Photoelectrochemical studies on colloidal copper (I) oxide/modified with some organic semiconductors: Incentive for use of nanoparticle systems

KASEM K KASEM* and CARMEN DAVIS

National Information Mathematical Sciences Department, School of Arts and Science, Indiana University Kokomo, Kokomo, IN 46904, USA

Abstract. Colloidal Cu_2O solutions were used to explore photonic activities at the semiconductor/electrolyte interface. Fluorescence spectroscopic studies were performed on Cu_2O colloidal particles modified with some conjugated organic monomers such as 2-amino-phenyl pyrrole (2-APPy), tri-phenyl amine (TPA), or 2-thionyl pyrrole (2-Th-Py) to investigate the quantum absorbance efficiency at this inorganic/organic interface (IOI). Our study shows that colloidal *p*-type Cu_2O possesses a bandgap with direct transition of $\approx 2\cdot2$ eV and indirect transition of $1\cdot85$ eV. The recorded rates of charge injection into colloidal Cu_2O, k_{ct}, were $2\cdot31 \times 10^9$ s^{-1}, $5\cdot05 \times 10^8$ s^{-1}, and $7\cdot22 \times 10^8$ s^{-1} for 2-APPy, TPA and 2-Th-Py, respectively. The studied systems show more stability in colloidal form than in thin solid form. Results were interpreted using the optical and electrical parameters of the organic monomer such as ionization potential (IP), electron affinity (EA) and energy bandgap (Eg), and the barrier height at the IOI interface. Stability of the colloidal system is attributed to the physical dimensions of the photoactive system. The nano-colloidal particle offers a condition where its size is less than $\sqrt{Dt}$.

Keywords. Photoelectrochemistry; nano-particles; semiconductors; interface; colloidal.

1. Introduction

The great demand for renewable sources of energy has increased interest in the use of semiconductors in capturing solar radiation. The fact that some metal oxides possess semiconductor characteristics with bandgaps matching visible solar radiation adds great advantages to these inexpensive metal oxides over other more expensive semiconductors. The conversion of solar radiation into a controllable form can be more efficient if we focus on the range of the radiation spectrum with a relative high photon flux. Wavelengths within the range between 450 and 800 nm fit these criteria. Semiconductors with bandgaps between $3\cdot1$ eV and $1\cdot5$ eV can be used to capture and convert these radiations into chemical or photo-chemical energy.

A tangible effort is being made to develop a number of semiconductors in the form of thin film-electrodes or colloidal systems which might be used in solid or liquid photovoltaic cells (Spanhel *et al* 1987; Kamat and Dimitrijevic 1989; Gruszecki and Holmstrom 1998; Kumar *et al* 1998; Willner *et al* 1998; Cahen *et al* 2000; Shipway *et al* 2000; Kamat 2002; Adams *et al* 2003; George Thomas and Kamat 2003). Several methods were used to prepare

these semiconductors as single crystals or as polycrystalline materials. Examples of these methods are chemical vapour deposition and vacuum evaporation. In most of these methods, one material with a specific bandgap is being produced. Some studies were performed on metal chalcogenides such as sulfides, selenides, tellurides, but low conversion efficiencies were reported (Goidas *et al* 1990; Vogel *et al* 1990, 1994; Kohtani *et al* 1993; Liu and Kamat 1993; Graetzel 1997, 2001; Plass *et al* 2002; Peter *et al* 2003). Ordered assemblies of narrow bandgap semiconductor nanostructures, if employed, can be convenient systems to harvest visible light energy. The photocurrent obtained using such nanoparticle assemblies is often low, as fast charge recombination limits photocurrent generation. By employing composite semiconductors, however, it has been possible to improve the efficiency of charge separation through charge rectification by modifying the surface of the base semiconductor with either inorganic or organic semiconductors. As thin films of Cu_2O show poor resistance to photo corrosion (Nagasubramanian *et al* 1981; Hara *et al* 1998a), an alternative form of Cu_2O may show a greater stability than that of the thin solid film.

