



# Improved performance of dye-sensitized solar cells with novel conjugated organic dye using aluminum oxide-coated nanoporous titanium oxide films



Hyo Jeong Jo<sup>a</sup>, Jung Eun Nam<sup>a</sup>, Dae-Hwan Kim<sup>b</sup>, Jin-Kyu Kang<sup>a,\*</sup>

<sup>a</sup> Advanced Convergence Research Center, DGIST, Hyeonpung-Myeong, Daegu 711-873, South Korea

<sup>b</sup> Division of Energy, DGIST, Hyeonpung-Myeong, Daegu 711-873, South Korea

## HIGHLIGHTS

- We reported our findings on solution-process-deposited Al<sub>2</sub>O<sub>3</sub> barriers in DSSCs.
- We focused on the effect that adsorption properties of dye can have on the interfacial charge transfer reactions.
- These results were supported by the Raman spectroscopy, IMPS and IMVS.

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## ABSTRACT

This work introduces the TiO<sub>2</sub>/dye/electrolyte interface in the recombination and offers an interface treatment method using solution process for dye-sensitized solar cells (DSSCs). Solution-processed ultra-thin metal oxides introduce to treat the surface of mesoporous TiO<sub>2</sub> to reduce the defect density and improve the electronic quality. Among the metal oxides, an Al<sub>2</sub>O<sub>3</sub> barrier is incorporated into DSSCs as a carrier-recombination blocking layer. In all instances, the short-circuit current density increase and the dark current is suppressed after Al<sub>2</sub>O<sub>3</sub> deposition. The impact of the Al<sub>2</sub>O<sub>3</sub> barriers is also studied in devices employing different dyes. To compare the behavior of metal-free organic dyes and Ru dyes when Al<sub>2</sub>O<sub>3</sub> barrier layers are involved, the charge transfer between the dye and TiO<sub>2</sub> electrodes, associated with interfacial electron injection, is investigated by Raman spectroscopy. The metal-free organic dye had a high molar extinction coefficient and better adsorption properties compare to Ru dye, which resulted in higher charge-collection efficiency. To verify the strategy, the DSSCs photovoltaic performances containing these dyes are compared using their current–voltage curves. Electrochemical impedance spectroscopy (EIS), Intensity Modulated Photocurrent Spectroscopy (IMPS), and Intensity Modulated photoVoltage Spectroscopy (IMVS) were used to further investigate the kinetics process of the TiO<sub>2</sub> film electrodes.

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## 1. Introduction

Since the historic paper on dye-sensitized solar cells (DSSCs) was published in 1991 by Grätzel et al., DSSCs have been widely investigated because of their special advantages such as low fabrication costs and fairly high solar-energy-conversion efficiencies relative to conventional p–n junction solar cells [1,2]. In DSSCs, dye molecules are chemisorbed on the surface of a TiO<sub>2</sub> porous layer, and visible light is absorbed by the sensitizer dye to generate excited electrons. Electron injection from the excited state

of the dye into the conduction band of TiO<sub>2</sub> is followed by subsequent regeneration of the dye by an I<sup>−</sup>/I<sub>3</sub><sup>−</sup> redox couple [3–5]. Efficient operation of a DSSC device relies upon the minimization of possible recombination pathways occurring at the TiO<sub>2</sub>–dye–electrolyte interface, allowing efficient charge transport through the TiO<sub>2</sub> film and electrolyte and subsequent charge collection at the device contacts. There are two possible recombination losses to consider: the injected electrons may recombine either with oxidized dye molecules or with the oxidized redox couple; the latter reaction is thought to be particularly critical to device function (Scheme 1) [6].

