Development of a Low-Cost TiO_2/CuO/Cu Solar Cell by using Combined Spraying and Electroplating Method

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Abstract. A simple method is proposed to develop a low-cost TiO_2/CuO/Cu based solar cell. The cell is made by employing a lower grade (technical grade) of TiO_2 as the active material. CuO powder is synthesized using a wet chemical method and mixed with TiO_2 powder to give impurity to the TiO_2. A layer of TiO_2/CuO is then deposited onto fluorin-doped tin oxide (FTO) by spraying. Copper particles are grown on the spaces between the TiO_2 and/or CuO particles by electroplating for more feasible electron migration. The TiO_2/CuO/Cu solar cell is finalized by sandwiching a polymer electrolyte between the film and the counter electrode. Current-voltage measurement was performed for various parameters, such as the molarity of NaOH for producing CuO particles, the weight ratio of CuO over TiO_2, and the current in the electroplating process. A highest efficiency of 1.40% and a fill factor of 0.37 were achieved by using this combined spray and electroplating method.

Keywords: *Copper particles; CuO; electroplating; solar cell; spraying;* TiO_2.

1 Introduction

Titanium dioxide (TiO_2) is widely used as a primary material for many purposes, for example as for a photocatalyst, as a color pigment in paint, for solar cells, etc. [1-3]. The advantage of TiO_2 is that it is a non-toxic and low-cost material [4]. In dye-sensitized solar cells (DSSC), where electrons are generated by the dye after being illuminated by light, TiO_2 is commonly used as electron transporting medium. A highest efficiency of 11% in DSSC employing TiO_2 has been reported by O'Regan and Grätzel [5]. However, the use of TiO_2 as a light harvesting material has rarely been reported. There are only a few papers about solar cells that use TiO_2 as electron-producing medium, among

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which Rahman, *et al.* [6] and Zainun, *et al.* [7]. However, they reported the resulting efficiency as being too small [6,7].

Our preliminary paper [8] reports a highest efficiency result of 0.35% and 1.24% in a solar cell using TiO_2 as a light-harvesting media before and after NaOH post-treatment respectively. The structure of the cell was a multilayer sandwich containing a fluorin-doped tin oxide (FTO), a layer of TiO_2 particles inserted by copper metal particles, a polymer electrolyte, and an aluminum counter electrode. The layer of TiO_2 was made by spraying and the copper particles were deposited on the spaces between the TiO_2 particles by electroplating. In that work, an aqueous solution of copper(II) nitrate trihydrate was added to the TiO_2 suspension prior to the spraying process [8]. Unfortunately, this addition caused the final TiO_2 suspension to be too viscous, so it was very difficult to spray.

In the present work, a low-cost TiO_2/CuO/Cu solar cell was developed with a similar structure to the one from our previous paper [8]. The solar cell is based on the use of a low-grade/low-cost TiO_2 powder as the primary material and a simple production method. This method consists of a number of steps: spraying of a TiO_2-CuO suspension onto the FTO's surface; depositing of copper particles by electroplating; adhesion of the polymer electrolyte; and fixing of the counter electrode. To avoid difficulties in the spraying process [8,9], we did not use copper(II) nitrate trihydrate liquid but CuO particles, which were synthesized by a wet chemical method [10]. The presence of CuO, which is a p-type semiconductor and has a narrow bandgap (1.2 eV), in the TiO_2 layer is expected to improve the absorbance level of the TiO_2. Meanwhile, the insertion of copper particles using electroplating was still used in an attempt to improve the electron transport in the TiO_2/CuO layer.

2 Materials and Experiment

FTO from Solaronix (Switzerland) and LiOH from Kanto (Japan) were used. A technical grade of TiO_2 anatase, alcohol 70%, aquadest, polyvinyl alcohol (PVA), copper(II) sulphate ($CuSO_4$), aluminum, and copper(II) nitrate ($Cu(NO_3)_2$) were obtained from Bratachem (Indonesia).

