H₂ EVOLUTION FROM GRAPHENE DEPOSITED / N-CU2O

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ABSTRACT

n type cuprous oxide (n-Cu₂O) is a widely used and low cost material which can be fabricated by boiling a Cu plate in a CuSO₄(5×10^{-3} M). Synthesis of Cu plate with reduced graphene oxide (rGO) before synthesis of n-Cu₂O increases the photo effect of n-Cu₂O, means rGO acts as an electron acceptor to exact photogenerated electrons from n-Cu₂O. rGO is synthesized using electrophoretic deposition (EPD) technique. Fabricated samples are characterized using diffuse reflectance spectra, photocurrent response and stability of the cells. It can clearly say that there is a remarkable enhancement in photo effects in n-Cu₂O when it is fabricated with rGO.

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 effect¹. Therefore it is encouraged the fabrication of low cost materials for energy conversion devices². The potential for Cu₂O 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 Cu₂O, but the simplicity of preparation and the non-toxicity of n type Cu₂O, it has considerable attention for research on this material in the past². For this study n-Cu₂O layer is formed by boiling a well cleaned Cu plate in a CuSO₄ solution. Since the beginning of the last century, carbon based systems played major role in energy conversion applications³. 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}. For the ease of synthesizing of graphene layer, graphene oxide is used. For

further increasing of conductivity reduced graphene oxide is used. For this, electrophoretic deposition technique is used because of its high deposition rate, good thickness controllability, good uniformity, and simplicity of scale up coating⁶. The diffuse reflectance spectra, photocurrent response and pH variation of the cell are discussed.

2. EXPERIMENTAL

Cu plates (3 cm \times 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 method⁷. 2 g of graphite powder was mixed with 46 ml conc. H₂SO₄ and 1 g NaNO₃ solution at 0 $^{\circ}$ C. 6 g of KMnO₄ was added slowly to the flask while the temperature kept below 15 $^{\circ}$ C with vigorous stirring for 30 minutes. The suspension was mixed until the temperature exceed 35 $^{\circ}$ C then it became a brownish in color. 92 ml of deionized water was added slowly while stirring for further 15 min. Finally, 10 ml of H₂O₂ (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 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

GO was dispersed in distilled water and a solution of pH of 4 was made. Figure 1 shows the diagram of the EPD cell experiment. When 10 V DC voltage was applied between Pt plate and Cu plate, the rGO platelets migrated towards the Cu plate (positive electrode). After deposition, samples were dried⁶.



Figure 1: Experimental setup of the EPD technique

2.3 Preparation of Cu/rGO/n-Cu₂O layer

Cu/rGO substrate was immersed in a 5×10^{-3} M CuSO₄ solution and boiled to obtain Cu₂O layer on the substrate. Boiling time controls the amount of Cu₂O formed on it. During the boiling a fixed volume of CuSO₄ solution was maintained to provide the same experimental conditions for different preparations. The pH readings of the CuSO₄ solution after boiling were obtained using Adwa AD1030 pH/mV & Temperature Meter.

2.4 Characterization Techniques

Diffuse reflectance spectra of Cu/n-Cu₂O and Cu/rGO/n-Cu₂O 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. 0.025 M FeSO₄ solution was used as the electrolyte.

3. RESULTS AND DISCUSSION

3.1 Photo current response curves

Figure 2 shows the photo current variation of $Cu/n-Cu_2O$ substrates for different boiling times in $CuSO_4$ solution. As in Figure 2, a peak can be observed according to the boiling time of 45 min.



Figure 2: Photo response curve of Cu/n-Cu₂O for various boiling times in CuSO₄ Solution



Figure 3: Photo Current response curve of Cu/rGO/n-Cu₂O for various rGO depositing time Figure 3 shows the photo current variation of Cu/rGO/n-Cu₂O for various rGO depositing time and boiling time in CuSO₄ solution is 45 min as it is the best time observed from Figure 2. According to Figure 3 it is clear that the ultimate photo current is observed when rGO depositing time is 30 s.

3.2 pH variation

The pH variation of $CuSO_4$ solution, when Cu_2O layer grows on the Cu plate as a function of boiling time, is shown in Figure 3. It shows rapid reduction at the beginning and saturating at a value around 3.8, which means the acidity of the solution increases rapidly and then settles at a constant value. So it is clear that at the beginning, the oxide layer grows rapidly and slows

down after some time. The formation of Cu_2O on a copper surface can be explained from following chemical reaction.

$$Cu^{2+} + Cu + H_2o \to Cu_2o + 2H^+$$
 [1]

It is clear that the acidity of the CuSO₄ solution increases as a result of the rapid growth of the Cu₂O layer⁸.





3.3 Diffuse Reflectance Spectra

Figure 4 shows the absorption spectra of Cu/n-Cu₂O (curve-a) and Cu/rGO/n-Cu₂O (curve-b). The estimated band gap from the absorption edge corresponding to the light absorption of n-Cu₂O was $\approx 1.9 \text{ eV}$ ($\lambda \approx 640 \text{ nm}$) [8]. It can be clearly seen that a relatively high absorption when Cu/n-Cu₂O substrate synthesize with rGO layer.



Figure 5: Absorption Spectra of (a) Cu/n-Cu₂O (b) Cu/rGO/n-Cu₂O

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5. CONCLUSIONS

The optimum Cu/rGO/n-Cu₂O layer is produced by depositing rGO layer for 30 s and boiling Cu/rGO substrate in a 0.005 M CuSO₄ solution for 45 min. The absorption spectra indicates the band gap of this material as 1.9 eV and rGO exhibits the enhanced visible-light absorption. To conclude, we can say that rGO can act as an electron acceptor to enhance the photo effect of n-Cu₂O due to the formation of n-Cu₂O-rGO junction.

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