Hybrid TiO$_2$-Gigantochloa Albociliata Charcoal in Dye Sensitized Solar Cell

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Abstract. The Dye Sensitized Solar cell (DSSC) is an alternative to the silicon solar cell because it is low cost and easy to fabricate. In previous work, Remazol Orange (RO) was used as a dye sensitizer in DSSC but the efficiency is still low, 0.13%. In order to increase the device performance, TiO$_2$ thin film as the working electrode is hybridized with high conducting and absorption material which is bamboo charcoal powder (BCP). It is founded that the nanoparticle size of TiO$_2$-BCP composite was smaller compared to pristine TiO$_2$. The ratio of TiO$_2$ and BCP did not give any significant effect towards the particle size. The efficiency of RO DSSC was highly improved by 84.6% at higher carbonization temperature, 1100 °C compared to 500 °C during pyrolysis process due to its capability in absorbing more dye as it has larger specific area.

1. Introduction
Dye Sensitized Solar Cell (DSSC) is one of photovoltaic device that aroused world’s attention due to its low cost production and high efficiency. There are many efforts that have been applied in order to enhance the efficiency of DSSC. One of the recent techniques is by hybridizing all parts with carbon based materials like carbon nanotubes [1], graphene [2] and even carbon nanotubes-graphene hybrid system [3]. Carbon based material such as carbon nanotubes and graphene are highly favoured due to their extraordinary structure, conductivity and other properties. However these materials are quite expensive.

Bamboo charcoal is a newly developed material with high conductivity, high absorption and other extraordinary properties. Bamboo is an abundant plant in tropical countries including Malaysia, thus it offers a low cost alternative towards other carbon family. The most noticeable one is a micro-porous material with excellent adsorption property due to its large surface area where it could absorb more dye when the electrode (TiO$_2$-BCP) was immersed in the dye solution [4].

In the previous work, an alternative to Ruthenium as dye sensitizer was studied and investigated as this material was very expensive and not environmental friendly [5]. The results found that a water based dye, Remazol Orange potential to be used as a dye sensitizer with efficiency of 0.2% at the condition of 2.5 mM immersed for 24 Hours. In this project, TiO$_2$ as the nanomaterial for working electrode was hybridized with BCP in order to improve Remazol Orange DSSC device performance as illustrated in figure 1. Herein, the structural investigation on the hybrid system and also the efficiency of the DSSC were investigated.
2. Materials and Methods

2.1. Bamboo Charcoal Powder Preparation

There are two types of BCP using in this experiment which are the commercial sample and in-house sample. For commercial sample, the BCP was purchased from the JitraGrow Resources (carbonized at 500°C). While for in-house sample, the BCP was prepared using furnace at the temperature of 1100°C. For carbonization process, firstly, the bamboo was chopped into small segments. The carbonization process of bamboo was as followed: (1) the temperature was set to 300°C within 10 minutes and retained for 5 minutes before increased to 600°C and retained for 15 minutes and (2) the temperature was ramped up to 1100°C within 30 minutes and this temperature retained for one hour. Then, the time was set for 2 hours to let it ramped down to the room temperature.

2.2. Remazol Orange Dye Preparation

Remazol Orange (RO) dye is a water based dye which was used as the dye sensitizer in this experiment. It is easily to get as it is widely used in textile industry. RO was purchased from the AR Alatan Sdn. Bhd and was diluted before being used. The powder of RO has a molarity weight at 617.54 g/mol. The solution is prepared by mixing 23 mg powder and 15 mL DI water to form 2.5 mM concentration. The calculation was show as Equation 1.

\[
\text{Molar mass (mg)} = \frac{\text{Molecular weight (g/mol)} \times \text{concentration (mMolar)} \times \text{volume (mL)}}{1000}
\]  

2.3. TiO$_2$-bamboo charcoal powder hybrid

The preparation procedures for a working electrode of TiO$_2$ (P25)-BCP composite were as followed: (1) preparation of the stabilizer by mixing the 0.1 mL of high concentration of acetic acid solution ($\text{C}_2\text{H}_4\text{O}_2$) with 50 mL DI water to produce 0.035 molar solution; (2) preparation of the suspension by mixing TiO$_2$-BCP composite particles (1:0.08 g) with stabilizer (15 mL) and Triton X-100 (0.05 mL); (3) deposition of suspension on top of the ITO glass substrate using Doctor Blade method; (4) annealing of this substrate at 450°C for 30 minutes on hot plate and (5) immersion of TiO$_2$-BCP thin film into the solution of RO for 24 hours in order to produce the working electrode.

2.4. Assembling and testing the DSSC

The counter electrode was produced using a black deposition from the soot of combustion of flame. The working electrode was sandwiched with soothed conductive glass by facing each other the active sides of anode and cathode and held together using binder clips as shown in figure 2. Then, a drop of
iodine electrolyte was injected between the two electrodes. The PV Cell Testing LS1000 Solar Simulator was used to illuminate the DSSC and a digital source meter (Keithley 2450) was used to obtain the $I_{sc}$ and $V_{oc}$. From the graph, the efficiency of the DSSC can be calculated by using Equation 2 and 3:

$$\text{Efficiency, } \eta = \frac{J_{sc} \times V_{oc} \times FF}{Pin}$$

(2)

where

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}}$$

(3)

2.5. Structural investigation

The structural and morphology of the TiO$_2$-BCP composite were analyzed using Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscope (FESEM).

