Mesoporous TiO₂ hierarchical structures: preparation and efficacy in solar cells†

Dae-Kue Hwang,* Jeong-Hwa Kim, Kang-Pil Kim and Shi-Joon Sung†

We investigated an electrospray-based method to manufacture photoelectrodes for dye-sensitized solar cells (DSSCs). TiO₂ doughnut-, spherical-, and disk-shaped particles with a large surface area, high crystallinity, uniform nanostructure, and good light scattering properties were fabricated via a simple electrospray method. The control of the morphology of the nanostructured particles prepared by electrospraying a dispersion of nanoparticles was investigated experimentally; the results are qualitatively explained on the basis of the available theory. The solvent in the droplet, droplet size, surface tension, process temperature, and process humidity are crucial to the morphology of the resulting particles. The effect of the particle morphology on the performance of DSSCs is demonstrated. Compared to the DSSCs with conventional photoelectrodes (with a power conversion efficiency of 8.4%), the DSSCs based on doughnut-, spherical-, and disk-shaped particle photoelectrodes yielded higher power conversion efficiencies of 8.8%, 9.3%, and 10.4%, respectively. The DSSC utilizing the disk-type photoelectrode showed the best performance under AM1.5 global illumination through a photo-mask at an illumination power of 100 mW cm\(^{-2}\). This is because the generated TiO₂ disks provide a large surface area and exhibit excellent light scattering capabilities, thus resulting in a low total internal resistance and long electron lifetime.

1. Introduction

The advantages of simple fabrication using low cost materials and high energy conversion efficiency make dye-sensitized solar cells (DSSCs) very attractive candidates for next generation solar energy conversion technologies.\(^1\) In order to improve the efficiency of DSSCs, various techniques such as deposition of a thin tunneling barrier layer on the substrate\(^2\) or the oxide surface,\(^3\) co-sensitization using different dyes,\(^7\) post-treatment with a TiCl₄ precursor,\(^8,9\) and use of reflection layers\(^10\) have been proposed. Light-scattering particulate films with a bilayer structure have also been adopted widely because they confine the incident light within an electrode and thereby enhance the photocurrent density.\(^11\)–\(^13\) The size of the scattering particle should be large enough to scatter the incident light efficiently since small-sized (10–30 nm) nanocrystalline particles cause Rayleigh scattering that is too weak to scatter the light backward.\(^16\) Large TiO₂ particles with spherical shapes or flat surfaces are normally used as scattering particles. However, except for their role in the actual light scattering, these scattering particles hardly offer any additional effect, for instance electron generation, because dye adsorption is expected to be much less for these particles than that for nanocrystalline TiO₂ owing to their much smaller surface area.\(^17,18\) The use of hierarchically structured films having submicrometer-sized aggregates assembled by nanocrystallites appear to be a promising approach to meet such conflicting requirements. Hierarchically-structured TiO₂ (HS-TiO₂) has been suggested as the most promising photoelectrode for DSSCs because of the advantages of (1) large surface area and dye adsorption; (2) light scattering effects of the submicrometer-sized structures; and (3) better penetration of electrolytes through the relatively large pores between the HS-TiO₂ particles.\(^19\)–\(^21\) Recently, several groups have reported that the morphology of hierarchical structured TiO₂ spheres is optimal for DSSCs.\(^19,20,22\)–\(^26\) However, it is not simple to obtain such hierarchical structures using multi-step processes such as the sol–gel method,\(^25\) solvothermal reactions,\(^27\) or hydrolysis.\(^19\) These processes are neither practical nor cost-effective for the large-scale production of DSSC modules. The electrospray technique has recently evolved as a cheap and simple process to directly deposit thin films from their colloidal solutions. The film size and uniformity of TiO₂ photoelectrodes could be easily controlled by varying the number of nozzles, volume of the syringe pump, and the motion-controlled system with a micro-processor. Photographs of the 10 × 10 cm and 30 × 30 cm films are shown in the ESI (Fig. S1†). This technique can be applied widely in modern material technologies such as microelectronics and nanotechnology\(^28\) and in industries for the deposition of various ceramic powders, polymer powders,\(^29\) and TiO₂ electrodes for DSSCs.\(^30,31\)
In this paper, we report an innovative particle processing technique to produce electrosprayed nanocrystalline-TiO₂ (nc-TiO₂) with several morphologies (spherical, biconcave, doughnut, and disk) for DSSC photovoltaic devices. A comparison between theoretical and current experimental results is shown to clarify how the particles of various sizes and morphologies are formed. When compared to the traditional photoanode, the present electrosprayed doughnut, spherical-, and disk-shaped particle photoelectrodes showed several advantages. Firstly, the electrosprayed TiO₂ photoelectrode particles were composed of nanocrystallites with diameters of approximately 15–20 nm, and thus, they did affect the dye-loading capacity of the photoelectrodes adversely. Secondly, the diameter of the electrosprayed TiO₂ photoelectrodes particles was submicron-sized, resulting in much higher diffusion reflection properties, thereby effectively improving the light harvesting characteristics of the device. Thirdly, the morphology of the photoelectrodes could be easily engineered and fine-tuned by changing the operating parameters of the electrospraying process.

