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To cite this article: Dui Yanto Rahman *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **599** 012004

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Fabrication of Flexible Graphite Film Using a Mechanical Method and Its Application in TiO_2 /Graphite Solar Cell as a Flexible Counter Electrode

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Abstract. We have successfully fabricated solar cell using flexible counter electrode of graphite powder. TiO_2 /graphite suspension was simply poured onto heated Fluorine Tin Oxide (FTO) substrate and kept heated at 200°C for 2 hours. PVA.LiOH polymer electrolyte was employed as a positive charge transfer medium. The counter electrode was made of graphite powder which is manually deposited on transparent plastic using tube-shaped metal which its surface covered with tissue of 2 mm thick. Graphite powder was deposited by straight motion of 20 movements for one coating or one layer. The same activity was repeated on the stacked film to increase the conductivity of the film. Resistivity and transmittance measurement of the film was performed by four-point probe method and UV-Vis equipment respectively. The film thickness and 2-D porosity were measured using an electronic microscope and ImageJ software orderly. The film resistivity and transmittance gradually decreased with the increase of coating number and reached the resistivity of $0.35 \Omega.\text{cm}$ and transmittance of 5% for 40 times of coating. At the same time, the film thickness was saturated at the 30 times coating and reached the thickness of $9.4 \mu\text{m}$. The film 2-D porosity which indicated how well the surface of the film covered the graphite also decreased to reach the film porosity of 18%. The most conductive film (40 times coating) was used as a flexible counter electrode in TiO_2 /graphite solar cell. The efficiency of this structure was 0.4 %, a reasonable efficiency achievement for a cheap material and easy method used.

1. Introduction

The dependence of worldwide people on the polluting energy source such as gas, coal, natural oil has motivated the search of non-polluting energy source. In addition, the availability of this kind of energy was limited and not abundant. Solar cell as a clean energy source was one of the most promising energy source to provide the need on energy in the future due its wide availability source. Various types of solar cell have been produced since it was firstly found such as bulk silicon solar cells [1-3], thin-film solar cells [4-6] and organic solar cells [7-9]. Each development has been carried out mainly on the concern of much easier method of fabrication, much cheaper materials used, much comparable efficiency to the present applied solar cell especially silicon based solar cell.

The development of organic solar cells was mainly dominated by the dye-sensitized solar cell (DSSC) which used the dye as a photon absorbing material and titanium dioxide (TiO_2) as the medium for the electron injected by the dye to flow towards the front electrode, iodide/triiodide redox couple



electrolyte as hole transport medium and Pt-counter electrode [10, 11]. However, the solar cell efficiency was relatively small to compete with most commercially silicon-based solar cells. In addition, the cost of producing such a solar cell which consisted mainly of material and process was relatively expensive. It made this type of solar cell still in the distance to its realization and commercialization.

Having participated in developing the solar cell using much less expensive material and a simpler method, we have developed a new type of solar that uses TiO_2 as a photon absorbing material, metal particles as a means of transporting the electron out to the front electrode (FTO), PVA.LiOH polymer electrolyte as the medium for transporting positively charge and Aluminium as counter electrode [12-17].

Further improvement is required to increase the performance of the solar cell. Due to the limited range absorption of TiO_2 in the ultraviolet range, it is essential to have a material assisting TiO_2 in absorbing wider range absorption to get a higher current. Besides, the development of using flexible counter electrode should be an important concern to realize inexpensive plastic solar cell. The attempt of using flexible graphite sheets has been demonstrated [18], but meet the problem of sophisticated method.

In the present research, we proposed a new kind of graphite based counter electrode which is deposited on the plastic using a manual method. The method was easier compared to the previous method [19]. Previously, we have fabricated flexible graphite-based film using manual circle motion but produced low conductivity and has not been employed as flexible counter electrode [20,21]. Another manual straight motion needs to be employed to increase its conductivity. Deposition other materials such as TiO_2 on the transparent plastic using spray method has been successfully conducted and employed in photocatalyst application [22-24]. The flexible graphite based counter electrode was then applied to a solar cell using graphite/ TiO_2 as photon absorbing material. The use of flexible counter electrode was aimed at preparing the future whole flexible solar cell using cheap materials and easy method of fabrication.

2. Material and Experiment

2.1 Preparation of flexible graphite counter electrode.

1 g of Graphite powder (Giva utama, Indonesia) was manually lubricated on the surface of the tube-shaped metal covered with tissue of 2 mm thickness. Manual straight motion was employed to attach the graphite powder on the surface of transparent plastic (Yashica, Indonesia) with the size of $2 \times 2 \text{ cm}^2$ using 20 movements for one coating time. To increase the conductivity of the film, repeated process was conducted on the previous attached graphite film.

Keithley 224 current source and Keithley 182 voltmeter were employed to measure film resistivity by using Four-Point Probe method. To investigate the transmittance of the film, we used UV-Vis electrometer (Mikropack Brands, NanoCalc 2000, Florida, USA). Scanning Electron Microscope (SEM) (JEOL JSM-6360LA, operated at 20 kV) was to observe film morphology. The film thickness was characterized by using an electronic microscope. 2D-porosity characterization was conducted to know how well the graphite powder covered the surface of the plastic homogeneously. The image was observed using an electronic microscope with 40 times of magnification.

ImageJ software was employed to measure the 2-D porosity of graphite film. The procedure of porosity measurement was easily conducted by opening the image of the film followed by adjusting the threshold of the film on the image feature. The porosity was automatically measured through the information of film uncovered by the graphite powder (white color) in percent unit (%).

2.2 Preparation of solar cell.

5 g of graphite powder (technical grade, Giva Utama, Indonesia) was stirred homogeneously in 12 ml of mineral water (Aqua, Indonesia) for 15 minutes. TiO_2 powder (technical grade, Bratachem, Indonesia) was then added to the suspension with the amount of 10% of the amount of graphite powder.

The suspension of TiO_2 and graphite was stirred for 30 minutes. In a separate place, the FTO glass was heated on a hot plate at 100°C for 30 minutes. Using a small spatula, the last suspension was then poured onto the FTO surface. The suspension was then stuck evenly on the FTO surface. To increase the good contacts between the FTO surface and the TiO_2 /graphite particles, the formed film was then held at 200°C for 2 hours. Separately, 0.38 g of LiOH (Kanto, Japan) was dissolved in 20 ml of mineral water placed in a beaker for 15 minutes. 1.8 g of polyvinyl alcohol (PVA) (Bratachem, Indonesia) was then added to the solution and heated at 100°C for 60 minutes to form a gel polymer electrolyte. The solar cell module was constructed by manually spreading the polymer electrolyte on the surface of the TiO_2 /graphite film and fixing the flexible graphite based counter electrode on the opposite side using two clampers on both sides of the cell.

3. Result and Discussion

The success of graphite powder deposition on the plastic was seen at figure 1. The graphite powder was homogeneously and strongly stuck on the plastic. It is confirmed by touching activity of hands and the investigation of its conductivity property for more than a month which still has the same value of resistivity.

