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Full Length Research Paper

Electrical and optical properties of nanostructured copper (I) iodide (CuI) incorporated with ligand agent for dye sensitized solar cell applications (DSSC)

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Dispersion of CuI solution incorporated with ligand or stabilizer in acetonitrile solvent has been deposited on glass substrates, where it formed a mixture of inorganic/organic thin film in order to study its characteristics for dye sensitized solar cell applications (DSSC). CuI thin film has been prepared by sol-gel process with incorporation of TMED as a ligand into the CuI solution. Particle size of the solution is measured after few hours of stirring. Then, the thin film was deposited by spin coating technique with appropriate parameters. The optical properties of the composite thin film have been examined to display the energy shifting, which support the improved band gap compared to that of the pure CuI film, while the electrical properties show improved conductivity of the hole conductor to be a function of the p-type semiconductor for DSSC. This result indicates that the electrical and optical properties of CuI film can be easily adjusted by the formation of composite film with proper ligand agents.

Key words: solar cell, ligand agent, iodide.

INTRODUCTION

Throughout the years, researchers made an effort in improving the performances of liquid electrolyte based dye-sensitized solar cells (DSSC) when some problems were identified within this device. Problems that have been identified by liquid electrolyte based DSSC are dye desorption, solvent evaporation, seal imperfection, reaction of the sealant with the electrolyte and other reaction of the redox cycle (Bin, 2006; Wei, 2010). One of the approaches to the replacement of liquid electrolyte is by utilizing p-type semiconductor. An inorganic p-type semiconductor based on a copper compound which works as a hole conductor, such as CuI, copper bromide (CuBr) or copper thiocynate (CuSCN), was found to be suitable for the task (Bin, 2006; Wei, 2010; Fujishima and Zhang, 2005). After extensive experimentations, CuI is the most common precursor to be used as p-type hole conductor (Bin, 2006). Until date, in order to improve the functionality of CuI as hole conductor, few changes were made to the CuI solution. The change which was made is by incorporating a ligand agent. Even though the change was made, the original properties of the solution itself were still not destroyed. Synthesizing CuI thin film with incorporation of ligand agent for dye-sensitized solar cells application was started by Kumara (2002) and Konno et al. (2008). It is believed that the ligand they used work as CuI crystal growth inhibitor and could be adopted for fabricating solid state dye-sensitized solar cells (DSSC). Furthermore, it was reported that the stability of CuI based DSSC greatly improved with the existence of ligand agent (Konno et al., 2008). This paper introduced an alternative ligand to be used as CuI crystal growth inhibitor and as an option to the fabrication of DSSC, as discussed previously. However, a novel approach used to obtain a new CuI-related composite film is demonstrated by making use of CuI-acetonitrile solution. The ligand agent is called tetramethylethylenediamine (TMED

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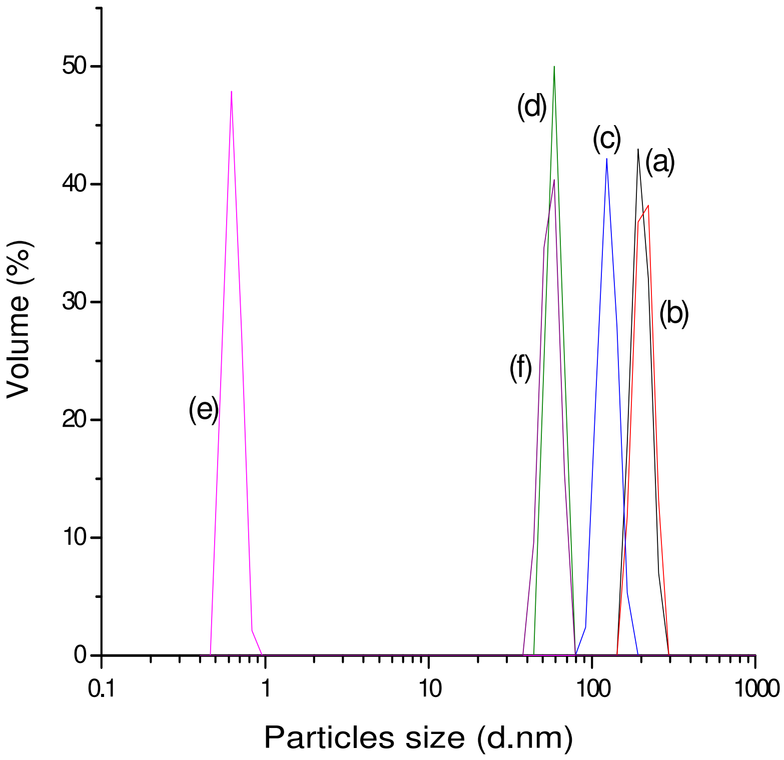

Figure 1. Particles size distribution of 0.05 MCuI incorporated with different volumes of TMED; (a) without TMED, (b) 0.1 mLTMED, (c) 0.2 mLTMED, (d) 0.3 mLTMED, (e) 0.4 mLTMED, (f) 0.5 mLTMED.

