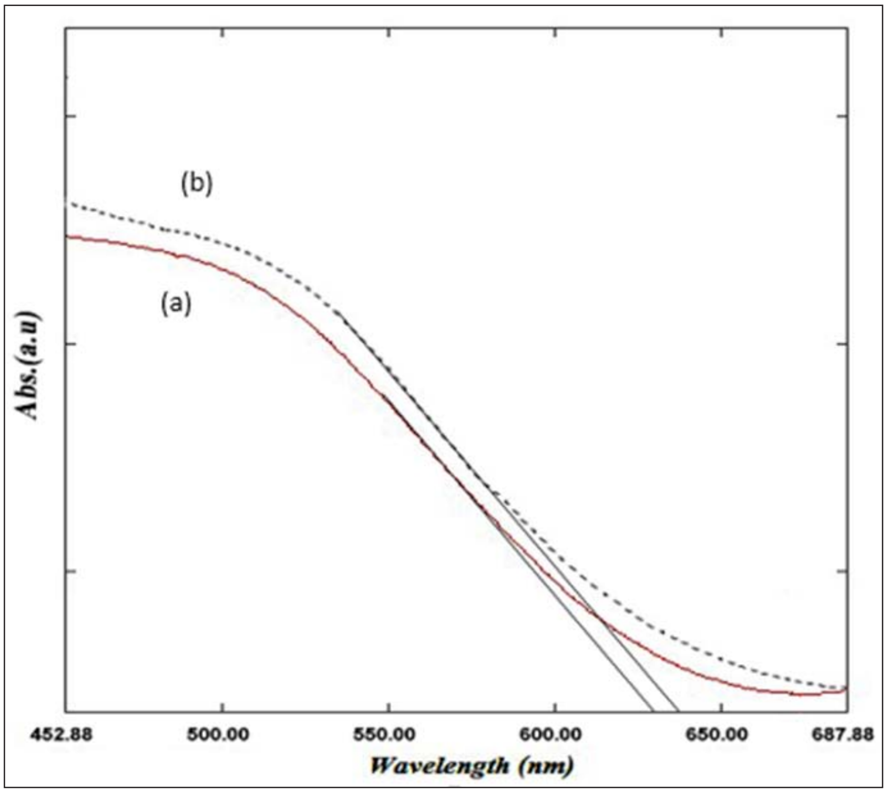

Fig. 3: **Diffuse Reflectance Spectra a-Cu/p-Cu_2O b-Cu/p-Cu_2O/rGO**

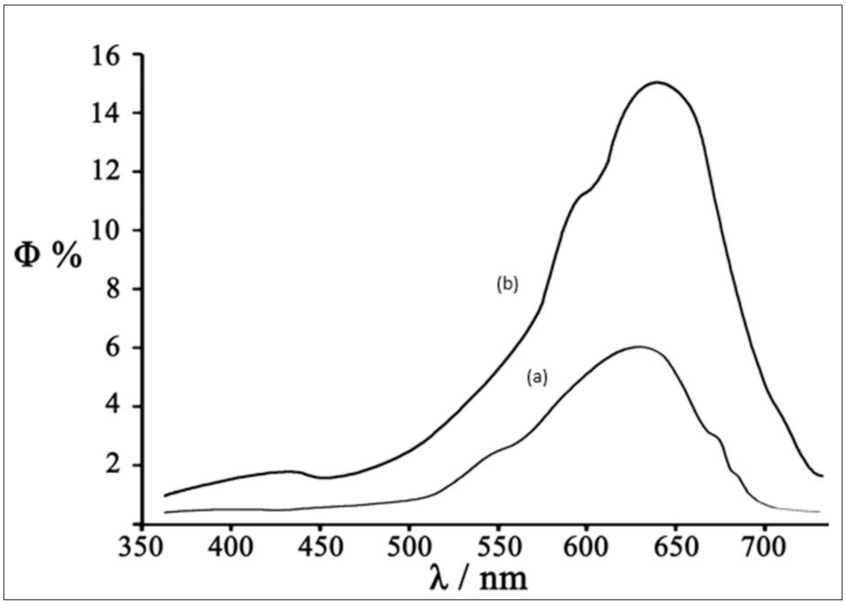

Fig. 4: **Photocurrent Action Spectra a-Cu/p-Cu_2O b- Cu/p-Cu_2O/rGO**

of Cu/p-Cu_2O photo-electrochemical cell. Improvement of the stability of the photocurrent can be explained as follows. It is well known that the photocurrent decay at the p-Cu_2O–electrolyte interface is due to the chemical dissolution of the following reaction.ie

$$Cu_2O + 2H^+ \rightarrow 2Cu + H_2O$$

After depositing rGO on p-Cu_2O, photo-generated electrons accumulate on rGO layers before transferring to the electrolyte species. So that the possibility to contact Cu_2O layers with electrolyte species is minimized suppressing the above photo-degradation reaction avoiding the forming of anodic region on the surface of the p-Cu_2O. Fig. 6 shows the FTIR spectrum for the Cu/p-Cu_2O/rGO photo-electrode before irradiation. It shows the formation of rGO by the EPD processes on p-Cu_2O. It should be mention even after long time irradiation, FTIR spectrum of Cu/p-Cu_2O/rGO photo-electrode does not

