Photo-Current Enhancement in the Cu/rGO/n-Cu_2O Photo-Electrode at Electrolyte Interface

S.P.A.U.K. Samarakoon[1], K.A.S.K. Hemachandra[1], C.A.N. Fernando[1*]

Abstract

A simple method was found to fabricate Cu/rGO/n-Cu2O photo-electrode to enhance the photocurrent with compared to the device Cu/n-Cu_2O photo-electrode at semiconductor-electrolyte interface. Reduced graphene oxide (rGO) was fabricated on a well cleaned copper sheet using electrophoretic deposition (EPD) technique to fabricate Cu/rGO. Thereafter Cu/rGO electrode was boiled in a 10^{-4}M $CuSO_4$ solution to fabricate Cu/rGO/n-Cu_2O photo-electrode for the first time. Here The rGO acts as a good electron acceptor ton-Cu_2O photo-generated electrons enhancing the charge separation process suppressing the recombination process of the photo-generated charge carriers.

Keywords: n-Cu_2O, rGO, Photoelectron Chemical Cell

1. Introduction

The renewable energy sources are one of the greatest challenges facing us to address the increasing energy demand of our society. Solar energy is the largest energy source available us and can be converted into electricity through the photovoltaic effect[1]. Therefore it is encouraged the fabrication of low cost materials for energy conversion devices[2].

The potential for Cu_2O to be used in semiconducting devices has been investigated as it is timely and attractive, since this material with a band gap around 2 eV. Many researches are based on p type Cu_2O, but the simplicity of preparation and the non-toxicity of n type Cu_2O, it has considerable attention for research on this material in the past[2]. For this study n-Cu_2O layer is formed by boiling a well cleaned Cu plate in a $CuSO_4$ solution.

Since the beginning of the last century, carbon based systems played major role in energy conversion applications [3]. Graphene with two-dimensional structure has been used as excellent charge transfer medium, due to its high conductivity, excellent conductivity, high mobility of charge carriers and light transmission[4-5]. Ease of synthesizing of graphene layer, graphene oxide (GO) is used. For further increasing of conductivity, reduced graphene oxide (rGO) is used. Electrophoretic deposition technique (EPD) is used to deposit rGO because of its high deposition rate, good thickness controllability, good uniformity, and simplicity of scale up coating [6].

From this study n-Cu_2O were fabricated on rGO deposited copper sheets for the first time. A photocurrent enhancement with improved absorption properties and higher steady state photocurrents were found at Cu/rGO/n-Cu_2O electrolyte interface in a photo-electrochemical cell as a low cost solar energy conversion device.

2. Experimental

Cu plates (3 cm × 1 cm) were cleaned and polished with sand papers to obtain a mirror like surface. Then the plates were thoroughly washed with distilled water.

2.1. Preparation of Graphene Oxide

The Graphene Oxide (GO) used in this study was prepared from purified natural graphite by the modified Hummers method [7].2 g of graphite powder was mixed with 46 ml conc. H_2SO_4 and 1 g $NaNO_3$ solution at 0 ^{0}C. 6 g of $KMnO_4$ was added slowly to the flask while the temperature kept below 15 ^{0}C with vigorous stirring for 30 minutes. The suspension was mixed until the temperature exceed 35 ^{0}C then it became a brownish in color. 92 ml of de-ionized water was added slowly while stirring for further 15 min. Finally, 10 ml of H_2O_2 (30 wt. %) solution was added slowly to the mixture and the color of the mixture change into yellow in color. The mixture was centrifuged and

[1] Nano-Technology Research Laboratory, Department of Electronics, Wayamba University of Sri Lanka, Kuliyapitiya, Sri Lanka.
[*] Correstonding author: nandanaf@phy.ruh.ac.lk

washed with water and HCl based on a volume ratio 10:1 for several times to remove the residual ions. The powder was dried at room temperature in a vacuum desiccator for an overnight.

2.2. Deposition of rGO Layer

At first GO was dispersed in distilled water pH of 4. Fig.1.a shows the diagram of the EPD cell experiment. When 10V DC voltage was applied between Pt plate and Cu plate, the rGO platelets migrated towards the Cu plate (positive electrode). After deposition, samples were dried[6].