In this paper, we investigate the photonic behaviour of diverse sizes of Cu_2O colloidal nanoparticles with special emphasis on the effectiveness in capturing solar radiation. Furthermore, because of the great surface area that a colloidal solution can offer, adsorption of organic semi-

*Author for correspondence (kkasem@iuk.edu)

conductor material is very likely and inorganic/organic interface (IOI) assemblies can be produced. Three conjugated organic compounds were chosen, 2-APPy, TPA, 2-Th-Py. We investigate the effect of these organic semiconductors on the photonic behaviour of these assemblies and judge how much of solar radiation can be harvested.

2. Experimental

2.1 Reagents

All reagents were of analytical grade. All solutions were prepared using deionized water, unless otherwise stated.

2.2 Instrumentation

All electrochemical experiments were carried out using a conventional three-electrode cell consisting of Pt wire as a counter electrode, Ag/AgCl as a reference electrode and BAS 100W electrochemical analyser (Bioanalytical Co.) was used to perform the electrochemical and impedance studies. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer 5500 ESCA. An Amery 1000A was used to produce scanning electron micrographs of the polymer films. Both UV-VIS spectrophotometer and reflectance UV-VIS were used to generate absorption spectra of the thin solid films on ITO electrodes or for the colloidal oxide. An Olympus BX-FLA60 reflected light fluorescence microscope working with polarized light at a range between λ 330 and 550 nm was used to determine the particle size of colloidal particles.

Fluorescence lifetime measurements were recorded using a Chronos (ISS, Champaign, IL) with a laser diode as the excitation source (Tatarets *et al* 2006).

2.3 Synthesis of colloidal Cu₂O

Colloidal *p*-type Cu_2O was generated using a hydrolysis method. In this method, a buffered basic solution of copper acetate in the presence of hydrazine or with Fehling reagent, was heated to 90°C under constant stirring for 2 h. In all cases, colloidal oxide was allowed to stile, then filtered, rinsed and dried at 200°C for 10 h. The colloidal particles were further dispersed into water using high energy sonicators.

3. Results and discussion

3.1 Redox potential of organic semiconductors

Cyclic voltammetric studies were carried out, unless otherwise stated, in acetonitrile solutions for the 2-APPy, 2-Th-Py, and TPA. Figure 1 displays the CV for the polymer film of each of the studied monomers. The CVs of the

monomers were not different from those of the polymer films. The onset oxidation potential corresponding to each of these molecules are recorded in table 1.

3.2 Characterization of Cu₂O nanoparticles

Figure 2 illustrates the absorption spectra of meso-size particles of Cu_2O. In large particles direct and indirect transitions are possible. We used the following equations (Robert *et al* 1998) to calculate the direct and indirect transition band structures for Cu_2O spectra displayed in figure 2.

$$(\alpha E_\gamma)^2 \propto E_\gamma - E_{gd}, \tag{1}$$

$$\alpha \propto \frac{(E_\gamma + E_p - E_{gi})^2}{e^{(E\gamma/kT)} - 1} + \frac{(E_\gamma - E_p - E_{gi})^2 e^{(E\gamma/kT)}}{e^{(E\gamma/kT)} - 1}, \tag{2}$$

