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# *In-situ* fabricated transparent conducting nanofiber-shape polyaniline/coral-like $TiO_2$ thin film: Application in bifacial dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cell (DSSC) is the most promising of third generation solar cells for large scale applications due its low cost, flexibility, and scalable manufacturability. However, enhancing the efficiency of the DSSC is still highly desired. In this study, we designed a novel bifacial DSSC based on a transparent Polyaniline (PANI) films as counter electrode (CE) associated with coral-like $TiO_2$ nanostructured films, which can be used as the photoanode. PANI-based CEs were prepared by a facile *in situ* polymerization, while coral-like $TiO_2$ films were chemically synthesized at low temperature through the sol–gel process. Owing to the light irradiation from both the front and the rear sides, it is expected that higher density of dye molecules should be excited. In addition, due to the excellent light scattering of the coal-like $TiO_2$ and high specific surface area of PANI nanofibers (NFs), more carriers are generated. Both these factors resulted in the increase of the conversion efficiency. The bifacial DSSC fabricated by combining the PANI NFs-based film and the coral-like $TiO_2$ film in the presence of the expensive N719 dye molecules showed the efficiency of 8.22% corresponding to the both-side irradiation. In comparison, similar cells employing either a cross-linked PANI- or Pt-based CE showed efficiencies of 7.81% and 7.75%, respectively. The results of the similar cells in the presence of the low cost CoPC dye molecules showed efficiencies of 0.29%, 0.22%, and 0.27%, for DSSCs comprised of PANI NFs-, cross-linked PANI-, and Pt-based CEs, respectively. The low fabrication cost as well as the improved light absorption highlights the potential application of the coral-like $TiO_2$ and PANI NFs-based films in fabrication of bifacial DSSCs.

## 1. Introduction

Exploration for green energy resources will be among one of the humanity's top ten problems for the next 100 years, which can potentially be solved by numerous renewable energy technologies. Dye-sensitized solar cells (DSSCs) have been extensively used as a potential alternative to the conventional solar cells because of their simple preparation process [1–4], low fabrication cost [5–7], and comparable efficiency. Generally, a standard DSSC consists of a dye-sensitized titanium dioxide ($TiO_2$) photoanode, a redox couple of iodide/tri-iodide ($I^-/I_3^-$), organic liquid electrolyte, and a counter electrode (CE). Commonly CEs, such as conductive glasses including indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), platinum (Pt) film, and carbon-based material, catalyzes the reduction of redox electrolyte to keep a low overvoltage at reasonable photocurrent density. The conductive glasses without a catalyst have exhibited a low rate of reduction reaction in comparision with the Pt electrodes. Pt is one of the most expensive rare metals, which is a limiting factor for the large-scale commercial application. Therefore, researchers are encouraged to the replacement of this precious metal with other less expensive materials to decrease the final price of the fabricated-DSSCs.

DSSCs based on nanocrystalline $TiO_2$ have attracted much attention since their first introduction at early 1990s by O'Reagan and Grätzel [8]. The specific physical properties of porous $TiO_2$ thin films have been extensively investigated over the years mainly due to its potential device applications. For example, $TiO_2$ nanostructured thin films have been used as optical coatings for their high refractive index, high chemical stability, and favorable band gap energy, i.e. 3.02 eV and 3.23 eV for rutile and anatase phases, respectively [9–11]. The performance of $TiO_2$-based DSSCs are affected by the optical transparency, thickness, morphology and surface structure of the prepared films. These factors undoubtedly play pivotal roles and must be optimized to attain high efficiency. It has been shown that the two-dimensional (2D) structures including nanosheets and three-dimensional (3D) nanostructures,

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such as flower-like and cauliflower-shaped $TiO_2$ clusters have superior photoelectron–catalytic properties. These structures have shown entirely different reaction pathways compared to the nanoparticles with smooth surfaces [12–14].

In the case of $TiO_2$-based DSSCs prepared by carbon-based materials, such as activated carbon, graphite, and carbon nanotubes used as a CE, the film thickness is required to be up to several micrometers to achieve the desired conductivity and catalytic activity. Such large thicknesses will reduce the transparency of the film. Although a thin Pt layer deposited on glass can be used as semi-transparent CE, besides its high cost, it would have a high reflectivity that would reduce the efficiency. Therefore, finding alternative materials with improved properties and low cost is an essential need for the construction of DSSCs at commercial scale.

The catalytic activity and transparency of conducting polymers such as poly (9,9- dioctylfluorene- *co*- benzothiazole) (F8BT) [15], poly (3,4- ethylenedioxythiophene) (PEDOT) [16], poly (9,9- dioctylfluorene) (PFO) [17], poly (phenylene vinylene) (OxdEh-PPV) [18], 2,2′-bis(3,4-ethylenedioxythiophene) [19] and polyaniline (PANI) has been studied for their favorable electrical conductivity and high catalytic activity to replace the opaque carbon-based and expensive Pt-based CE [20]. For instance, PEDOT doped with poly(styrenesulfonate) (PEDOT:PSS) has emerged as a promising CE because of its suitable mechanical stability and easy processability. Also, this polymer exhibits favorable conductivity of approximately 450 S/cm after the addition of the organic polar solvents including of dimethylsulfoxide and ethylene glycol via a secondary doping effect [21,22]. However, there remain the problems of low conductivity and high cost for a flexible substrate compared with a rigid substrate.