Firstly, CuO particles were prepared from 0.2 M of copper(II) nitrate ($Cu(NO_3)_2$) using the simple wet chemical method from [10] with the help of sodium hydroxide (NaOH). The concentration of NaOH was varied (0.5, 0.75, 1.0 and 1.5 M) in different experiments. A 1 x 1 cm^2 active area of FTO substrate was cleaned by immersion in distilled water for 20 minutes and in alcohol for 40 minutes respectively by using an ultrasonic bath (Branson 1510). The TiO_2 suspension was prepared by mixing 5 grams of TiO_2 and CuO powder in 20 ml of distilled water. The mixture was stirred using a magnetic stirrer so it was dispersed evenly. TiO_2/CuO was deposited onto the surface of the FTO by spraying at a pressure of 120 psi. The FTO/TiO_2/CuO film was then heated on a hot plate at a temperature of 200 °C for 10 minutes and in a furnace at 450 °C for 30 minutes.

To grow copper particles on the spaces between the TiO_2/CuO particles, the electroplating process from [8,9] was employed, but this method was further explored by using an alternative source, i.e. a current source instead of a voltage source. Also, a polymer electrolyte was used consisting of PVA and LiOH as reported by Saehana, *et al.* [9]. Prototype solar cells were produced by sandwiching the FTO/TiO_2/CuO/Cu film, a polymer electrolyte and an aluminum counter electrode. Finally, to improve the contact between the counter electrode, the electrolyte and the film, NaOH post-treatment was used [8].

To observe the morphology and the elemental composition of the CuO or TiO_2/CuO/Cu film, scanning electron microscopy (SEM) (JEOL-JSM 6360LA) and energy-dispersive X-ray spectroscopy (EDS) were used, respectively. An X-ray diffractometer (XRD, PW 1710) was also used to ensure that CuO and Cu particles were formed. Finally, an IV meter (Keithley 617) was used to obtain the current-voltage (IV) characterization of the solar cells. During measurement, the solar cell sample was illuminated under the light of a halogen lamp. Using a solar power meter (Tenmars TM206), the light intensity on the sample was measured to be 120 W/m^2.

3 Result and Discussion

The morphology of the CuO particles prepared by the simple wet chemical method was investigated by SEM characterization (Figure 1). Figures 1(a), 1(b) and 1(c) are SEM images of the CuO particles made with the addition of 1.0 M, 0.75 M and 0.5 M concentrate of NaOH solution to the copper nitrate solution after annealing, respectively. The addition of NaOH is an important parameter to avoid the presence of NO_2 in producing CuO from $Cu(NO_3)_2$. As can be seen from the SEM images (Figure 1), the morphology of the particles reveals seed-like structures. These results are in agreement with those reported by Singh and Srivastava [10].

The concentration of NaOH influences the purity of the CuO particles, as was observed by EDS characterization. The results of the EDS characterization are summarized in Table 1. As can be seen in Table 1, the CuO particles prepared with the aid of 0.75 M NaOH had the highest purity.

Table 1 Composition of precipitate (based on EDS characterization).

Concentrate of NaOH (M)	Composition (%wt)					
	Na	N	C	O	Cu	CuO
0.5	17.90	28.10	7.14	14.40	32.45	40.62
0.75	-	-	6.12	18.88	75.00	93.88
1.0	-	-	9.35	18.5	72.15	91.04
1.5	-	-	12.88	17.52	69.60	87.12

