

# Room temperature-processed TiO<sub>2</sub> coated photoelectrodes for dye-sensitized solar cells

Dae-gun Kim<sup>\*,\*\*</sup>, Kyung-min Lee<sup>\*</sup>, Hyung-bok Lee<sup>\*\*</sup>, Jong-woo Lim<sup>\*,†</sup> and Jae-hyuk Park<sup>\*,†</sup>

<sup>\*</sup>Research Center, IONES Co., Ltd., Hwaseong 18487, Korea

<sup>\*\*</sup>Department of Material Science and Engineering, Myongji University, Yongin 17058, Korea

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**Abstract** The depletion of fossil fuels and the increase in environmental awareness have led to greater interest in renewable energy. In particular, solar cells have attracted attention because they can convert an infinite amount of solar energy into electricity. Dye-sensitized solar cells (DSSCs) are low cost third generation solar cells that can be manufactured using environmentally friendly materials. However, DSSC photoelectrodes are generally produced by screen printing, which requires high temperature heat treatment, and low temperature processes that can be used to produce flexible DSSCs are limited. To overcome these temperature limitations, this study fabricated photoelectrodes using room-temperature aerosol deposition. The resulting DSSCs had an energy conversion efficiency of 4.07 %. This shows that it is possible to produce DSSCs and flexible devices using room-temperature processes.

**Key words** Dye-sensitized solar cell, Aerosol deposition, Photoelectrode, TiO<sub>2</sub>, Room temperature process

## 1. Introduction

The energy conversion efficiency of dye-sensitized solar cells (DSSCs) is comparable to that of amorphous-silicon solar cells. Furthermore, their simple structure and low manufacturing costs mean that they are more likely to be commercialized than other third-generation or hybrid designs. DSSCs consist of four main components: dyes with selective light absorption bands to effectively absorb visible light which comprises 44 % of the energy from the sun; photoelectrodes to transport excited electrons from the dyes; oxidized/reduced liquid electrolytes; and a transparent conductive oxide (TCO) counter electrode to allow the transmission of visible light.

TiO<sub>2</sub> is the most widely used photoelectrode because it is inexpensive, has a wide bandgap (3.2 eV), and good stability. The n-type photoelectrodes used in DSSCs are usually produced by screen printing with paste and ink [1-4]. Photoelectrodes manufactured using this method are heat treated at approximately 500°C to burn-off the binder and to develop particle-to-particle connections. However, this process is costly and limits the choice of substrate materials.

In an attempt to overcome this problem, Gutierrez-

Tauste et al. [5] and Jiang et al. [6] conducted numerous studies on low temperature processes using ultraviolet (UV)-irradiation and nanowires. However, they only achieved energy conversion efficiencies of less than 2 %.

This study aims to present an improved method for manufacturing photoelectrodes using a new coating technique. Here, photoelectrodes are produced using aerosol deposition on polyethylene naphthalate (PEN) films coated with transparent indium tin oxide (ITO) electrodes at room temperature. A DSSC fabricated using the new photoelectrode will then be compared to a traditional design.

## 2. Experiments

### 2.1. Materials

TiO<sub>2</sub> powders, with particles 200 and 15 nm in diameter, were used to produce the photoelectrodes (NanoPac, Korea). Anatase phase TiO<sub>2</sub> was used as it is a well-known nanocrystalline particle that is stable at room temperature. Figure 1 shows a field electron scanning electron microscopy (FE-SEM) image of the TiO<sub>2</sub> particles.

A PEN film (surface resistance: 15 Ω/□) coated with a 100 nm thick layer of ITO was used as the substrate and N719 (Solaronix, Switzerland), a ruthenium com-

<sup>†</sup>Corresponding author

E-mail: blast62@naver.com, rndpark@iones.co.kr

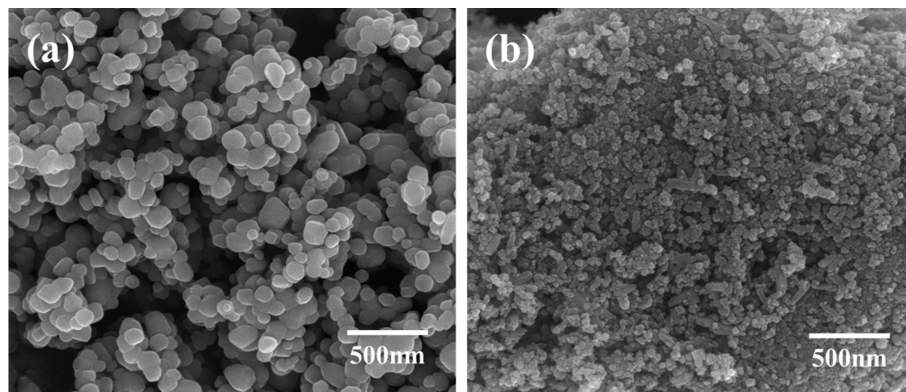


Fig. 1. FE-SEM images of used  $\text{TiO}_2$  Particles and XRD patterns of the particles. (a) 400 nm, (b) 15 nm.

plex that can absorb light, was used as the dye. In addition, 1-methyl-3-propyl imidazolium iodide (PMII) in 3-methoxypropionitrile (MPN), a common conventional ionic liquid type electrolyte, was used as the electrolyte.