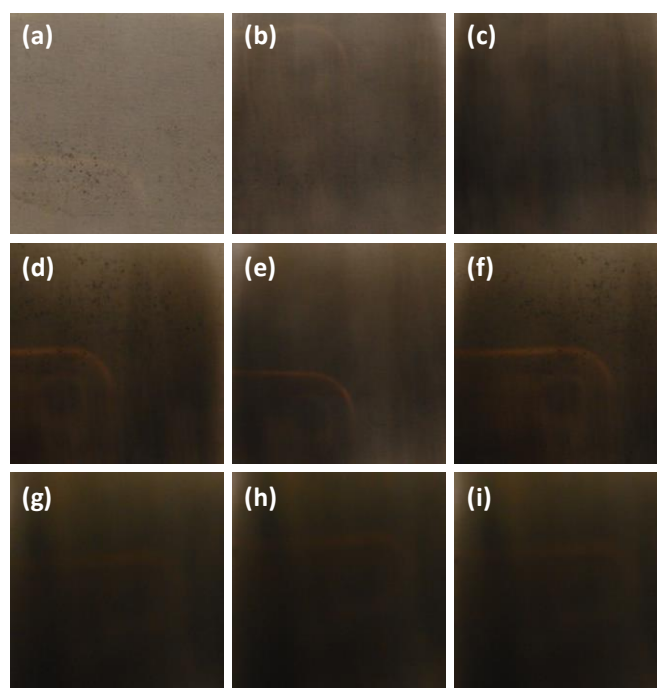


Figure 1. Photo of graphite-based flexible film with size of 2 cm x 2 cm after (a) 1 times (b) 5 times (c) 10 times (d) 15 times (e) 20 times (f) 25 times (g) 30 times (h) 35 times and (i) 40 times of coating.

Figure 2 (a) was the SEM image of flexible graphite film confirming that graphite powder was homogeneously deposited on the plastic. Figure 2(b) describes the cross section of graphite film informing that graphite film was well deposited on the surface of the plastic.

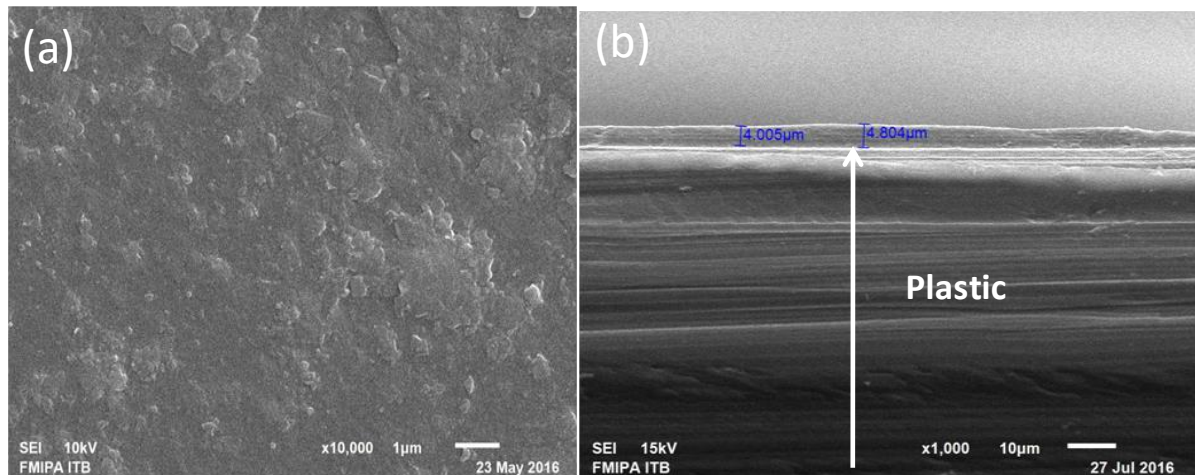


Figure 2. SEM image of (a) surface morphology of graphite-based flexible film. (b) Cross section of graphite-based flexible film after 5 times of coating.

The investigation of the influence of number of coating to the properties of the film was fully described at Table 1. Table 1 informed us that in general that the film conductivity was increased with the increase of number of coatings. This is mostly caused by the increase of film thickness as we see at Table 1. The increase of the film conductivity affected by the film thickness was also reported by Liu et al. who used copper materials [25], Dayal et al. who used silver materials [26], Camacho and Oliva who used Aluminium, copper, and gold materials [27] Those experimental data was theoretically calculated and well fitted by Fred [28].

