Modification of CuI based Hole Transport Material for Solid State DSSC Application

Q A Hanif1, A H Ramelan2, I N M Z Saputri1, and S Wahyuningsih1*
1Inorganic Material Research Group, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Ir. Sutami street 36A, Surakarta Indonesia
2Electronic Materials and Energy, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Ir. Sutami street 36A, Surakarta Indonesia

Email: sayekti@mipa.uns.ac.id

Abstract. Modification of Hole Transport Material (HTM) with addition of tetramethylethylenediamine (TMED) and ammonium thiocyanate (NH4SCN) have been conducted. Copper Iodide (CuI) were used as the main component of HTM. Several volume variations of TMED (0.1; 0.2; and 0.4 mL) was added into 0.05 M CuI solutions. While TMED: NH4SCN ratio were 1:1,1:2,2:1 also introduced to the dissolved CuI. Optical properties of these materials showed the band gap energy value ranging from 2.38 to 3.79 eV. The conductivity of HTM has been measured and showed the maximum value in CuI added with 0.4 mL TMED = 0.29 S m⁻¹, and ratio of TMED: NH4SCN=2:1 added into CuI = 0.39 S m⁻¹, these value were increased compared to the CuI conductivity itself (0.26 S m⁻¹). The effect of this modification towards SS DSSC efficiency also has been monitored. The SS DSSC construction consists of TiO2 nanorods sensitized by N3, HTM, and platinum as a counter electrode. The performance of SS DSSC showed rising efficiency as follows TiO2|N3|CuI<CuI-TMED<CuI-TMED: NH4SCN|Pt. The highest conversion was increased 3.28 times when CuI-TMED: NH4SCN used as a HTM. Therefore, both TMED and NH4SCN incorporated with CuI be able to improve the electrical properties in SS DSSC system.

1. Introduction

Global energy demands is increased in the last past years. Its increase predicted will occur to a couple years ahead because the dependence of many sectors towards energy. Transportation, industrial, residential, and commercial sectors contribute to the high energy consumption [1]. Until now, the most utilized energy, comes from unrenewable energy fossil fuel. Therefore, the study of renewable energy is the interesting field topic to be concern about. One of massive renewable energy source is sun/ solar. Silicon solar cell as a device to convert solar energy to electrical energy was commercially producing. Despite the relatively high efficiency, the synthesis of this material requires a high purity of Si that lead to high cost fabrication [2]. Another type of solar cell device pioneered by O’Regan B and Grätzel is Dye Sensitized Solar Cell (DSSC). Compared to the silicon solar cell, DSSC is relatively low cost, less toxic, easy in fabrication, good performance, doesn’t require very high purity of material, and environmentally friendly [3,4]. Typically, DSSC consists of 1) photoanode, TiO2 is commonly used, 2) complex compound as dye usually ruthenium based complex, 3) liquid electrolyte I⁻/ I₃⁻, and 4) cathode or counter electrode [4]. Photovoltaic performance of DSSC containing protonated N3 complex as

* To whom any correspondence should be addressed.
sensitizer yielding efficiency 11.18% [5]. Unfortunately, DSSC shows several drawbacks such as corrosion, photoreactive, dye desorption, evaporation, and leakage of solvent while using liquid I/ I3 as electrolyte, thus lead to changing to quasi solid and solid state DSSC [6,7]. Replacement of liquid electrolyte with inorganic hole transport material was investigated by Tennakone and coworkers with copper iodide (CuI) [8]. CuI more promising for HTM compared to CuSCN [9], since it difficult to be dissolved [10] and CuBr [11]. However, CuI remains unstable and to obtain fulfilled area with CuI is not easy because its rapid crystallization leaves porous surface thus giving only few contact interface [12]. Chelating agent compounds such as 1-methyl-3-ethyl-imidazolium thiocyanate (MEIT) [14] and triethylamine hydrothiocyanate (THT) could improve the efficiency of SS DSSC [15]. Another research shown that interaction CuI with functional groups from dye also supports for the better performance [16]. Because of the fairly expensive of MEIT, Zainun et al. add tetramethylethylenediamine (TMED) into CuI. TMED addition prevents CuI from fast crystallization, filling pores, yielding well covered layer [17]. Nevertheless, the effect of TMED and NH4SCN addition to performance of SS DSSC haven’t been studied.