## 2.2. DSSC fabrication process

To make stable photoelectrodes using aerosol deposition, it is important to control the moisture on the surface of the  $\text{TiO}_2$  nanoparticles. Therefore, the nanoparticles were stored in a vacuum oven at  $150^\circ\text{C}$  for 24 h prior to use and 5 wt% of 15 nm particles were mixed with the 200 nm particles using a high speed mixer as required. Figure 2 and Table 1 show a schematic of the aerosol deposition (AD) system and the main operating conditions used to produce the porous  $\text{TiO}_2$  coating, respectively. AD is a coating technique that can produce high density and high quality ceramic layers in room-tem-

perature and low-vacuum environments. Therefore, it is of interest for applications in large screen displays and plasma semiconductor equipment components where there are extreme environments. The AD system consisted of a coating chamber with a holder for the stream nozzle and substrate, a vacuum system, and a powder feeding system to supply the nanoparticle aerosols. Nitrogen was used as the carrier gas for the powder and the vacuum was maintained at approximately 15 Pa as the carrier gas was injected. The  $\text{TiO}_2$  powder was aerosolized by the carrier gas, transported, and sprayed at a high speed (greater than 300 m/s) through the nozzle. The  $\text{TiO}_2$  powder collided forcefully with the substrate and formed the  $\text{TiO}_2$  coating. The properties of this film, such as the thickness and quality, were controlled by adjusting the angle of the nozzle, the speed, and the number of scans.

This preparation was used to apply a layer of  $\text{TiO}_2$  ( $10 \times 4$  mm) to the ITO coated PEN film ( $20 \times 15$  mm). This sample was immersed in 0.5 mM of N719 in acetonitrile/tert-butanol solution for 24 h which adsorbed onto the porous surface of  $\text{TiO}_2$ . Fluoride doped tin oxide (FTO) coated glass was used as a counter electrode. This was prepared by immersing it in an aqueous solution of 7 mM of platinum in 2-propanol. The pre-

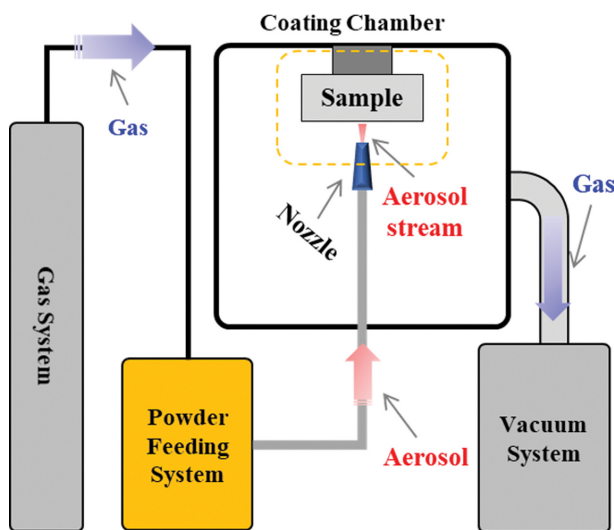


Fig. 2. Schematic of aerosol deposition system.

Table 1  
Critical parameters for aerosol deposition of the  $\text{TiO}_2$  semiconductor film

| Parameters                     | Value               |
|--------------------------------|---------------------|
| Nozzle slit size               | $10 \times 1.0$ mm  |
| Angle of nozzle                | $15^\circ$          |
| Working distance (Sub.-nozzle) | 10 mm               |
| Carrier gas                    | $\text{N}_2/15$ SLM |
| Number of scan and scan pitch  | 2 times/ $0.25$ mm  |
| Scan speed                     | 10 mm/s             |

pared components were assembled using an adhesive material and electrolytes were then injected into the unit to complete the DSSC.

