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# Enhanced performance of a flexible dye-sensitized solar cell with a composite semiconductor film of ZnO nanorods and ZnO nanoparticles

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ABSTRACT

A composite thin film of only 6 μm, consisting of a first layer of ZnO nanorods (ZNRs) and a second layer of ZnO nanoparticles (ZNPs), was deposited on a flexible Ti foil. The structures and morphologies of the films of ZNRs, ZNPs, and their composite (hereafter ZNRs/ZNPs) were studied by X-ray diffraction (XRD) patterns, scanning electron microscopic (SEM) and transmission electron microscopy (TEM) images. The Ti foil with the composite film was used as the photoanode of a flexible dye-sensitized solar cell (DSSC); an indium doped tin oxide/polyethylene naphthalate (ITO/PEN) substrate with a thin layer of platinum was used as the counter electrode. A power conversion efficiency ($\eta$) of 2.19% was achieved for the DSSC with ZNRs/ZNPs, through back-illumination, which is higher than that of the cell with only ZNPs (1.80%); the DSSC with bare ZNRs showed a very poor efficiency of 0.90%. Explanations are substantiated by electrochemical impedance spectra (EIS), laser-induced photo-voltage transients, and incident photon-to-electron conversion efficiency (IPCE) curves.



## 1. Introduction

Dye-sensitized solar cells (DSSCs) are important power devices, as they are expected to provide an answer to many environmental and energy problems. Recently, numerous efforts have been made to endow DSSCs with flexibility to extend their application. Lightweight and flexible DSSCs have advantages of easy transportation and roll-to-roll production, which makes them cost-effective. Among various substrate materials, metal foil is most promising for making the electrode substrate of a flexible DSSC [1–6], because large range of annealing temperatures can be used for preparing its photoanode or counter electrode.

The electron-collecting layer of a DSSC is traditionally composed of randomly packed $TiO_2$ nanoparticles (TNPs). The electron transport and recombination rate for $TiO_2$ based DSSCs have been investigated. Enache-Pommer et al. determined the electron transport and recombination time constants in DSSCs made from $TiO_2$ nanowires, by using transient photocurrent and photovoltage measurements [7]. They reported that a DSSC made with single-crystal rutile $TiO_2$ nanowires shows similar electron transport rate to that of a cell made with TNPs [8]. Huang et al. described the charge recombination between a dye-sensitized nanocrystalline $TiO_2$ electrode and the $I_3^-/I^-$ couple in nonaqueous solution [9]. The review by Frank et al. highlighted several significant advancements in the understanding of electron transport and recombination in DSSCs, and the limitations that these processes impose on cell performance [10]. Zhu et al. reported on the dynamics of electron transport and recombination in DSSCs with oriented $TiO_2$ nanotube arrays [11]. Benkstein et al. applied percolation theory to understand the influence of network geometry on the electron transport dynamics in dye-sensitized nanocrystalline $TiO_2$ solar cells, and compared the predicted results with those measured by transient photocurrent [12]. It is now well-accepted that a photoelectrode with high light-harvesting efficiency requires not only a high surface area for the loading of a large amount of dye molecules but also a tailored microstructure for light harvesting and fast electron transport [13–15]. Strategies to enhance the cell efficiency include the promotion of rate of electron transfer through $TiO_2$ and the reduction of the rate of recombination between injected electrons in the conduction band and $I_3^-$ ions. One of the ways for enhancing the electron transfer in a $TiO_2$ photoanode is to convert the $TiO_2$ material into nanotubes or rods, since these structures can conduct electrons far better than their particulate forms. Xu et al. obtained a rapid electron transport in one-dimensional (1-D) titanium dioxide nanotubes (TNTs) in the case of a bilayer-structured film, with a TNP underlayer and a TNT overlayer [16]. Nakayama et al. fabricated a DSSC with TNTs as an underlayer to raise the light-harvesting efficiency [17]. ZnO has been investigated as a promising photoanode material for DSSCs. Keis et al. prepared ZnO films consisting of 150-nm sized particles and sensitized them with different ruthenium dyes; they investigated the influences of

