p-CuSCN (band gap=3.1eV) Sensitized Cu_2O Quantum Dots (QDs) Photoelectrochemical Cell

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Abstract— *This work focuses on making photoelectrochemical cell for the first time by sensitizing p-CuSCN with Cu_2O quantum dots (QDs). Copper (I) thiocyanate (CuSCN) is wide band gap material which is sensitive only to UV light. This wide band gap semiconductor can be made sensitive to visible light by sensitization with quantum dots. Cu_2O QDs were prepared on Cu/p-CuSCN photoelecrode by boiling Cu/p-CuSCN in a 1M $CuSO_4$ solution. Boiling time controlled the size of the quantum dots. It was found that the boiling time below 20min, QDs of Cu_2O can be fabricated on p-CuSCN and for longer period of boiling above 20min Cu_2O micro crystals were fabricated on p-CuSCN forming a p-CuSCN/n-Cu_2O junction photoelectrode. Higher photocurrents were shown from the QD sensitized photoelectrochemical cells with compared to that of the Cu/p-CuSCN/n-Cu_2O junction photoelectrochemical cells. Photocurrent measurements and diffuse reflectance spectra were presented to explain the mechanism of photocurrent enhancement for the p-CuSCN sensitized QDs of Cu_2O.*

Keywords— *CuSCN, n-Cu2O, Quantum Dots*

I. INTRODUCTION

In recent years, all the technologies are allowing the production of low cost, highly efficient solar energy converting devices such as photoelectrochemical (PEC) cells (Gratzel, 2001). Photoelec (Kamat, 2008)trochemical cell is a photocurrent generated device has a semiconductor in contact with an electrolyte. Extending the spectral response of wide band gap semiconductors by quantum dots sensitization related to Photo-electrochemical cells is an interesting phenomenon (Fernando, et al., 1999) (Kamat, 2008). The p- type CuSCN with a band gap of ~ 3.0 eV is a good semiconductor material since it has the ability to operate stable sensitized photocurrents with disordered and ordered molecular arrangements (Fernando, et al., 1994). Because of the band gap of p-CuSCN is relatively high, the visible spectrum cannot be absorbed. To avoid it, dyes are used for many years to absorb visible spectrum. Since each passing year, dyes are often unable to meet the expectations (Singh, et al., 2013), nowadays dyes are being replaced by QDs due to instability compared with semiconductor QDs. A QD is a portion of matter (e.g. semiconductor) whose excitons are confined in all three spatial dimensions. In this study n-Cu_2O QDs are used. Cu_2O is considered to be an attractive material for photovoltaic energy conversion because it absorbs visible light due to its proper band gap (2.0 eV) with a higher absorption coefficient, showing more than a 10% theoretical energy conversion efficiency proving that the material is extremely useful for solar energy conversion devices. And also it is a non-toxic semiconductor material (Colleen , et al., 2009) (Garuthara & Siripala, 2006).

From this study p-CuSCN was sensitized from Cu_2O QDs for the first time. A photocurrent enhancement was observed with compare to the photoelectrochemical cells made from p-CuSCN/n-Cu_2O junction photoelectrode.

II. EXPERIMENTAL

Cleaning process of the copper sheets

The outer impurity layer in commercially available (purity 99.9%) copper plate (1 cm × 3 cm) was removed by sand papers and polished until a mirror like surface and cleaned with distilled water.

Preparation of Cu/ p-CuSCN photoelectrode

Well cleaned and mechanically polished copper plate was immersed in a solution containing 0.1 M KSCN, 0.1 M acetic acid and 1 M acetone (pH-value ≈ 3.5) for 30 minutes in order to prepare p-CuSCN layer. Immersing time controlled the thickness of the thin film of p-CuSCN deposited on Cu.

$$KSCN + CH_3COOH \rightarrow CH_3COOH + HSCN$$

$$2\,Cu + 2\,HSCN + \frac{1}{2}\,O_2 \rightarrow 2\,CUSCN + H_2O$$

Acetone (C_3H_6O) favours the formation of uniform layers on the copper substrate.

Preparation of Cu/ p-CuSCN / n-Cu_2O QD photoelectrode

The resultant Cu/p-CuSCN substrate was boiled in a 1 M $CuSO_4$ solution for certain time period to obtain an n-Cu_2O layer on top of the p-CuSCN layer. The amount of Cu_2O, formed on Cu/p-CuSCN substrate (g cm^{-2}) was controlled by controlling the boiling time.

Experimental techniques

Defuse reflectance spectra of bare p-CuSCN and p-CuSCN / n-Cu_2O were measured by using a Shimdzu 1800 UV Spectrophotometer. Conventional potentiostat (Hokuto Denko HA-151) with three electrode configuration was used to measure the photocurrent of Cu/ p-CuSCN / n-Cu_2O junction photoelectrode. Where, a Ag/AgCl electrode employed as the reference electrode and a Pt plate was used as the counter electrode.