where α is absorption coefficient, E_g the optical bandgap. Figures 3A and B display Tauc's plots from which we obtained the direct and indirect bandgap transitions
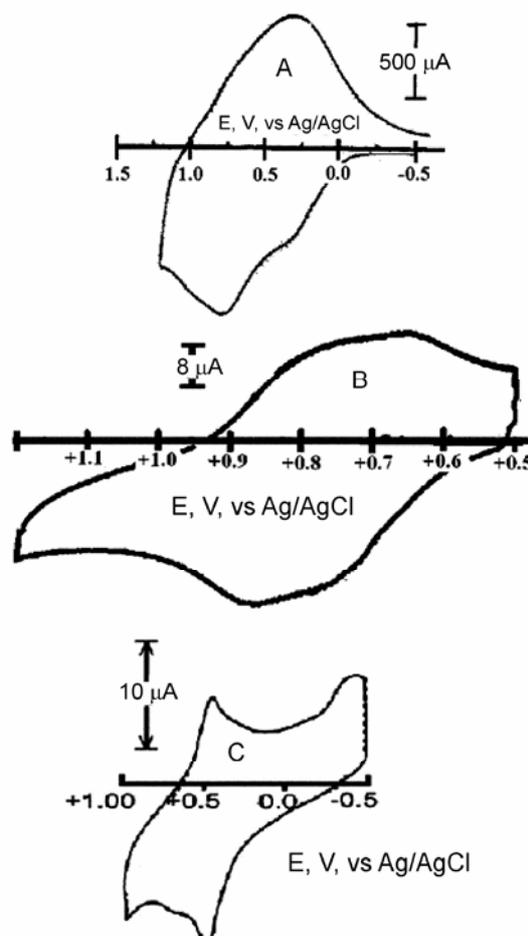

Figure 1. CV in acetonitrile perchlorate electrolyte of Pt electrode modified with **A**. poly 2-Th-Py, **B**. poly TPA, and **C**. poly 2-APPy (protonated in aqueous $HClO_4$). Scan rate (100 mV/s).

shown in the inset diagram of figure 3. This diagram indicates that colloidal Cu_2O possesses bandgaps with a direct transition of ≈ 2 eV and an indirect transition of 1·85 eV. The nano particles of Cu_2O show greater bandgap than larger particles (500–1000 nm). The calculated optical bandgap for nano-crystals of Cu_2O (data not displayed) is 2·52 eV, a value that is consistent with nano or quantum dot size particles.

3.3 *Photo-absorption activities of IOI*

Fluorescence emission studies were performed on a copper (I) oxide colloid modified with 2-APPy, 2-Th-Py, and TPA. To detect the absorption of the emitted photon from organic semiconductors, a reference system consisting of colloidal SiO_2 ($Eg > 5$ eV) and an organic semiconductor was studie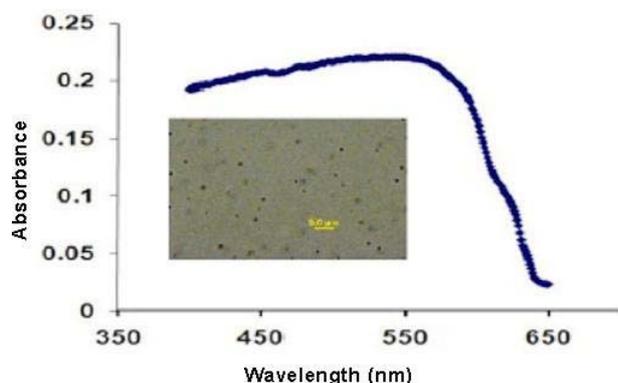d before and after doping with Cu_2O. In the absence of Cu_2O, all fluorescence emissions were detected, as no injection will take place into SiO_2 particles due to the very large bandgap and band positions with HUMO and LOMO in the organic semiconductors. In the presence of Cu_2O, less fluorescence emission was recorded as Cu_2O absorbed some of these emitted photons. Figure 4 displays the fluorescence emission spectra of the colloidal system consisting of SiO_2 and 2-APPy (figure 4A), 2-Th-Py (figure 4B), and TPA (figure 4C) before and after doping with Cu_2O.

Understanding the photonic activities at the studied IOI shown in figure 4 requires information about the characteristic energies at IOI such as EA, IP, and *Eg* of the organic semiconductor and φ (barrier potential) at IOI

Figure 2. Absorption spectra of meso-sized particles of Cu_2O. Inset: the fluorescence-microscopic image of the particles.