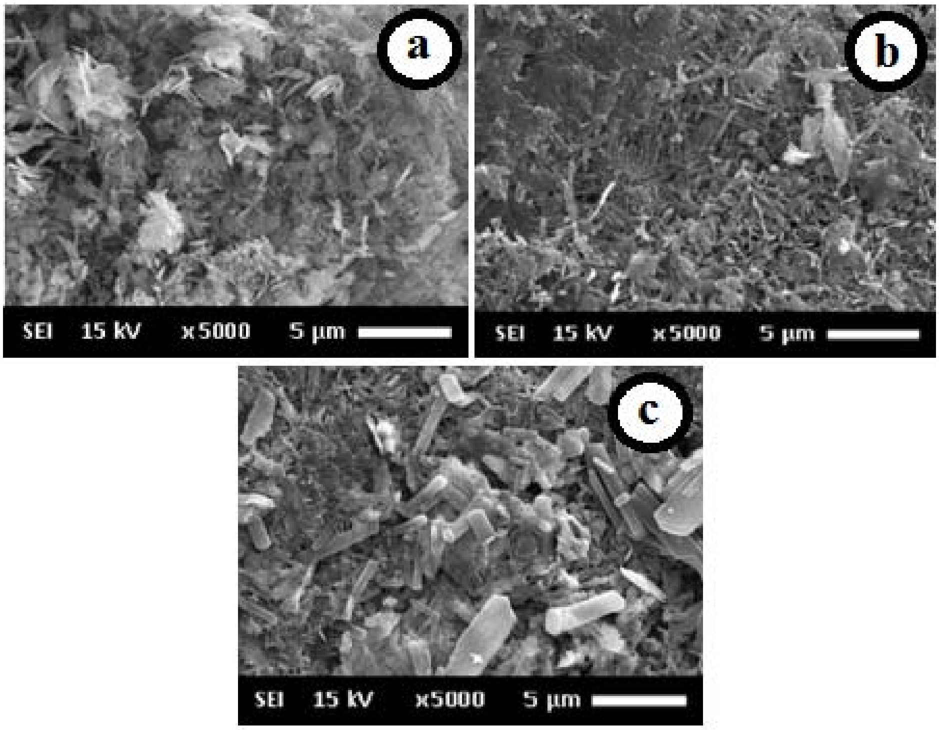

Figure 1 SEM image of CuO particles (precipitate) prepared by a simple wet chemical method using (a) 1.0 M NaOH, (b) 0.75 M NaOH, and (b) 0.5 M NaOH.

Subsequently, the performance of the TiO_2/CuO solar cells was observed through current-voltage characterization. The result of current-voltage characterization with the concentrate of NaOH as the parameter can be seen in Table 2. In general, it can be seen that adding CuO particles on the TiO_2 film can improve the efficiency of the cell. The solar cell produced with the use of NaOH 0.75 M generated an efficiency of 0.14% with a fill factor of 0.37 (see Table 2). This is an enhancement of about 70 times compared to the solar cell using pure TiO_2 (solar cell A in Table 2). If we look at the results of the EDS characterization, the highest efficiency was obtained with an NaOH concentration of 0.75 M, while at this concentration the highest purity of CuO was obtained (see Table 1).

This indicates that the addition of impurity to the TiO_2 film using CuO particles enhanced the performance of the solar cells. These results are in accordance with Perazolli, *et al.* [11]. They state that the combination of CuO and TiO_2 can broaden the absorption spectra of visible light [11], so that the solar cell is able to better absorb light. After illumination, electrons on the TiO_2 surface that have been excited will flow to the CuO particles that have a smaller bandgap. The presence of materials with a smaller bandgap may reduce the recombination of electrons and holes in the TiO_2 layer.

Table 2 Performances of TiO_2/CuO solar cells with NaOH concentrate as the parameter.

Solar cell	Concentrate of NaOH (M)	Isc (mA)	Voc (V)	FF	Efficiency (%)
A	-	0.008	0.13	0.20	0.002
B	0.5	0.065	0.61	0.37	0.08
C	0.75	0.102	0.62	0.37	0.14
D	1.0	0.091	0.63	0.38	0.12
E	1.5	0.084	0.60	0.35	0.09

The performances of the TiO_2/CuO solar cells under illumination in a variety of weight ratios of CuO over TiO_2 is shown in Table 3. It can be seen that the performance of the cells increased as the weight ratio of CuO fraction increased from 0 to 1.8 %wt. However, it decreased again after the weight ratio of CuO was more than 1.8 %wt. This indicates that 1.8 %wt is the optimum weight ratio of CuO with a highest efficiency of 0.17% and a fill factor of 0.37 (denoted by solar cell C3 in Table 3).

Table 3 Performances of TiO_2/CuO solar cells in a variety of weight ratios of CuO as the parameter.

Solar cell	Weight ratio of CuO (%)	Isc (mA)	Voc (V)	FF	Efficiency (%)
C1	1,2	0.069	0.60	0.34	0.08
C2	1,5	0.102	0.62	0.37	0.14
C3	1,8	0.192	0.62	0.37	0.17
C4	2,1	0.091	0.63	0.35	0.11
C5	2,4	0.048	0.61	0.32	0.06

Addition of CuO to TiO_2 over 1.8 %wt will reduce the performance of the cell. In this case, too much CuO impurities can inhibit the TiO_2 as the main active layer from absorbing the light. Increasing the CuO content causes the TiO_2 content as the active layer supplying electrons to be reduced, so that the performance of the solar cells will decrease again [8]. In addition, the presence of excessive dopant (in this case: CuO) is thought to provide a new recombination center for electrons that have been produced by TiO_2 layers to recombine indirectly with holes in the CuO valence band. This is in accordance with the statement reported by Yin, *et al.* [12] that the addition of excessive dopant may provide a trap or a new recombination center.

