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Particles Size and Conductivity Study of P-Type Copper (I) Iodide (CuI) Thin Film for Solid State Dye-Sensitized Solar Cells

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Abstract Copper Iodide based dye-sensitized solar cells (DSSC) has been reported either deliver small photocurrents or highly unstable. In this research, by added in a small amount of Tetra-methyl-ethylene-diamine (TMED) into CuI sol-gel (CuI in acetonitrile), performance of electrical properties and optical properties of CuI based DSSC have been studied. Particles size and conductivity of CuI solution were measured when addition of TMED to the sol at 0.05M concentrations. Spin-coating technique has been explored to prepare nano-crystalline CuI films at room temperature. The film was examined for their surface morphology, optical and electrical properties by field emission scanning electron microscope (FESEM), ultraviolet visible spectroscopy (UV-Vis), Photoluminescence (PL) and current-voltage (I-V) measurement respectively. The results were then compared with CuI sol-gel which prepared by dissolving CuI powder with acetonitrile only. It showed some improvement to the CuI-based DSSC by incorporation of a small quantity of TMED in the solution of precursor.

1. Introduction

It is obvious that we need to find alternative sources of energy for human life when human population and energy consumption are increasing. One of alternative we have now is by approach to nature sources such as solar energy. Solar energy provides huge energy power and free, at least for the next few billion years. The challenge is to utilize it efficiently and use it on much larger scale. There are two basic attempts in manipulating solar energy for human use, first is by chemically approaching through artificial photosynthesis (converting biomass to energy) and second are solar cells (photovoltaic technology). At the moment the efficiency of solar cells are still in the stage of improving. Research for improving the solar technology is still continuing until recently an alternative approach to solar cells has been found which is known as *Dye Sensitized Solar Cells (DSSC)*.

Through his reviewed, Bin Li et al highlighted the problem of device instability when liquid electrolyte is used in DSSC. If the cell is imperfectly sealed, evaporation of electrolyte may occur and this will lead to permeation of water or oxygen molecules into the device. This will cause the performance of the cell degrade when their reaction with the electrolytes worsen. One of the way to improve the stability of DSSC is by replacing the electrolyte to solid state hole conductor. The hole conductors employed in solid-state DSSC can be classified as p-type semiconductors, ionic liquid electrolytes and polymer electrolytes.

So far, using p-type semiconductors to fabricate solid-state DSSC is the most common approach by which need to fulfill some conditions. Many of these semiconductors match several of the conditions. However, the familiar large-band gap p-type semiconductors such as SiC and GaN are not suitable for use in DSSC since the high-temperature deposition techniques for these materials will certainly degrade the dye [2]. After extensive studies, a type of inorganic p-type semiconductor based on copper compounds such as copper iodide (CuI) was found to meet all of these conditions. It is likely that this chemical compound is replacing at least part of the function of the iodide mediator electrolyte in the solar cell. A number of research groups are currently investigating p-type conductors like CuI as a possible replacement for an aqueous iodide electrolyte in DSSC.

Utilizing chelating agent to improve the efficiency of solid state dye-sensitized solar cells has been introduced by Tennakone et al using 1-methyl-3-ethyl-imidazolium thiocyanate (MEIT). However, MEIT is fairly expensive as purification involves a chromatographic separation [6]. In the following stage, he and his group had found more effective chelating agent called triethylamine hydrothiocyanate (THT) for fabrication of dye-sensitized solar cells. In both cases his claims that these chelating agents work as CuI crystal growth inhibitor where it control the crystal size of p-CuI while depositing it and at the same time can filling the pores of the nano crystalline n-type semiconductor (e.g., TiO₂, ZnO)[6]. Until present, the efficiency of DSSC with THT has been reported at about 4%.

Following to the above, this paper is to introduce another chelating agent to give an alternative for fabrication of DSSC. The chelating agent is called tetra-methyl-ethylene-diamine (TMED) and it is hope that introduced chelating agent can be worked either equally or much effective than MEIT or THT.

2. Experimental procedure

All the chemicals used in this work were as obtained from the supplies and without any further purification. CuI coating solution was produced by dissolving 0.05M CuI powder (ALDRICH 99%) in acetonitrile at room temperature. 0.5 mL of TMED (Sigma-Aldrich 99%) were added in to be work as chelating agent. The solution is stirred around three hours. The glass substrates were cleaned with acetone, followed with methanol and finally rinsed with deionizer water. All stages were put in dip ultrasonic water within 15 minutes each. The glass was pre-heated at 50°C for a while before depositing process. CuI coating solution was deposited onto glass substrates using spin coating technique (LAURELL) which produced transparent CuI thin film. Layers of the thin film are about 10 layers which produced by dripping 10 drops in each layer.