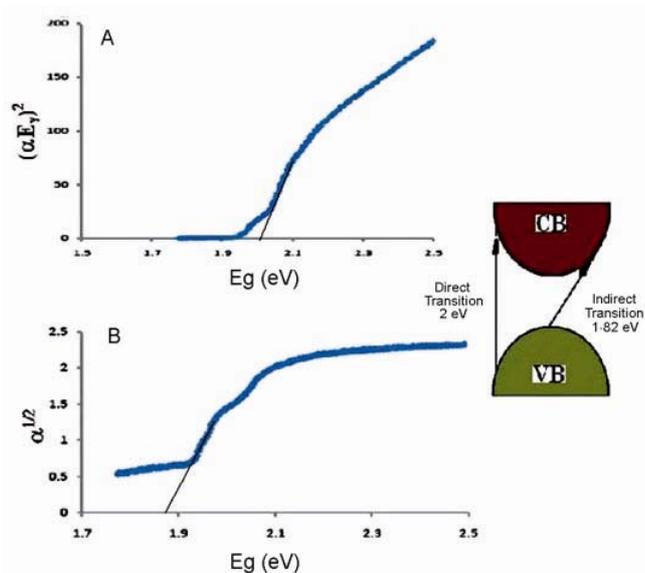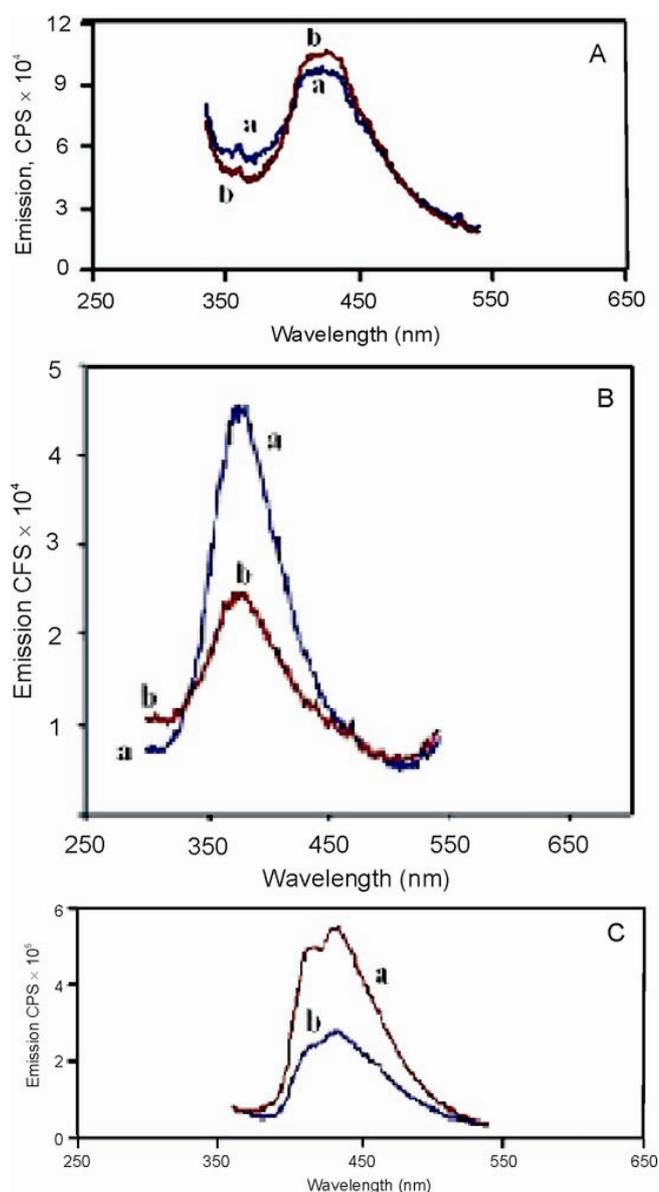**Figure 3. A**. Direct and **B**. indirect bandgap meso-size particles of Cu_2O (Inset: bandgap diagram).

