RSC Advances

RSCPublishing

PAPER

Cite this: RSC Advances, 2013, 3, 3017

Received 2nd November 2012, Accepted 17th December 2012

DOI: 10.1039/c2ra22746k

www.rsc.org/advances

1. