In-situ Fabricated Transparent Conducting Nanofiber-shape Polyaniline / Coral-like TiO₂ 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 TiO₂ nanostructured films, which can be used as the photoanode. PANI-based CEs were prepared by a facile *in situ* polymerization, while coral-like TiO₂ 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 coral-like TiO₂ 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 TiO₂ 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 TiO₂ and PANI NFs-based films in fabrication of bifacial DSSCs.

Keywords: Polyaniline nanofibers, Coral-like TiO₂ nanostructures, transparent thin films, bifacial dye-sensitized solar cell, conversion efficiency.

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 compared 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, 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 Figure 1). In 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/TiO₂ 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 TiO₂, while the valence band maximum (VBM) lies much higher than the HOMO level.^[36] When PANI/TiO₂ film is illuminated under visible light, both the TiO₂ and PANI absorb the photons at their surface and then the charge separation occurs. Since the conduction band of TiO₂ and the LUMO level of the PANI are well matched for the charge transfer, the electrons, which are promoted from a π - π^* absorption band of the outside PANI film upon the incident light, are easily injected into the conduction band of the inner TiO₂ nanostructured film. Whereas electrons in the valence band of TiO₂ are transferred into the PANI film and leaving behind holes which lead to increase the fast reaction of I⁻/I₃⁻ 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 TiO₂ 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 TiO₂ 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 TiO₂ nanostructured film as photoanode, as shown in Figure 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/cm², respectively. The bifacial DSSC fabricated in this study allows clarification of the specific morphology with favorable energy loss light and high surface area for the fabrication of the assembled bifacial DSSCs with high conversion efficiency.

2. Experimental section

2.1. Materials. Titanium tetra-isopropoxide (TTIP 99.9%), ammonium peroxydisulfate [(NH₄)₂S₂O₈], Nitric acid (HNO₃, ≥90%), hydrofluoric acid (HF, 40%), hydrochloric acid (HCl 37%, ACS reagent grade), Aniline (99.5%, ACS reagent grade), 1-methyl-2-pyrrolidinone (NMP), ruthenium (II) 535 *bis*-TBA (N 719, Solaronix), N719 (*cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) *bis*-(tetrabutylammonium), (cobalt (II) phthalocyanine (CoPC) dye, 1,2-dimethyl-3-propylimidazolium iodide (DMPII), Iodine (I₂, 99.8% ACS reagent), Lithium iodide anhydrous beads (LiI), 4-tert-butylpyridine (TBP, 96%), Acetonitrile anhydrous (99.8%), propylene carbonate and ethanol were purchased from Sigma-Aldrich Corp.

2.2. Synthesis. The synthesis of each of PANI and TiO₂ solutions were carried out through two steps: (1) TiO₂ nanostructures were synthesized via hydrolysis reaction of an inorganic precursor through sol-gel process. First, an aqueous solution was prepared by mixing of 1M TTIP, as the precursor, and ethanol in deionized water under stirring at room temperature. A series of HNO₃ and HF, as catalysts, were dissolved in deionized water to make acidic solutions with different concentrations of 0.1 M, 0.15 M and 0.2 M according to a procedure which has been reported previously.^[37] Then, the TTIP solution was slowly added into the latter one under stirring for 30

min at the temperature of 90 °C in a three-necked refluxing pot. The solution was allowed to react for 4 h at the mentioned temperature while the volumes of aqueous solution reached to the half of the initial value. After stirring and refluxing, a homogenous milky solution was formed. The deionized water was slowly added to the milky solution until its volume reached to the initial value. The obtained solution was allowed to stir slowly during 48 h at 50 °C until the hydrolysis reaction was completed and a light bluish solution was formed. (2) Polymerization of 0.55 mmol aniline was carried out by mixing aqueous solutions of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and HCl at room temperature under vigorous stirring for 12 h. The initial concentrations of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and HCl were 0.25 M and 0.5 M, respectively. The PANI-EB precipitate was washed with ethanol and deionized water, respectively. The precipitate was filtered and subsequently dried under vacuum conditions at 55 °C. Finally, the NMP as the solvent was added to PANI-EB powder to make a 10 wt. % solution, which was stirred for 2 h at room temperature until a homogenous and stable solution with a brownish green color was obtained.

2.3. Preparation of PANI and TiO_2 films. PANI and TiO_2 nanostructured films were prepared via two steps: (1) a series of ITO glasses as a substrate were cleaned in an ultrasonic bath containing ethanol for 10 min and treated in UVO cleaner for 15 min. The TiO_2 thin films were obtained by the immersion of the cleaned substrate in the solution using a dip-coater with withdrawal velocity of 0.5 cm/min. TiO_2 thin film used in this work comprised of two layers. The under-layer was composed of dense TiO_2 nanostructured film coated on the FTO glasses. The coral-like TiO_2 film was coated on the under-layer according to the procedure reported previously.^[33] The mean thickness of the dense TiO_2 nanostructured film and the coral-like TiO_2 film were determined as 94 ± 5 nm and 1.0 μm , respectively. The prepared homogeneous films were preheated at the temperature of 125 °C in an electric oven and cooled down slightly to room

temperature. The same process was repeated two times and the obtained films were annealed at 400 °C in vacuum with temperature ramp rate of 3 °C/min. (2) The nanofiber-shape PANI-EB films were prepared by immersing a piece of well-cleaned fluorinated tin oxide (Pilkington, TEC 8 glass, 8 Ω per square, 2.3 mm thick FTO) glass in the solution using the dip-coater with withdrawal velocity of 1 cm min⁻¹. Finally, the PANI film coated on the FTO glass substrates were heated in the oven under vacuum conditions at two drying temperatures of 45 and 200 °C to achieve the PANI thin films. The mean thicknesses of all PANI films were adjusted to 350 $\pm$ 20 nm based on the dipping process. The Pt electrode was prepared by depositing a thin layer of Pt film with thickness of 500 $\pm$ 5 nm on FTO glass using magnetron sputtering.

2.4. Fabrication of DSSCs.

At first, the prepared TiO₂ nanostructured films as photoanode were separately immersed in two types of purified dye molecules including 0.3 mM N719 and 0.2 mM CoPC dye solutions for 24 h. It was then rinsed with ethanol solution and dried under vacuum at 60°C. Subsequently, the DSSCs were assembled by sandwiching the sensitized TiO₂ photoanode with Pt or PANI film as CE by introducing a liquid electrolyte containing 1 M DMPIImI, 60 mM I₂, 0.5 M LiI, and 0.5 M TBP in Acetonitrile and propylene carbonate (v/v=1:1) between them.^[20, 31, 33] Figure 1a illustrates the solution-processed DSSC architecture. As shown in this figure, the commonly used redox couple is iodide/tri-iodide (I⁻/I₃⁻) in an organic liquid electrolyte. A schematic diagram of the energy levels of the TiO₂, N719 dye and PANI, is shown in Figure 1b.