2. Experimental section

Preparation of various TiO₂ particles

First, 10 wt% of nc-TiO₂ (Degussa P-25, particle size ~15–20 nm) was dispersed in ethanol using a Kotobuki UAM-015 Ultra Apex mill. The dispersion of 10 wt% nc-TiO₂ in ethanol was then dispersed in an ethanol/butanol (9/1 v/v) solution. The diluted 5 wt% nc-TiO₂ dispersion solution was loaded into a plastic syringe, which was connected to a Bertan 205B high-voltage power supply. The dispersed nc-TiO₂ solution was electrosprayed directly onto the conducting fluorinated tin oxide (FTO) substrates having the dimensions of 10 cm × 10 cm. The process temperature and humidity were controlled by a heater and humidifier, respectively. Table 1 lists the temperature and humidity values used to produce different particle morphologies in this experiment. An electric field of 15 kV was applied between the metal orifice and the conducting substrates, which were separated by a distance of 10 cm. The feed rate was controlled by a syringe pump at 35–30 μL min⁻¹. In order to obtain a uniform thickness over a large area, the nozzle and the substrate were placed on a motion-control system with a microprocessor. The surface areas of the resulting nanoparticles were determined by the Brunauer–Emmett–Teller (BET) method; the distributions of the pore volume and particle size were determined by the Barrett–Joyner–Halenda (BJH) method using the adsorption branches of the N₂ isotherms. Dye desorption experiments were carried out using the nanoparticle photoelectrode films coated with the N719 dye prepared from a 0.3 mM ethanolamine solution. For each sample, the dye was desorbed from the nanoparticle photoelectrode by treatment with a certain volume of 0.1 M NaOH (aq). The absorbance of the resulting solution was then quantified with a UV-vis spectrophotometer by calculating the number of molecules from the obtained UV-vis absorption spectra of the desorbed sensitizers using the extinction coefficient of the N719 sensitizer. The optical properties were measured by a UV/VIS/NIR spectrometer (Perkin Elmer LAMBDA 1050) within the wavelength range of 185–330 nm. The surface and cross-sectional morphologies of the TiO₂ nanoparticles were analyzed by field-emission transmission electron microscopy (FE-TEM) (Hitachi, HF-3300) and field-emission scanning electron microscopy (FE-SEM; Hitachi, S-4800). The structural properties of the TiO₂ nanoparticles were analyzed by X-ray diffraction (XRD; PANalytical, X’pert PRO-MPD with Cu Kz irradiation) in the 2θ–20 mode.

