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Biotemplated hybrid TiO₂ nanoparticle and TiO₂–SiO₂ composites for dye-sensitized solar cells

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ABSTRACT

Hybrid TiO₂-nanoparticle (NP)/TiO₂–SiO₂ (TS) composites, prepared using rice straw biotemplates were used as photoelectrodes in dye-sensitized solar cells. The hybrid TiO₂-NP/TS composite showed increased dye loading due to a faster electron diffusion pathway. This could effectively improve the photoelectrode properties of this nanocomposite material, which would improve its solar conversion efficiency. TiO₂-NP/TS (10 wt%) based DSSC demonstrated a $\tau_{\rm t}$ of 1.17 ms, $\tau_{\rm r}$ of 37.14 ms, and showed a maximum power conversion efficiency of 5.81%. $V_{\rm oc}$, $J_{\rm sc}$, and fill factor values of TiO₂-NP/TS were found to be 0.69 V, 14.01 mA cm⁻², and 60.11%, respectively under AM 1.5 simulated sunlight illumination (100 mW cm⁻²).

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1. Introduction

Since O'Regan and Grätzel demonstrated a dve-sensitized solar cell (DSSC) in 1991, they have been extensively studied [1]. As reported earlier, DSSCs have sandwich type structures consisting of three components: (1) a photsensitizer adsorbed mesoporous semiconductor (TiO₂, ZnO, SnO₂, etc.) photoelectrode layer, (2) an electrolyte containing an I^-/I_3^- redox couple, and (3) a counter electrode [2]. However, DSSCs are not yet ready to be made commercially available because they have some weaknesses such as lower conversion efficiency than silicon solar cells, relatively poor long-term stability, and the material limitation for application to DSSCs. Of the challenges these weaknesses present, increasing the solar conversion efficiency is a big challenge for their commercialization. Although several methods have been proposed to enhance the solar conversion efficiencies of DSSCs, it seems that one of the most promising methods is to use nanostructured TiO₂ as a photoelectrode to enhance light harvesting, surface area, dye adsorption, and electron transfer as well as to improve photocurrent density, photovoltage, and fill factor [3-6]. Son et al. [7] reported that deposition of SiO_2 powder onto TiO_2 in DSSCs was an effective tool for retarding charge recombination, which lead to enhanced charge collection and substantially increased overall conversion efficiency. In addition, TiO₂-SiO₂ (TS) composite films have

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demonstrated increased light harvesting ability and improved charge transport [8].

A new method for the synthesis of TS that utilizes rice straw (RS) as a biotemplate, which is simple, inexpensive and ecofriendly, has been reported for preparation of TS. RS was chosen **Q2** because, as an agricultural bioresource, it contains a large amount of silicon [9]. In this work, TS was prepared by impregnating RS biotemplates with $TiCl_4$ and its was used to produce a hybrid TiO_2 nanoparticle (NP)/TS composite, which was incorporated into DSSCs to improve the solar conversion efficiency by increasing surface area and electron transfer speed.

2. Experimental details

RS consists of cellulose, hemicellulose, lignin, and inorganic materials (Si etc). The RS has large numbers of surface functional groups, such as OH and C=O, which offer an important chemical environment for the adsorption of metal cation such as Ti^{4+} [10]. To form the precursor, RS (Jeonnam province, South Korea) was used as a biotemplate for impregnation with titanium tetrachloride (TiCl₄; 99.99%, Aldrich). Washed RS was treated with ethanol (99.9%, Aldrich) at 60 °C for 24 h. Next, a 0.4 M aqueous solution of TiCl₄ was made and then added to the solution for impregnation at 25 °C for 6 h; the amount of TiCl₄ impregnation was controlled so that a 1:1 weight ratio of SiO₂ to TiO₂ was achieved. Thereafter, TiCl₄ impregnated RS samples were washed with ethanol and dried under vacuum at 80 °C for 4 h. Finally, samples were

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Fig. 1. X-ray diffraction patterns of photoelectrodes.

calcinated at 700 °C for 4 h to remove the RS templates. The sample code was subsequently indexed as TS. Surface area, pore volume and average pore size of the prepared TS composite were measured to be 92.3 m²g⁻¹, 0.18 cm³g⁻¹ and 3.77 nm, respectively and its surface area is higher than that of TiO₂-NP (P25: 50 m²g⁻¹) [11]. Such a high surface area of the TS composite might bring about an increase in the amount of dye loading and the rate of electron transfer in the semiconductor layers.

TiO₂-NP powder (12 g) was treated in dilute nitric acid solution (0.83 v/v%, HNO₃/DI water) at 80 °C for 8 h to enhance dispersion of TiO₂ particles [12]. Thereafter, the solution was dried at 100 °C for 24 h. The acid treated TiO₂-NP was mixed with TS particles in a ball mill for 10 h. The weight ratios of TiO₂-NP in the TiO₂-NP/TS composite were 5, 10, 20, and 30 wt%. TiO₂-NP/TS composites were used to produce pastes. Pastes were prepared by mixing 1 g TiO₂-NP/TS composite, 2 ml distilled water, 0.35 g hydroxypropyl cellulose (MW 80,000, Aldrich), and 0.4 ml acetyl acetone (99.5%,



Fig. 2. (a), (b) are FE-SEM images, (c), (d) are EDS analyses, and (e), (f) are the corresponding elemental map of Ru for TiO₂-NP and TiO₂-NP/TS (10 wt%) based photoelectrodes.

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