Figure 1. (a) The solution-processed bifacial DSSC architecture. [The adsorbed dye molecule absorbs a photon from a light source and forms an excited state (dye^*). This excited dye transfers an electron to the TiO₂ and a hole to the electrolyte. This separates the electron-hole pair leaving the hole on the dye (dye^{*+}). The hole is filled by an electron from an iodide ion. The reaction is $2\text{dye}^{*+} + 3I^- \rightarrow 2\text{dye} + I_3^-$]. (b) Energy level diagram of the prepared bifacial DCCS structure. The ground state (HOMO level) and excited states (LUMO level) of N719 dye is also shown. The energy scale is referenced to the vacuum level. ΔE , e^- and h^+ show the value of the band gap energy, electron and hole, respectively.

2.5. Physical characterization. The morphology and microstructure of the nanostructured films were examined by scanning electron microscopy (SEM) using a Cam Scan MV2300 microscope. The mean surface roughness of the films were characterized by atomic force microscopy (AFM) using a DME DS-95-50 instrument. Analysis of the AFM data was performed with the image analysis software package Scanning Probe Image Processor (SPIP, Image Metrology A/S, Denmark). The roughness of the films was calculated at different length scales of the AFM images with a customized extension for this program. The thickness of TiO₂ and PANI thin films were measured by ZeScope optical profilometer. Spectroscopic analyses of TiO₂ thin films were performed by a UV–vis spectrophotometer (Hitachi 3140) operating in the 300–1000 nm region. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2020 surface area analyzer. Pore size distribution was calculated by the Barrett-Joyner -Halenda (BJH) method by the adsorption branch of N₂-sorption isotherms. Cyclic voltammetry (CV) of different CEs were carried out on a traditional three-electrode electrochemical workstation (CH Instruments Model 600E, Shanghai, China) at a scan rate of 50 mV/s under the potential range from -0.4 to 1.0 V using electrochemical station with a Pt film as CE, a saturated Ag/AgCl as reference electrode, and PANI/FTO as working electrode. The electrolyte was a mixture of an acetonitrile solution containing 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄. The electrochemical impedance spectroscopy (EIS) measurement was carried out on the CHI 600E electrochemical workstation with the method reported in the literature.^[24, 38-40] The incident photon-to-current conversion efficiency (IPCE) spectrum for the solar cell was measured at AC mode on an IPCE measuring system (PV measurement Inc.). A 75 W xenon lamp as an original light source for monochromatic beam and a 75 W–12 V halogen lamp were used as a bias light source. The photovoltaic performance of the cell was measured under

standard Air Mass 1.5 global (AM 1.5G) sunlight simulation with a class A solar cell analyzer (Spectra Nova Tech.) with the intensity of 100 mW/cm². The intensity was calibrated by using KG5 filtered Si reference solar cell.

3. Results and Discussion

A highly uniform and transparent PANI/TiO₂ assembled-film for photovoltaic application was prepared using a facile method in low temperature. Figure 2 show the SEM images of the TiO₂ nanostructured film (a,b), coral-like TiO₂ film (c,d), and PANI film (e,f). The typical low- and high-magnification SEM images of TiO₂ nanostructured film annealed at 400 °C are seen in Figure 2a and 2b, respectively. According to a previous study, the main reason for choosing 400°C as annealing temperature might be explained by the smaller particle size, higher crystallization of anatase phase, and greater transmittance of the obtained TiO₂ film compared with the films that were annealed at lower temperatures.^[37] As shown, the TiO₂ film has a smooth surface comprised of 20-30 nm anatase TiO₂ nanocrystallites that interconnected in a 94 ± 5 nm thick coated on an optically transparent FTO glass. The crystal structure and phase of TiO₂ nanostructured film was investigated by XRD pattern (Figure S1 in Supplementary data). It can be seen that anatase phase, which can be ascribed to the (101), (004), (200), (105) and (211) planes, was the dominant crystalline structure in the prepared TiO₂ film, which was annealed at 400 °C; however, the weak rutile phase peak according to the (110) plane was detected from XRD pattern of the TiO₂ film.

The surface roughness of TiO₂ nanostructured film was determined using AFM image (Figure S2 in Supplementary data) and AFM image analysis using the Scanning Probe Image Processor software package (Figure S3 in Supplementary data). As shown, the TiO₂ film surface has a uniform structure with mean surface roughness, R_a , of 2.54 nm and limited distribution particles

size of 35-43 nm. The surface roughness, associated with the fluctuations in the film thickness, is a significant factor characterizing the surface morphology which determines the scattering properties of TiO₂ nanostructured film. However, previous studies have shown that the surface roughness does not negatively affect the performance of the solar cells.^[29]

Figures 2c and 2d show high- and low-magnification SEM images of the coral-like TiO₂ film, respectively. Large quantities of coral-like anatase TiO₂ structures made of randomly aligned nanoparticles are observed on the film surface. It is difficult to determine the exact size of coral-like porous structures because of aggregation heterogeneously distributed size. However, it can be estimated that the size of most coral-shape structures are in the range between 200 to 700 nm. It is noteworthy that these aggregates seem to be formed by the superposition of several layers, which make interesting structures regarding their unique shape. As shown in figure 2c, the size of coral-like TiO₂ structures differs spatially from upper portion to the lower one. High magnification SEM image show that the surface of the coral-like structures is composed of nanoparticles with uniform particle size distribution and non-uniform shapes appearing in cashew-like forms (Figure 2d). The size of nanoparticles is in the narrow range of 25-40 nm with mean pore size of 14-19 nm. The observed mesopores structures are mainly resulted from intra-aggregated voids among the nanoparticles contributing to high specific surface area. The pore size distribution of coral-like TiO₂ film was determined using N₂ adsorption–desorption isotherm based on BJH method (Figure S4 in Supplementary data). The low-magnification SEM image of the PANI film dried at temperatures of 45 and 200 °C, which are below and above of the glass transition temperature T_g , are observed in figures 2e and 2f, respectively. The value of T_g for the PANI film are reported to be 378 K in the literature.^[29] As can be seen from these figures, the surface morphology of PANI films are not sufficiently dense and hierarchical porous structures

in an interwoven style can be observed. However, it can be seen that the increase of the drying temperature from 45 °C (Figure 2e) to 200 °C (Figure 2f) appears to favor the coalescing of the nanofibers, thereby yielding a less homogeneous surface morphology and formation of interwoven cross-linked structure.