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dye concentration and the residence time of the ZnO film in the dye solution on the incident photon-to-current conversion efficiencies of the pertinent DSSCs [18]. ZnO has a high electron mobility of 115–155 $cm^2 V^{-1} s^{-1}$ [19] and much higher electron diffusivity than $TiO_2$ [20,21]. These characteristics of ZnO make it more suitable for the fast electron transport, through the application of a 1-D structure. One dimensional nanostructures of ZnO, such as nanorods and nanotubes [22] have been used in DSSCs, intending to improve the electron transfer in the photoanodes; these structures can act as efficient light scattering centers for enhanced light-harvesting efficiency [20,23]. ZnO nanoflower photoanodes were hydrothermally prepared by Jiang et al., and a light-harvesting efficiency of 1.90% was achieved [24]. Hsu et al. fabricated a DSSC with nanorods on its photoanode and achieved a light-harvesting efficiency of 0.22% [25]. Baxter et al. grew ZnO nanowires of about 8 μm on a transparent conducting oxide substrate and found an overall power conversion efficiency of 0.3% for the pertinent DSSC [26]. Greene et al. formed textured ZnO nanocrystals with their c axes normal to the substrate, by the decomposition of zinc acetate at 200–350 °C, to provide nucleation sites for vertical ZnO nanowire growth; the nanorod arrays had a rod diameter, length, density, and orientation desirable for use in ordered nanorod-polymer solar cells [27]. Martinson et al. fabricated DSSCs based on ordered arrays of polycrystalline ZnO nanotubes with 64 μm in length and obtained an efficient electron collection over the entire photoanode array length [28]. In their case, the photoanode based on ZnO nanorod arrays exhibited dramatically faster electron transport while retaining similar recombination time, compared to those of a standard photoanode prepared with colloidal nanoparticles [29]. Galoppini et al. have investigated the electron transport in DSSCs with a film of ZnO nanorod array, grown by a metal organic vapor deposition-technique and with a mesoporous film prepared from ZnO colloids [30]. Chung and co-workers have reported that ZnO nanorods annealed in $N_2/H_2$ or $O_2$ have increased their dye loadings due to higher OH concentrations on the hydrophilic surface, and have thereby enabled an improved efficiency for the pertinent cell [31]. Although the 1-D structure of ZnO provides a favorable electron transport path, its low surface area renders only a low efficiency for its DSSC. The concept of adding nanoparticles in such structures was applied to increase the surface area for dye adsorption. Ku and Wu have prepared, by chemical bath deposition, vertical ZnO nanowires, and the pertinent photoanode had dense ZnO nanoparticles within the interstices of the nanowires [32]. Baxter et al. fabricated a DSSC using dendritic ZnO nanowires grown by metalorganic chemical vapor deposition, and obtained an efficiency of 0.5%; the addition of ZnO nanoparticles to these nanowires has resulted in a hybrid nanowire-nanoparticle structure and the pertinent DSSC has shown an overall efficiency of 1.3% [33]. Yodyingyong et al. investigated ZnO nanoparticle-nanowire hybrid photoanodes for DSSCs [34]; they mainly focused on the analysis for the morphology of ZnO materials and measured the photocurrent density–voltage characteristics to confirm their concept. Shiyanovskaya and Hepel prepared a bicomponent $WO_2/TiO_2$ film for the photoanode of a DSSC, and found a considerably higher photoresponse for the cell, in comparison to those of cells with single components in their photoanodes. They stated that the application of a porous $WO_2$ matrix layer with high open surface area as the substrate for a very thin nanoparticulate $TiO_2$ overlayer is beneficial for efficient photogeneration [35]. They also found, in bicomponent $WO_3/TiO_2$ films, that the porous films of the $WO_3$ can serve as substrates for nanocrystalline $TiO_2$ films to increase the efficiency of photocurrent generation at bandgap excitation [36].