So far, it can be concluded that by adding CuO particles to the TiO_2 film will enhance the performance of the solar cell due to improvement of the light capturing ability of the TiO_2/CuO. On the other hand, we also want to increase the performance of the cell by improving its electron transport ability. To increase the electron transport ability of the cell, copper metal particles were inserted into the TiO_2/CuO film (in this case, TiO_2/CuO film as in solar cell C1 was used) by electroplating. Different sources were used as electroplating source. The performances of the TiO_2/CuO/Cu solar cells with the electroplating source as a parameter are shown in Table 4.

Table 4 Performances of TiO_2/CuO/Cu solar cells with electroplating source as a parameter.

Solar cell	Isc (mA)	Voc (V)	FF	Efficiency (%)
C31	0.442	0.64	0.37	1.31
C32	0.324	0.60	0.35	0.92
C33	0.565	0.65	0.37	1.40
C34	0.210	0.61	0.32	0.68

Table 4 represents the performances of the TiO_2/CuO/Cu solar cells under illumination. The electric source for electroplating was taken as a parameter and the time of electroplating was kept at 20 seconds. C31 is a solar cell with copper particles grown on the TiO_2/CuO film by using electroplating with a voltage source of 5 V, while for C32, C33, and C34 it was done with a current source of 1 mA, 10 mA, and 50 mA, respectively. The highest efficiency (for cell C33) was 1.40% with a fill factor of 0.37. This result is higher than that reported in our previous paper [8]. This indicates that the structure of a TiO_2/CuO/Cu solar cell is better than of a TiO_2/Cu cell. This result can also be considered high compared to those reported in previous papers [7,13,14,15]. Saehana and Muslimin [13] reported that the highest efficiency was only 1.05% with a similar cell structure. Zainun, *et al.* [7] reported the highest short circuit current and open circuit voltage as 0.0031 mA and 0.47 V, respectively. Moreover, Li, *et al.* [14] reported a highest efficiency of only 0.01% and a fill factor of 0.27. In addition, our efficiency result is also higher than the older results reported by Rahman, *et al.* [15] with a similar cell structure.

The increased efficiency of the solar cell after insertion of copper particles is in line with the result reported by Rokhmat, *et al*. in [16]. They state that the presence of copper particles (Cu) can improve the process of transporting electrons to the main electrode, thereby reducing the recombination between electrons and holes [16]. Basically, the insertion of copper particles in the space between the TiO_2 particles provides more paths for the electrons to migrate to the FTO by Cu-TiO_2 contact. Electrons will move more easily toward the FTO with thermionic processes due to the Schottky barrier on the metal-semiconductor junction (TiO_2-Cu) [9,16].

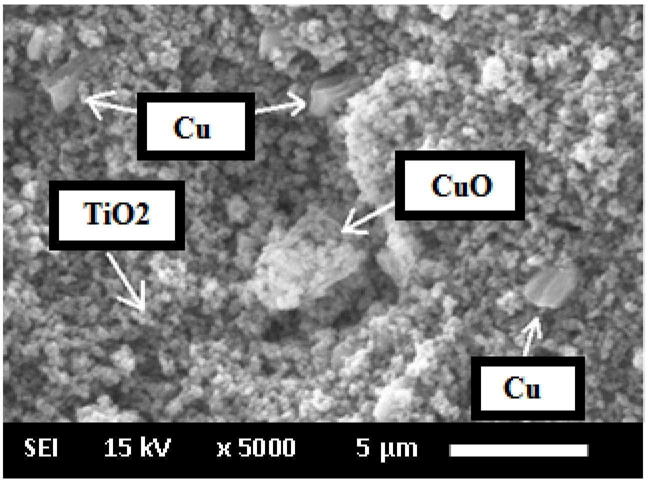

Figure 2 SEM image of TiO_2/CuO/Cu film.