Figure 2. (a-f) SEM images of the prepared nanostructured films. (a) low-magnification image of TiO₂ film (b) high-magnification image of TiO₂ film, (c) low-magnification image of coral-like TiO₂ film, (d) high-magnification image of coral-like TiO₂ film, (e) PANI film dried at 45°C, (f) PANI film dried at 200°C. (g, h) TEM images of the PANI films. (g) PANI NFs-based film dried at 45°C. (h) Cross-linked PANI dried at 200°C

Figures 2g and 2h shows the TEM images of PANI films prepared at drying temperatures of 45 and 200 °C, respectively. As shown in Figure 2g, the smooth surface shows well-defined single PANI NFs morphology with diameters of 20-40 nm and the length of above 500 nm. With the increase of the drying temperature from 45 to 200 °C, it can be found that the irreversible thermal reaction such as physical cross-linking junctions, which probably weakens the interaction of the inter-chains in the PANI structure, is occurred (Figure 2h). It can be expected that the free volume of the PANI film surface decreases upon a cross-linking phenomena. Therefore, the nanofiber shape and porous structure of the prepared PANI NFs-based film with high surface area is expected to enhance the electrocatalytic performance of the iodide/tri-iodide electrolyte. In fact, high surface area of PANI film led to greater catalytic current densities per unit surface because of the greater surface-to-volume ratio for the iodide reduction.^[2, 20]

Figure 3 shows the N₂ adsorption-desorption isotherm and the corresponding pore size distribution curve for the PANI-NFs-based film obtained at drying temperature of 45 °C and cross-linked PANI film obtained at 200 °C. Using BET measurements, surface area of PANI-NFs-based and cross-linked PANI films were estimated to be 173 and 122 m²/g, respectively. Therefore, the surface area was increased by the presence of micropores and nanofibers shape structures in the PANI film. Based on BJH method, mean pore diameter of NFs-based and cross-linked PANI films were estimated to be 11.9 nm and 14.6 nm, respectively. Therefore, it can be expected that the NFs-based PANI film represents a good sorption ability and solar-to-electricity conversion efficiency because of a high surface area.

Figure 3. (a) N_2 adsorption-desorption isotherms of the PANI-NFs-based film obtained at drying temperature of 45°C and cross-linked PANI film obtained at 200°C and (b) pore size distribution plots.

Optical properties of the thin films were evaluated by UV-vis spectroscopy. Figure 4a shows the transmittance spectrum of the FTO glass in the visible light. It can be seen that the transmittance of the FTO thick film varied slightly around 80 to 83% in the range of 300–1000 nm. The transmittance of PANI NFs-based film coated on the FTO glass is compared with Pt, and cross-linked PANI film in Figure 4b. The Pt film showed better average transmittance in the wavelength range of 300–1000 nm, but the cross-linked PANI and PANI NFs-based films showed the higher transmittance in the range of 480–705 nm and 465–780 nm, respectively. Interestingly, the PANI NFs-based film exhibited a maximum transmittance of $\sim 71\%$ in the visible region, which indicated that the PANI NFs-based film is better candidate as CE than Pt electrode for fabrication of the bifacial DSSC.

Figure 4c shows the transmittance spectrum of the dense TiO_2 nanostructured film annealed at 400°C . The transmittance of film increases suddenly above 395 nm and reaches to a relatively stable value with maximum transmittance ($\sim 80\%$) due to the interference between the TiO_2 film

and the FTO glass at high wavelengths. The large decrease approximately below 395 nm is due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of the TiO₂ nanostructured films.

Based on the solid-state band theory, the absorption coefficient for the direct transition can be defined as a function of the incident photon energy, i.e. $(\alpha h\nu)^2 = (h\nu - E_g)$. In this equation, α and E_g are the absorption coefficient and the band gap energy, respectively. The value of α was calculated as a function of the photon energy and plotted in Figure 4c (inset image). The linear extrapolation in the transition region using Tauc's plot^[41] on the photon energy-axis gives the E_g of 3.22 eV for TiO₂ nanostructured film annealed at 400 °C. The value of E_g calculated for TiO₂ nanostructured film is similar to the values of E_g reported in the literature (E_g = 3.2 eV for anatase TiO₂ nanowalls,^[42] E_g = 3.15 eV for single-layered TiO₂ nanosheets and E_g = 3.2 eV for anatase TiO₂ film^[43]). The small difference in the E_g of the TiO₂ nanostructures reported in the literature is due to the ratio of anatase to rutile phase, because the E_g of the anatase (3.2 ± 0.1 eV) is larger than that of the rutile phase (3.0 ± 0.1 eV).^[44]

Figure 4d shows the UV-vis spectrum of coral-like TiO₂ film deposited on the FTO glass/dense TiO₂ nanostructured film that annealed at 400 °C. This spectrum reveal that the transmittance of film is less than 35% and the E_g of film is 3.05 eV (Figure 2d, inset). The value of E_g calculated for coral-like TiO₂ film is close to similar structures reported in literature (E_g = 3.02 eV for TiO₂ hierarchical nanostructures and E_g = 3.02 ± 0.1 eV for flower-like TiO₂ film^[45]). The low transmittance of the porous film evidences that most part of the incident light is absorbed by the organic dye molecules. However, small part of the incident light directly passes through, scattered or reflected, and is not utilized in DSSC.

It clearly indicates that the film with coral-like TiO₂ structure has excellent light scattering and favorable optical absorption performance that can also yield better performance for the solar cell.

Figure 4. UV-vis spectra of (a) FTO glass, (b) the transmittance spectra of three kinds of CEs: Pt film, cross-linked PANI film, and PANI NF film, (c) the transmittance spectra of the dense TiO₂ nanostructured film and (inset) the band gap estimation, (d) the transmittance spectra of coral-like TiO₂ film and (inset) the band gap estimation.

To compare the optical response of the bifacial DSSC consisted of the PANI NFs-based CE and coral-like TiO₂ nanostructured film as photoanode; we studied their UV-vis spectra using

dye molecules of CoPC and N719 with initial concentrations of 1 mM and 0.3 mM, respectively. As shown in Figure 5, the optical absorbance spectrum of the cells consisting of CoPC dye/coral-like TiO_2 nanostructures (black line) and, especially, N719/coral-like TiO_2 film (green line) are compared with a conventional Grätzel cell, (red line), which the latter was prepared with N719 dye/nanoporous TiO_2 film.^[1,2,5,8,46]

Figure 5. Optical response of fabricated-DSSC based on the PANI NFs electrode with two different photoanode consisting of 1 mM CoPC dye/coral-like TiO_2 film (black line) and the 0.3 mM N719 dye/coral-like TiO_2 nanostructures (green line) with a conventional Grätzel cell, which prepared with 0.3 mM N719 dye/nanoporous TiO_2 film (red line)

Optical absorption measurements show that the prepared cell containing of the N719/coral-like TiO_2 film exhibit a red-shifted absorption edge (at 558 nm) compared to that of the conventional Grätzel cell (at 660 nm) and outperform it in the red and near-infrared spectral regions. Therefore, the fabricated cell based on the coral-like TiO_2 film has a higher light absorption and is more efficient than the conventional Grätzel cell. It can be also noted that the main drawbacks of N719 dye sensitizer in both cells are the lack of light absorption caused by the high transmittance of the TiO_2 film and the low molar extinction coefficient of the dye molecule

above the wavelength of 600 nm. In fact, the lack of absorption peak in the red and near-infrared spectral regions and the high fabrication cost are challenging issues for ruthenium-based dyes such as N719.