DSSC fabrication

To fabricate a conventional DSSC, an nc-TiO₂ paste (Solaronix T/SP, R/SP) was applied to an FTO-glass slide using a doctor blade and subsequently heat treated. Cellophane tape was used to control the film thickness. To produce the final structure, a conventional scatter layer was pasted onto the nc-TiO₂ layer by a doctor blade. After the electrospray process, each as-prepared TiO₂-coated FTO photoelectrode was placed between two planar steel plates for mechanical pressing with a Teflon film to prevent the delamination of the TiO₂ photoelectrodes. Mechanical hot-pressing process can indeed improve the adhesion between the TiO₂ photoelectrode and the substrate, thus improving the interfacial performance of TiO₂ photoelectrodes in DSSCs. The typical pressure applied to fabricate the solar cells was 12 MPa at 120 °C for 10 min. The photoelectrodes coated with the TiO₂ spherical-, doughnut-, and disk-shaped particles were sintered under air at 500 °C for 30 min. The TiO₂ biconcave particles separated from the substrate by peeling after the mechanical pressing process. This might have resulted because of the hollow particle structures, as shown in Fig. 1. Therefore, the device performance could not be tested for the biconcave particle morphology. For post-treatment, the TiO₂ films were soaked in a 0.05 M TiCl₄ aqueous solution for 20 min at 80 °C, rinsed with water, and then sintered again at 450 °C for 30 min. After cooling to 80 °C, the TiO₂ photoelectrodes were immersed in a purified 3 × 10⁻⁴ M cis-disothiocyanato-bis[2,2'-bipyridyl-4,4'-dicarboxylato]ruthenium(II)bistetraphenylbistetralen)(solution (N719, Solaronix) for 15 h at room temperature (25 °C). For the counter electrode, the FTO plates were drilled by a micro-drill, washed with a 0.1 M HCl solution in ethanol, and subsequently cleaned in an ultrasonic bath with water and ethanol for
15 min. A solution of 5 mM H$_2$PtCl$_6$ in isopropyl alcohol was drop-cast onto the washed FTO plates and then sintered at 400 °C for 20 min under air. The dye-adsorbed TiO$_2$ photoelectrodes were rinsed with ethanol and dried under nitrogen flow. The dye-adsorbed TiO$_2$ photoelectrodes were then assembled and sealed with the Pt counter electrodes using thermal adhesive films (Surlyn, Dupont 1702, 25 μm-thick) as spacers to produce sandwich-type cells. The liquid electrolyte consisted of 0.7 M 1-propyl-3-methylimidazolium iodide (PMII), 0.03 M iodine (I$_2$), 0.1 M guanidinium thiocyanate (GSCN), and 0.5 M 4-tert-butylpyridine (TBP) in a mixture of acetonitrile (ACN) and valeronitrile (VN) (85/15 v/v). The electrolyte solution was introduced through the holes drilled in the counter electrodes. Finally, the holes were sealed with a hot-melt film and a cover glass.

Photovoltaic and photoelectrical measurements

The photovoltaic measurement of the DSSCs employed an AM1.5G solar simulator between the sample and a 450 W xenon lamp. The intensity of the simulated light was calibrated by a silicon reference solar cell equipped with a KG5 filter for approximating AM1.5 global solar radiation. The photovoltaic characteristics of the DSSCs were obtained by applying an external potential bias to the cells and measuring the generated photocurrent with a Keithley Model 2400 source meter. The incident photon-to-electron conversion efficiency (IPCE) was measured as a function of the wavelength from 350 to 800 nm using a specially designed IPCE system for DSSCs (PV measurement, Inc.). A 75 W xenon lamp was used as the light source to generate a monochromatic beam. The calibration was performed using a NIST calibrated silicon photodiode as the standard. The IPCE values were collected at a low chopping speed of 5 Hz. The electrical impedance spectra (EIS) were measured using an impedance analyzer (Solatron 1260) at an open-circuit potential under an AM1.5G full-sun illumination (100 mW cm$^{-2}$) at frequencies in the range of ~0.1–10$^5$ Hz. The obtained spectra were fitted using ZView software (v3.2c, Scribner Associates, Inc.).