@TMEDA). It is found that highly (111) oriented CuI film with improved quality could be easily prepared on glass substrate. Furthermore, the composite film exhibit obviously improved band gap photoluminescence, indicating that TMED@TMEDA is a kind of reagent in inorganic synthesis exhibiting a special function for this composite film. So far, the use of TMED for studying the electrical and optical properties of the semiconductor CuI thin film has not been reported yet.

EXPERIMENTAL PROCEDURE

All the chemicals used in this work were obtained from the supplies and without any further purification. The powder of copper (II) iodide and liquid of tetramethylethylenediamine (TMED) was purchased from ALDRICH and SIGMA-ALDRICH respectively. The glass substrate was chosen to study the characteristics of the new CuI thin film. The glass was cleaned with acetone, followed with methanol and finally rinsed with deionized water. All stages were put in dip ultra sonic water for 15 min each. The next step is the preparation of the CuI solutions with and without ligand agent. CuI coating solution, also known as CuI sol-gel, was prepared by dissolving 0.4761 g CuI powder (ALDRICH 99%) into 50 ml acetonitrile (0.05 M) at room temperature. For CuI solution with ligand agent, 5 beakers were prepared with a volume from 0.1 to 0.5 ml of TMED (Sigma-Aldrich 99%) and were added to the solution. The solutions were stirred for about 3 h before particles size was measured by MALVERN zeta sizer nano-s. Before the deposition process took place, the glass was pre-heated at 50°C for a while. Then, CuI solutions were deposited into the glass substrates using spin coating technique (LAURELL) at 1000 rpm for 20 s where a nano meter thickness of CuI thin film was then produced. This thin film is heated into a furnace at 50°C for about 30 min. The properties of CuI thin film nanostructure with and without TMED have been studied by their atoms arrangement within CuI crystal using X-ray diffraction (XRD), absorption and emission of photon toward CuI thin film by photoluminescence (PL) measurement (HORIBA JOBIN YVON) and direct current voltage measurement for determination of the difference in electrical potential between two points by two probe (I to V) measurement.

RESULTS AND DISCUSSION

To investigate the role of TMED in the formation of CuI thin films, particles size measurement was conducted after 3 h and stirred in CuI solution with and without TMED. Figure 1 shows particles size results of CuI solution without TMED (a) and with TMED (b to f).

Evaluating the size distribution of particles by volume, the solution obtained in the absence of TMED by Figure 1 (a) is composed of large CuI grains, and the particle size is about 0.2 µm. The peak value is around 200 (d.nm) with about 43% volume. On the other hand, CuI solution existing in TMED as shown in Figure 1 (b to f) produced much better outcome with smaller crystallites that can be observed. Size distribution by volume show that CuI solution with TMED give better results within 38 to 50% of