In order to reduce the recombinations, many research groups have proposed device architectures that include the use of insulating polymers. The use of very thin-layered, high band-gap,

\* Corresponding author. Tel.: +82 53 785 3700; fax: +82 53 785 3739.  
E-mail address: [apollon@dgist.ac.kr](mailto:apollon@dgist.ac.kr) (J.-K. Kang).

semiconductor metal oxides like ZnO, MgO, and Al<sub>2</sub>O<sub>3</sub> between the TiO<sub>2</sub> and the dye interface has also been attempted [6–11]. The application of a metal-oxide barrier layer should improve the collection efficiency of electrons successfully injected into TiO<sub>2</sub> by reducing the number of charge carriers lost via recombination. Aluminum oxide is especially attractive owing to its wide bandgap [8], high iso-electric point (IEP, which can enhance dye adsorption) [8,12], and ability to raise the TiO<sub>2</sub> conduction band edge (which can improve the open-circuit voltage,  $V_{oc}$ ) [13]. On the other hand, the high conduction band of Al<sub>2</sub>O<sub>3</sub> will inhibit electron injection from an excited dye state into TiO<sub>2</sub>. Therefore, if the Al<sub>2</sub>O<sub>3</sub> barrier layer is too thick, the device current will drop as relaxation of the dye excited state competes with electron injection via tunneling.

In this paper, we reported our findings on solution-process-deposited Al<sub>2</sub>O<sub>3</sub> barriers in DSSCs. In order to reduce the defect density and improve the electronic quality, solution-processed ultra-thin metal oxides have been introduced to treat the surface of mesoporous TiO<sub>2</sub> [14]. In addition, we focused on the effect that adsorption properties of sensitizer can have on the interfacial charge transfer reactions and ultimately on the device efficiency. We illustrated, as an example, adsorption properties by sensitizer affect not only to increase the electron injection efficiency but also to slow recombination on the Al<sub>2</sub>O<sub>3</sub>-coated TiO<sub>2</sub> electrode compared to TiO<sub>2</sub> electrode. By comparing the behavior of the Ru dye and a metal-free organic dye, we demonstrated the importance of dye chemistry on current collection (Fig. 1).

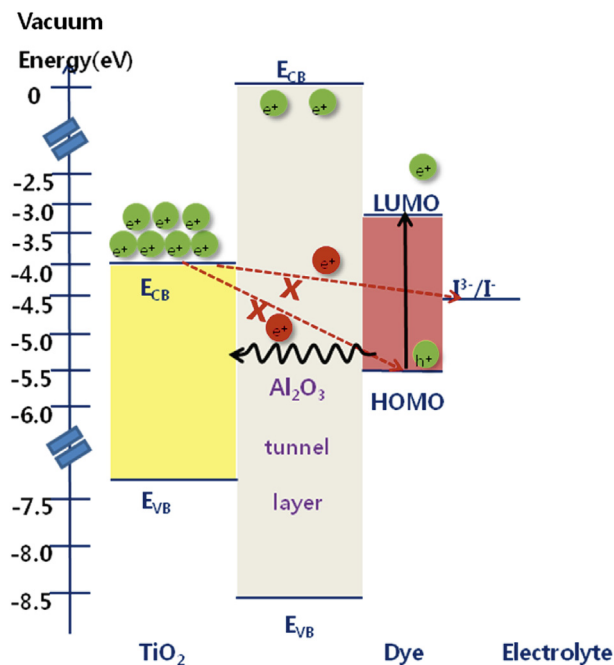
## 2. Experimental details

### 2.1. Fabrication of DSSC using Al<sub>2</sub>O<sub>3</sub>

In order to prepare a working electrode, fluorine-doped thin oxide (FTO) for a conductive transparent electrode was purchased from Pilkington ( $\sim 8 \Omega \text{ sq}^{-1}$ ) and cleaned using the general cleaning process for electronic applications: ultrasonic treatment in detergent, deionized water, acetone, and 2-propanol in that order for 15 min for each at room temperature. The transparent and porous titanium oxide film was formed on the cleaned FTO substrate using 20-nm particle-size TiO<sub>2</sub> paste (Solaronix, T/SP) with the doctor-blade coating method. The coated TiO<sub>2</sub> film was sintered at 500 °C in air for 60 min. An air-stable solution of aluminum 2-propoxide (15 mM in isopropanol) under aerobic conditions was used to conformally coat the TiO<sub>2</sub>. The film was dipped in the coating solution for 15 min at 25 °C. After this, the film was dried to water vapor for 1 min at 100 °C. For dye adsorption, the Al<sub>2</sub>O<sub>3</sub>-coated TiO<sub>2</sub> electrodes were immersed in a dye solution (0.3 mM of dye in ethanol) at room temperature for 24 h. The dye-adsorbed TiO<sub>2</sub> electrode and Pt counter electrode were assembled using 60- $\mu\text{m}$ -thick Surlyn (Dupont, 1702) as a bonding agent. A liquid electrolyte was introduced through a pre-punctured hole on the counter electrode.