Figure 4. Fluorescence emission on **a**. SiO_2. **b**. SiO_2 doped with Cu_2O (excitation $\lambda = 320$ nm; A. 2-APPy; B. 2-Th-Py and C. TPA).

Table 1. Chemical and photo-electrochemical data of IOI components.

Property	2-APPy	TPA*	2-Th-Py
Onset oxidation potential (vs Ag/AgCl)	0·3 V	0·8 V	0·4
IP (ionization potential (eV))	4·7	5·2	4·8
Eg (Bandgap, eV)	≈2·8	≈2·2–2·4	≈1·8
EA (electron affinity, eV)	1·9	3·0 to 2·8	3·0
Barrier height φ (eV) at Cu_2O/molecule interface	3·0	1·9 to 2·1	1·9
Life time (ns)	0·437	1·98	1·4
% of Fluoresces emission absorbed by Cu_2O	0	72·7	65·0

*Two-photon emissions

interface. These quantities constitute the potential map of the IOI assemblies.

The potential maps of the studied organic semi-conductors were calculated using the following relations:

$$IP = E_{ox} = E'_{ox} + 4\cdot4 \ eV,$$

where E'_{ox} is onset oxidation potential, IP the ionization potential, and EA the electron affinity.

$$IP = EA + Eg.$$

Table 1 lists the data corresponding to the studied three organic compounds. These data give an insight to the potential map of the studied IOI assemblies.

The data listed in table 1 shows that the IOI made of Cu_2O/organic semiconductor absorbs the least amount of emitted fluorescence photons with 2-APPy adsorbent. The percentages of absorbed photons at the IOI assemblies were 0%, 65%, and 72% for 2-APPy, 2-Th-Py and TPA, respectively. The zero absorption percentage at Cu_2O/2-APPy can be attributed to the fact that 2-APPy is a *p*-type organic semiconductor as indicated by its low EA (1·9 eV), and Cu_2O is also *p*-type. The IOI favours charge separation and further injection when the condition for *p–n* junction is fulfilled. That is not the case with Cu_2O/2-APPy interface. The barrier height (barrier height, φ = work function of Cu_2O – EA of 2-APPy) is 3 eV. This value is high enough to make charge injection thermodynamically unfavourable. The greater absorption percentage recorded for TPA and 2-Th-Py can be explained by the fact that TPA and 2-Th-Py are *n*-type hole-transporting materials due to their higher EA (table 1), and thus has a lower barrier potential. It is worthwhile noticing that the physical quantities recorded in table 1, other than φ, assume symmetric conditions for each indi-vidual organic molecule. In reality IOI interface, symmetry of the adsorbed organic molecule is broken. This will cause shifts in some molecular energy of the adsorbed molecule in comparison with unadsorbed ones. As a result of this asymmetric status of the adsorbed organic mole-cules, the energy barrier for charge transfer is rearranged.

Table 1 also shows that the IOI with TPA has a greater absorption than that with 2-Th-Py. Furthermore, the measured life time of the excited state for TPA (1·98 ns) is longer than that of 2-Th-Py (1·4 ns). Both the structure

and the measured life time indicate that TPA offers larger surface area of delocalization of the formed radical cation. This allows for more stable intermediates with different energy states that favour charge injection into Cu_2O parti-cles at the IOI assembly.