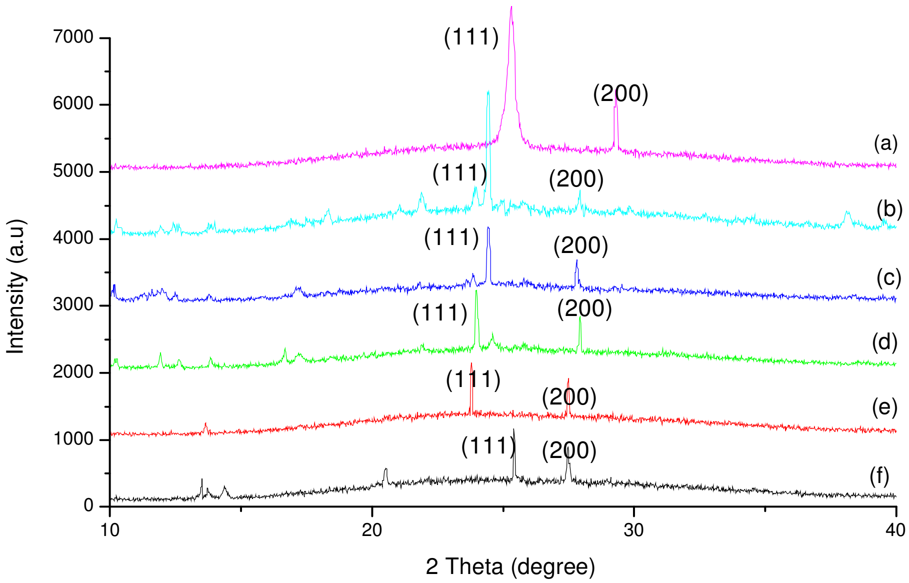

Figure 2. XRD patterns of 0.05 MCuI thin film incorporated with different volumes of TMED; (a) without TMED, (b) 0.1 mLTMED, (c) 0.2 mLTMED, (d) 0.3 mLTMED, (e) 0.4 mLTMED, (f) 0.5 mLTMED.

the volume, in which the particles' size is around 200~0.7 (d.nm). The results reveal that the size of CuI particles are going smaller or its growth is inhibited by the suitable amount of the volume of TMED. This indicates that with the existence of TMED, the particles of CuI solution are controllable within the nano size and also, it made the particles disperse well, which prevents the scale or precipitate to occur.

Figure 2 shows the XRD pattern of CuI composite thin film with and without TMED, in which a very strong and weak peak could be detected. These peaks could be assigned to the (111) and (200) planes of the face-centered-cubic structure (fcc) of CuI. The very high peak intensity of the (111) and coexistence of the (200) plane indicate that the deposited CuI incorporating TMED film is highly oriented along the (111) crystal axis perpendicular to the substrate surface (Yang and Gao, 2005). In addition, owing to the very strong (111) diffraction of CuI film, the broadened XRD pattern originating from the glass substrate could not be observed. Therefore, the prepared film is high in crystalline even at room temperature. It is noted that in this case the substrate property has minor effects on the film orientation. Highly (111) oriented film can be obtained on different substrates such as silicon and quartz by this method. The aforementioned results indicate that it is with the assistance of TMED that the deposited CuI films can be of highly oriented growth.

Evaluating the photoluminescence of this thin film should and suppose to be done since emission properties of CuI are strongly affected by the coordination environments, surface states and dopant substances (Yang and Gao, 2005). Photoluminescence spectra for CuI thin film prepared with and without TMED are shown in Figures 3 and 4. The emission spectrum of CuI thin film deposited without TMED can be seen with one peak structure at about 410 nm. From the energy point of view, the peak at 410 nm (~ 3.1 eV) is assumed to be the recombination band gap of CuI. On the other hand, the emission spectrum of CuI thin film prepared with TMED exhibited emission peak at about 583 nm (~ 2.13 eV). This shows that shifting of energy from the blue region to red region could be due to the crystalline size in this film smaller than that from CuI solution without TMED, which might also increase the population of the iodine related surface defects due to the increase of the ratio surface area [6]. By evaluating their intensity, it can be seen that the CuI thin film with TMED exhibits higher crystallinity than CuI thin film without TMED. Thus, through the re-crystallization process in acetonitrile solvent, CuI material with better crystallization could be produced. However, the intensity of CuI thin film without TMED is still low which indicates that the trapping of holes at CuI surface sites still remains the major cause of recombination for this film (Yang and Gao, 2005). Consequently, the intensity of CuI thin film with or without TMED peak increases, thereby indicating that the recombination efficiency of the optical transition has been altered.

In addition, some papers have been reported on photoluminescence of materials doped with Cu1+ and Cu2+ ions. For example, two luminescent peaks were observed at 450 and 530 nm when ZnS was doped with Cu1+ ions. Also, two luminescent peaks were observed at 500 and 540 nm when zeolites were doped with Cu1+