As shown in figure 5, the visible absorption band appeared at the range of 600–700 nm when 1mM CoPC dye molecules used in the prepared DSSC. In the mentioned spectral region, relatively more electrons transferred from the ground state (HOMO level) to the excited state (LUMO level) in the CoPC dye molecules at the surface of the coral-like TiO_2 film during illumination, which leads to the enhancement of the charge separation and electron transfer processes under illumination. There are three bands of 690 nm, 668 nm and 625 nm in the absorption spectrum of DSSC at the presence of CoPC dye molecules. Two strong absorption bands at 670 nm and 690 nm represent the monomer form of the CoPC, while the weak absorption band at 649 nm reveals the dimer form of the CoPC dye molecules. The main disadvantage of CoPC is the significant reduction of the absorption band in the blue region of the visible spectrum in comparison with N719 dye molecules.

It should be noted that the complementary absorption properties of PANI NFs-based film associated with each of the dye molecules (N719 or CoPC) are crucial for the high performance of the fabricated DSSC prepared in this work when the incident light was reflected from the rear side of the electrode.

Cyclic voltammetry (CV) was used to investigate the electrocatalytic activity of the fabricated DSSC based on different CEs toward to I^-/I_3^- redox couple. Generally, in DSSC, electrons are injected into photo-oxidized dye from I^- ions in the electrolyte, and the produced I_3^- ions are reacted at the CE (see Figure 1). The PANI film in fabricated DSSC serves as an electrocatalyst for reducing I_3^- to I^- ; therefore, the cathodic reduction peak current density in CV curves can be

applied to evaluate the electrocatalytic activity of the film. Figure 6 shows the repeated CV of the PANI NFs electrode recorded continuously in a supporting electrolyte consisting of 10 mM LiI, 1 mM I₂ acetonitrile solution containing 0.1 M LiClO₄ at the potential range between -0.4 V to 1.0 V. Here, PANI/FTO as working electrode and Pt wire or PANI as CEs were combined with Ag/AgCl in saturated KCl as a reference electrode immersed in the electrolyte solution. Calibration was done using ferrocene as standard. The positive and negative pairs of redox waves are observed on each of the electrodes; the left and the right pairs are explained to be the oxidation and reduction of I⁻ / I₃⁻ and I₂ / I₃⁻ redox couple, respectively. The performance of the cell prepared with the PANI NFs-based CE was compared with Pt- and cross-linked PANI-based CEs that used for fabrication of DSSC. From figure 6, it can be found that the cathodic (*I_c*) and anodic peak current (*I_a*) density of PANI NFs-based CE is higher than that of the cross-linked PANI and Pt electrodes. The analysis of the CV curves shows that the PANI NFs electrode attains reasonably high values for *I_c* and *I_a* in the range of 0.98 and -1.61 mA/cm², respectively, associated with a considerably high switching point value of 0.87 mA/cm². However, the cross-linked PANI electrode showed the lower *I_c* of 0.82 mA/cm² and *I_a* of -1.49 mA/cm² with a lower switching point of 0.79 mA/cm² compared with the PANI NFs electrode. It is notable from the cathodic peak position that the overpotential for reducing I₃⁻ in cross-linked PANI electrode and especially PANI NFs-based CE electrodes are higher redox current density and stronger electrocatalytic activity toward the reduction of the I₃⁻ to I⁻ ions in the redox couple compared with Pt-based CE. However, the bridge effect of PANI NF's electrode has the largest peak current density, which compensates its disadvantage of the overpotential. Therefore, the PANI NFs-based film as an efficient CE is very promising for fabrication of DSSCs considering its high surface area and low cost compared with the Pt-based CEs.

Figure 6. Cyclic voltammograms for Pt-, cross-linked PANI-, and PANI NFs-based CE recorded in a supporting electrolyte consisting of 10 mM LiI, 1 mM I₂ acetonitrile solution containing 0.1 M LiClO₄ at scan rate of 50 mV s⁻¹.

To explore the potentials for photovoltaic applications, the performance of a DSSC assembled based on coral-like TiO₂ nanostructured film with different CEs was investigated at AM 1.5 G simulated irradiation under intensities from the front and the rear of 100 and 68 mW/cm², respectively. Figure 7a demonstrates the current density–voltage (J–V) characteristic curves of the DSSCs using Pt, cross-linked PANI, and PANI NFs-based CEs at the presence of 0.3 mM N719 dye molecules under simulated light irradiation from both the front and the rear sides. The J–V characteristic curves of the fabricated cells at the presence of 1 mM CoPC dye molecules are also shown in Figure S6 (Supplementary data). The photovoltaic characteristics of the fabricated DSSCs are summarized in Table 1. The cell employing PANI NFs-based CE showed a short-circuit current density (J_{sc}) of 16.17 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.734 V, and a fill factor (FF) of 0.710, resulting in a conversion efficiency ($\eta = V_{oc} \times J_{sc} \times FF$) of 8.22%, which was comparable to the efficiencies of 7.75% and 7.81% when the CE was fabricated based on Pt and

cross-linked PANI film, respectively. The results of the present cells showed an increase in conversion efficiency compared with the solar cells consisted of PANI/nanoporous TiO_2 film ($FF = 0.604$ and $\eta = 6.54\%$), and Pt/nanoporous TiO_2 film ($FF = 0.643$ and $\eta = 6.69\%$) reported in the literature.⁴⁸ The improvement by using the coral-like TiO_2 nanostructures can be attributed to the larger surface area, which enables more adsorption of CoPC dye molecules and relatively suitable dye loading. It can be seen from table 1 that the FF values for the prepared DSSCs based on different CEs are slightly higher than that of the most reported ones in the literature (0.6-0.7).^[1, 14, 48-51] This may be attributed to the low recombination rate between photo-excited carriers in the photo-anodes and the tri-iodide ions in the electrolyte.

Figure 7. (a) J-V characteristic curves of the DSSCs fabricated based on the coral-like TiO_2 nanostructures and CEs including Pt, cross-linked PANI and PANI NFs-based CEs at the presence of 0.3 mM N719 dye molecules under simulated sunlight irradiation from both the front (100 mW/cm²) and the rear (68 mW/cm²) sides, (b) J-V curves of the fabricated-DSSCs using three kinds of CEs under simulated sunlight irradiation (100 mW/cm²) from only the front (F) or the rear (R).

Figure 7b shows the J-V curves of the fabricated-DSSCs irradiated only from the front or the rear side. The results are summarized in Table 1. When the incident light irradiated from the front side of the cell, the fabricated DSSC based on Pt film showed a conversion efficiency of 6.72%, which is same as the typical values reported in the literature.^[47, 52-53] Also, the low conversion efficiency of 2.84% is obtained by irradiation only from the rear side of cell, which was due to the high reflectivity of the Pt-based CE. However, the obtained efficiency is still slightly higher than that of the similar cell reported in the literature (2.73%).^[54] This may be associated with the higher light scattering capacity of the coral-like TiO₂ film as photoanode improving the light harvesting and the cell performance. The reduced J_{sc} is due to the decrease of the incident light intensity through reflection from the Pt-based CE.^[51, 52] Although Pt electrode has high reflectivity, the transmitted light from the rear can produce photogenerated charge carriers and photocurrent, resulting in higher efficiency for both-side irradiation than one-side irradiation. When the DSSC fabricated based on cross-linked PANI electrode irradiated from the front side, a low efficiency of 5.91% was obtained, which is the lower than the values reported in the literature.^[34, 44, 52] However, the DSSC with cross-linked PANI-based CE irradiated from the rear side showed an efficiency of 3.03%.