Table 1. Relationship between number of coatings and resistivity, thickness, transmittance, 2-D porosity of graphite-based film

Number of coatings (times)	Resistivity ($\Omega \cdot \text{cm}$)	Thickness (μm)	Transmittance (%)	2-D Porosity (%)
1	1.18	1.3	53	34
5	6.5	4.5	47	30
10	2.1	6.6	36	21
15	1.9	7.5	14	25
20	1.8	9	13	24
25	2.1	9.5	11	24
30	1.9	10.4	8	20
35	1.35	9	7	17
40	0.35	9.4	5	18

Furthermore, we investigated the influence of coating number on the film properties more completely. The increase of coating number influenced not only the conductivity and thickness of the film but also its transmittance. As the number of coating increased, the transmittance of the film decreased. This is also due to the increase of the film thickness. We can see it clearly in figure 3(c) that the transmittance of the film decreased from 53 % to 5 % with the increase in the number of coatings. The increase of film thickness caused the increase of photon absorption by the film as the amount of graphite powder attached on the surface of the plastic increased. The investigation of the effect of the film thickness on the light absorbance was also reported by Islam et al. who found that the absorption of the blend of poly (3-hexylthiophene) (P3HT) and Phenyl C61 butyric acid methylester (PCBM) film

increased with the increase of the film thickness [27]. This is then strongly confirmed by Yu Xie et al. who found that the light absorbance of P3HT:PCBM thin film increased with increase of film thickness from 60 nm to 80 nm [29].