### 3. Results and Discussion

Figure 3(a) shows the DSSC processed at room temperature including the photoelectrode with a porous TiO<sub>2</sub> coating fabricated using AD. To evaluate its photovoltaic properties, a 10 μm thick TiO<sub>2</sub> coating was applied. For comparison, DSSCs were manufactured using TiO<sub>2</sub> photoelectrode layers of the same thickness that were fabricated by screen-printing with a binder-free paste consisting of a mixture of the same 200 and 15 nm TiO<sub>2</sub> particles used for the AD. The current density-voltage (I-V) curves of the DSSCs were measured using a solar simulator consisting of a xenon lamp with a light illumination intensity of 100 mW/cm<sup>2</sup>. The results are shown in Table 2 and Fig. 3(b). The DSSC fabricated at room temperature by screen printing with the binder-free paste had a current density ( $J_{sc}$ ) of 4.46 mA/m<sup>2</sup> and an open circuit voltage ( $V_{oc}$ ) of 0.62 V. The fill factor (FF) and

Table 2  
Photovoltaic properties of the DSSCs processed at room temperature

| Sample  | $J_{sc}$<br>(mA/cm <sup>2</sup> ) | $V_{oc}$<br>(V) | FF<br>(%) | $\eta$<br>(%) |
|---|-----------------------------------|-----------------|-----------|---------------|
| AD-TiO <sub>2</sub>                           | 8.08                              | 0.72            | 69.41     | 4.07          |
| Screen printed TiO <sub>2</sub> (binder-free) | 4.46                              | 0.62            | 55.56     | 1.54          |

solar energy efficiency ( $\eta$ ) were 55.56 % and 1.54 %, respectively. In contrast, the DSSC prepared using the AD process had a current density of 8.08 mA/m<sup>2</sup>, open circuit voltage of 0.72 V, fill factor of 69.41 %, and solar energy efficiency of 4.07 %, indicating overall improvement.

Figure 4 shows a cross-sectional SEM image of the photoelectrodes produced using a mixture containing 5 wt% of 15 nm particles in 200 nm TiO<sub>2</sub> powder, or 200 nm TiO<sub>2</sub> powder. In general, the microstructural properties of the ceramic coating produced using AD depends on the size of the particles and the spraying speed [7-9]. For example, if the granules are too large, then the substrate may be eroded or the coating may not adhere as the collision energy of the particles is too high. In con-

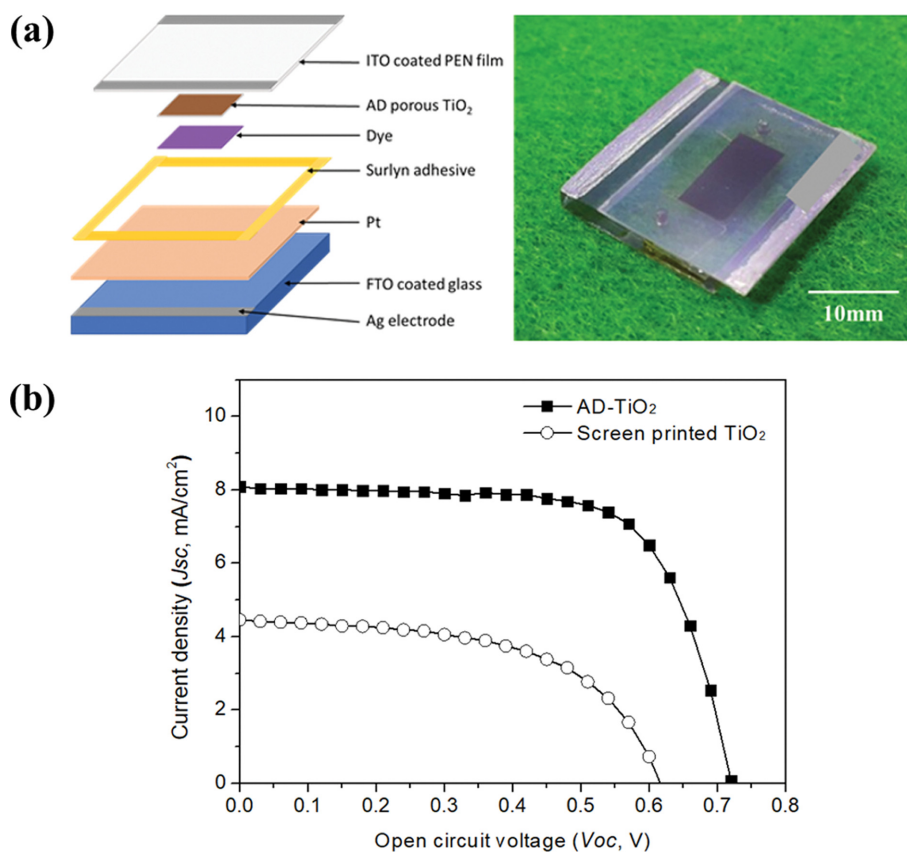


Fig. 3. (a) Schematic and photograph of room temperature processed DSSC including AD coated porous TiO<sub>2</sub> as semiconductor oxide and (b) measured photovoltaic properties (I-V curve) of DSSCs.