III. RESULTS AND DISCUSSION

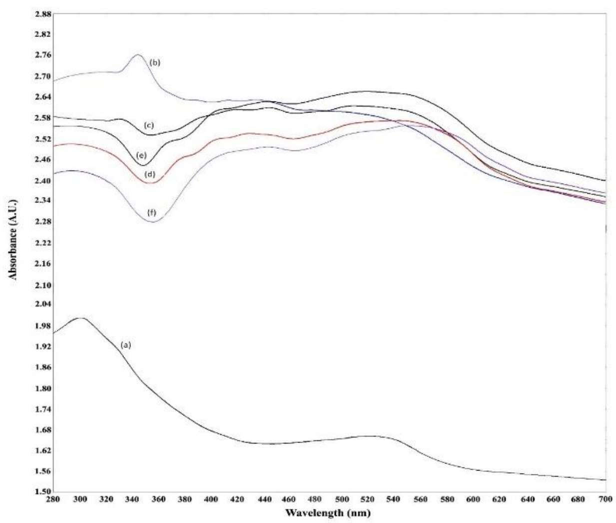

Figure. 1: Diffuse reflectance spectra for (a) Cu/p-CuSCN and Cu/p-CuSCN/QD cells for various boiling time in 1 M $CuSO_4$ solution for making of various n-Cu_2O layers. b) 8 min, c) 18 min, d) 26 min, e) 30min, f) 44min

Fig.1 shows the diffuse reflectance spectrum for the Cu/p-CuSCN and Cu/p-CuSCN/Cu_2O (QDs). Curve (a) shows an absorption edge ≈ 380nm corresponding to the band gap 3.1eV. It is further confirmed that p-CuSCN is a wide band gap semiconductor. It is clearly seen that bare p-CuSCN shows very poor absorption properties in the visible region and the absorption properties are much improved by fabricating QDs of Cu_2O on p-CuSCN thin film as shown in curves (b) to (f). Broad absorption spectrum can be observed in the visible region for Cu/p-CuSCN/Cu_2O (QDs). The formation of broad absorption spectrum may be due to the improved absorption properties of different sizes of Cu_2O QDs. Further it was observed when the boiling time increases the broad absorption spectra becomes slightly narrow around 680nm absorption confirming the formation of crystalline n-Cu_2O with its absorption edge on p-CuSCN showing a 2.0eV band gap. Each absorption spectra of p-CuSCN/Cu_2O (QDs) shows the absorption properties of p-CuSCN. This observation confirms that the duration of boiling in $CuSO_4$ solution considerable chemical dissolution of p-CuSCN was non-significant.

Fig.2 shows the variation of boiling time of Cu/p-CuSCN electrode in the 1M $CuSO_4$ solution with photocurrent. It is interesting to mention that the photocurrent increases with the boiling time in 1M $CuSO_4$ and shows two photocurrent maxima. The first maximum occurs when the boiling time is nearly 18 min and second maximum occurs when it at 30min. The reason for the sharp photocurrent enhancement in the first maximum may be due to the enhancement of the light absorption of Cu_2O QDs and the sensitization of p-CuSCN efficiently by Cu_2O QDs. When the boiling time increases further increase of the size of the QDs can be expected. So that the possibility of the QD sensitization process suppresses gradually with increase of the size of the QDs. Further when the boiling time around 30 min, it is observed that photocurrent increases again and maximized. The reason for the photocurrent enhancement at the second stage as shown in Fig.2 is the formation of n-Cu_2O thin film on p-CuSCN forming a p-CuSCN/n-Cu_2O junction providing an efficient charge separation for the photogenerated charge carriers at the n/p junction. After 18min boiling time QDs gradually increases their sizes showing large n-Cu_2O microcrystals reducing the photocurrent until n-Cu_2O forms a n-p junction with p-CuSCN to exhibit the second photocurrent enhancement as shown in Fig.2.

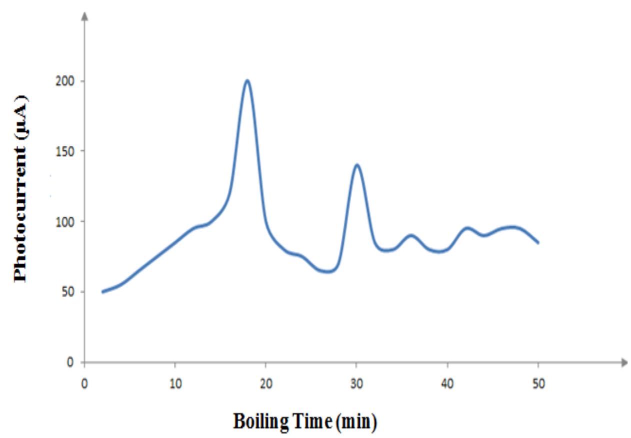

Figure. 2: Photo Current vs Boiling Time of the Cu/p-CuSCN photoelectrode in 1M $CuSO_4$

IV. CONCLUSION

p-CuSCN was sensitized by Cu_2O quantum dots for the photoelectrochemical cell at low cost and easy fabrication processes on a well cleaned commercially available copper sheets. When the size of the QD increased, photocurrent and absorbance enhancement were observed.

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