The thin films were then have been examined and analyzed by it surface morphology using ZEISS SUPRA 40VP field emission scanning electron microscope (FESEM), optical properties by UV/VIS spectrometer (PerkinElmer Lambda 750) and photoluminescence spectra by PL spectrometer (HORIBA JOBIN YVON).

3. Results and discussion

The particles size results of CuI solution with and without TMED are shown in Figure 1. Particles size measurement was conducted after 3 hours stirred of CuI solution with and without TMED. As expected, CuI solution without TMED produced well result but with TMED it produced much better outcome. The peak value without TMED is around 105 (d.nm) at about 38% of volume. However, size distribution by volume with TMED where within 47% of the volume, the particles size are around 1.5 (d.nm). Meaning, with existence of TMED the particles of CuI solution are within nano size, stable and disperse well. These results are supported with image taken by FESEM in figure 2.

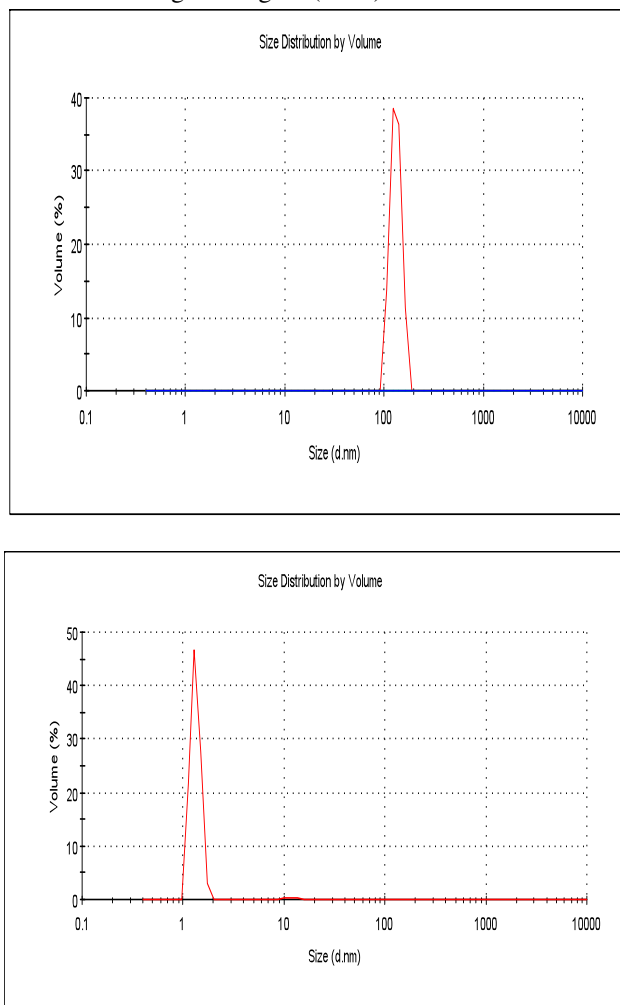


Figure 1. Particles size distribution (d.nm) in CuI solution vs. volume (%), without TMED (above) and with TMED (below).

Surface morphology of 0.05M CuI thin film without (top) and with TMED (middle & bottom) taken by FESEM are shown in figure 2. As from the results, CuI crystals shaped from images (top) can be clearly seen over a large area. This indicates that crystallization is very quick and not easily controlled. Furthermore, it forms chain like structure which forming an empty space between them. The reason of this could be dispersion among the crystal is not good enough to make them controllable and attach with each others.

As of image (middle) was deposited by using the same precursor and maintaining the same condition as in images (top) but with addition of TMED. Referring to these images, when compared with that of images (top), it is clearly that the size of CuI crystals decreases dramatically to nanometer order. No more empty space between the CuI crystals but covered with the well distributed CuI crystals. This proved that the TMED can control the size of CuI crystals and make well distribution within each others. This could be a benefit in filling the voids of TiO₂ or ZnO porous film.