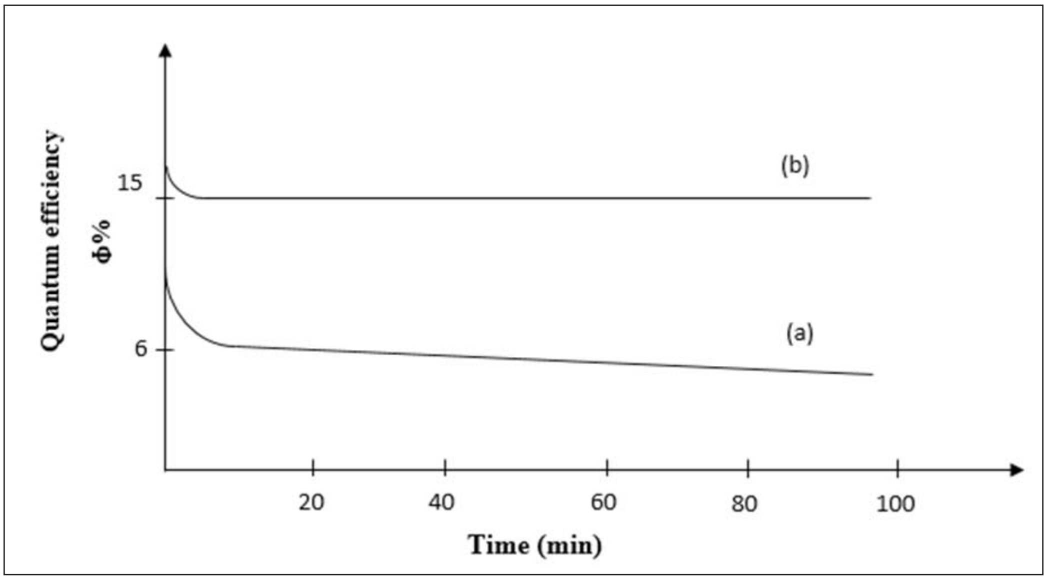

Fig. 5: **Time Development of the Photocurrent Cu/p-Cu_2O b-Cu/p-Cu_2O/rGO**

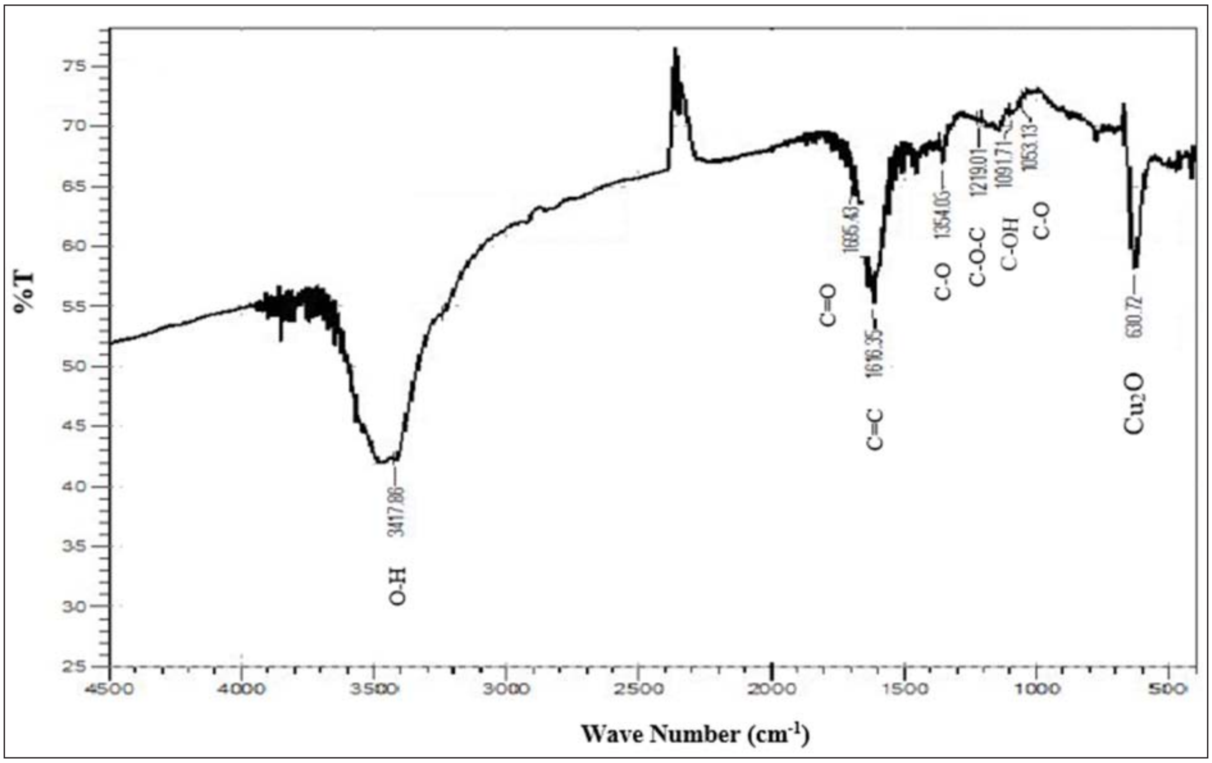

Fig. 6: **FTIR Spectrum of Cu/p-Cu_2O/rGO before Irradiation.**

show any vibrations corresponding to p-CuO confirming the remarkable stability after depositing rGO on p-Cu_2O. Further rGO can act as an electron pool of photo-generated electrons to reach redox species to collect the photo-generated electrons effectively in order to enhance the steady state photocurrent at Cu/p-Cu_2O/rGO-electrolyte interface. So that the possibility to contact H^+ ions presence in the electrolyte with Cu_2O surface minimize by the rGO layer avoiding the contact to reduce Cu_2O into metallic Cu or CuO suppressing the photodegradation.

5. Conclusions

Remarkable stability and the higher steady state photocurrents was found from the Cu/p-Cu_2O/rGO – electrolyte interface in the photo-electrochemical cells. FTIR spectrum confirms the formation of rGO on p-Cu_2O thin films.

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