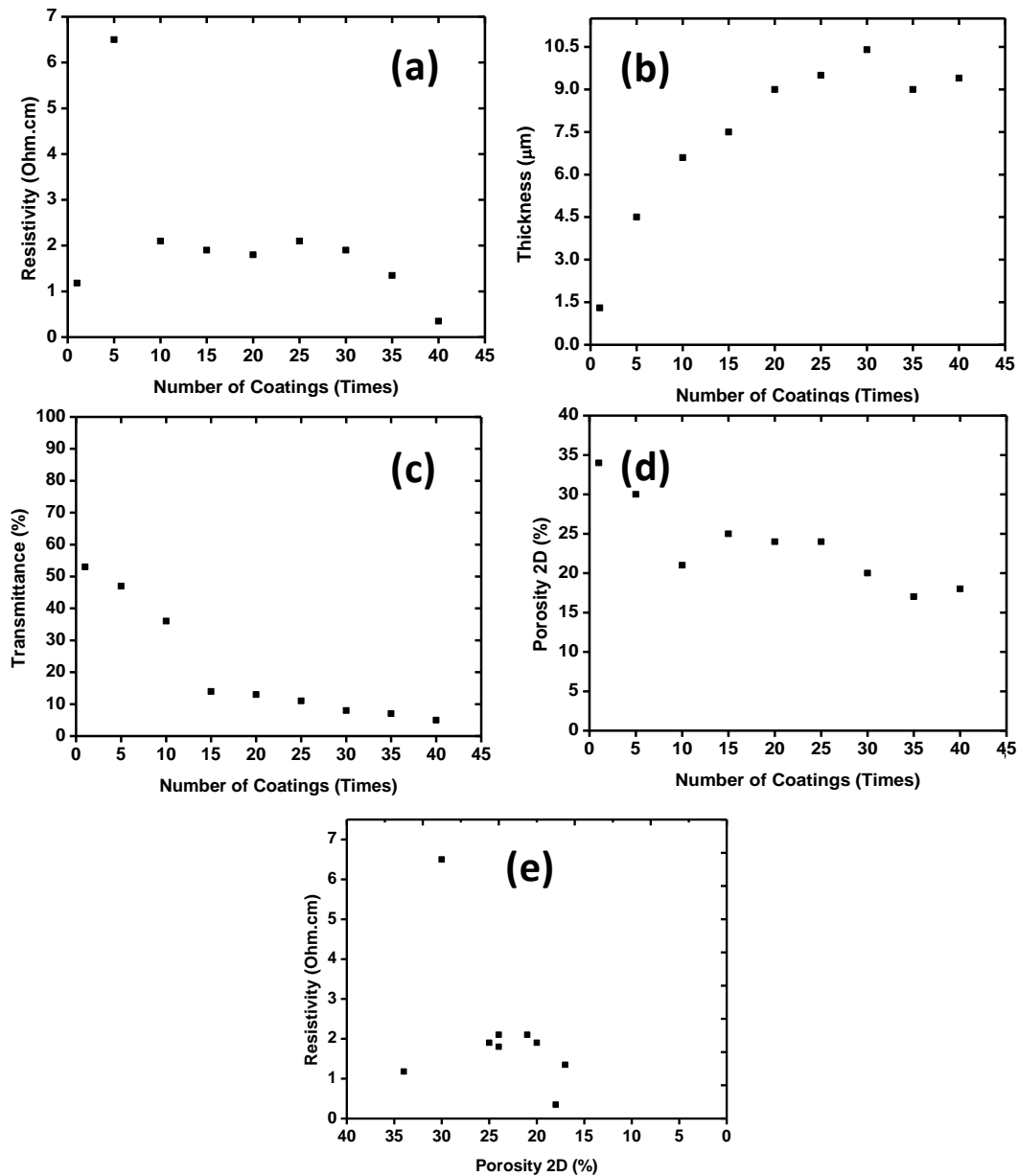


Figure 3. Graph of relationship between (a) number of coating and film resistivity (b) number of coatings and film thickness (c) number of coating and film resistivity (d) number of coating and film 2-d porosity and (e) 2-D porosity and film resistivity.

The film transmittance decrease was supported by the decrease of 2-D film porosity which tends to decrease with the increase of the coating number. It means that the film was increasingly covered by the graphite powder deposition on the surface of the film with the increase of coating number (figure 3(d)). The film 2-D porosity also revealed that the film conductivity was affected not only by the increase of the film thickness, but also how homogeneously the surface of the plastic was covered by the graphite

powder. It is clearly observed from table 1 that the thickness of the film was not increased any more after 30 times of coating but the conductivity of the film continuously increased. The reason for this phenomenon was clearly obtained by observing the 2-D porosity behavior that still continuously decreased from 20% to 17% with the increase of coating after 30 times of coating. Figure 4 is the 2-D porosity of the film describing clearly the covering of the graphite powder to the surface of the plastic. From figure 4, we can find that the increase of coating number influenced the covering of graphite powder to the surface of the plastic. It is obviously understood that the more homogeneously the film is covered by the graphite powder, the more conductive the film is. The film 2-D porosity can likely be compared to the surface roughness of the film. The increase of 2-D porosity indicates the increase of the surface roughness of the film. The resistivity of the film highly depends on the surface roughness of the film [27]. The increase in the surface roughness makes the film resistivity increase. The film resistivity is caused by electron scattering from the surface [30, 31]