Table 1. Photovoltaic characteristics of DSSCs fabricated based on different CEs in the presence of 0.3 mM N719 and 1 mM CoPC dye molecules

CE	Dye type	Irradiation direction	R_s ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Efficiency (%)
Pt	N719	front	-	-	12.78	0.727	0.723	6.72
		rear	-	-	5.33	0.679	0.784	2.84
		front & rear	12.89	2.92	14.79	0.742	0.706	7.75
	CoPC	front	-	-	0.94	0.226	0.942	0.20
		rear	-	-	0.56	0.166	0.971	0.09
		front & rear	13.61	4.25	1.23	0.240	0.915	0.27
Cross-linked PANI	N719	front	-	-	13.19	0.616	0.728	5.91
		rear	-	-	6.03	0.671	0.749	3.03
		front & rear	15.09	4.39	15.45	0.722	0.700	7.81
	CoPC	front	-	-	0.77	0.217	0.954	0.16
		rear	-	-	0.49	0.166	0.982	0.08
		front & rear	16.08	5.67	0.99	0.239	0.927	0.22
PANI NFs	N719	front	-	-	13.60	0.729	0.712	7.06
		rear	-	-	6.48	0.689	0.764	3.41
		front & rear	13.01	3.14	16.17	0.738	0.688	8.22
	CoPC	front	-	-	0.97	0.228	0.945	0.21
		rear	-	-	0.62	0.166	0.972	0.10
		front & rear	14.64	4.75	1.34	0.243	0.893	0.29

As shown in table 1, when the DSSC fabricated based on PANI NFs-based CE was irradiated only from the front or the rear, the efficiency was 7.06% and 3.41%, respectively. Therefore, using PANI NFs electrode, the both-side and the rear side efficiency are increased by 7.55% and 13.76%, respectively, in compared with the DSSC fabricated based on the cross-linked PANI-based CE. The PANI NFs-based fabricated DSSC has better photovoltaic performance than the Pt-based CE and cross-linked PANI-based CE. The both-side efficiency (8.22%) of DSSC with

PANI NFs electrode is enhanced by 16.4 % compared to the front-side efficiency. The efficiency of 8.22% is the highest reported value for the DSSCs fabricated by PANI NFs-based CE.

The electrochemical impedance spectroscopy (EIS) analysis is carried out to investigate the correlations between the properties of the CEs and the J-V performances of the fabricated-DSSC. Figure 8 presents the corresponding Nyquist plots obtained from symmetrical dummy cells relative series resistance (R_s) and charge-transfer resistance (R_{ct}) on the PANI NFs-, cross-linked PANI-, and Pt-based CEs tested in the presence of 0.3 mM N719 dye (Fig. 8a and 8c) and 1 mM CoPC dye (Fig. 8b and 8d) dye solutions. The results are presented in Table 1. It is generally recognized that, in the order of increasing frequency, the response can be attributed to the Warburg diffusion processes in the electrolyte and electron transport at the CE/electrolyte interface.

As shown in figure 8a, the cross-linked PANI-based CE in the presence of N719 dye molecules has a high R_s and R_{ct} values of 15.11 and 4.39 $\Omega \text{ cm}^2$, respectively, indicating an unsuitable CE in DSSC compared with the other electrodes. The Pt electrode in the presence of N719 dye has moderate R_s value of 12.89 $\Omega \text{ cm}^2$ and low R_{ct} value of 2.84 $\Omega \text{ cm}^2$. PANI NFs electrode has almost similar R_s and R_{ct} as the Pt electrode with values of 13.01 $\Omega \text{ cm}^2$ 3.14 $\Omega \text{ cm}^2$, respectively. This result is in the same range as those of other nanostructured porous films used as CE.^[51, 52, 54]

The cell aging stability was investigated by checking the efficiency decay as a function of aging time. Figures 8c and 8d show the impedance spectra using the Z-view software for the fresh and aged dummy cells from PANI NFs-based CE in the presence of 0.3 mM N719 and 1 mM CoPC dye molecules, respectively. All cells were kept in the dark place at room temperature (25 °C). There is a reasonable stability for R_s , which indicates that PANI NFs-based CE has a good stability in redox electrolyte solution. In contrast, the R_{ct} of the cross-linked PANI-based

CE in the presence of N719 dye molecules increases from 3.14 to 4.53, 5.08, and 5.24 $\Omega\cdot\text{cm}^2$ after aging for 7, 14, and 28 days, respectively. However, R_{ct} of the cross-linked PANI electrode in the presence of CoPC dye molecules significantly increased from 4.75 to 6.84 $\Omega\cdot\text{cm}^2$ after aging time of 7 days. The poor long-term stability of cell in the presence of CoPC dye is attributed to weakly bound dye molecules on the surface of film comprised of coral-like TiO_2 nanostructures. In addition, desorption of CoPC dye molecules from the TiO_2 surface can be strongly correlated with the decay of light harvesting efficiency, resulting in poor long-term stability. The increase of R_{ct} with aging time and especially in presence of CoPC dye molecules can possibly be attributed to the decrease in transferring charges due to saturation of active sites by the electroactive ionic species and decrease of electrocatalytic activity to redox electrolyte that can be result in the reduction of J_{sc} . The reduced J_{sc} is the main reason for the efficiency loss. However, at high frequencies there is no significant difference on the electrolyte resistance through aging time (Figs. 8b and 8c). An equivalent circuit is applied to model the complex impedance in the prepared DSSC (inset of Figure 8 a and 8c).

Figure 8. Nyquist plots obtained from dummy cells relative series resistance (R_s) and charge transfer resistance (R_{ct}) from the Pt, cross-linked PANI, and PANI NFs-based CE tested in the presence of 0.3 mM N719 dye (a and b) and 1 mM CoPC dye (c and d). The insets are the equivalent circuit [C_{dl} corresponded to the double layer capacitance value at electrode surface and the solution interface]. Nyquist plots of EIS for the cells with PANI NFs electrode tested at different aging times at room temperature (b and d).

According to the results of table 1 and figure 8, the following points should be noted: (1) Since R_{ct} of the PANI NFs electrode is slightly higher than that of Pt and especially cross-linked PANI electrode, the increase of electrocatalytic activity to redox electrolyte and the improvement of J_{sc} is attributed to the high surface area of the PANI NFs-based CE due to its porous nature, which is evident from the results of SEM, TEM and BET analysis. (2) The porous PANI NFs electrode has a high internal surface area; hence, it gives high electrochemical rates per unit surface area of the electrode, but the internal area cannot be completely utilized at high current densities due to the internal effect from mass transfer and ohmic polarization in an electrolyte that is dependent on the surface morphology of PANI film. (3) Because the charge capacity of an electrode for a specific reaction is proportional to the electrode surface, CV result indicates that the reaction surface area increases when the surface morphology of PANI film exhibits a nanofiber shape. (4)

The R_{ct} of the PANI NFs electrode in the presence of N719 dye molecules are significantly higher than that of CoPC dye molecules. (5) The efficiency of the fresh cell in the presence of N719 dye molecules gradually decreased over 28 days while the efficiency of the fresh cell in the presence of CoPC dye molecules abruptly decreased during 7 days, indicating poor long-term stability of the cell. (6) The efficiency decay is mainly correlated with the decrease of J_{SC} . On the other hand, a slight increase of FF can retard the efficiency decay.