2. Experimental

2.1. Synthesis of CuI and its Modification TMED
The synthesis of CuI was conducted according to reference [9], with minor addition procedure. Copper iodide 0.19 gram was then dissolved in 20 mL acetonitrile. The TMED (Sigma Aldrich, 96%) was added into this 0.05 M CuI. The addition of TMED was varied in three different volumes of 0.1, 0.2, and 0.4 mL. The mixture was then stirred in 3 hours, yield CuI-TMED.

2.2. Modification of CuI-TMED with NH4SCN
The first step of this modification was conducted similar with modification with TMED, but we only used same volume addition (0.4 mL). NH4SCN (Merck) 1.5 gram was dissolved in 20 mL acetonitrile. Then the CuI-TMED was added by NH4SCN in ratio of 1:2,1:1, and 2:1 (TMED: NH4SCN) (v/v). All solution after modification were characterized with uv vis spectrophotometer (Perkin Elmer Lambda 25), Fourier Transform Infra-Red (FTIR, Prestige-21 Shimadzu type 8201PC, KBr pellet), I V measurements (El Kahfi 100, Cu electrode) and Scanning Electron Microscopy (SEM, Quanta 250).

2.3. Application in SS DSSC
Each CuI, CuI-TMED, and CuI-TMED: NH4SCN compound was utilized in SS DSSC system as a HTM. SS DSSC in this test consists of TiO2 nanorods as working electrode [18], platinum (Brataco) as counter electrode (Sigma Aldrich) each coated in separate Fluorine doped Tin Oxide (FTO) (dyesol), dye N3 complex (N3=cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'dicarboxylato ruthenium (II)) (Sigma Aldrich), and HTM. FTO containing sensitized TiO2 was added with HTM via drop coating method in 80 °C. I V measurement of SS DSSC was conducted with I V Keithley 2602 System source.

3. Results and Discussion

3.1. Optical Properties of CuI and Modified CuI
The spectra of CuI with and without TMED shows different profile. CuI itself has no absorption peak in visible area, similar with previous result [19]. The shifting peak in UV ranged (200-300 nm) to the lower wavenumber or higher energy may the cause of the complexation between inorganic compound (Cu+) and bidentate ligand TMED [20]. TMED as chelating agent for CuI, contributes to the broad absorption in visible area (550-800 nm), and its intensity increase while increasing amount of TMED was added. Not only TMED, but NH4SCN also shown higher absorption at visible range, depicted in Figure 1.

The energy band gap was calculated with Kubelka-Munk equation [21]. According to Beranek and Kisch [22], CuI likely to have direct band gap, so the n value is 0.5. Energy band gap of CuI, CuI-TMED
0.4 mL addition, and CuI-TMED: NH₄SCN 2:1 are 3.79, 3.63, 3.55 eV, respectively. The utilization of smaller band gap, relates to the better conductivity and electrical property [23].

![Graph](image)

**Figure 1.** UV Vis absorption spectra of CuI and modified CuI

### 3.2. Infra-Red Spectra

FTIR spectrum with specific atomic bond signal of CuI, TMED, and NH₄SCN can be seen in Figure 2. The broad peak between 3400-3100 cm⁻¹ in NH₄SCN represent N-H or amine bond [24]. This peak was changed into hydrogen bonding characteristic after mixed with TMED, shown from a broaden peak in the same area. The transformation into hydrogen bonding may occur due to the effect of interaction between hydrogen atom from NH₄SCN with lone pair electron in nitrogen from TMED. The interaction causes extending distance between hydrogen and nitrogen in NH₄SCN. Besides that, hydrogen atom attracted by nitrogen yielding closer distance, thus hydrogen bond rather dominates than amine bond.