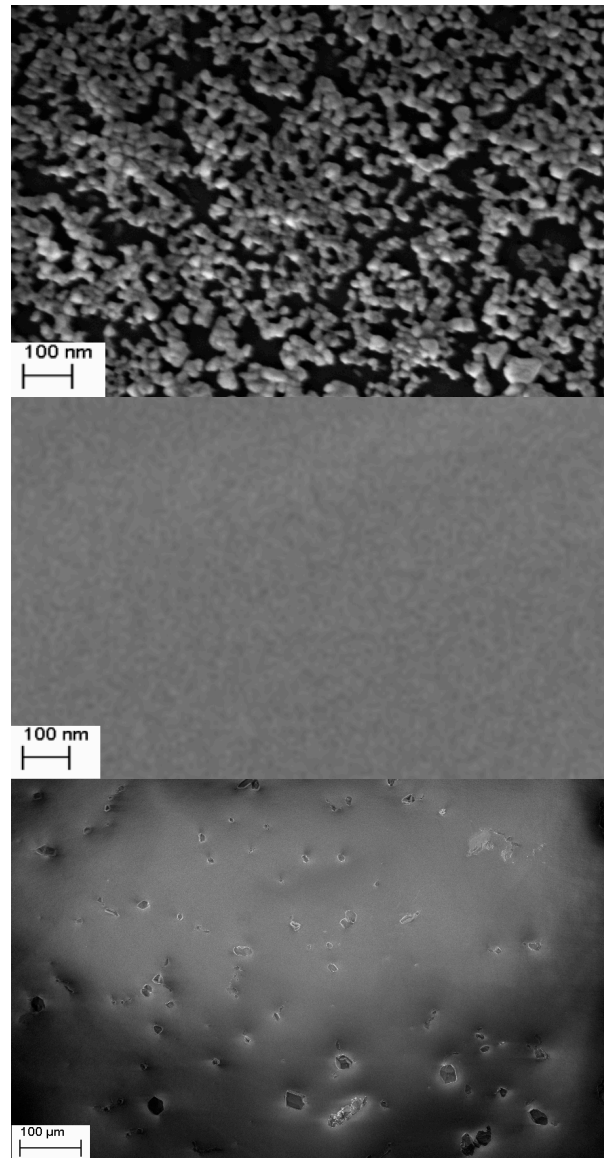


Figure 2. FESEM image of CuI thin film prepared without TMED (top) and with TMED (middle & bottom)

Also from image (bottom) which same conditions as image (middle), a soft shell (layer) can be seen on the surface of the CuI crystal. One function of this layer is to reduce direct contact between the CuI crystals and uncovered part of the dyed TiO₂ or ZnO film, therefore significantly decreasing short circuiting between them [6]. Another function of this layer is to reduce deterioration of the CuI itself [6], improving the lifetime of the solar cell.

Absorption and transmittance spectrums of the CuI thin film with and without TMED are shown in figure 3. As shown in the figure, the absorption value of CuI thin film prepared with TMED started to be seen at 350 nm which is almost close to the TUPAC plot (not shown in the text). While the absorption for CuI thin film prepared without TMED is shifted toward shorter wavelength (408 nm) region. The evaluated band gap energy for the thin film with TMED is 3.26eV and without TMED is 3.04eV. Electron transitions at higher energies than the band gap (E_g) are observed for the CuI film with TMED. The reason for this is spin-orbital splitting of the upper most valence band and sub energy levels in the conduction band [2][3]. This blue shift transition could be due to the existing of nanoparticles in the film [4]. Also the increased in absorption of CuI solution can be considered as increases in pH solution since the pH value without TMED is 3.817pH while with TMED is 10.709pH. As in general, changes in pH can affect the absorption spectrum. The effect of conductivity in form of solution also could be the reason to higher energy shift of the thin film. Before the thin film was

deposited, the conductivity of CuI solution has been taken. CuI solution without TMED measured at $1343 \mu\text{S}$ while CuI solution with TMED measured at $1510 \mu\text{S}$. The different between the two data is very obvious and excellent. The average transmittances for CuI thin film with TMED and without TMED are above 85% and 70% respectively, in the range of wavelength from 800 and 300nm.

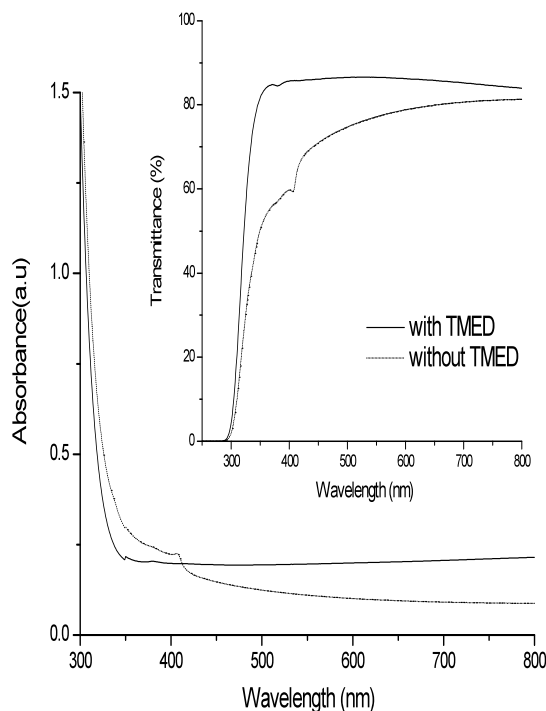


Figure 3. Optical absorption and transmittance (inside) spectrum of CuI thin film with TMED and without TMED