The light response of the photovoltaic devices was measured using IPCE spectrum, which is directly related to the short-circuit current. Figure 9 compares the IPCE as a function of incident wavelength for the DSSC assembled based on coral-like TiO_2 nanostructured film with different CEs in the presence of N719 dye molecules under light irradiation from both sides (front and rear irradiations were 100 and 68 mW cm^{-2} , respectively) over the wavelength range of 400-900 nm. The IPCE curves of fabricated DSSCs in the presence of CoPC dye molecules at same conditions are shown in Figure S7 (Supporting Information). As shown in Figure 9, the DSSC fabricated with cross-linked PANI-based cell exhibits the IPCE value of ~60% in the absorption range of 440-670 nm. In the same spectral range, PANI NFs-based DSSC produces a higher and broader photocurrent density with the IPCE of ~70% under the external circuit illumination (per photon flux). In addition, for the case of the cell based on PANI NFs electrode, in the visible region from about 440 to 570 nm, a strong and relatively constant conversion efficiency associated with the nearly flat profile was seen in the absorption range of ~65-70%. The IPCE red-shift phenomenon can be ascribed to the extended optical path by the light scattering, just as mentioned elsewhere.^[50, 55-57] The high both-side conversion efficiency of the DSSC with PANI NFs-based CE and coral-like TiO_2 nanostructured film can be explained by considering a combination of several effects. Firstly, the enhanced photon absorption associated with the

augmented surface area results in higher dye loading and correspondingly to a larger J_{sc} , as shown in Figure 7b. Secondly, mesoporous structures of coral-like TiO_2 film can increase the electron diffusion length because the pores provide more direct conduction paths for electron transfer in the TiO_2 film-electrolyte interface and then hole transfer in the electrolyte-PANI CE interface, which all occur in the fabricated bifacial DSSC (see Figure 1b). This result indicates that higher electrons were trapped in the coral-like TiO_2 structures. Thirdly, cashew-like shaped and randomly aligned nanoparticles which have been formed on the coral-like TiO_2 structures, promote enhanced light-dye interaction without sacrificing the efficient electron transport. Finally, owing to the transparent CE, the rear light can penetrate and be absorbed by the dye molecules in the DSSC, which will enhance the J_{sc} and thus the overall conversion efficiency. It is also believed that the value can be further improved by designing a better light-splitting device with vertical incidence.

Figure 9. IPCE spectrum as a function of incident wavelength for bifacial DSSCs with different CEs under light irradiation from both sides (front and rear irradiances were 100 and 68 mW/cm^2 , respectively)

Conclusion

We presented a novel bifacial dye-sensitized solar cell (DSSC) based on transparent conducting Polyaniline (PANI) films as the counter electrode (CE) combined with coral-like TiO_2 nanostructured films used as the photoanode. PANI-based films with the thickness of 350 ± 20 nm were prepared on an FTO glass by a facile *in situ* polymerization. The coral-like TiO_2 films with the thickness of $1.0 \mu\text{m}$ were prepared on an FTO glass. They were chemically synthesized at low temperature through the sol-gel dip-coating method. The images from the SEM and the TEM showed that the PANI films dried at 45°C and 200°C were composed of nanofibers (NFs) and cross-linked surface morphology, respectively. This type of morphology, which reveals hierarchical porous structures, resulted in the surface area of 173 and $122 \text{ m}^2/\text{g}$ for PANI NFs and cross-linked PANI structures, respectively. According to CV and EIS, the PANI NFs-based CE exhibited higher catalytic activity and smaller charge transfer resistance at the electrolyte/CE interface in the cell filled with N719 dye molecules. These features resulted in the reduction of I_3^- and the improvement of the short-circuit current density ($16.17 \text{ mA}/\text{cm}^2$) compared with that of the cross-linked PANI ($15.45 \text{ mA}/\text{cm}^2$) and Pt ($14.79 \text{ mA}/\text{cm}^2$) electrodes. Furthermore, the PANI NFs-based CE showed a maximum transmittance of $\sim 70\%$ in the visible region, which enabled the fabrication of the bifacial DSSC. Owing to the light irradiation from the front and rear sides, more dye molecules were excited by the dye molecules and more carriers were generated because of the excellent light scattering property of the coral-like TiO_2 and high specific surface area of the PANI nanofibers (NFs). Consequently, we observed the increase of the solar-to-electricity conversion efficiency. We concluded that the PANI NFs-based CE has favorable catalytic activity. The bifacial DSSC fabricated by the PANI NFs-based film associated with the coral-like TiO_2 film in the presence of N719 dye molecules showed efficiency of 8.22% corresponding to the both-side irradiation, while similar cells employing a

cross-linked PANI- and Pt-based CE showed efficiencies of 7.81% and 7.75%, respectively. In comparison with PANI NFs-based CE, the low conversion efficiency of the DSSC fabricated by cross-linked PANI-based CE, especially when the CE irradiated only from the rear side, was because of the low transmittance and the low electrocatalytic activity of the cross-linked PANI electrode. The results of similar cells irradiated from both sides at presence of CoPC dye molecules showed low efficiencies of 0.27%, 0.22% and 0.29%, when the DSSCs were comprised of Pt, cross-linked, and PANI NFs-based CEs, respectively. The low efficiencies of these devices were due to the absorption band of the CoPC dye molecules which is in the red region of the visible range although this dye is less expensive than the ruthenium-based dyes such as N719. The bifacial DSSCs prototyped in this work are promising for commercial scale applications due to their improved photovoltaic performance as well as the low cost of the PANI NFs as the CE and the high light scattering of the TiO₂ film as the photoanode.

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References

- [1] M. Grätzel, Photoelectrochemical cells, *Nature* 414 (2001) 338-344.
- [2] M. Grätzel, Recent advances in sensitized mesoscopic solar cells, *Acc. Chem. Res.* 42 (2009) 1788–1798.
- [3] J-W. Lim, D-Y. Cho, J. Kim, S-I. Na, H-K. Kim, Simple brush-painting of flexible and transparent Ag nanowire network electrodes as an alternative ITO anode for cost-efficient flexible organic solar cells, *Sol. Energ. Mat. Sol. C.* 107 (2012) 348-354.

