The use of carbon black-TiO$_2$ composite prepared using solid state method as counter electrode and $E$. conferta as sensitizer for dye-sensitized solar cell (DSSC) applications

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**ABSTRACT**

In this paper, counter electrodes based on carbon black (CB)-TiO$_2$ composite are proposed as a cost-effective alternative to conventional Pt counter electrodes used in dye-sensitized solar cell (DSSC) applications. CB-TiO$_2$ composite counter electrodes with different weight percentages of CB were prepared using the solid state method and coated onto fluorine-doped tin oxide (FTO) glass using doctor blade method while Eleiodoxa conferta ($E$. conferta) and Nb-doped TiO$_2$ were used as sensitizer and photoanode, respectively, with electrolyte containing $I^-/I_3^-$ redox couple. The experimental results revealed that the CB-TiO$_2$ composite influenced the photovoltaic performance by enhancing the electrocatalytic activity. As the amount of CB increased, the catalytic activity improved due to the increase in surface area which then led to low charge-transfer resistance ($R_{ct}$) at the electrolyte/CB electrode interface. Due to the use of the modified photoanode together with natural dye sensitizers, the counter electrode based on 15 wt% CB-TiO$_2$ composite was able to produce the highest energy conversion efficiency (2.5%) making it a viable alternative counter electrode.

1. Introduction

Dye-sensitized solar cells (DSSCs) have received great attention due to the low cost and ease of its fabrication process as well as its high power conversion efficiency [1,2]. A typical DSSC consists of multiple components i.e. transpiring conducting glass which usually utilizes fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO). The mesoporous metal oxide layer developed from TiO$_2$ acts as photoanode with the inclusion of sensitizers (dye molecules), electrolyte (iodide-tri iodide electrolyte is mostly used) and counter electrode. There are several ways to enhance the performance of DSSCs including increasing light harvesting capabilities which can be achieved with good surface area and absorption of broader range of solar light [3], increasing the electron injection speed by improving the electron injection over-potential [4,5], moving the redox couple Fermi level ($E_F$) to enhance the dye regeneration rate [6,7], enhancing the lifetime of electrons by retarding the probability of charge recombination [8] and improving the charge transfer rate in TiO$_2$ [9,10].

In the DSSC structure, the counter electrode acts as a catalyst to reduce the oxidized species of redox couples. Platinum (Pt), thus far, is the preferred material for the counter electrode since it is an excellent catalyst for $I_3^-$ reduction [9]. The platinized FTO substrate exhibits electrocatalytic activity which improves the reduction of $I_3^-$ by facilitating electron exchange. It also has high light-reflection due to the mirror-like effect of Pt [10].

However, Pt is a rare metal, hence not cost effective for large-scale production. Besides the high cost, Pt corrodes with the redox mediator $I_3^-$ which leads to the generation of undesirable platinum iodides like PtI$_4$ [11,12]. This means that the Pt counter electrode has a durability issue. Therefore, other materials such as carbon nanotube, graphite and conductive polymer are being investigated as alternatives to Pt [13,14]. Among these materials, carbon has the advantages of being low cost, environmentally-friendly, exhibits high catalytic activities as well as has high corrosion resistance [15]. Highly orientated carbons, such as graphite and carbon black (CB) have lower crystallinity and more catalytic sites which may be helpful for the improvement of charge-transfer ability. Grätzel et al. [16] explored CB counter electrodes in different thicknesses by EIS and photoelectric tests. By increasing the thickness of CB, they greatly decreased the charge-transfer resistance but increased the serial resistance. A similar result was also confirmed...
by Rhee et al. [17]; they found that fine-sized CB (20 nm) with increased electrode thickness (9 μm) guarantee excellent catalytic activity owing to the increased surface area and good conductivity of CB. To enhance the catalytic performance of CB, carbon composites are also widely investigated. Wang et al. [18] prepared highly crystalline graphene/CB composite by tuning the composite content. The obtained composite with a weight ratio of 3:1 combined rapid electron transport of graphene and high surface area of CB, resulting in superior catalytic activity and higher power conversion efficiency. A poly (3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) used as the conductive polymer was also mixed with CB to prepare a new PEDOT:PSS/Carbon (PEDOT:PSS/C) CE for DSSC [19]. The composite with the desirable features of good conductivity (1.73 S cm⁻¹) and low resistance revealed superior catalytic activity for I⁻/I₃⁻ redox reaction, yielding a high light-to-electric conversion efficiency of 7.01% under a standard simulated solar light irradiation. Much research has been conducted on the photovoltaic performance of CB as counter electrode but its use for the fabrication of CB-TiO₂ composite with various weights of CB using the solid state method has not been reported. Fabrication using the solid state method tends to produce a homogeneous powder with high crystalline structure, making it the preferred method in this study.