3. Results and discussion

Fig. 1 shows the formation mechanisms for different particle morphologies using the electrospay method. Various particle morphologies could be produced by changing the processing conditions and the initial droplet shapes. A modified Peclet number (Pe) can be used to characterize the morphology of nanoparticles fabricated using the electrospay process.\textsuperscript{32}

Based on this idea, Pe value can be used to determine the solvent evaporation rate, the particle diffusion coefficient within the droplet, and the particle diffusion rate. This relationship is similar to that suggested by Okuyama and Wuled Lenggoro\textsuperscript{33} and can be written as

$$\text{Pe} = \frac{\frac{\partial r_d}{\partial t}}{r_d D_{AB}}$$

where $\frac{\partial r_d}{\partial t}$ is the rate of change of the droplet radius because of the solvent evaporation, $r_d$ is the droplet radius, $D_{AB}$ is the diffusion coefficient of the nanoparticle solute inside the droplet, and Pe is the ratio of the solvent evaporation rate from the droplet surface and the diffusion rate of the nanoparticles inside the droplet. The electrospay method typically yields spherical particles. We could easily fabricate spherical particles using the nc-TiO$_2$ dispersion solution (Fig. 1, R1). The solution exhibits the maximum structural stability when the particles are in spherical form. This is the fundamental reason for the production of this shape.\textsuperscript{34} When the humidity is low, the solvent evaporation rate is high, and the nanoparticles can re-homogenize as droplet shrinks, promoting the formation of less porous particles. The low porosity corresponds to a high mechanical strength inside the particles, so the particles do not experience shrinkage or collapse, and a spherical morphology is
formed. For the same droplet shrinkage rate, the Pe value is the lowest in this case because of the small droplet radius.\textsuperscript{32}

However, changing this parameter, which is related to the solvent evaporation rate, can result in the formation of different particle morphologies.\textsuperscript{44} When the solvent evaporation rate was slow because of the use of the ethanol/butanol (9/1 v/v) solvent mixture (boiling points of 78.4 and 117.7 °C, respectively), as shown in Table 1, the removal of the solvent from the droplet surface caused an increase in the concentration of nanoparticles near the surface.

As more of the solvent evaporated, the concentration increased until a thin crust of solid nanoparticles was formed at the droplet surface. As more solvent was removed, the thickness of the crust increased until finally a large hollow particle was formed; this hollow shell collapsed to form the observed biconcave particle (Fig. 1, R2). At this droplet shrinkage rate, the Pe value was high in this case. The particle was spherical at low values of Pe and became biconcave when the value of Pe increased.\textsuperscript{32}

A toroid morphology of the produced particles can be considered to arise from an initial deformation of the droplet, which changed the initial spherical shape to either a doughnut-like shape or a disk form. This is possible by the loss of structural stability of the droplet in a two-phase field because of the additional macro- and microhydrodynamic effects during the drying process.\textsuperscript{35}

The structural stability of droplets can be explained by the bond’s number \( \beta \), the ratio of the inertial force to the surface tension effects. The bond number is given by

\[
\beta = \frac{\Delta \rho ad}{\sigma}
\]

where \( \Delta \rho \) is the difference in the densities of the droplet and the surrounding fluid, \( a \) is the acceleration (change in gas velocity with time), \( d \) is the droplet size, and \( \sigma \) is the surface tension.\textsuperscript{36,37}

The droplet is nearly spherical when \( \beta \rightarrow 0 \) and becomes flat when the value of \( \beta \) increases. The value of \( \beta \) can be set experimentally by varying the process temperature or humidity. It follows that the destabilization of the initial shape of a droplet could be achieved by (i) increasing the droplet size and (ii) decreasing the surface tension (\( \sigma \)) of the droplet. A decrease in \( \sigma \) can be set experimentally by increasing the process temperature to \( \sim 35 \) °C using a heater, as shown in Table 1, destabilizes the droplet. For droplets at high temperatures, the values of \( \beta > 1 \) are attained from eqn (2), and a doughnut-like form is obtained (Fig. 1, R3). At high values of humidity (\( \sim 40\% \)) obtained by using a humidifier, the droplet radius increases with the decreasing solvent evaporation rate, and the destabilization of the initial droplet shape occurs. The values of \( \beta > 1 \) are also attained from eqn (2), and the disk form is obtained (Fig. 1, R4). Detailed formulae for the determination of shape in all the cases are available in previous reports.\textsuperscript{37–40}

The selection and adjustment of the initial physicochemical properties of the droplet is known as the bond-number correlation. The changes in the hydrodynamics, structural stability, and droplet behavior cause the transformation of the shape of a droplet from spherical to doughnut or disk-like (Fig. 1, R3 and R4).\textsuperscript{35}

The effectiveness of the above mentioned mechanism for fabricating particles with various morphologies is discussed using the SEM images shown in Fig. 2(a–d).