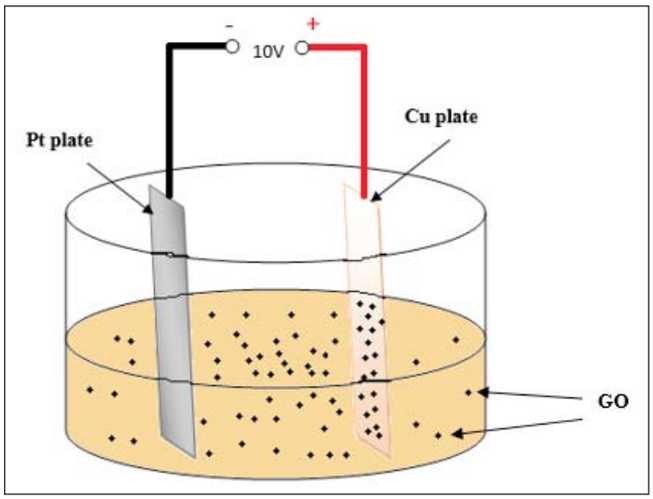

Fig. 1.a: Experimental Setup of the EPD Technique

2.3. Preparation of Cu/rGO/n-Cu_2O layer

Cu/rGO substrate was immersed in a 5×10^{-3} M $CuSO_4$ solution and boiled to obtain Cu_2O layer on the substrate to prepare Cu/rGO/n-Cu_2O. Boiling time controls the amount of Cu_2O formed on it. During the boiling a fixed volume of $CuSO_4$ solution was maintained to provide the same experimental conditions for different preparations. The pH readings of the $CuSO_4$ solution after boiling were obtained using Adwa AD1030 pH/mV and Temperature Meter. Schematic structures were presented in Fig.1.b for both Cu/n-Cu_2O and Cu/rGO/n-Cu_2O photo-electrodes.

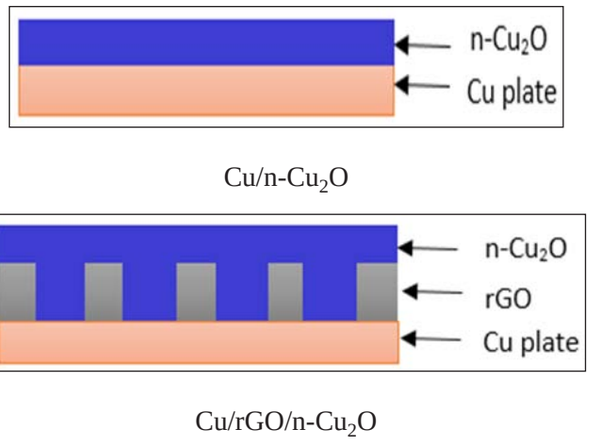

Fig. 1.b: Schematic Diagrams for Electrons Flowing of Cu/ n-Cu_2O Electrode Before and After Introducing rGO

2.4. Characterization Techniques

Diffuse reflectance spectra of Cu/n-Cu_2O and Cu/rGO/n-Cu_2O were obtained by using SHIMADZU 1800 UV spectrophotometer. The photocurrent measurements were done using Hokuto Denko HA-131 potentiostat. Here a Pt plate was used as the counter electrode, an Ag/AgCl electrode was used as the reference electrode and fabricated samples were used as the working electrode. (10^{-2}M)Fe^{2+}/Fe^{3+}(10^{-4}M) solution was used as the electrolyte.

3. Results and Discussion

3.1. The Variation of the Photocurrent with Boiling Time in $CuSO_4$ (10^{-4}M) Solution

Fig. 2.a shows the variation of the photocurrent with boiling period of copper sheets in 10^{-4}M $CuSO_4$ solution. It is clearly seen that photocurrent is maximized at 45 min boiling period producing n-Cu_2O on copper sheets reporting ≈1mA/cm^2. Fig. 2.b shows the variation of the photocurrent with boiling period in 10^{-4}M $CuSO_4$ solution of Cu/rGO electrodes. In this case at around 30 min boiling period higher value of steady photocurrent ≈ 1.5mA/cm^2 is reported with compared to that of bare n-Cu_2O as shown in Fig. 2.b.

