Development of activated carbon-doped TiO$_2$ nanoparticle thin film for application in dye-sensitized solar cells

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Abstract. Carbon This research aims to study the preparation of activated carbon-doped TiO$_2$ nanoparticle thin films with basellaceae, malvaceae and hylocereus dyes for application in dye-sensitized solar cells (DSSCs). The physical and chemical properties of as-prepared thin films were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-vis diffuse reflectance spectra (UV-vis DRS) techniques. Results revealed that the basellaceae dye (JSC is 13.5 mA/cm$^2$, VOC is 0.450 V and η (%) is 1.59) on thin film showed the highest efficiency compared with the malvaceae (JSC is 10.2 mA/cm$^2$, VOC is 0.425 V and η (%) is 1.08) and hylocereus (JSC is 12.1 mA/cm$^2$, VOC is 0.325 V and η (%) is 1.17) dyes. Moreover, we observed that activated carbon/TiO$_2$ nanoparticle thin film exhibited a higher efficiency than other thin film samples. This might be due to the activated carbon doped into the TiO$_2$ leading to facilitate the separation of photogenerated charge carriers, resulting in its enhanced efficiency.

Keywords: Dye-Sensitized Solar Cells, Thin film, TiO$_2$, Activated carbon

1. Introduction

Dye-sensitized solar cells (DSSCs) are a photovoltaic technology used for converting light energy into electricity with dyes coating on semiconductor film, which have received extensive attention due to their low cost, simple production and high stability [1–3]. Generally, the materials of DSSCs creation included oxide semiconductor film (photoanode), sensitizing dyes, carbon powder or metal particle (counter electrode) and iodide/triiodide (I$^-$/I$_3^-$) redox couple (electrolyte) [4,5]. Recently, DSSCs based on SiO$_2$ nanoparticles, have been receiving much interest for applying electricity generation in the past a decade. However, the limitation of SiO$_2$ is an expensive, simply breakable and complicated manufacturing procedure [6,7]. To solve the drawbacks of SiO$_2$, Titanium dioxide (TiO$_2$) is an oxide semiconductor with wide band gap energy of 3.1-3.2 eV which has gained large popularity for employing in DSSCs [8]. Nowadays, TiO$_2$ is broadly employed as a photoanode in dye-sensitized solar cells (DSSCs) system because the unique properties such as non-toxicity, low cost, high stability and being environmentally friendly [9]. Importantly, the property and efficiency of TiO$_2$ also depend on the phase structure, morphology, surface area and so on [10]. TiO$_2$ is mainly consisted of three crystalline structures which are brookite, rutile and anatase [11]. Among the three phase structures, the anatase TiO$_2$ structure has the highest efficiency compared to brookite and rutile structures for its application in DSSCs [8]. However, the disadvantage of individual TiO$_2$ is low performance in DSSCs due to its smaller surface area and swift recombination of charge carriers [12], resulting in the limitation of
adsorbed dye molecule onto TiO₂ and the decrement of DSSCs efficiency. Therefore, in order to solve the problem of isolated TiO₂, the combination of TiO₂ with other materials to reduce the charge carrier recombination and increase specific surface area is considered. Activated carbon (AC) is regarded as being adsorbent and photocatalyst, with numerous unique properties such as large specific surface area, high porosity, high stability and being eco-friendly [13]. Especially, a high surface area property of AC has been drawing much attention for the adsorption of dye molecules in DSSCs. Moreover, the DSSCs production depends not only on the semiconductor material alone, but also relates to dyes such as synthetic and natural dyes. Especially, natural dyes are an alternative dye, which has received extensive popularity owing to its low cost, easy extraction and environmentally friendly. To the best of my knowledge, Activated carbon-doped TiO₂ nanoparticle thin film for DSSCs is an extremely challenging job to lead to the enhanced efficiency. Many methods for the preparation of Activated carbon-doped TiO₂ nanoparticle thin film have reported such as sputtering, spay pyrolysis, spin coating, dip-coating and doctor blade [14–18].

In this research, Activated carbon-doped TiO₂ nanoparticle thin film was produced through a doctor blade technique with natural dye coating such as basellaceae, malvaceae and hylocereus as a photocathod for application in DSSCs. Moreover, the efficiency of activated carbon-doped TiO₂-based DSSCs was studied under solar light illumination.

2. Experiment

2.1 Preparation of Activated carbon
The Activated carbon was prepared via a chemical activation method using HNO₃ as an activating agent. Firstly, the bamboo was heated to form a charcoal, and then the charcoal was washed with deionized water and dried at a temperature of 80 °C for 24 h. Secondly, the obtained charcoal was dipped into HNO₃ solution to make porosity. Finally, the activated carbon was ground and heated at 600 °C for 1 h.