Photoluminescence spectra for CuI thin film prepared with and without TMED are shown in figure 4. The range of wavelength for without TMED (inside) is from 350–800nm and for with TMED is from 350–900nm. As shown in the figure, CuI thin film prepared with and without TMED exhibited different characteristics. In this work, CuI film prepared with TMED exhibited emission peak at 583 nm. Some papers have been reported on photoluminescence of materials doped with Cu^{1+} and Cu^{2+} ions. For example, two luminescent peaks were observed at 450 and 530 nm when ZnS doped with Cu^{1+} ions. Also, two luminescent peaks were observed at 500 and 540 nm when Zeolites doped with Cu^{1+} ions. This emission bands is due to electron transition of Cu^{1+} ions shifting from $3d^{10}$ to $3d^94s^1$ [2][3]. Therefore, the observed luminescence peak at 583 nm for CuI film prepared with TMED is due to recombination of electron and holes at Cu^{1+} centers, since the existing of TMED is functioning as ligand to metal ions and form stable complexes with copper (I) iodide. Moreover, quenching of excited luminescence centers and repulsion of ions are the reasons for the observed shift of emission toward the longer wavelength [2].

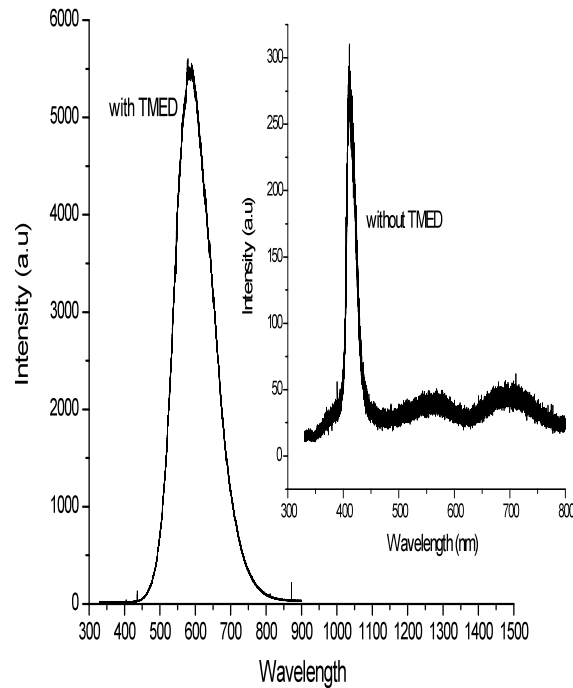


Figure 4. Photoluminescence spectrum of CuI thin film, with TMED and without TMED (inside).

Current-voltage characterization of CuI thin film is shown in Figure 4. It was measured using two-point probe method at room temperature. The value taken were the average of measurements made at different location on the film surface. It was found that the total electric conductivity of the CuI thin film with TMED increased remarkably compare to CuI thin film without TMED. This experimental results proves that the particles size effect the conductivity of the CuI thin film, which mean the smaller particles size better conductivity. This also proves CuI particles size become smaller when TMED was added into the CuI solution.

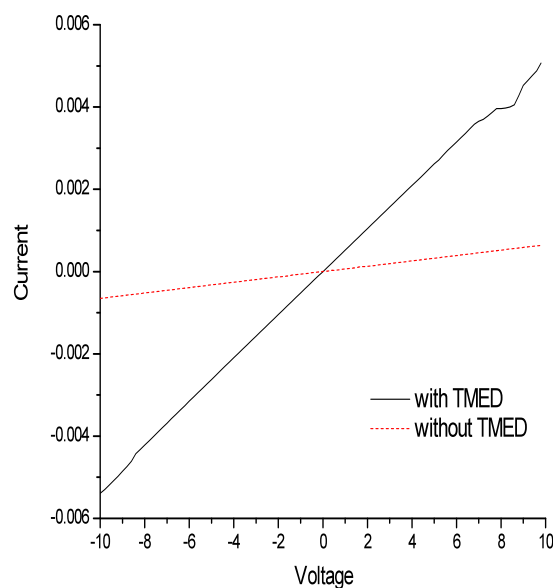


Figure 4. Current-voltage characteristics of CuI thin film with TMED and without TMED.

4. Conclusion

The characterization of highly transparent CuI thin film prepared with TMED and deposited by spin coating technique is presented. High intensity is observed for the CuI film prepared with TMED compare to that without TMED. The optical properties measurements of CuI thin film with TMED show an expansion of band gap energy. This energy shifting is due to recombination of electrons and holes in the Cu^{1+} centre. Also, energy difference between curve at 350nm and peak at 408nm in optical absorption spectra is almost cause by the spin orbit splitting. Particles size measurement, FESEM and current-voltage measurement results prove that the particles size of CuI thin film with TMED improve better than without TMED.

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