- [4] Q. Chen, H. Zhou, Z. Hong, S. Luo, H-Sh. Duan, H-H. Wang, Y. Liu, G. Li, Y. Yang, Planar heterojunction Perovskite solar cells via vapor-assisted solution process, *J. Am. Chem. Soc.* 136 (2014) 622–625.
- [5] M. L. Parisi, S. Maranghi, R. Basosi, The evolution of the dye sensitized solar cells from Grätzel prototype to up-scaled solar applications: A life cycle assessment approach, *Renew. Energ.* 39 (2014) 124-138.
- [6] W. Chen, Y. Liu, J. Luo, J. Sun, L. Gao, A bifunctional TiO_2 sol for convenient low-temperature fabrication of dye-sensitized solar cells, *Mater. Lett.* 67 (2012) 60-63.
- [7] Y. Hou, D. Wang, X. H. Yang, W. Q. Fang, B. Zhang, H. F. Wang, G. Z. Lu, P. Hu, H. J. Zhao, H. G. Yang, Rational screening low-cost counter electrodes for dye-sensitized solar cells, *Nature Commun.* 4 (2013) 1583-1583.
- [8] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature* 353 (1991) 737–740.
- [9] Y. Masuda, T. Ohji, K. Kato, Multineedle TiO_2 nanostructures, self-assembled surface coatings, and their novel properties, *Cryst. Growth Des.* 10 (2009) 913-922.
- [10] J. J. Wu, C. C. Yu, Aligned TiO_2 nanorods and nanowalls, *J. Phys. Chem. B* 108 (2004) 3377-3379.
- [11] Z. Ma, Q. Guo, X. Mao, Z. Ren, X. Wang, Ch. Xu, W. Yang, D. Dai, Ch. Zhou, H. Fan, X. Yang, Photocatalytic dissociation of ethanol on TiO_2 (110) by near-band-gap excitation, *J. Phys. Chem. C* 117 (2013) 10336–10344.
- [12] S. Prabakar, C. W. Bumby, R. D. Tilley, Liquid-phase synthesis of flower-like and flake-like titanium disulfide nanostructure, *Chem. Mater.* 21 (2009) 1725-1730.

- [13] Z. Sun, J. H. Kim, Y. Zhao, F. Bijarbooneh, V. Malgras, Y. Lee, Y.-M. Kang, S. X. Dou, Rational design of 3D dendritic TiO₂ nanostructures with favorable architectures, *J. Am. Chem. Soc.* 133 (2011) 19314-19317.
- [14] S. H. Lee, J. Kwon, D. Y. Kim, K. Song, S. H. Oh, J. Cho, E. F. Schubert, J. H. Park, J. K. Kim, Enhanced power conversion efficiency of dye-sensitized solar cells with multifunctional photoanodes based on a three-dimensional TiO₂ nanohelix array, *Sol. Energ. Mat. Sol. C.* 132 (2015) 47-55.
- [15] K.-J. Yoon, J. S. Park, S.-J. Lee, M. Song, I. A. Shin, J. W. Lee, Y.-S. Gal, S.-H. Jin, Synthesis and characterization of fluorene-based copolymers containing benzothiadiazole derivative for light-emitting diodes applications, *J. Polym. Sci. A: Polym. Chem.* 46 (2008) 6762–6769.
- [16] H. V. Patten, E. Ventosa, A. Colina, V. Ruiz, J. López-Palacios, A. J. Wain, S. C. S. Lai, J. V. Macpherson, P. R. Unwin. Influence of ultrathin poly-(3,4-ethylenedioxythiophene) (PEDOT) film supports on the electrodeposition and electrocatalytic activity of discrete platinum nanoparticles, *J. Solid State Electrochem.* 15 (2011) 2331-2339.
- [17] R. Palacios, P. Formentin, E. Martinez-Ferrero, J. Pallarès, L. F. Marsal. β -phase morphology in ordered poly(9,9-dioctylfluorene) nanopillars by template wetting method, *Nanoscale Res. Lett.* 6 (2010) 35-38.
- [18] R. M. Moslin, Ch. G. Espino, T. M. Swager. Synthesis of conjugated polymers containing *cis*-phenylenevinylenes by titanium mediated reductions, *Macromolecules.* 42 (2008) 452–454.
- [19] Y. Kiya, A. Iwata, T. Sarukawa, J. C. Henderson, H. D. Abruña, Poly[dithio-2,5-(1,3,4-thiadiazole)] (PDMcT)–poly(3,4-ethylenedioxythiophene) (PEDOT) composite cathode for high-energy lithium/lithium-ion rechargeable batteries, *J. Power Sources* 173 (2007) 522-530.

- [20] Q. Tai, B. Chen, F. Guo, Sh. Xu, H. Hu, B. Sebo, X.-Zh. Zhao, In situ prepared transparent polyaniline electrode and its application in bifacial dye-sensitized solar cells, *ACS Nano* 5 (2011) 3795–3799.
- [21] F. Zhang, M. Johansson, M.R. Andersson, J.C. Hummelen, O. Inganas, Polymer photovoltaic cells with conducting polymer anodes, *Advanced Materials* 14 (2002) 662–665.
- [22] J. Ouyang, Q. Xu, C.W. Chu, Y. Yang, G. Li, J. Shinar, On the mechanism of conductivity enhancement in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment, *Polymer* 45 (2004) 8443–8450.
- [23] S. J. Pomfret, P. Adams, N. Comfort, A. P. Monkman, *Polymer* 41 (2000) 2265–2269.
- [24] T. H. Lim, K. W. Oh, S. H. Kim, Self-assembly supramolecules to enhance electrical conductivity of polyaniline for a flexible organic solar cellsanode, *Sol. Energ. Mat. Sol. C.* 101 (2012) 232-240.
- [25] J. Stejskal, I. Sapurina, M. Trchová, E. N. Konyushenko, Oxidation of aniline: Polyaniline granules, nanotubes, and oligoaniline microspheres, *Macromolecules*, 41 (2008) 3530–3536.
- [26] L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C.-K. Tee, Y. Shi, Y. Cui, Zh. Bao, Hierarchical nanostructured conducting polymer hydrogel with high electrochemical activity, *PNAS Early Edition* 109 (2012) 9287-9292.
- [27] E. M. Scherr, A. G. MacDiarmid, S. K. Manohar, J. G. Masters, Y. Sun, X. Tang, M. Druy, P. J. Glastokowski, V. B. Cajipe, J. E. Fischer, K. R. Cromack, M. E. Jozefowicz, J. M. Ginder, R. P. McCall, A. J. Epstein, Polyaniline: Oriented films and fibers, *Synth. Met.* 41 (1991) 735-738.
- [28] S. G. Pawar, S. L. Patil, M. A. Chougule, B. T. Raut, Shashwati Sen, V. B. Patil, Camphor sulfonic acid doped polyaniline-titanium dioxide nanocomposite: Synthesis, structural,

morphological, and electrical properties. *Int. J. Polymer. Mater. Polymer. Biomater.* 60 (2011) 979-987.

[29] A. Bahramian, The effect of heat treatment on the surface structure of Polyaniline nanostructured film: An experimental and molecular dynamics approach, *Appl. Surf. Sci.* 311 (2014) 508–520.