2.2 TiO₂ synthesis
The process of anatase-TiO₂ synthesis was operated via a sol-gel method. Firstly, the nitric acid (2.5 M) solution was used as a solvent to dissolve TTIP with magnetic stirring. Then, the mixtures were dripped into a cellophane membrane sheet, followed with ethylene glycol and ammonia solution under magnetic stirring till homogeneous solution. The as-synthesized precipitates were filtered and cleaned with deionized water by using centrifuge. Finally, the particles of anatase-TiO₂ were dried with an electric oven at a temperature of 80 °C for 24 h.

2.3 Preparation of Activated carbon-doped TiO₂ nanoparticles
The impregnation method was employed to prepare the activated carbon-doped TiO₂ nanoparticles. 0.1 g of activated carbon and 1.0 g of TiO₂ was mixed into crucible with 1.0 ml deionized water, and then the solution was shaken with ultrasonic water bath until homogeneous. The as-prepared activated carbon-doped TiO₂ was dried and heated at calcination temperature of 400 °C for 1 h.

2.4 Preparation of thin film
The activated carbon-doped TiO₂ nanoparticle thin film was coated on FTO glass substrates via a doctor blade method. Firstly, 0.5 g of activated carbon-doped TiO₂ powders was mixed with 1 ml acetic acid and 0.5 ml Triton x-100 in a mortar. Then, the ethanol absolute was dropped and ground until becoming homogeneous paste. The as-papere past was coated on FTO glass substrates by a doctor blade method. Finally, the obtained thin films were annealed at 400 °C for 1 h.

2.5 Preparation of DSSCs
The natural dyes derived from basellaceae, malvaceae and hylocereus were decorated on an activated carbon-doped TiO₂ nanoparticle thin film to use as a photocathode. While the photoanode was used, the graphite coating on a FTO glass substrate, and then both photocathode and photoanode were dovetailed with clip in sandwich-like form. The as-prepared DSSCs were injected with an iodide to act as an
electrolyte. Finally, the obtained DSSCs were investigated for the efficiency by detecting open-circuit voltage (VOC) and short-circuit current density (ISC) under solar light illumination (80 mW/cm²).

2.6 Characterization of DSSCs
The phase composition of activated carbon-doped TiO₂ nanoparticle thin film was studied via X-ray diffraction (XRD, Philips X'Pert MPD). The morphology of activated carbon-doped TiO₂ nanoparticle thin film was monitored by scanning electron microscopy (SEM, JEOL JSM-6335F). The absorption property of activated carbon-doped TiO₂ nanoparticle thin film was measured through UV-vis diffuse reflectance spectroscopy (UV-vis DRS, PerkinElmer Lambda 1050).

3. Results and Discussion
3.1 Crystalline structure analysis
The crystalline structures of activated carbon, TiO₂ and activated carbon-doped TiO₂ nanoparticle thin films were measured using XRD technique, as seen in Figure 1. The main XRD peak of activated carbon shows weakly two broad peaks at approximately 24.23° and 43.10°, matching with (002) and (100) planes of carbon [19]. While the XRD peak of TiO₂, it can be indexed as anatase phase, with main peaks locates at about 25.14°, 37.88°, 47.99°, 54.13°, 55.16° and 62.65° corresponding to the (101), (004), (200), (105), (211) and (204) planes respectively. The XRD peak of activated carbon-doped TiO₂ nanoparticle thin film exhibits similar peak to TiO₂, indicating that activated carbon doping into TiO₂ does not affect the phase transition.

![Figure 1 XRD diffraction patterns of activated carbon, TiO₂ and activated carbon-doped TiO₂ nanoparticle thin films.](image)

3.2 Morphology analysis
The SEM technique was used to identify the morphologies of activated carbon, TiO₂ and activated carbon-doped TiO₂ nanoparticle thin films, as displayed in Figure 2. From SEM image of activated carbon in Figure 2a, the morphology shows plate-like structure with particle size of approx. 100-200 nm. While, the SEM image of TiO₂ in Figure 2b plays spherical-like structure with uniform morphology and an average size of about 20-50 nm. For the SEM image of activated carbon-doped TiO₂ nanoparticle thin film, the morphologies are included plate-like structure of activated carbon and spherical-like structure of TiO₂ as represented in Figure 2c.
Figure 2 SEM photographs of (a) activated carbon, (b) TiO$_2$ and (c) activated carbon-doped TiO$_2$ nanoparticle thin films.