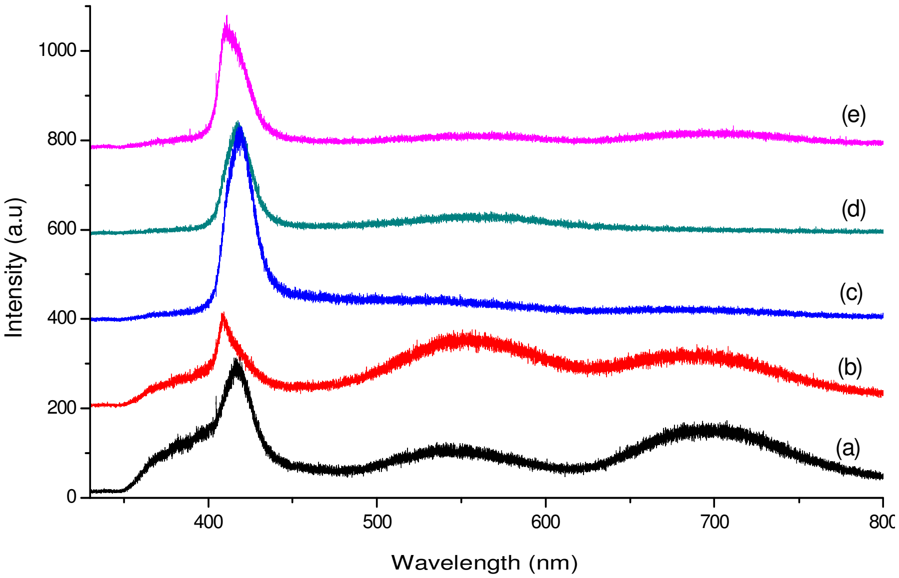

Figure 3. Photoluminescence spectra of CuI thin film without TMED; (a) 0.01 M CuI, (b) 0.02 M CuI, (c) 0.03 M CuI, (d) 0.04 M CuI and (e) 0.05 M CuI.

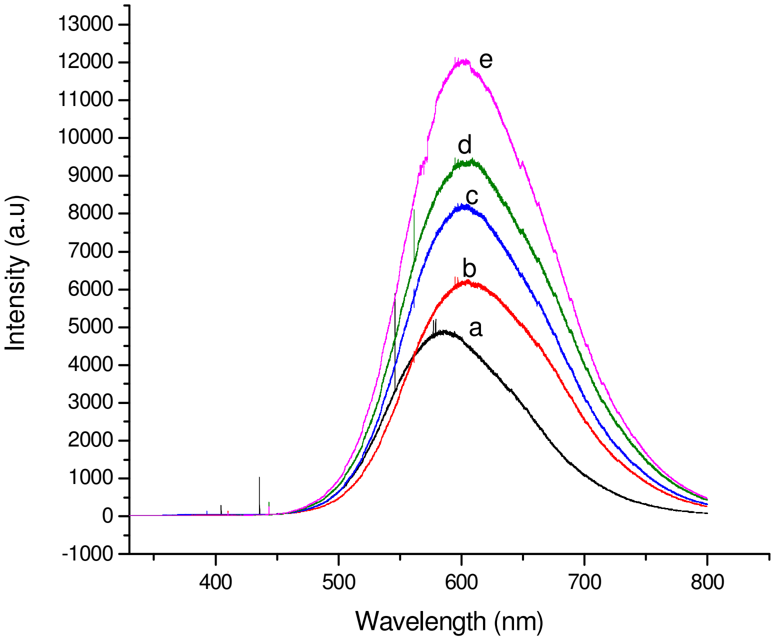

Figure 4(a). Photoluminescence spectra of 0.05 MCuI thin film incorporated with different volumes of TMED; (a) 0.1 mLTMED, (b) 0.2 mLTMED, (c) 0.3 mLTMED, (d) 0.4 mLTMED, (e) 0.5 mLTMED.

ions. This emission band is due to electron transition of Cu1+ ions shifting from 3d10 to 3d94s1 (Wei, 2010; Konno et al., 2008). Therefore, the observed luminescence peak at 583 nm for CuI film prepared with TMED is due to recombination of electron and holes at Cu1+ centers. Moreover, quenching of excited luminescence centers and repulsion of ions are the reasons for the observed shift of emission toward the longer wavelength (Sirimanne and Tributsch, 2006).

Electrical characterizations of CuI thin film with different volumes of TMED are shown in Figures 4 and 5 by different approaches. Electrical characteristics are