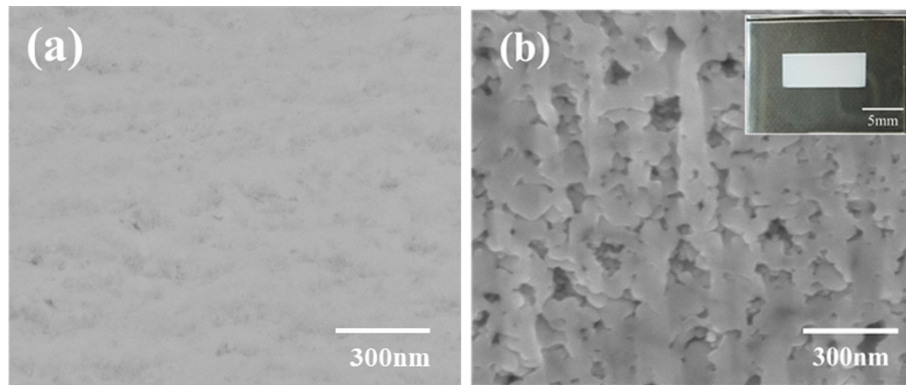


Fig. 4. Cross-sectional SEM images of AD-TiO<sub>2</sub> films. (a) using only 400 nm-TiO<sub>2</sub> powder and (b) 5 wt% 15 nm-TiO<sub>2</sub> mixed with 400 nm-TiO<sub>2</sub>. Inset shows the AD coated porous TiO<sub>2</sub> film on ITO-PEN film.

trast, if the particles are smaller than several tens of nanometers, they will not have sufficient energy to form a coating because they will be scattered due to fracture-plastic deformation. Therefore, the particle size required for AD coating is approximately 1  $\mu\text{m}$  or less, and 200 nm TiO<sub>2</sub> particles are suitable for coating. However, when only 200 nm particles are used, as shown in Fig. 4(a), the coating is very dense. This is not suitable for photoelectrodes which must be porous in order to absorb the dye. Fan et al. mixed a polymer with TiO<sub>2</sub> to create a porous TiO<sub>2</sub> coating for use in DSSCs [10]. However, this required the polymer to be burnt-off at a high temperature of 450°C. Therefore, in this experiment, we have mixed 200 nm-sized TiO<sub>2</sub> powder, which can create a dense and hard coating film, with 15 nm-sized TiO<sub>2</sub> powder, which can induce a porous coating film by mitigating collision energy, to create a coat. As described, 15 nm TiO<sub>2</sub> particles cannot form a coating alone because they do not have sufficient collision energy during the AD process [11]. However, if they are mixed with 200 nm particles, they can limit the collisions of the 200 nm particles or reduce their collision energy, resulting a porous coating [12]. Figure 4(b) shows a cross-sectional SEM image of a porous TiO<sub>2</sub> coating produced by AD without subsequent heat treatment using a 5 wt% 15 nm and 200 nm TiO<sub>2</sub> mixture.

These results show that the TiO<sub>2</sub> coating produced using AD was sufficiently porous to adsorb the dye and that there were proper connections between the TiO<sub>2</sub> particles without the need for heat treatment. Therefore, it effectively leads the flow of electrons.

#### 4. Conclusion

The photoelectrodes in a DSSC must be porous to

ensure the dye is adsorbed and there must be stable connections between particles to guarantee the smooth flow of electrons. Therefore, it is necessary to consider the composition of the powder used to form the porous TiO<sub>2</sub> layer via AD. We improved the powder by mixing 5 wt% of 15 nm TiO<sub>2</sub> fine powder with 200 nm TiO<sub>2</sub> granulated powder. Then, AD was used to form a 10  $\mu\text{m}$  thick TiO<sub>2</sub> layer at room temperature and the DSSC was completed without subsequent heat treatment. To demonstrate that the AD-TiO<sub>2</sub> coating had a microstructure that was suitable for DSSC application, a comparison sample was prepared using screen printing with binder-free paste containing the same powder without high temperature heat treatment. The photovoltaic properties were then measured. The DSSC containing AD-TiO<sub>2</sub> performed significantly better than the comparison sample. This shows that DSSCs can be manufactured at room temperature without the need for high-temperature heat treatment, which increases the potential applications of flexible DSSCs.

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