PERFORMANCE OF n-TiO₂/dye/p-CuI INCORPORATED WITH NEW CHELATING AGENT FOR SOLID STATE DYE SENSITIZED SOLAR CELL APPLICATIONS

A.R. Zainun¹,a,b, M. Ichimura²,c

¹Faculty of Electrical & Electronics Engineering, Universiti Malaysia Pahang (UMP), 26600 Pekan, Pahang, Malaysia.
²Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Nagoya 466-8555, Japan.
email: aayibrsd@yahoo.com, ayib@ump.edu.my, ichimura.masaya@nitech.ac.jp

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Abstract
A new approach to produce Cul-related composite film for dye-sensitized solar cell applications is demonstrated. This paper introduced an alternative organic chelating agent, called tetramethylethylenediamine (TMEDA), to be used as Cul crystal growth inhibitor and as an alternative to the previously used chelating agents in the fabrication of DSSCs. Investigation was conducted on the use of the proposed chelating agent in conjunction with eco-friendly p-type materials in the preparation of dye-sensitized solar cells. It is found that highly (111) oriented Cul film with improved quality could be easily prepared on FTO glass substrate using TMED. Furthermore, the TMED-chelate Cul film exhibit improved band-gap photoluminescence, indicating that TMED is a kind of reagent in inorganic synthesis that is more effective than using either 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) or triethylamine hydrothiocyanate (THT). So far, the use of TMED in Cul solution in the fabricating of solid-state DSSC has not yet been reported. Subsequently, an n-TiO₂/dye/p-Cul solid-state DSSC cell was fabricated and characterized. The chelating agent or ligand that was introduced not only controls the Cul crystal growth and acts as a protective coating for Cul nanocrystals but improves the electrical contact between Titanium dioxide (TiO₂) particles thus improving the cell performance. Current-voltage characteristics highlighted a larger conversion efficiency of fabricated samples.

Introduction
Attempts have been made to convert electrolyte-based DSSC cells to solid-state DSSC cells and p-type semiconducting materials such as spiro-OMeTAD and copper (I) iodide (Cul) have been tested as hole conductor for the cells [1-2]. Also, studies were conducted to improve the performance of the solid-state DSSCs as the device has been reported to deliver small photocurrents and are found to be unstable. However, one major restriction in the fabrication of DSSCs is to fill the pores of an n-type semiconductor TiO₂ film with a p-type semiconductor in order to establish firm and stable contacts with the dyed surface. The crucial problem that needs studying is related to the contact between dye monolayer and holes conductor as the n-type TiO₂ pores could only be partially filled with the p-type material, particularly when using thicker films [3].

To date, one well-known approach that most researchers was to employ in the fabrication of DSSC is to use Cul as holes conductor probably because it is not water-soluble, however, Cul is soluble in acetonitrile at room temperature. Its solubility in acetonitrile is attributed to the
formation of weak CuI-acetonitrile adducts whose coordination originates from a significant π bank-bonding from cuprous ion to nitrogen, as confirmed by infrared and Raman spectra investigations [4-5]. The formed CuI-acetonitrile adducts are metastable and can easily revert to Cul materials with a ligand missing, but the Cul deposited from acetonitrile solution usually consists of large cubic crystallites resulting in a film with a rough surface. Such a structure cannot form stable and firm contact with other functional materials, hence limiting its application in many optoelectronic devices [6]. Besides, Cul films prepared by evaporating the solution when exposed to light will emit radiation with higher energy than Cul band-gap causing Cul to photo-decompose and iodine is liberated; this photo-decomposition will strongly affect the stability of optical and electronic properties of the film. One example of this emission is when there is variation in the amount of iodine adsorbed on the surface the Cul film resulting in instability of the film.

Tennakone et al. has formulated and synthesized Cul thin film using 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) by incorporating ligand for DSSC [7-8], but MEISCN is rather costly to produce as the separation process during its purification involves a rigid chemical procedure. However, a more effective ligand, called triethylamine hydrothiocyanate (THT) has been identified that could be used in the fabrication of Cul for application in DSSC cells [9-10] with efficiency of approximately 3.8 %. In both cases, the function of the ligand is to suppress the expansion of Cul particles as it is able to inhibit the growth of Cul crystal size and to fill the pores of the nanocrystalline n-TiO₂ semiconductor [3].