Another important part of DSSC is the sensitizer. The sensitizer is the central component in DSSC as it harvests sunlight and produces photo-excited electrons at the semiconductor interface. There are several requirements for the sensitizer to perform efficiently. These involve chemical adsorption to load on the semiconducting material, high molar extinction coefficient in the visible and near-infrared region for light harvesting [20] and good photostability and solubility to create space between the electrolyte and photoanode for recombination prevention [20]. Various metal complexes and organic dyes have been utilized as sensitizers and the best, to date, is ruthenium-bipyridyl dye (N719) which displays a high energy conversion efficiency of about 11% [21]. In conventional DSSC, ruthenium complexes are the best known, most effective and scientifically proven sensitizers. However, ruthenium dye is complicated to synthesize, expensive and not environmentally friendly due to its high toxicity [22,23]. Therefore, a search for novel and alternative dye-sensitizers, especially from natural sources, has become the focus for many researchers [24]. To this end, organic dyes containing anthocyanin pigment which is suitable for DSSC applications have been extracted from different parts such as the leaves, flowers, fruits and barks of various plants [25–27].

The present work is devoted to CB-TiO₂ composite prepared using the solid-state method and its use as a counter electrode with dye extracted from E. conferta as sensitizer. E. Conferta was selected as the sensitizer in this study due to its raw natural dye extract. It is expected to perform better with the presence of natural extracts like organic acids and alcohols which behave as co-absorbrates [28]. These suppress the recombination of dye with electrolyte, favors charge injection and reduces dye aggregation [29]. The solid state method was chosen as it is a better approach due to the ease in fabrication as it avoids processes such as pH control and temperature and chemical preparation, and the provision of high sample crystallinity. These advantages induce electron injection and transportation which provide better catalytic ability. Hence, it increases the photovoltaic performance. The mechanism provided by CB-TiO₂ composite with E. conferta as sensitizer was also investigated in terms of phase analysis, surface morphology, and electronic behaviors.

2. Experimental

2.1. Preparation of natural dye sensitizers

The flesh of E. conferta fruits were separated from the seed and completely dried at room temperature. The flesh was crushed to powder form using a mortar. 50 g of the powder was put into a beaker, added with 500 ml ethanol (1:10) and stirred. The mixture was left for 24 h in the dark at room temperature. The solid residues of the mixture were filtered out to obtain a pure and clear natural dye solution. Further details on the E. conferta dye characterization results can be found in our previous work [30].

2.2. Preparation of Nb-doped TiO₂ photoanodes

TiO₂ doped with 1.0 wt% of Nb were synthesized via the solid state method. The mixture was prepared using the ball mixing method. The mixture was filled into 250 ml polyethelene containers with zirconia balls with a ball to powder weight ratio of 10:1. Zirconia balls were used as a mixing media due to its high degree of hardness and to minimize contamination. The containers were placed on the ball mixing roller and mixed for 6 h at 120 rpm and then sintered at 600 °C for 6 h [31].

2.3. Preparation of counter electrode

The counter electrode was synthesized using the solid state method. Various amounts of CB powder (5–20 wt%) were mixed with 5 wt% of TiO₂, respectively. The mixture was filled into 250 ml polyethelene containers with zirconia balls (ball to powder weight ratio of 10:1). The containers were placed on the ball mixing roller and mixed for 3 h at 120 rpm. The homogeneous mixture was then mixed with 0.1 ml Triton X-100 and stirred using hotplate for 30 min. The conducting side of the FTO glass was coated with 10 mM H₂PtCl₆ solution in ethanol and the mixed paste was applied onto the FTO glass using the doctor blade technique and sintered at 500 °C for 1 h.

2.4. Assembly of DSSC

ITO conductive glass with a sheet resistance of ~7 Ω/cm² was cleaned in a detergent solution, rinsed using deionized water and ethanol and then dried. The photoanode paste was prepared with 0.3 g of 1.0 wt% of Nb-doped TiO₂, 0.5 ml acetonic acid, 1:1 (5 ml) mixture of deionized water and ethanol and was ground for 20 min. Triton-X was added (0.5 ml) to the mixture and continued to be ground until a homogenous paste was achieved. The Nb-doped TiO₂ pastes were deposited onto FTO glass using the doctor blade technique. The coated films were sintered at 450 °C for 30 min. The sintered photoanode electrodes were immersed in E. conferta dye solution for 24 h at room temperature. The sensitized electrodes were then rinsed using ethanol to remove unanchored dye. A drop of redox electrolyte (iodolyte HI-30 with a concentration of 30 mM (Solaronix) and acetonitrile as solvent) was cast on the surface of the sensitized photoanodes. The counter electrode was then clipped onto the top of TiO₂ working electrode with a cell active area of 6.5 cm² and then sealed using slurry tape.

2.5. Cell characterisation

Phase identification of the nanomaterials was conducted using Bruker D8 Advance operated in Bragg Brentano geometry and exposed to CuKα radiation (λ = 1.540 Å). The X-ray diffraction (XRD) pattern was scanned with a step size of 0.02° (2θ) at a fixed counting time of 71.6 s from 10° to 90° 2θ. The resulting powder diffraction patterns were analyzed using Highscore Plus software. The grain size and surface morphology analysis of the samples was carried out using FESEM (Zeiss Supra 35VP) at 5 kV. The photocurrent–voltage (J–V) curves of DSSCs were recorded with a computer-controlled digital source meter (Keithley 2400) under an irradiation of 100 mW cm⁻². The Brunauer–Emmet–Teller (BET) surface area of CB-doped TiO₂ powder samples were measured using a surface area analyzer (Micromeritics ASAP, 2020). The charge-transfer resistance of a DSSC was analyzed by electrochemical impedance spectroscopy (EIS, GamryREF 3000, USA). The test was conducted under a light intensity of 100 mW cm⁻² in a
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