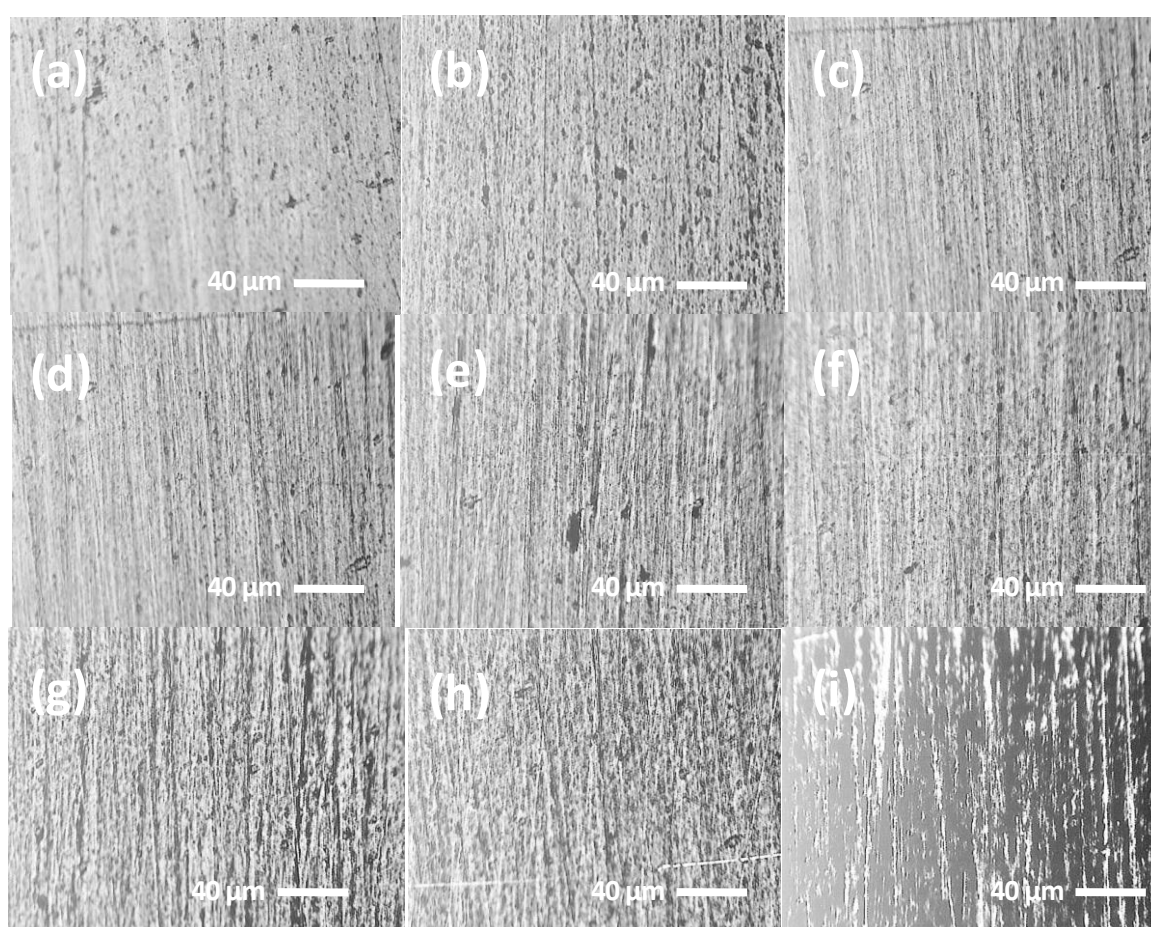


Figure 4. Image of 2-D porosity of graphite-based flexible film (a) one coating (b) 5 times (c) 10 times (d) 15 times (e) 20 times (f) 25 times (g) 30 times (h) 35 times and (i) 40 times, of coating.

After successfully coating graphite powder on the surface of the plastic, we tried to apply the flexible graphite film of 40 times coating as flexible counter electrode of solar cell containing FTO as front electrode, graphite/TiO₂ as photon absorbing materials, PVA polymer electrolyte as a positive charge transfer medium and flexible graphite film as counter electrode. The performance of this structure was compared to the same solar cell structure, but with a different counter electrode (Aluminium). Figure 5

(a) describe the morphology of graphite/TiO₂ anode film while figure 5(b) describes I-V characteristic of solar cell using flexible graphite counter electrode and Aluminium counter electrode.