### 2.2. Synthesis of PREDCN2 dye

We designed and synthesized organic dyes containing a phenothiazine derivative as an electron donor and a cyanoacrylic acid moiety as an electron acceptor and anchoring group, connected with electron-rich ethylene-di-oxythiophene (EDOT) as a  $\pi$ -conjugated group in a chromophore with moderate yields. The synthetic procedures were followed using known methods [15–17]. The product obtained was a dark red powder. Yield: (0.48 g, 81.3%), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.01 (s, 2H), 7.50–7.48 (d,  $J$  = 8.4 Hz, 2H), 7.38–7.37 (d,  $J$  = 2.0 Hz, 2H), 7.35–7.33 (d,  $J$  = 8.4 Hz, 2H), 7.20–7.17 (m, 2H), 6.12–6.01 (d,  $J$  = 8.8 Hz, 2H), 2.71–2.65 (m, 2H), 1.64–1.53 (m, 4H), 1.33–1.30 (m, 4H), 0.88 (m, 3H). MALDI-TOF



Scheme 1. Illustration of interfacial charge-transfer processes in DSSCs.

MS: Calcd. for C<sub>44</sub>H<sub>35</sub>N<sub>3</sub>O<sub>8</sub>S<sub>3</sub>  $m/z$ : 829.16; found  $m/z$ : 830.85 [M + H]<sup>+</sup>; anal. calcd. for C: 63.67; N: 5.06; S: 11.59; H: 4.25; found, C: 63.86; N: 5.58; S: 11.29; H: 4.68%.

### 2.3. Characterization of physical, electrochemical, and electrical properties

The morphologies of Al<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> electrode were measured using transmission electron microscopy (TEM, Hitachi HF-3300).

Structural analysis was conducted using <sup>1</sup>H NMR spectra recorded via a Bruker Advance NMR 400 Hz spectrometer for DMSO-*d*<sub>6</sub>. Matrix Assisted Laser Desorption Ionization-Time Of Flight mass spectra were obtained using a Voyager DE-STR spectrometer. UV–Vis spectra were recorded using a CARY5000 UV/Vis/NIR spectrophotometer. The redox properties were examined using cyclic voltammetry (model: Iviumstate). The electrolyte solution was 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF6) in freshly dried dimethylformamide (DMF). Ag/AgCl and platinum wire (0.5 mm in diameter) electrodes were used as reference and counter electrodes, respectively.

Raman spectra were obtained using an Alpha XR Raman spectrometer (Thermo scientific) with 532 nm solid-state laser.

The photocurrent-density–voltage characteristic of the DSSCs was measured using a Keithley 2400 source meter and a solar simulator equipped with a 1 kW xenon arc lamp (ORIEL, Newport). A standard silicon solar cell (PV Measurement Inc.) was used for calibration with the power of the AM 1.5 simulated light (100 mW cm<sup>-2</sup>).

To perform electrochemical impedance spectroscopy (EIS), the DSSCs were measured under dark condition by a potentiostat (IVIUM, Iviumstat); the frequency range was from 0.1 Hz to 100 kHz. The data obtained from this measurement was fitted by simulation software (Scribner Associates, Z-View), which proposed an equivalent circuit to model the data. Intensity Modulated Photocurrent Spectroscopy (IMPS) and Intensity Modulated

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