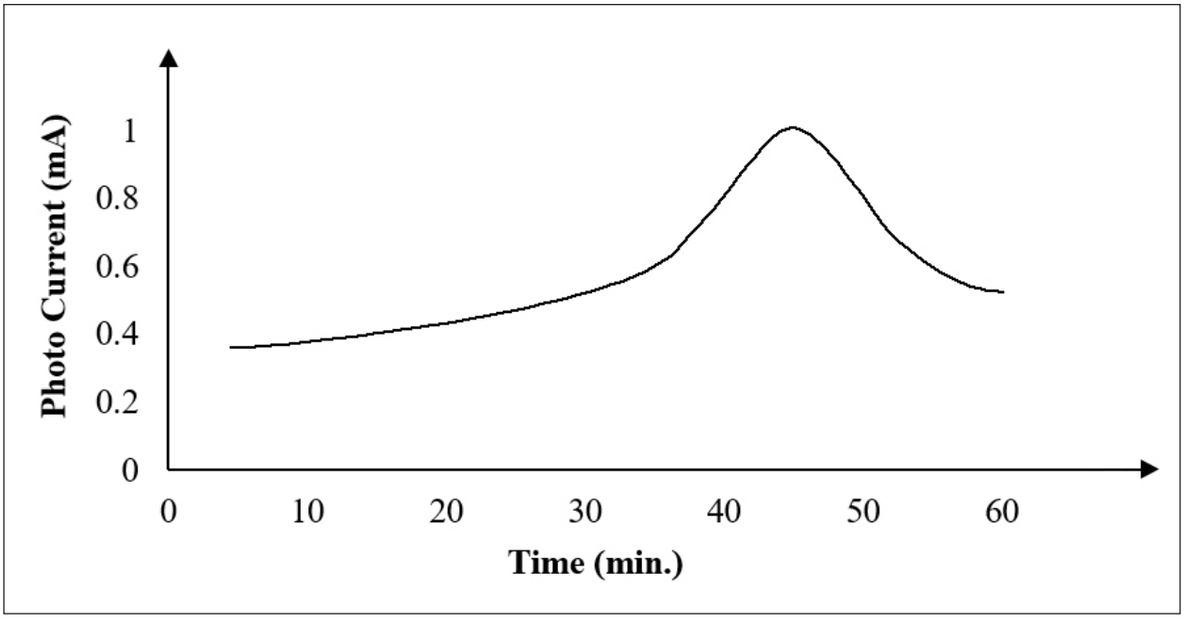

Fig. 2.a: **The Variation of Photocurrent with Various Boiling Periods of Copper Sheets in 10-4M $CuSO_4$ Solution**

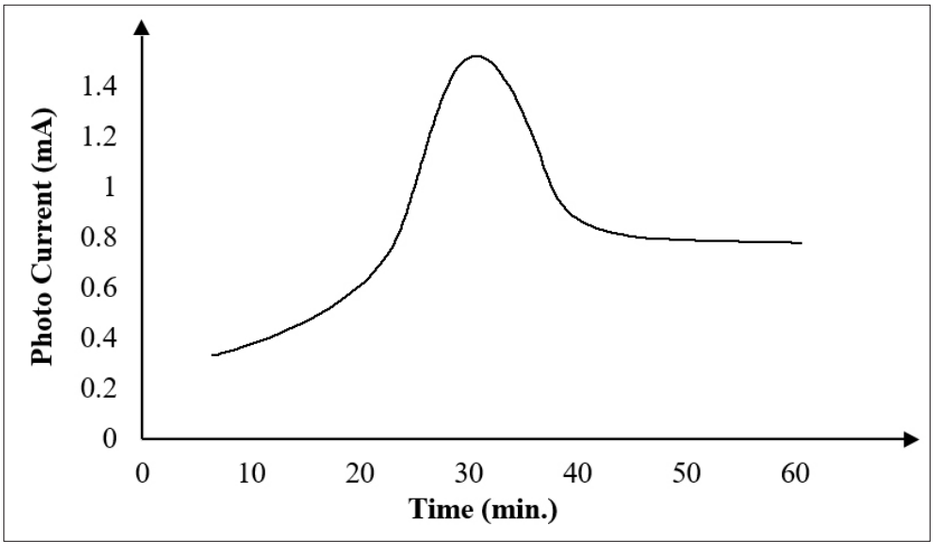

Fig. 2.b: **The Variation of Photocurrent with Different Boiling Periods of Cu/rGO Electrodes in 10^{-4}M $CuSO_4$ Solution**