Fig. 2a shows the spherical TiO\textsubscript{2} particles produced using the electrospray method. The SEM images confirm that under typical conditions, the electrospray method generates spherical particles.\textsuperscript{41} The adjustment of some experimental parameters produces particles with different morphologies. The change in the solvent evaporation rate causes the production of biconcave particles (Fig. 2b), which is attributed to the component movements within the droplet\textsuperscript{42} and to the decreased

![Fig. 2](image-url)  
SEM images of particles of (a) spherical, (b) biconcave, (c) disk –, and (d) doughnut -like morphologies.
Fig. 3(d) shows the XRD patterns for the TiO$_2$ sphere, doughnut, and disk-shaped particles prepared by electrospraying on FTO substrate. Furthermore, the anatase (101) peak using the Scherrer equation, were 15.3, 31 nm, and 3.98 nm, respectively. The mesoporous TiO$_2$ hierarchical structures were annealed under high temperature at 500 °C for 30 min. After annealing, these structures were soaked in a TiCl$_4$ aqueous solution for 20 min at 80 °C for post-treatment and then sintered again at 450 °C for 30 min. It is well known that post-treatment by a TiCl$_4$ aqueous solution and the high-temperature annealing process both improve connections between the nanoparticles by changing the ratio of surface to interface. Post-treatment with TiCl$_4$ aqueous solution also changes the surface area by modifying the roughness factor of the nanoparticles. Consequently, these post-treatments can change the surface area and interface; these changes can strongly affect the disk-, spherical-, and doughnut-shaped TiO$_2$ hierarchical structures because the different assembly patterns produce varied pore sizes and interfaces. Therefore, we can assume that the surface area is different for each type of mesoporous TiO$_2$ hierarchical structure, despite the constant primary unit of the samples of P-25. The amount of the dye adsorbed on the disk-, spherical-, and doughnut-shaped TiO$_2$ conventional particles was 4.53 × 10$^{-7}$, 4.35 × 10$^{-7}$, 4.12 × 10$^{-7}$, and 3.98 × 10$^{-7}$ mol cm$^{-2}$, respectively. The pore-size distributions for these four films were analyzed by N$_2$ adsorption–desorption isotherms. As shown in Fig. S2, the average pore size of the film from conventional TiO$_2$ NPs was 31 nm, a reasonable result considering the constituent particle size. Conspicuously, two kinds of pores were observed in the films fabricated from the disk-, spherical-, and doughnut-shaped TiO$_2$ structures. Pores of ~26–30 nm and ~120–160 nm were found in the films derived from TiO$_2$ hierarchically structured particles. The ~26–30 nm-sized pores were the internal pores of the nanoporous disk-, spherical-, and doughnut-shaped TiO$_2$ structures, whereas the ~120–160 nm-sized pores originated from the interstitial voids formed by the closed-packed sub-micrometer TiO$_2$ hierarchical structures. These pores allowed the electrolyte to penetrate through the TiO$_2$ film. The HS-TiO$_2$ particles exhibited a high surface area, high pore volume per gram, and high dye-loading as compared to those exhibited by the conventional TiO$_2$ particles.

Fig. 4 shows the cross-sectional images of the electrosprayed electrodes (~15 μm thick) with uniform spherical, doughnut-, and disk-like shapes from the bottom to the top of the deposited layers. The photovoltaic properties of the DSSCs formed using each of the TiO$_2$ photoelectrodes are shown in Fig. 5(a) and Table 3. The DSSC with the conventional photoelectrode showed a short circuit current ($J_{sc}$) of 14.7 mA cm$^{-2}$, an open circuit voltage ($V_{oc}$) of 0.805 mV, and a fill factor of 71%, resulting in a power conversion efficiency (PCE) of 8.4%.