![Graph](image)

**Figure 2.** IR Spectra of a) TMED, b) NH₄SCN, c) TMED: NH₄SCN, d) CuI, e) CuI-TMED: NH₄SCN

The intensity of SCN⁻ group in frequency of 2050 cm⁻¹ decreased after it mixed together with TMED and CuI. It indicates that other functional group from each compounds and metal Cu influence the SCN⁻
nature. Furthermore, it is also possible for SCN\textsuperscript{−} act as counter ion for Cu\textsuperscript{+} beside I\textsuperscript{−}. Because there are two peaks reveal in 461.97 and 428.22 cm\textsuperscript{-1} in e) spectrum, represent interaction of C and I. The decrease intensity also found in 1036.78 cm\textsuperscript{-1} as C-N signal [24]. The interaction of Cu\textsuperscript{+} with nitrogen from both TMED and NH\textsubscript{4}SCN may the cause of its decrease.

From the FTIR characterization, we assumed that the interaction between CuI and TMED is dominates in the coordination bonding between Cu\textsuperscript{+} and lone pair electron from nitrogen in TMED then form complex compound. When NH\textsubscript{4}SCN introduced to CuI-TMED, it has many probabilities of interaction. Ion SCN\textsuperscript{−} can play role whether as counter ion of Cu\textsuperscript{+} or another ligand source beside TMED.

3.3. Surface Morphology

Figure 3 is the morphology of HTM observed with SEM instrument. In the absence of TMED, CuI apparently cannot fulfill all of the surface because the existence of porous in some area. After addition of TMED, there is no porous have been found. The reaction between CuI and bidentate ligand TMED yield complex compound that lead to formation of agglomerates as can be seen in the Fig. 2b. Crystallization of CuI, happened spontaneously in a short time. The chain in crystallite binding leaves empty porous which not good for SS DSSC application. Addition of TMED could prevent CuI from rapid crystallization and facilitate pores filling [17]. The incorporation of NH\textsubscript{4}SCN into CuI-TMED prevents the large agglomeration of CuI-TMED. Therefore, relatively more distributed materials in the surface layer, smaller size aggregates, and no porosity was obtained.

![Figure 3](image)

**Figure 3.** Morphology of CuI a) pretreatment 1000x magnification, b) after addition of TMED, and c) TMED: NH\textsubscript{4}SCN 100x magnification

3.4. The Conductivity of HTM

The result of conductivity of all HTM measured with I V el kahfi depicted in Figure 4. It may conclude that the better conductivity achieved when 0.4 mL TMED added (0.29 Sm\textsuperscript{-1}), also the incorporation of NH\textsubscript{4}SCN in 2:1 ratio (TMED: NH\textsubscript{4}SCN) perform maximum conductivity (0.39 Sm\textsuperscript{-1}). This result is an agreement with the previous research, stated that both conductivity and photoenergy conversion were greatly improved with the addition of thiocyanate salt [25].
Figure 4. The conductivity value of A) CuI, B) CuI-TMED 0.1 mL, C) CuI-TMED 0.2 mL, D) CuI-TMED 0.4 mL, E) CuI-TMED: NH₄SCN (1:1), F) CuI-TMED: NH₄SCN (1:2), G) CuI-TMED: NH₄SCN (2:1)

3.5. The Electrical Properties of SS DSSC

The result of I V measurement of SS DSSC conducted with Keithley is present in Table 1. The decrease of open circuit voltage as well as short circuit current is followed by the increase of conversion efficiency. The highest absorption capability, smallest band gap energy, highest conductivity, are contribute to the highest photoenergy conversion of CuI-TMED: NH₄SCN compared to other HTM. Both TMED and NH₄SCN provide intense interactions, that prevent CuI from fast crystallization, have an impact in pore filling, thus be able to improved conductivity, and photoenergy efficiency [13, 17].

| HTM                | Voc (V) | Isc (10⁻³ mA) | η (10⁻³ %) |
|--------------------|---------|---------------|------------|
| CuI               | 0.70    | 8.37          | 0.46       |
| CuI-TMED           | 0.67    | 8.35          | 0.90       |
| CuI-TMED: NH₄SCN   | 0.52    | 5.33          | 1.52       |

4. Conclusion

TMED compound introduced to the CuI solution, influence the optical characteristic which is shown from broaden absorption spectrum into visible area. The conductivity of the material was increased after addition of TMED due to the interaction that occur between these two compounds and the change of its optical characteristic. The addition of NH₄SCN into mixture CuI-TMED also be able to improve both optical characteristics and conductivity. The electrical properties of all HTM together in SS DSSC system with the use of TiO₂ as photoanode, N₃ as dye, and platinum as counter electrode was monitored. The highest efficiency was achieved when HTM CuI-TMED: NH₄SCN utilized. Its efficiency value was increased 3.28 higher compared to the control CuI. The addition of organic compound (TMED) and thiocyanate salt (NH₄SCN) not only lead to better electrical properties, but also prevent the CuI deterioration which affects to the stabilization of SS DSSC system.
Acknowledgment
Authors express gratitude for The Ministry of Research Technology and Directorate General of Higher Education (KEMENRISTEK DIKTI), Indonesia for support this research in financial, through Hibah Mandatory Project.