Fig. 3 shows the variation of n-Cu_2O amount produced with time, on bare copper sheets and Cu/rGO respectively. In case of Cu/rGO/n-Cu_2O, saturation was reached before the saturation of n-Cu_2O amount produced on copper sheets. So that it can be concluded that the formation of n-Cu_2O is much efficient on Cu/rGO electrode with compared to the n-Cu_2O fabrication on bare copper sheets according to the chemical reaction presented as follows. ie

$$Cu^{2+} + Cu + H_2O \rightarrow Cu_2O + 2H^+ \quad (1)$$

3.2. pH Variation of the 10^{-4}M $CuSO_4$ Boiling Solution

The pH variation of $CuSO_4$ solution, when Cu_2O layer grows on the Cu plate and Cu/rGO electrodes as a function of boiling time, is shown in Fig. 4. It shows rapid reduction

at the beginning and saturates at around 4 for both cases. However it should be mentioned that the saturation of pH immediately occurs for Cu/rGO electrodes with compared to that of n-Cu_2O produced bare copper system. This observation also confirms that the formation of n-Cu_2O is much efficient when it is fabricated on Cu/rGO. It is well known that rGO can acts as a good electron acceptor [9]. So that rGO facilitates repelling Cu^{2+} ions from the solution to reach Cu on the copper substrate very fast to form quality n-Cu_2O layer on Cu/rGO decreasing the pH very rapidly.

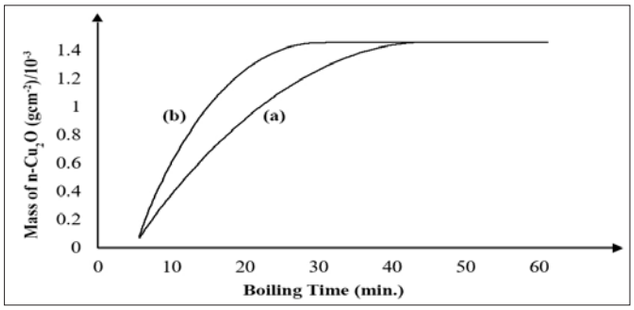

Fig. 3: The Growth Rate of Cu_2O Layer as a Function of Boiling Time for (a) Cu/ n-Cu_2O (b) Cu/rGO/n-Cu_2O

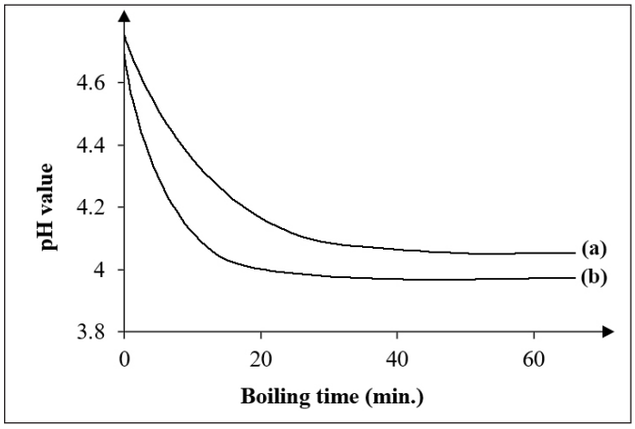

Fig. 4: pH Variation in $CuSO_4$ Solution as a Function of Boiling time for (a) Cu/ n-Cu_2O (b) Cu/ rGO/n-Cu_2O