In this paper, a novel approach to produce a new Cul-related composite film is introduced where an alternative organic chelating agent, called tetramethylethylenediamine (TMED@TMEDA), to be used as Cul crystal growth inhibitor. Subsequently an n-TiO₂/dye/p-Cul solid-state DSSC cell was fabricated and characterized. Highly efficient solid-state DSSC (TiO₂/dye/Cul) with improved efficiency was fabricated by controlling the pore-filling of the dyed porous TiO₂ layer with chelating agent capped nanosized Cul crystals. The chelating agent or ligand that was introduced not only controls the Cul crystal growth and acts as a protective coating for Cul nanocrystals but improves the electrical contact between TiO₂ particles thus improving the cell performance. The electrical characteristic of the cells shows a very good electrical rectification and photovoltaic efficiency. This shows that the performance of solid-state solar cells is very much dependent on the role of p-type materials pore-filling into TiO₂. So far, the use of TMED in Cul solution in the fabricating of solid-state DSSC has not yet been reported.

**Experimental procedure**

All the chemicals used in this research were as obtained from the suppliers and no further purification was carried out. TiO₂ films of approximately 15 µm thick were prepared using squeegee technique and Figure 1 shows the flow diagram of the process involved in the preparation and deposition of the TiO₂ thin film.

After the TiO₂ films have been prepared, the films are soaked for 24 hours in Rhodamine B dye. The preparation and deposition procedure of Cul thin films and TMED-chelate Cul thin films onto dye/TiO₂/FTO glass substrates is done using a technique of drop and leave for a while then spin coated. Figure 6.2 shows the flow diagram of the process involved in the preparation and deposition of the Cul thin film.
Results and Discussion

1  Structural Properties

In this study, the morphology of the deposited films produced after each process was investigated, including that of the TiO₂ film, and this is shown in Figure 3. In Figure 3(A), shows the morphology of TiO₂ using squeegee method; it is observed that large pores are formed on the surface of the film and the pores are assumed to also exist inside the film. Theoretically, when these pores are filled with p-type materials, the contact between the dye and p-type materials would be improved [11-12]. The deposition method employed produces films with a rough surface and the roughness of the surface influences the amount of light that is absorbed, hence affecting the efficiency of energy conversion [13]. The pores and surface roughness of TiO₂ films produces here is very much dependent on the volume of polyethylene glycol (PEG) and triton X used, and an appropriate amount of both materials is necessary to prevent the formation of heavy cracks.

The morphology of Cul film prepared without the addition of TMED is presented in Figure 3(B), and large Cul crystals are observed scattered on the deposited film indicating that the crystallization process happened very fast and is uncontrolled [3]. However, the Cul films morphology prepared with the addition of TMED, as shown in Figure 3(C), shows significant reduction in the Cul particles compared to that prepared without the use of TMED showing that TMED can control the crystallization of Cul by acting as a surfactant. From the result, the smaller Cul crystals can better fill the TiO₂ pores, hence improving the contact with the dye monolayer. Another phenomenon observed in Figure 3(C) is a fine layer covering the Cul crystal surface; the layer serves to reduce immediate contact between the unexposed dyed TiO₂ particles to the Cul crystals, thus reducing the probability of short-circuiting between them. Also, this layer helps decrease degeneration of the Cul due to aging, hence increasing the lifetime of the solar cell [3]. Figure 3(D) shows the morphology of the Cul thin film with the addition of TMED deposited on dye/TiO₂/FTO substrate. The film is a very thin layer and its surface difference can be seen compared to the TiO₂ only film shown in Figure 3(A) because the reduced Cul crystals size has penetrated deeper into the TiO₂ film, other than covering the surface of the film.

One reason for the phenomenon is that the smaller Cul crystals penetrated the pores in the TiO₂ film gradually from surface down into the film, and finally cover the top of the film. Since the adsorption of TMED in Cul film results in smaller crystals, its average size is determined by the monolayer covering the film. Again, the optimum TMED concentration required was found to be the same order of magnitude as the amount of TMED needed for monolayer coverage of µm Cul crystallites. TMED being a ligand, its residue, formed at the grain boundaries after evaporation of the solvent, spread into a thin film around the surfaces.