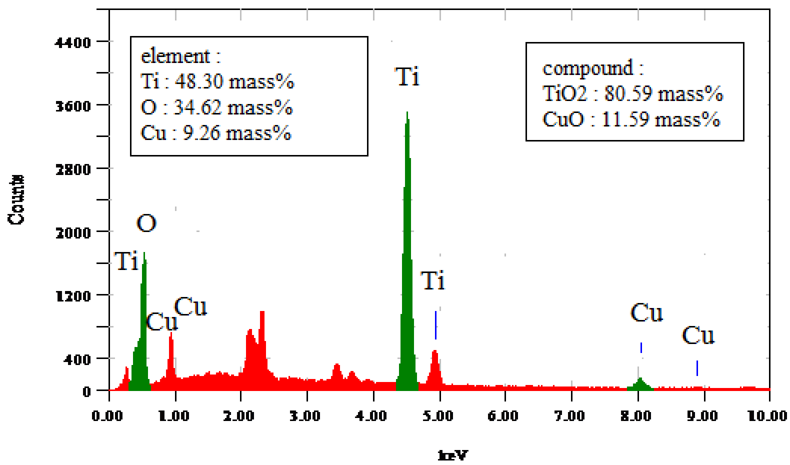

Figure 3 Result of EDS characterization for TiO_2/CuO/Cu film.

Figures 2 and 3 respectively show SEM images and the EDS characterization result of the TiO_2/CuO/Cu. It can be seen in Figure 2 that the TiO_2 particles have a spherical form, the CuO particle have a seedlike structure, and the copper (Cu) particles have a pyramidal structure. The pyramidal form of the copper particles is in line with previous papers [8,13,16]. The peaks of Cu in Figure 3 show that the copper metal was successfully deposited on the TiO_2/CuO film.

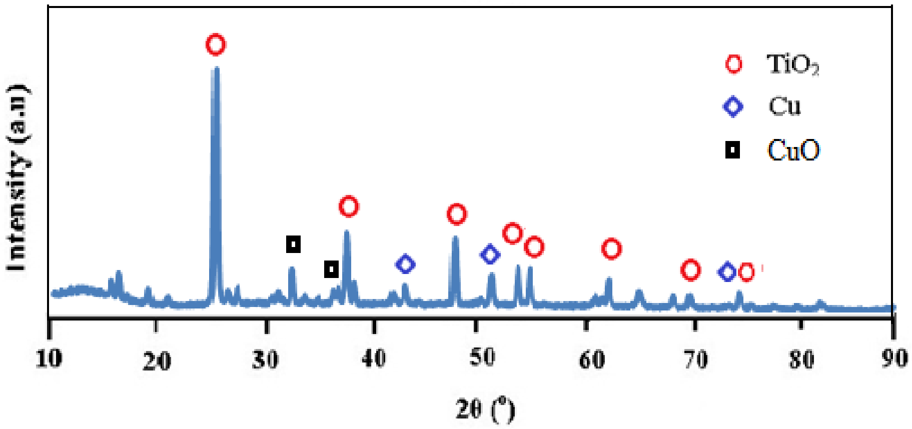

Figure 4 Result of XRD characterization for TiO_2/CuO/Cu film.

The presence of CuO and copper particles (Cu) among the TiO_2 particles was also investigated by XRD characterization. The XRD characterization result is shown in Figure 4. There were additional diffraction peaks for copper particles (Cu) at diffraction angles of 43.6°, 50.8°, and 74.4° between the diffraction angles of TiO_2, 25.3°, 38°, and 49°. The additional diffraction angle for Cu corresponds to JCPDS No. 04-0836, which is the reference for copper particles (Cu). In addition, there are also diffraction angles for CuO particles in accordance with JCPDS No. 80-1917, as shown in Figure 4. The diffraction angles of Cu and CuO show that copper metal particles and CuO were successfully deposited on the TiO_2 film.

4 Conclusion

A simple method to develop a low-cost TiO_2/CuO/Cu based solar cell was proposed. A highest efficiency of 1.40% and a fill factor of 0.37 were achieved by using spraying and electroplating. The combination of CuO and Cu to improve the light capturing ability and electron transport ability yielded the best treatment for a good efficiency result.

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