In this study, a composite thin film of only 6 μm, consisting of a first layer of ZnO nanorods (ZNRs) and a second layer of ZnO nanoparticles (ZNPs) was created on a Ti foil. This Ti foil with the composite film (ZNRs/ZNPs) was used as a photoanode for a flexible back-illuminated DSSC. The structure of ZNRs was intended to provide 1-D electron transfer pathways between the ZNPs layer and the Ti foil substrate; they are also regarded as efficient light scattering centers for enhanced light-harvesting efficiency. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were applied to characterize the structure and morphology of the ZnO-based films, while electrochemical impedance spectroscopy (EIS) was employed to analyze the charge transfer resistances in the DSSCs. Moreover, the electron lifetime was estimated by Bode-phase plots and laser-induced photovoltage technique. An efficiency of 2.19% was achieved for the flexible DSSC with a 6 μm thin film of ZNRs/ZNPs in its photoanode and with an indium doped tin oxide/polyethylene naphthalate (ITO/PEN) as its substrate for counter electrode, which is higher than that of the cell with only ZNPs (1.80%); the DSSC with bare ZNRs also showed a very poor efficiency of 0.90%. To the best of our knowledge, this is the first report on a flexible DSSC containing a photoanode with a composite semiconductor film of ZNRs and ZNPs and a counter electrode based on an ITO/PEN.

## 2. Experimental

### 2.1. Materials

Iodine ($I_2$, synthetical grade) was obtained from Merk; tert-butyl alcohol (tBA, 96%) was obtained from Acros. Neutral cleaner, isopropyl alcohol (IPA, 99.5%), polyethylenimine (PEI, low molecular weight, water-free), zinc acetate dihydrate ($Zn(C_2H_3O_2)_2 \cdot 2H_2O$, reagent grade) and 2-methoxyethanol were obtained from Sigma–Aldrich. Acetonitrile (ACN, 99.99%) and zinc nitrate with 6-hydrate crystal ($Zn(NO_3)_2 \cdot 6H_2O$, 99.5%) were obtained from J. T. Baker. 1-Propyl-2,3-dimethylimidazolium iodide (DMPII) was obtained from Solaronix. Hexamethylenetetramine (HMT, 99.5%) and triethanolamine (TEA, 99%) were purchased from Riedel-de Haen. For the electrolyte, a mixture of 0.03 M $I_2$ and 0.6 M DMPII in ACN was used, which was optimized in our previous report [37].

### 2.2. Preparation and characterization of photoanode and Pt counter electrode

The flexible Ti foils (99.8% purity, Fuu Cherng Co. Ltd., Taiwan) were polished to remove any metal oxides or any other adhesive substances on the surface, and cleaned with a neutral cleaner, and then washed with DI-water, acetone, and IPA, sequentially. The ZNPs paste was synthesized by a hydrothermal process. A 0.2 M $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution was mixed with a 0.2 M TEA aqueous solution of the same volume (both of them turned out to be 0.1 M after mixing) under stirring for 10 min at room temperature. The obtained solution was then heated to ca. 60 °C for 24 h on hot bath, and then cooled at room temperature. The solvent of the resultant ZNPs paste was replaced by ethanol in the final step. The films of ZNR and ZNP, and their composite film of ZNRs/ZNPs were deposited on the Ti foils as follows. A ZnO seed layer was first deposited on the Ti foil by spin coating a solution of 0.01 M $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 2-methoxyethanol, and the Ti foil was then annealed at 200 °C for 30 min. The ZNRs were grown by immersing the ZnO-seeded Ti foil in an aqueous solution, containing 50 mM $Zn(NO_3)_2 \cdot 6H_2O$, 50 mM HMT, and 10 mM PEI, at 92 °C for 2.5 h [23]. The ZNRs were then rinsed with ethanol and kept for drying; the Ti foil with this ZNRs structure was the photoanode with ZNRs. Afterwards, the ZNPs were deposited on the ZNRs by doctor blade technique; the Ti foil with this combination was the photoanode with the composite film of ZNRs/ZNPs. Also, the photoanode with only ZNPs was made by directly applying the ZNPs paste