EDX has been performed to verify that the film is composed only of TiO₂ and Cul, and this found to be so as can be seen in spectrum 1 and spectrum 2 shown in Figures 4. The EDX revealed that the composite film has only TiO₂ and Cul except that carbon dioxide is also detected which could be from the unresolved TMED element when the film is annealed or due to contamination from the surrounding environment. Furthermore, since the Cul film is prepared from saturated solutions, all the particles will not be completely reduced. The particles that underwent incomplete process as growth inhibitor will be left on top of the film as can see in the
area of spectrum 1 while the completely reduced particles will gradually penetrate into the pores of TiO\textsubscript{2} as in spectrum 2.

Figure 5 shows the EDX measurement, simultaneously represents the SEM images, and of the cross-section of the fabricated films and it is observed that pore-filling in the TMED-chelate Cul thin films is more advanced. The large opaque areas found in cross-sectional SEM images of the TiO\textsubscript{2} layer signify good pore-filling in those areas, and the EDX measurements proved the covered area is a composite of TiO\textsubscript{2} and Cul film. Other elements that appear in the spectrum, like indium (In), are because the cross-sectional images was taken after the metal contact is deposited on top of the films. Elements like carbon dioxide and aluminum (Al) originate from unresolved TMED element after undergoing the annealing process or are contaminants from the surrounding environment.

Figure 6 shows X-ray diffraction spectra (XRD) for the TiO\textsubscript{2} film, TMED-chelate Cul film, TiO\textsubscript{2}/dye/Cul (TMED) composite film and FTO substrate. The peaks noted in the TiO\textsubscript{2} film spectra can be assigned to the TiO\textsubscript{2} anatase structure and the peaks noted in the TMED-chelate Cul film spectra can be assigned to the Cul polycrystalline γ-phase structure. In the case of TiO\textsubscript{2}/dye/Cul film spectra, other than the TiO\textsubscript{2} peaks, Cul peaks are also observed. A very strong TiO\textsubscript{2} (101) and TMED-chelate Cul (111) peaks at 2θ value around 25.5° can be seen in the composite film proving that it is TiO\textsubscript{2}/dye/Cul film.

2 Electrical Properties

The Current-Voltage (I-V) characteristics of the fabricated cells were examined using two-probe solar simulator (BUNKOH KEIKI-CEP2000) where all procedure and measurements are performed under room temperature. An array of indium (In) spots, each 1-mm in diameter, was evaporated on top of composite film as metal contact as shown in Figure 7. Also shown in the figure is the incident light, maintained at AM1.5 (100mW/cm\textsuperscript{2}) that illuminated the p-type material during the measurement.

Figure 8 is the investigated photovoltaic performance of TiO\textsubscript{2}/dye/Cul cell prepared without TMED. The characteristic values of the cell are $V_{oc} = 0.076\text{V}$, $I_{sc} = 0.026\text{ mA/cm}^2$, a fill factor $\text{FF} = 0.178$ so that the resulting energy conversion efficiency is $3.54 \times 10^{-4}\%$. For comparison purposes, the performance of TiO\textsubscript{2}/dye/Cul (TMED) solid-state device DSSC are conducted, and is shown in Figure 9. The characteristic values for Sample A are as follows: $V_{oc} = 0.536\text{V}$, $I_{sc} = 10.12\text{mA/cm}^2$, a fill factor $\text{FF} = 0.7156$, and the resulting conversion efficiency of the cell is 3.88%.

All the devices under study were annealed at 80°C of temperature. In the case of Cul films without TMED, it is suggested that the Cul crystals large size results in poor electrical contact between the TiO\textsubscript{2} porous surface and the Cul crystal, and improper filling of the pores. The very poor electrical contact decreases the transfer of holes from the dye molecules to the Cul crystal. The uneven pore-filling of the films’ void causes a lack in holes transportation in the Cul layer thus decreasing the overall efficiency of the solid-state DSSC [8].

In the case of Cul films with TMED, the Cul crystals small size together with an almost complete absence of voids in the Cul layer permits good contact between the dyed TiO\textsubscript{2} porous surface and the Cul crystals. Thus, as indicated by the increase in the short-circuit current, the
device performance is affected by the pore-filling of the TiO$_2$ by the p-Cul (TMED) crystals together with the effect of heat energy from the annealing process. From the results, it is noted that there is an increase in short-circuit current in sample with the use of TMED. This increase indicates an intensification of the charge carriers mobility which create strong electric field inside the cell and is further supported by the complete filling of the pores between the nanoparticles by the transparent holes conductor [8].