3.3 Optical absorption analysis

The UV-vis DRS technique was employed to analyze the optical properties of activated carbon, TiO$_2$ and activated carbon-doped TiO$_2$ nanoparticle thin films, as illustrated in Figure 3. In Figure 3a-c, the optical absorption edges of activated carbon, TiO$_2$ and activated carbon-doped TiO$_2$ nanoparticle thin films are in the wavelength range of UV light. While the band gap values of activated carbon, TiO$_2$ and activated carbon-doped TiO$_2$ nanoparticle thin films can be evaluated by following the equation: 

$$E_g = \frac{1240}{\lambda}$$

where, $E_g$ and $\lambda$ are the band energy of samples and the wavelength of samples [20,21], respectively. The band gap values of activated carbon, TiO$_2$ and activated carbon-doped TiO$_2$ nanoparticle thin films are 3.73 eV, 3.10 eV and 3.66 eV, respectively.
3.4 Absorbance of natural dyes

The absorbance of natural dyes such as basellaceae, malvaceae and hylocereus was investigated by using UV-vis spectrometer, as showed in Figure 4. The absorbance spectra of basellaceae dye are in the range of UV-light and visible light, with the wavelength of approx. 360-500 nm. Meanwhile, the malvaceae dye shows the absorbance spectra at the wavelength of approx. 450-600 nm, which is in good accordance with visible light. In the part of the hylocereus dye, the absorbance spectra are in the region of visible light, which is the wavelength of approx. 500-600 nm. The results can be observed that the basellaceae dye shows a broader absorbance range than malvaceae and hylocereus dyes, suggesting that basellaceae has higher transfer of electron on LUMO of basellaceae dye to the conduction band of thin film than malvaceae and hylocereus dyes [22]. Therefore, it can be inferred that the basellaceae is a suitable dye for being used as a sensitizing dye to coat on thin film for utilization in DSSCs.

Figure 3 UV-vis DRS of (a) activated carbon, (b) TiO$_2$ and (c) activated carbon-doped TiO$_2$ nanoparticle thin films.

Figure 4 The absorbance spectrum of basellaceae, malvaceae and hylocereus dyes.
3.5 Photovoltaic efficiency

The photovoltaic performance of activated carbon-doped TiO$_2$ nanoparticle thin film with natural dyes such as basellaceae, malvaceae and hylocereus for acting as a photocathode in DSSCs was carried out by the plot between current density (JSC) versus open-circuit voltage (VOC), as shown in Figure 5. The various parameters have effect on the photovoltaic efficiency as displayed in Table 1. From experimental results, the activated carbon-doped TiO$_2$ nanoparticle thin film with basellaceae dye in DSSCs shows the photovoltaic efficiency of 1.59% with (JSC is 13.5 mA/cm$^2$, VOC is 0.450 V and FF is 0.21). For the photovoltaic efficiency of activated carbon-doped TiO$_2$ nanoparticle thin film with malvaceae dye in DSSCs is 1.08% with (JSC is 10.2 mA/cm$^2$, VOC is 0.425 V and FF is 0.20). In the case of activated carbon-doped TiO$_2$ nanoparticle thin film with hylocereus dye in DSSCs, the photovoltaic efficiency is 1.17% with (JSC is 12.1 mA/cm$^2$, VOC is 0.325 V and FF is 0.24). From the results, it can be seen that the efficiency of activated carbon-doped TiO$_2$ nanoparticle thin film with basellaceae dye in DSSCs shows the highest compared with malvaceae and hylocereus dyes under solar light irradiation. This may be due to broader absorbance range [22]. Moreover, TiO$_2$ doping with activated carbon also can help to narrow band gap energy and facilitate the separation of photogenerated charge carriers, resulting in its enhanced efficiency [23–26].

![Figure 5](image_url)

**Figure 5** The photovoltaic efficiency of activated carbon-doped TiO$_2$ nanoparticle thin film with basellaceae, malvaceae and hylocereus dyes for use as a photocathode in DSSCs.

| Dyes       | JSC (mA/cm$^2$) | VOC (V) | FF  | η (%) |
|------------|----------------|---------|-----|-------|
| basellaceae| 13.5           | 0.450   | 0.21| 1.59  |
| malvaceae  | 10.2           | 0.425   | 0.20| 1.08  |
| hylocereus | 12.1           | 0.325   | 0.24| 1.17  |

4. Conclusions

In summary, the activated carbon-doped TiO$_2$ nanoparticle thin film on a FTO glass substrate was prepared by using a doctor blade method. The sensitizing dyes were extracted from natural dyes such as basellaceae, malvaceae and hylocereus. The results inferred that the activated carbon-doped TiO$_2$
nanoparticle thin film with basellaceae in DSSCs exhibited the highest efficiency, reaching up 1.59%. This phenomenon might be attributed to a wider absorbance range. Therefore, it can be summarized that the basellaceae dye coating on the activated carbon-doped TiO₂ nanoparticle thin film is most proper for employing as a sensitizing dye in DSSCs.

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