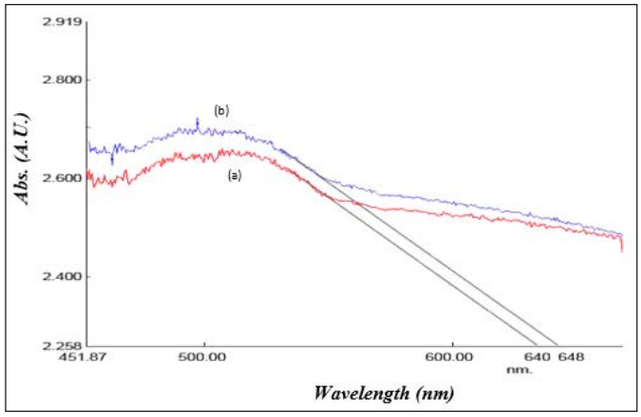

Fig. 5: Absorption Spectra of (a) Cu/n-Cu_2O (b) Cu/rGO/n-Cu_2O

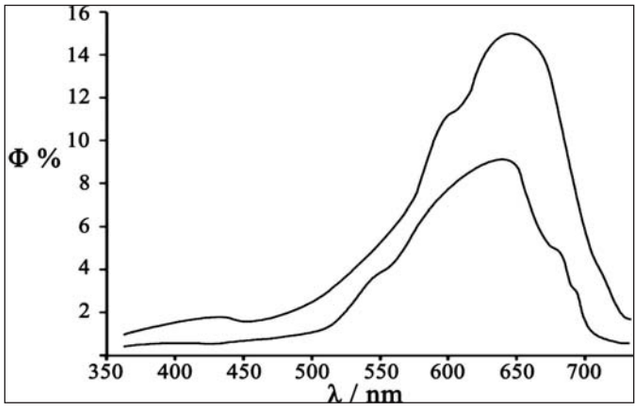

Fig. 6: Photo Current Action Spectra of (a) Cu/ n-Cu_2O (b) Cu/ rGO/ n-Cu_2O

3.3. Diffuse Reflectance Spectra and Photocurrent Action Spectra

Fig. 5 and 6 shows the diffuse reflectance spectra and photocurrent action spectra of Cu/n-Cu_2O and Cu/rGO/ n-Cu_2O photo-electrodes reporting the absorption edges ≈648nm and ≈640nm respectively. Both materials exhibit ≈ 2.0eV as the band gap. Both shapes of the spectra are almost similar confirming that the photocurrent generation occurs only due to the light absorption of the Cu_2O films. In the photocurrent action spectra photocurrent peaks can

be observed around the corresponding absorption edges confirming the photocurrent generation operates due to band to band transitions of both semiconductor films. The photocurrent enhancement is clearly observed for the Cu/rGO/n-Cu_2O photo-electrodes. Since the rGO facilitates to reach the Cu^{2+} ions towards the copper surface uniform film formation and good crystalline properties can be expected for the n-Cu_2O films prepared on rGO with improved absorption properties. Another advantage of the rGO film under the n-Cu_2O is the facilitation to collect photo-generated electrons readily suppressing the electron hole pair recombination.

4. Conclusions

Cu/rGO/n-Cu_2O photoelectrodes exhibit enhanced photocurrent at electrolyte interface. Good crystalline properties and efficient electron – hole separation can be expected for n-Cu_2O deposited rGO films. rGO supports to improve the absorption properties of the n-Cu_2Ofilms deposited on Cu/rGO.

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References

1. Tran, P. D., Batabyal, S. K., Pramana, S. S., Barber, J., Wong, L. H., and Loo Nanoscale, S. C. J. (2012). A cuprous oxide–reduced graphene oxide (Cu 2 O–rGO) composite photocatalyst for hydrogen generation: employing rGO as an electron acceptor to enhance the photocatalytic activity and stability of Cu 2 O, 4, 3875-3878
2. Fernando, C. A. N., and Wetthasinghe, S. K. (2000). *Sol. Energy Mater. Sol. Cells*, 63, 299-308
3. Prashant, V. K. (2011). *Journal of Physical Chemistry Leters,* 2, 242-251
4. Guo, S., Zhang, G. K. Guo, Y. D., and Yu, J. C. (2013). *Carbon,* 60, 437-444
5. Hu, S. J., Chi, B., Pu, J., and Jian, L., (2014). RSC Advances, 4, 60437-60444
6. An, S. J., Zhu, Y., Lee, S. H., Stoller, M. D., Emilsson, T., Park, S., Velamakanni, A., An, J., and Ruoff, R. S. (2010). *The Journal of Physical Chemistry Letters,* 1, 1259
7. Hummers, W. S., and Offeman, R. E. (1958). *Journal of the American Chemical Society,* 80, 1339
8. Fernando, C. A. N., De Silva, P. H. C., Wethasinha, S. K., Dharmadasa, I. M., Delsol, T., and Simmonds, C. M. (2002). *Renew. Energy,* 26, 521-529
9. Zhang, Y., Tang, Z., Fu, X., and Xu, Y. (2010). *ACS Nano,* 4, 7303-7314