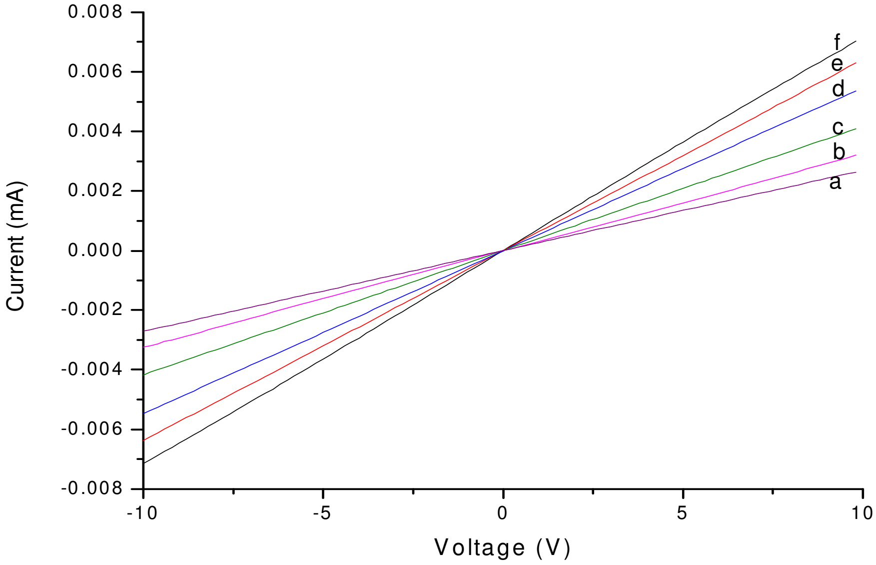

Figure 4(b). Measurement of current-voltage of 0.05 MCuI incorporated with different volumes of TMED; (a) without TMED, (b) 0.1 mLTMED, (c) 0.3 mLTMED, (d) 0.2 mLTMED, (e) 0.5 mLTMED, (f) 0.4 mLTMED.

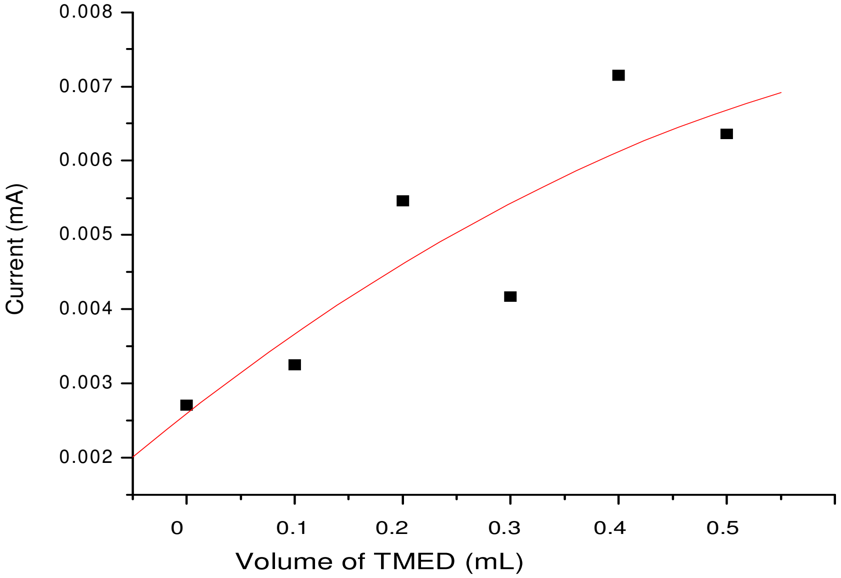

Figure 5. Comparison of conductivity (sheet resistance) with different volumes of TMED.

used to determine the resistivity and contact resistance of the CuI thin film. The results show that the produced CuI thin films have ohmic contact with the place where the current is a linear function of the voltage. It was measured using two-point probe method via platinum-plated contact at room temperature. The value taken was the average of measurements made at different locations on the film surface.

As regards the results taken for the case of the existing TMED into CuI solution, the linearity of conductivity is ruined due to some factors, such as the thicknesses and crystalline size of the thin films which vary. Also, it could be suggested that an appropriate amount of TMED should be used so that it will match with the molarities of CuI solution, which is the main factor to be considered. On the other hand, conductivity of CuI without TMED depends on the presence of iodine. However, prolonged heating will remove iodine from the film, thereby increasing the resistance.

Conclusion

In this paper, a new ligand called TMED was introduced in CuI solution dissolved with acetonitrile. At the beginning of the study, the particle size of the CuI solution was presented. In addition, excitation of electron within metal ions of solution was viewed by photoluminescence (PL) measurement. TMED is widely employed as a ligand for metal ions and it forms stable complexes with metal halides, such as copper (I) iodide, giving complexes that are soluble in organic solvents. In such complexes, TMED serves as a bidentate ligand. Based on the given results, existence of TMED in CuI solution is very much needed so that it will hopefully increase the performance of DSSC in future.

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