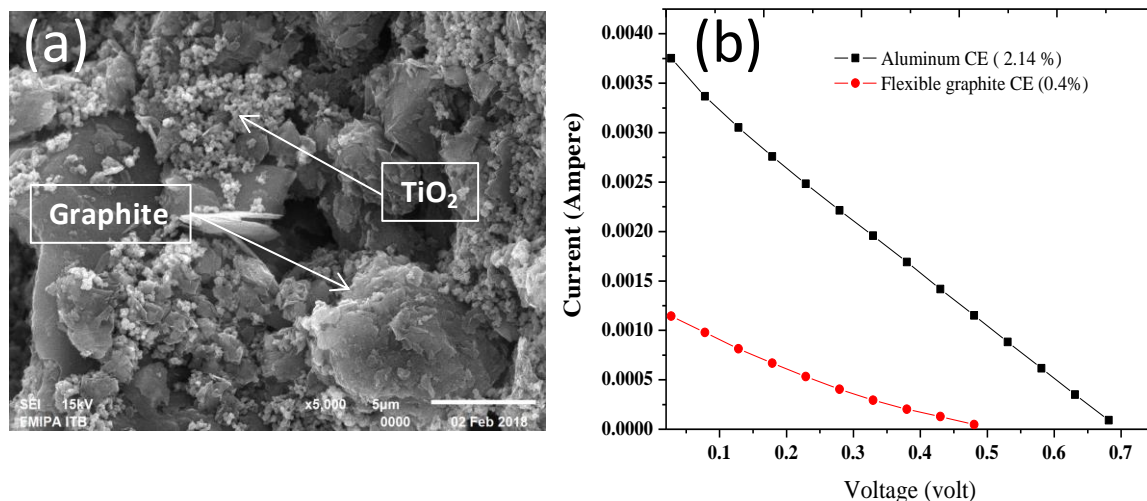


Figure 5. (a) SEM image of graphite/TiO₂ film photo anode (b) I-V characteristic of solar cell using aluminium and flexible graphite film.

From figure 5(b) we can see that solar cell using flexible graphite film work well with current-voltage value when applied to I-V characterization measurement. This solar cell structure achieved the efficiency of 0.4 % with current of 1.1 mA and voltage of 0.43 V. The efficiency was lower compared to the efficiency of the structure solar cell, but using Aluminium counter electrode which achieved the efficiency of 2.14 % with current of 3.7 mA and Voltage of 0.68 V. This is due to the low conductivity of flexible graphite counter electrode which have resistivity of 0.35 $\Omega\cdot\text{cm}$ while Aluminium counter electrode has a resistivity of $2.3 \times 10^{-4} \Omega\cdot\text{cm}$. It is clearly understood since the solar cell efficiency strongly depends on the conductivity of the counter electrode [19]. The performance of this solar cell still has a chance to be improved when the resistivity of the graphite counter electrode can reach the value of $10^{-4} \Omega\cdot\text{cm}$. The way of improving the conductivity of the film is to increase the number of coating to more than 40-80 times. It is requested that coating more than 40 times will increase the covered area of graphite film. It will be clearly observed from 2-D porosity characterization. Another way to improve the conductivity of the film is by combining straight and circle motion when depositing the graphite powder on the surface of the plastic.

4. Conclusion

We have successfully fabricated the flexible graphite based counter electrode using a manual method. The film reached the resistivity value of 0.3 $\Omega\cdot\text{cm}$ for 40 times of coating. The most conductive flexible film has been applied as counter electrode of solar cell using graphite/TiO₂ composite as absorbing material. This solar structure achieved the efficiency of 0.4%. Although the efficiency of the solar cell was below 1%, but it still has a room of improvement by increasing the conductivity of the graphite-based film through increasing the number of coating and combining the straight and circle motion when depositing the graphite powder aimed at homogeneously covering the surface of the plastic with graphite powder.

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Acknowledgments

This work was supported by fellowship grant from Indonesia Endowment Fund for Education (LPDP). The PMDSU fellowships from the Ministry of Research, Technology and Higher Education, Republic of Indonesia F.D.U. is highly acknowledged. This work was also supported by KK Research Grant from Bandung Institute of Technology 2019.