An important factor that may influence the photonic activities at these IOIs is the relative life times of the excited states created after illumination. The determined fluorescence life time of 2-APPy, TPA and 2-Th-PY are 0·437 ns, 1·98 ns and 1·4 ns, respectively. The shorter life time of the organic semiconductor compared to that reported for Cu_2O suggests that organic semiconductors will inject charges into the copper (I) oxide colloidal parti-cles, because the hole in the valence band has longer life than the excitons generated from 2-APPy or TPA, or 2-Th-Py. For illuminated Cu_2O, there are three possible ways for the generated electron–hole pairs to be con-sumed; first is the recombination of electron-hole, second is electron transfer to another chemical agent, and the third is the reduction of Cu^+ ions to metallic copper. The shorter lifetime of organic semiconductors excitons com-pared with Cu_2O suggests that these electrons can be injected to neutralize the holes in VB of Cu_2O. This will certainly reduce the electron–hole recombination process. The lifetime of the polaron shown in figure 4 determines whether these polarons will be partially or totally con-sumed in an oxidation of a chemical agent in conjunction with this illuminated IOI.

3.4 *Stability of colloidal Cu_2O/organic interface*

The IOI were used several times which generated the same results. This indicates its stability towards photo-corrosion. Colloidal nano-particles of Cu_2O show a great stability against illumination for almost 1900 h (Hara *et al* 1998b). A thin solid film of Cu_2O prepared electro-chemically using cycling the potential of pure copper sheet between –0·6 V and +0·1 V vs Ag/AgCl electrode (figure 5A and inset) shows a very poor stability upon illuminations as shown in figure 5B. The greater stability of nano particles of Cu_2O than that of thin solid film of Cu_2O can be attributed to two factors: (I) Morphological factor: We believe that photo corrosion is mostly due to the galvanic action that takes place following the forma-

tion of excited state. If the dimension of the Cu_2O cluster is greater than $\sqrt{Dt}$, (where D is the diffusion coefficient of $Cu +$ ions in the cluster, and t the excited state life time in s), the galvanic cell will be formed and degradation of Cu_2O takes place. As the thin solid film offers continuous, polycrystalline structure with larger area which is greater than $\sqrt{Dt}$, such phenomena will not take place in nano structure. Cu_2O nanoparticles (50 nm or less) have more resistance to photo corrosion than particles of meso- or micro-sizes. Certainly Cu_2O quantum dot will have the greatest stability against photo-corrosion and (II) structural factor in which the nano structure offers larger bandgap than that offered in condensed thin solid film. This larger bandgap offers energy map in which a VB and CB energy shifts to energy edge where E OH^-/H_2O is less than the E pd (free energy of oxidation of the Cu_2O), and E H^+/H_2O is greater than the E nd (free energy of reduction of Cu_2O).

4. Conclusions

The use of organic semiconductors in conjunction with colloidal inorganic semiconductors will increase the process of light harvesting, suppress electron–hole recombination rate, and increases the quantum conversion efficiency of the IOI system. Unlike chemical doping of inorganic semiconductors, modification of the surfaces with organic semiconductors will expand the photon-absorption range and enhance the charge separation and injection as well. Our results give rise to more incentive of using colloidal metal oxide semiconductors in IOI assemblies due to the great stability and larger surface area that they can offer. The great absorption of photons generated by excitation using short UV radiation suggests that TPA or 2-Th-Py can be used as a major component in high UV radiation protection paint.

References

Adams D *et al* 2003 *J. Phys. Chem.* **B107** 6668

Cahen D, Hodes G, Graetzel M, Guillemoles J F and Riess I 2000 *J. Phys. Chem.* **104** 2053

George Thomas K and Kamat P V 2003 *Acc. Chem. Res.* **36** 888

Goidas K R, Bohorques Maraia and Kamat P V 1990 *J. Phys. Chem.* **B94** 6435

Graetzel M 1997 *Nanocrystalline electronic junctions.* in *Semiconductor nanoclusters – Physical, chemical and catalytic aspects* (eds) P V Kamat and D Meisel (Amsterdam: Elsevier Science) pp 353–375

Graetzel M 2001 *Nature* **414** 338

Gruszecki T and Holmstrom B J 1998 *Sol. Energy Mater., Sol. Cells* **51** 243

Hara Michikazu, Kondo Takeshi, Komoda Mutsuko, Ikeda Sigeru, Shinohara Kiyoaki, Tanaka Akira, Kondoa Junko N and Domen Kazunari 1998a *Chem. Commun.* 357