3. Results and discussions

3.1. Characterizations of BC and TiO$_2$-BCP composite

Figure 3 (a) shows the bamboo which was carbonized at 500°C for commercial sample before being grind to form powder as in figure 3 (b). According to the Kuromoto et al., bamboo which was carbonized at temperature above 500°C has higher adsorption capacity where the degradation of hemicellulose and cellulose of bamboo occur at this stage [6]. This process is important to provide porous structure in the BC. The adsorptive properties of the BC depend on the microporosities of the BC. Figure 3 (c and d) show the comparison of TiO$_2$ powder before and after being mixed with BCP powder.

The mass ratio of TiO$_2$-BCP was varied in order to obtain the best optimized ratio. It was observed that the white colour of TiO$_2$ powder turned to black pestle after mixed with BCP and it can be concluded that the mass of BCP increased the colour of TiO$_2$-BCP composite. Figure 4 shows the FESEM images of TiO$_2$ and TiO$_2$-BCP (prepared with commercial sample) composite after annealed at 450°C where the slurry was homogenously dispersed on the ITO substrate. It was also observed that the surface of the TiO$_2$-BCP thin film was quite rough compared to the TiO$_2$ sample. It can be seen that the TiO$_2$ nanoparticle was clearly in spherical shape. After hybrid with the BCP, it was observed that the TiO$_2$ nanoparticle become stick together with the BC and the size of the TiO$_2$-BCP becomes smaller.

The surface morphology of this thin film was further observed using AFM as shown in figure 5. Generally TiO$_2$ consist of three types of structure which are anatase, ructile and brookite and this structure formation depends on the annealing temperature.
Figure 3. Images of (a) bamboo charcoal, (b) bamboo charcoal powder, (c) TiO$_2$ (P-25) and (d) TiO$_2$ (P-25)-BCP composite.

Figure 4. FESEM images of (a) TiO$_2$ (P-25) and (b) TiO$_2$ (P-25)-BCP composite.

Figure 5. AFM images of TiO : BCP at different ratio (a) 1:0.02; (b) 1:0.04; (c) 1:0.08.
The annealing process was done at 450°C after being optimized in the previous work [5], where anatase structure which is more suitable for photocatalytic process was successfully obtained. From the images, it found that the particles of the TiO$_2$ are in irregular shape and it is expected to agglomerate and becomes larger as the temperature increased [5]. Table 1 shows the comparison of grain size for deposited TiO$_2$-BCP thin film at different mass ratio of 1:0.02, 1:0.06, 1:0.08 g respectively. The results show that TiO$_2$ film was very uniform and the crystal structure was quite small. The average diameter was measured between 65.70 nm to 71.58 nm. It shows that the grain sizes are not affected by the ratio of the composite. However, there was a big different of the TiO$_2$. These findings were consistent for all samples (commercial and in-house BCP). The average grain size between the pure TiO$_2$ and the TiO$_2$-BCP composite was decreased by 52%. This finding proved the result of FESEM images which were observed in figure 5 where the size of the TiO$_2$ becomes smaller after hybrid with the BCP.

| Mass Ratio | Averages Grain Size, nm |
|------------|-------------------------|
| TiO$_2$ only | 131                     |
| 1: 0.02    | 71.58                   |
| 1: 0.04    | 67.01                   |
| 1: 0.08    | 65.70                   |

3.2. Effect of BC carbonization temperature towards efficiency of the DSSC.

Figure 6 shows the current voltage characteristic (IV) graph for different carbonization temperature of BC towards efficiency of the DSSC. The carbonization temperature of in-house BCP at 1100°C shows the highest device efficiency which was 1% followed by 500°C (commercial sample) at 0.23 % and RO DSSC with efficiency of 0.13% as presented in table 2. The performance of RO DSSC was highly improved by 84.6% using hybrid TiO$_2$-BC composite. It was expected that the pyrolysis of bamboo during carbonization process resulted a high quality porous carbonaceous structure.

![Figure 6](image.png)

**Figure 6.** The IV graph of different carbonization temperature of BC towards efficiency of the DSSC.
This porous structure was obtained when the parenchyma cell wall of bamboo charcoal become thinner. The formation of crevice in the parenchyma cell wall is also one of the major factors to promote the formation of this porous structure, thus increase the surface area of the charcoal [7]. It was proved that higher carbonization temperature (> 800°C) has improved the porous structure, hence produce high conducting and adsorption material, and thus increase the device efficiency.

Table 2. The efficiency of DSSC.

| Sample               | V_{OC} | I_{SC} | J_{SC} | P_{MAX} | FF   | η % |
|----------------------|--------|--------|--------|---------|------|-----|
| TiO$_2$              | 0.54   | 0.003138 | 0.001569 | 0.000258 | 0.152538 | 0.13 |
| TiO$_2$/BCP(500 °C) | 0.6    | 0.004642 | 0.002321 | 0.00045  | 0.161608 | 0.23 |
| TiO$_2$/BCP(1100 °C)| 0.8    | 0.011866 | 0.005933 | 0.001919 | 0.202121 | 1.00 |

4. Conclusions
In this work, the efficiency of RO DSSC was improved by using TiO$_2$/BCP composite as the working electrode. Structural investigations at annealing temperature of 450°C were done using FESEM and AFM where the nanoparticle size of the composite was smaller compared to pristine TiO$_2$. It was also observed that the mass ratio of TiO$_2$ and BCP did not affect the size of nanoparticle. These findings were consistent for all samples; commercial and in-house prepared at 500°C and 1100°C respectively. The DSSC performance was investigated using solar cell simulator. From the result, the efficiency of the DSSC was increased by 84.6% as the carbonization temperature increased from 0.13% up to 0.23% for 500°C and 1% for 1100°C. It was expected that, carbonization process at higher temperature promotes porous structure which increase the surface area of the charcoal, hence increase the absorption of the dye.

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