Table 2 The physical properties of the films bearing the disk-, spherical-, doughnut-shaped, and conventional particles.

| Morphology     | Surface area (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Absorbed dye (10$^{-7}$ mol cm$^{-2}$) |
|----------------|-------------------------------|-------------------------------|---------------------------------------|
| Disk           | 99.5                          | 0.402                         | 4.53                                  |
| Sphere         | 90.9                          | 0.394                         | 4.35                                  |
| Doughnut       | 89.7                          | 0.374                         | 4.12                                  |
| Conventional   | 82.3                          | 0.353                         | 3.98                                  |
| Sphere         |                              |                               |                                       |
DSSC with the photoelectrode consisting of doughnut-shaped particles showed a $J_{sc}$ of 15.0 mA cm$^{-2}$, $V_{oc}$ of 0.817 mV, and fill factor of 71%, resulting in a PCE of 8.8%. The DSSC with the photoelectrode consisting of spherical particles showed an enhanced $J_{sc}$ of 15.7 mA cm$^{-2}$, $V_{oc}$ of 0.820 mV, and fill factor of 72%, resulting in an increased PCE of 9.3%. The DSSC with the photoelectrode consisting of disk-shaped particles showed a significantly enhanced $J_{sc}$ of 17.5 mA cm$^{-2}$, $V_{oc}$ of 0.825 mV, and fill factor of 72%, resulting in an increased PCE of 10.4%. The DSSC utilizing the disk-type photoelectrode showed the best performance with an active area of 0.25 cm$^2$, as shown in Table 3. In particular, the $J_{sc}$ was 11%, 16%, and 19% greater than that of the DSSCs using the spherical-, doughnut-shaped, and conventional photoelectrodes, respectively. Statistical analyses of the PCE values of the devices based on TiO$_2$ photoelectrodes with disk-, spherical-, doughnut-type, and conventional nanoparticles by using the integrating sphere-mode of a UV-spectrophotometer, as shown in Fig. 5(b). Throughout the wavelength region ($\lambda = 400$–800 nm), the disk-type photoelectrode maintains the highest reflectance ($R$) compared to the spherical-, doughnut-type, and conventional electrodes, indicating the superior light-scattering properties of the disk-type film. The enhanced light reflectance can be attributed to the unique planar structure of the disk-type film. Diffusive particles randomly scatter in all directions. Thus still much of the incident light is lost after the scattering layer. However, disk-type film with the planar structure can directly reflect a large fraction of light back into the devices. It is expected such a planar structure can significantly enhance light harvesting and improve the overall conversion efficiency.33,44

In order to compare the photovoltaic performance of the disk-type photoelectrode to that of the electrode using spherical-, doughnut-shaped, and conventional particles, the IPCE

![Fig. 4] SEM images of TiO$_2$ sphere-, doughnut-, and disk-shaped particles prepared by electrospray method. (a) and (b) Cross-sectional and surface images, respectively, of the disk-shaped particles deposited on FTO substrate; (c) and (d) show similar cross-section and surface images for spherical particles; (e) and (f) show cross-sectional and surface images for doughnut-shaped particles.
spectra of the TiO2 photoelectrodes using these materials were collected. As shown in Fig. 5(c), the photoelectrode prepared using the disk-shaped particles possessed higher IPCE values over a wide spectral range (from 400 to 750 nm) than a photoelectrode of similar thickness using the spherical, doughnut-shaped, or conventional particles. The higher IPCE values of the disk photoelectrode are ascribed to the enhanced light-scattering capacity of the photoelectrode, which promotes the light harvesting of the sensitizing dye in this region.

This is in good agreement with the Jsc and relectance results discussed above.