References
[1] Diefendorfer J R, Conti J J, Paul D, James R, Napolitano S A, Michael A, Turnure J T, and Westfall L D 2015 The Annual Energy Outlook 2015
[2] Tobías I, Canizo C, and Alonso J 2003 Handbook of Photovoltaic Science and Engineering: Crystalline Silicon Solar Cells and Modules New York John Wiley & Sons
[3] O’Regan B and Grätzel M 1991 Nature 353 737-740
[4] Grätzel M 2006 C. R. Chim. 9 578-583
[5] Yum J H, Chen P, Grätzel M, and Nazeeruddin M K 2008 Chem. Sus. Chem. 1 699-707
[6] Yanagida S, Yu Y H, and Manseki K, 2009 Acc. Chem. Res. 42 1827-1838
[7] Olson C, Veldman D, Bakker K, and Lenzmann F 2011 Int. J. Photoenergy Article ID 513089
[8] Tennakone K, Kumara G R R A, Kumarsininghe A R, Wijayantha K G U, and Sirimanne P M 1995 Semicond. Sci. Technol. 10 1689-1693
[9] Tennakone K, Kumara G R R A, Kottegoda I R M, Perera V P S, Aponsu G M L P, and Wijayantha K G U 1998 Sol. Energ. Mat. Sol. Cells 55 283-289
[10] Zhenzhen Y, Katherine C P, Jia L D, Yang R, and Tao X 2011 J. Renew. Sustain. Ener. 3 Article ID 063101
[11] Li B, Wang L, Kang B, Wang P, and Qiu Y 2006 Sol. Energ. Mat. Sol. Cells 90 549-573
[12] Kumara G R R A, Konno A, Senadeera G K R, Jayaweera P V V, Silva D B R A D, and Tennakone K 2001 Sol. Energ. Mat. Sol. Cells 69 195-199
[13] Sakamoto H, Igarashi S, Niume K, and Nagai M 2011 Org. Electron. 12 1247-1252
[14] Kumara G R R A, Konno A, Shiratsuchi K, Tsukahara J, and Tennakone K 2002a Chem. Mater. 14(3) 954-955
[15] Kumara G R R A, Kaneko S, Okuya M, and Tennakone, K 2002b Langmuir 18 10493-10495
[16] Sakamoto H, Igarashi S, Uchida M, Niume K, and Nagai M 2012 Org. Electron. 13 514-518
[17] Zainun R, Mamat M H, Noor U M, and Rusop M 2013 Adv. Mater. Res. 667 447-451
[18] S Wahyuningsih, Ramelan A H, and Saputri I. N M Z 2017 J. Phys. Conf. Ser. 75 012002 1-6
[19] Johan M R, Siwen K, Hawari N, Azri N, and Aznan K 2012 Int. J. Electrochem. Sci. 7 4942-4950
[20] Zainun R, Rusop M, and Noor U M 2010 Electrical and Optical Properties of Nanostructured Copper(I) Iodide (CuI) Incorporate with Ligand Agent for DSSC New Jersey IEEE Publisher
[21] Gaya U I 2014 Heterogeneous Photocatalysis Using Inorganic Semiconductor Solids New York Springer Dordrecht Heidelberg
[22] Beranek R and Kisch H 2008 Angew. Chem. Int. Ed. 47 1320-1322
[23] Amalina M N, Rasheid N A, and Rusop M 2012 J. Nanomater. 1-6
[24] Stuart B 2004 Infrared Spectroscopy: Fundamentals and Applications Chichester John Wiley & Sons
[25] Konno A, Kitagawa T, and Kida H 2005 Curr. Appl. Phys. 5 149-151