[30] G. J. Meyer, The 2010 millennium technology grand prize: Dye-sensitized solar cells, *ACS Nano* 4 (2010) 4337–4343.

[31] Md. K. Nazeeruddin, R. Humphry-Baker, D. L. Officer, W. M. Campbell, A. K. Burrell, M. Grätzel, Application of metalloporphyrins in nanocrystalline dye-sensitized solar cells for conversion of sunlight into electricity, *Langmuir* 20 (2004) 6514–6517.

[32] Y. Tachibana, S. A. Haque, I. P. Mercer, J. E. Moser, D. R. Klug, J. R. Durrant, Modulation of the rate of electron injection in dye-sensitized nanocrystalline TiO₂ films by externally applied bias, *J. Phys. Chem. B* 105 (2001) 7424–7431.

[33] T. Yuasa, R. Kawakami, Y. Sato, Y. Mori, M. Adachi, Sh. Yoshikado, Dye adsorption for dye-sensitized solar cell, *Sol. Energ. Mat. Sol. C.* 102 (2012) 2-7.

[34] A. K. Sarker, M. G. Kang, J.-D. Hong, A near-infrared dye for dye-sensitized solar cell: Catecholate-functionalized zinc phthalocyanine, *Dyes Pigments* 92 (2012) 1160-1165.

[35] F. Liang, F. Shi, Y. Fu, L. Wang, X. Zhang, Zh. Xie, Zh. Su, Donor–acceptor conjugates-functionalized zinc phthalocyanine: Towards broad absorption and application in organic solar cells, *Sol. Energ. Mat. Sol. C.* 94 (2010) 1803-1808.

[36] I. Chung, B. Lee, J. He, R. P. H. Chang, M. G. Kanatzidis, All-solid-state dye-sensitized solar cells with high efficiency *Nature* 485 (2012) 486-490.

- [37] A. Bahramian, High conversion efficiency of dye-sensitized solar cells based on coral-like TiO₂ nanostructured films: Synthesis and physical characterization, *Ind. Eng. Chem. Res.* 52 (2013) 14837–14846.
- [38] B. Arredondo, B. Romero, G. Del Pozo, M. Sessler, C. Veit, U. Würfel, Impedance spectroscopy analysis of small molecule solution processed organic solar cell, *Sol. Energ. Mat. Sol. C.* 128 (2014) 351-356.
- [39] S. Sarker, H. W. Seo, D. M. Kim, Electrochemical impedance spectroscopy of dye-sensitized solar cells with thermally degraded N719 loaded TiO₂, *Chem. Phys. Lett.* 585 (2013) 193-197.
- [40] Q. Wang, J. E. Moser, M. Grätzel, Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells. *J. Phys. Chem. B.* 109 (2005) 14945-14953.
- [41] G. Tamizhmani, M. Cocivera, R.T. Oakley, C. Fischer, M. Fujimoto, *J. Phys. D: Appl. Phys.* 24 (1991) 1015.
- [42] J. J. Wu, C. C. Yu, Aligned TiO₂ nanorods and nanowalls. *J. Phys. Chem. B* 108 (2004) 3377-3379.
- [43] W. Wunderlich, L. Miao, M. Tanemura, S. Tanemura, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabin, R. Belkade. AB-Initio calculations of the optical gap of TiO₂ thin films, *Int. J. Nanosci.* 03, (2004) 439-445.
- [44] D. O. Scanlon, Ch. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, A. A. Sokol. Band alignment of rutile and anatase TiO₂, *Nature Mater.* 12 (2013) 798-801.

- [45] K. Pan, Y. Dong, W. Zhou, Q. Pan, Y. Xie, T. Xie, G. Tian, G. Wang, Facile fabrication of hierarchical TiO₂ nanobelt/ZnO nanorod heterogeneous nanostructure: an efficient photoanode for water splitting, *ACS Appl. Mater. Inter.* 5 (2013) 8314-20.
- [46] P. Keeratithivakorn, B. Tunhoo, T. Thiawong, J. Nukeaw, CoPc/CdS hybrid photovoltaic device, *Adv. Mat. Res.* 93 (2010) 570-573.
- [47] Q. Tai, B. Chen, F. Guo, Sh. Xu, H. Hu, B. Sebo, X.-Zh. Zhao, In situ prepared transparent polyaniline electrode and Its application in bifacial dye-sensitized solar cells, *ACS Nano* 5 (2011) 3795–3799.
- [48] I. Chung, B. Lee, J. He, R. P. H. Chang, M. G. Kanatzidis, All-solid-state dye-sensitized solar cells with high efficiency, *Nature* 485 (2012) 486-489.
- [49] Y. Rong, X. Li, Zh. Ku, G. Liu, H. Wang, M. Xu, L. Liu, M. Hu, P. Xiang, Z. Zhou, T. Shu, H. Han, Monolithic all-solid-state dye-sensitized solar module based on mesoscopic carbon counter electrodes, *Sol. Energ. Mat. Sol. C.* 105 (2012) 148-152.
- [50] H. S. Kim, C. S. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Grätzel, N. G. Park, Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%, *Sci. Rep.* 2 (2012) 591-597.
- [51] G. Syrrokostas, A. Siokou, G. Leftheriotis, P. Yianoulis, Degradation mechanisms of Pt counter electrodes for dye sensitized solar cells, *Sol. Energ. Mat. Sol. C.* 103 (2012) 119-127.
- [52] P. Li, J. Wu, J. Lin, M. Huanga, Y. Huang, Q. Li, High-performance and low platinum loading Pt/Carbon black counter electrode for dye-sensitized solar cells, *Sol. Energy*, 83 (2009) 845–849.

- [53] M Rita Narayan. Review: Dye sensitized solar cells based on natural photosensitizers, *Renew. Sust. Energ. Rev.* 16 (2012) 208-215.
- [54] J. Wu, Y. Li, Q. Tang, G. Yue, J. Lin, M. Huang, L. Meng. Bifacial dye-sensitized solar cells: A strategy to enhance overall efficiency based on transparent polyaniline electrode, *Sci. Rep.* 4 (2014) 4020-4028.
- [55] S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. D. Censo, Md. K. Nazeeruddin, M. Grätzel, Molecular engineering of organic sensitizers for solar cell applications, *J. Am. Chem. Soc.* 128 (2006) 16701-16707.
- [56] L. Li, Y. Yang, R. Fan, Y. Jiang, L. Wei, Y. Shi, J. Yu, Sh. Chen, P. Wang, B. Yang, W. Cao, A simple modification of near-infrared photon-to-electron response with fluorescence resonance energy transfer for dye-sensitized solar cells, *J. Power Sources* 264 (2014) 254-261.
- [57] W. Yu, L. Shen, P. Shen, F. Meng, Y. Long, Y. Wang, T. Lv, Sh. Ruan, G. Chen, Simultaneous improvement in efficiency and transmittance of low band gap semitransparent polymer solar cells with one-dimensional photonic crystals, *Sol. Energ. Mat. Sol. C.* 117 (2013) 198-202.