In order to investigate the electron transport properties in the nc-TiO2 doughnut-, spherical-, disk-shaped, and conventional photoelectrodes, the EIS measurements were employed. Fig. 5(d) shows the Nyquist plots of the EIS of the disk-, doughnut-, and spherical-type devices, measured under 1.5 AM simulated solar conditions. Generally, the conventional three semicircles observed in the Nyquist plot indicate the internal resistances of the devices. The series resistance (R0) of the cells is estimated from the intercept on the real axis with the highest frequency; the first arc in the high-frequency range indicates the electrochemical reaction resistance or redox couple at the Pt counter electrode (R1); the second arc in the intermediate-frequency range demonstrates the charge recombination resistance at the interface between the TiO2 photoelectrode and the electrolyte (R2); and the third arc is caused by the Warburg diffusion of the redox species (W). CPE1 and CPE2 are the constant-phase elements of the capacitance, corresponding to R1 and R2, respectively.

Fig. 5(d) illustrates the origin of the differences in the electric properties between the devices using doughnut-, spherical-, disk-shaped, and conventional TiO2 photoelectrodes. As shown in Table 4, the disk photoelectrode had a smaller R2 resistance and larger CPE2 capacitance than the spherical-, doughnut-shaped, and conventional photoelectrodes.

This result implies that the DSSC with the disk photoelectrode had more efficient charge-transfer at the TiO2/electrolyte interface. The packing density is rather low due to the point attachment of spherical scattering particles, which is adverse to light harvesting and electron transfer. Therefore, a special scattering layer constructed from planar mesostructured particles with high surface area and sufficient attachment to each other is expected to be one of the good choices to improve electron transfer and light harvesting for benefiting cell performance. Moreover, it has an improved electron lifetime, as determined by the following formula:

\[ \tau_n = R_2 \times CPE_2 \]  

(3)

The calculated lifetimes (\( \tau_n \)) of the disk-, spherical-, doughnut-shaped, and conventional photoelectrodes are 15.2,
12.7, 11.9, and 4.3 ms, respectively. Under illumination, the relation between $V_{oc}$ and recombination lifetime can be described as:

$$V_{oc} = \frac{RT}{\beta F} \ln \left( \frac{A I}{n_0 k_1 (I^{-}) + n_0 k_2 (D^{+})} \right)$$

(4)

where $R$ is the molar gas constant, $T$ is the temperature, $F$ is the Faraday constant, $\beta$ is the reaction order for $I^{-}$ and electrons, $A$ is the electrode area, $I$ is the incident photon flux, $n_0$ is the concentration of electronic states in the conduction band, $k_1$ is the reaction constant for the back-reaction of injected electrons with triiodide, and $k_2$ is the reaction constant for the recombination of electrons with oxidized dye ($D^{+}$). If we assume that recombination with the oxidized dye molecules is negligible, then $V_{oc}$ becomes logarithmically dependent on $k_1$ under the conditions used in this study because the concentration of triiodide in the electrolyte and the incident photon flux were both constant. Furthermore, if $V_{oc}$ is proportional to $\ln(1/\tau_n)$, then this suggests that the DSSCs with longer lifetimes have higher $V_{oc}$ values. In particular, the long lifetime of the disk-shaped photoelectrode should increase the $V_{oc}$ to 0.825 V, compared to the $V_{oc}$ values of 0.820, 0.817, and 0.805 V for the spherical-, doughnut-shaped, and conventional photoelectrodes, respectively. The increased lifetime for the disk photoelectrode was directly related to the reduced possibility of multiple trapping, as well as the inhibition of the recombination reactions with the electrolyte. Finally, the $W_s$ value of the disk photoelectrode (3.9 $\Omega$) showed a smaller diffusion resistance than that of the doughnut (4.5 $\Omega$) and conventional (6.7 $\Omega$) photoelectrodes. This suggests that the disk photoelectrode had a good pore structure and allowed an efficient diffusion of the $I^{-}$/$I_3$ redox couple in the electrolyte as shown in Table 2. A three-dimensional network the interconnected pores in the disk photoelectrode promoted the electrolyte diffusion and reduced the diffusion resistance.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the DGIST R&D Program of the Ministry of Science, ICT and Future Planning of Korea (17-EN-03) and the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (2016M1A2A2936781).

### References

1. B. O'Regan and M. Gratzel, *Nature*, 1991, 353(6346), 737–740.
2. J. M. Kroon, N. J. Bakker, H. J. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien and G. E. Tulloch, *Prog. Photovoltaiacs*, 2007, 15(1), 1–18.