Hara Michikazu, Kondo Takeshi, Komoda Mutsuko, Ikeda Sigeru, Kondo Junko N, Domen Kazunari, Shinohara Kiyoaki and Tanaka Akira 1998b *Chem. Commun.* 357

Kamat P V 2002 *J. Phys. Chem.* **B106** 7729

Kamat P V and Dimitrijevic N M 1989 *J. Phys. Chem.* **93** 4259

Kohtani S, Kudo A and Sakata T 1993 *Chem. Phys. Lett.* **206** 166

Kumar M, Sharan K and Sharon M J 1998 *Sol. Energy Mater., Sol. Cells* **51** 35

Liu D and Kamat P V 1993 *J. Phys. Chem.* **97** 10769

Nagasubramanian G, Giods A S and Bard A J 1981 *J. Electrochem. Soc.* **128** 2158

Peter L M, Wijayantha K G U, Riley D J and Waggett J P 2003 *J. Phys. Chem.* **B107** 8378

Plass R, Pelet S, Krueger J, Graetzel M and Bach U 2002 *J. Phys. Chem.* **B106** 7578

Robert A, Leeuwen van, Hung Chen-jen, Kammler Danlel R and Switzer Jay A 1998 *J. Phys. Chem.* **99** 15247

Shipway A N, Katz E and Willner I 2000 *Chem. Phys. Chem.* **1** 18

Spanhel L, Weller H and Henglein A 1987 *J. Am. Chem. Soc.* 109

Tatarets Anatoliy L, Fedyunyayeva Irina A, Dyubko Tatyana S, Povrozin Yevgeniy A, Doroshenko Andrey O, Terpetschnig Edward A and Patsenker Leonid D 2006 *Anal. Chim. Acta* **570** 214

Vogel R, Pohl K and Weller H 1990 *Chem. Phys. Lett.* **174** 241

Vogel R, Hoyer P and Weller H 1994 *J. Phys. Chem.* **98** 3183

Willner I, Kaganer E, Joselevich E, Durr H, David E, Gunter M J and Johnston M R 1998 *Coord. Chem. Rev.* **171** 261
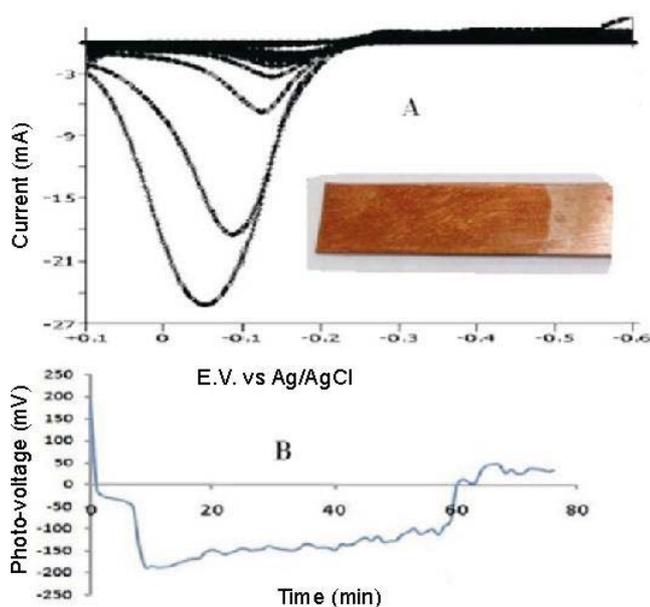

Figure 5. **A**. Electrodeposition of Cu_2O film from 0·1M LiOH aqueous electrolyte (Inset: film image of Cu specimen) and **B**. photo-voltage time curve for thin Cu_2O film shown in A, in aqueous KCl electrolyte under illumination.