**Conclusions and summary**

This research has demonstrated the operation of Cul solution without and with the incorporation of TMED using the drop and spin coating technique to deposit the films onto dye/TiO$_2$/FTO substrate, while squeegee method was applied to fabricate the TiO$_2$ films. Rhodamine B is used as dye in the cells for the purpose of absorbing photon. Indium was evaporated on top of the films in order to characterise the cell’s electrical properties. In conclusion, highly efficient solid-state DSSC (TiO$_2$/dye/Cul) with improved efficiency was fabricated by controlling the pore-filling of the dyed porous TiO$_2$ layer with chelating agent capped nanosized Cul crystals. The chelating agent controls the Cul crystal size and protects the Cul crystals from degeneration. Looking at the electrical characteristics of the cells, a very good electrical rectification and photovoltaic efficiency is noted and this shows that the performance of solid-state solar cells is very much dependent on the role of p-type materials pore-filling into TiO$_2$. With incomplete pore-filling, the cell’s resistivity is increased causing the degradation of current densities and resulting in poor energy conversion efficiency of the cell under sunlight.

This paper has shown that TMED-chelate Cul film is a very promising new holes-conductor that can be implemented in solid-state DSSC as it produces relatively high energy conversion efficiency, and it is found photocurrent can be increased with the use of thicker TiO$_2$ film. The dye used in this study is not necessarily the best absorber to be implemented in solid-state DSSC but the results show that, when interfaced with TiO$_2$/dye/Cul, Rhodamine B can produce significant photocurrents.

However, optimization of the various stages of the Cul film’s fabrication have yet to be conducted which include parameters such as reproducibility and stability of the cell. An efficient deposition technique should be improved to produce better penetration and distribution of the p-type materials into the TiO$_2$ pores. Although good penetration and pore-filling is observed, while high energy conversion efficiency has been achieved, there is still room for further improvement in pore-filling, especially down at the lower levels of TiO$_2$ film. Also, other factors such as electrical contact between the dye and hole conductor, and filling of the TiO$_2$ pores by p-type materials need further investigation as it gives significant influence on the performance of DSSC cells. As for future work, studies should be carried out to find new techniques that can facilitate more efficient and better distribution of Cul crystals to improve the energy conversion efficiency of DSSC cells.

**References**


Mix 4.0g TiO₂ powder (P25, Aerosil Japan) + 0.5ml acetyl acetone

Stir in 2ml of pure water for 5 minutes; stir in additional 3ml of pure water for another 5 minutes

Blend the mixed materials using mortar for 20 minutes.

Add 0.4g polyethylene glycol (PEG) and blend for 5 minutes

Add 2.5ml Triton X and continue blend for 5 minutes

Blended material ready for deposition using Squeegee technique

Heat and anneal deposited thin films at 100°C for 30 minutes; repeat process at 400°C

Figure 1: Preparation and deposition process flow of TiO₂ thin films.

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<tr>
<th>1. Solution preparation (without TMED)</th>
<th>1. Solution preparation (with TMED)</th>
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<tr>
<td>Precursor: Copper (I) Iodide</td>
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<tr>
<td>Solvent: Acetonitrile</td>
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<tr>
<td>Chelating agent: Tetramethylethylenediamine (TMED)</td>
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1. Stirring the solution
   Stirring speed: 2.5 (scale); Stirring time: 3 hours

3. Deposition onto dye/TiO₂/FTO substrate
   Method: drop a few drips and let it dry in ambient temperature for 5 minutes, then spin coating.
   Instrument speed: 500 rpm
   Deposition time: 20 minutes
4. Drying
   Place in ambient temperature for 5 minutes

5. Annealing using thermal furnace
   Temperature: 80°C; Annealing Time: 10 minutes

Figure 2: Preparation and deposition process flow of Cul thin films

Figure 3: The morphology of each deposited films; (A) TiO₂ film, (B) Cul film without TMED, (C) Cul film with TMED, (D) TiO₂/dye/Cul (TMED).
Figure 4: EDX measurements on top of TiO$_2$/dye/CuI(TMED) film surface.
Figure 5: EDX measurement on the cross-section of TiO$_2$/dye/CuI (TMED) film.
Figure 6: X-ray diffraction (XRD) spectra of the FTO substrate, TiO$_2$/dye/Cul(TMED) film, TMED-chelate Cul film, and TiO$_2$ film.

Figure 7: An array of electrodes for the I-V measurement.
Figure 8: I-V characteristic of TiO$_2$/dye/CuI film without TMED.

Figure 9: I-V characteristic of TiO$_2$/dye/CuI film with TMED.