Among conducting polymers that mentioned above, PANI is one of the most promising candidates as a CE due to its low cost, favorable electrical conductivity, processability, structural rigidity, environmental stability, and unique reversible protonic dupability. Recent studies demonstrated that polyaniline doped with camphorsulfonic acid (PANI:CSA) with a 2:1 molar ratio of PANI:CSA dispersed in *m*-cresol as solvent exhibit favorable conductivity of 400 S/cm and a high mechanical stability in the film with Young's modulus of 2 GPa. Also, conductivities as high as 600 S/cm have been reported for pure microstructured PANI films and fibers [23,24].

Therefore, considering these interesting properties, researches have focused on using PANI nanostructures for fabrication of novel nanoelectronic and energy storage devices [24].

PANI is typically synthesized by the chemical oxidation of aniline or anilinium salts, such as aniline hydrochloride or aniline sulfate, in acidic aqueous medium [25]. However, ammonium peroxydisulfate has been the most common oxidant. The half-oxidized emeraldine base (EB) form of the PANI can be doped into a highly conducting material. Scanning calorimetric measurement and dynamic mechanical analysis revealed that when PANI-EB is annealed above 400 K, cross-linking between PANI chains occurs [26]. Scherr et al. [27] reported that the cross-linking reaction proceeds between imine nitrogens and the quinoid rings, resulting in a two-dimensional “phenazine” type structure for the PANI. The electrical conductivity is reduced due to structural defects such as branched or cross-linked chains, which causes a reduction of electronic conjugation of the PANI backbone. There have been considerable studies on PANI characterizations. In particular, the effect of heat treatment, chemical reaction, and residual solvent content on the optical, electrical, and structural properties such as surface morphology and crystallinity of PANI films have been studied [28,29]. Recent investigations suggest using PANI nanofibers (NFs) to fabricate efficient electronic nanodevices, although the electrocatalytic performance of PANI NFs to $I^-/I_3^-$electrolyte still needs to be improves.

Anchoring of the dye molecules to the nanocrystalline semiconductors enables fast injection of electrons from the excited state of the molecule into the conduction band of the semiconductor. There have been also interests to make new dyes to substitute ruthenium complex as sensitizer due to their instability to long time solar exposure [30–33]. The most common dyes are the N3 and N719. The main disadvantages of these sensitizers are the lack of absorption in the red region of the visible range, low molar extinction coefficient above the wavelength of 600 nm, and high cost of the ruthenium complexes. In contrast, phthalocyanines (PCs), which are a class of organic compounds, have large absorption bands in the near-IR region and are well-known for their excellent chemical and thermal stability, and have suitable redox properties for fabrication of DSSCs [34,35]. Surprisingly, the PANI-EB and PC derivatives of cobalt, copper and nickel dyes have complementary absorption properties in the visible range. Therefore, when the incident light passes through a transparent PANI film, the energy loss, which can be used by PC dye, would be minimized.

After $TiO_2$ film as photoanode is excited with irradiation, the photogenerated electrons are captured by the transparent PANI film and are quickly transferred to the CE. Since CE is a conductive film, the recombination of photogenerated holes and electrons can be restrained.

The high photoelectrochemical conversion efficiency of PANI/$TiO_2$ films is expected in this charge transfer process that may be explained as follows. The first reason is the close matching of the band-gap energies of $TiO_2$ (3.2 eV) and PANI (2.8 eV) which enhances the charge separation and the electron transfer processes under illumination (see Fig. 1). On the other hand, the photogenerated electrons excited by irradiation enhance the conductivity and consequently improve the photoelectrochemical response and conversion efficiency of DSSC. Another explanation of the greater photocatalytic activity of PANI/$TiO_2$ film is on the basis of level energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Generally, the conduction band minimum (CBM) lies nearly in the same energy level as the LUMO level of the dye molecule and above the CBM of $TiO_2$, while the valence band maximum (VBM) lies much higher than the HOMO level [36]. When PANI/$TiO_2$ film is illuminated under visible light, both the $TiO_2$ and PANI absorb the photons at their surface and then the charge separation occurs. Since the conduction band of $TiO_2$ and the LUMO level of the PANI are well matched for the charge transfer, the electrons, which are promoted from a $\pi$–$\pi^*$ absorption band of the outside PANI film upon the incident light, are easily injected into the conduction band of the inner $TiO_2$ nanostructured film. Whereas electrons in the valence band of $TiO_2$ are transferred into the PANI film and leaving behind holes which lead to increase the fast reaction of $I^-/I_3^-$ redox species at CE. Owing to the light irradiation from both sides of the transparent film, more number of dye molecules can be excited; hence, generating more number of carriers that would increase the conversion efficiency of the DSSC.

In our previous study, a series of nanofiber-shape PANI and coral-like $TiO_2$ nanostructured films were prepared using a facile method under low-temperature conditions. The thermodynamics, dynamics and dynamic mechanical thermal properties of PANI films on a $TiO_2$ substrate were characterized and optimized [29,37]. In the present work, we designed a bifacial DSSC by combining transparent conducting PANI NFs-based CE with a coral-like $TiO_2$ nanostructured film as photoanode, as shown in Fig. 1. The incident light perpendicularly irradiates on the front side of the DSSC, and the transmitted light through the cell is reconstituted using reflecting it onto the rear side of the DSSC. The photovoltaic performance of the prepared bifacial DSSC is studied. The obtained solar-to-electricity conversion efficiency of the prepared bifacial DSSC with 0.3 mM N719 dye molecules is 8.22% under the light irradiation from the front and the rear sides of the cell with the intensity of 100 and 68 mW/cm$^2$, respectively. The bifacial DSSC fabricated in this study allows clarification of the specific morphology with favorable energy loss light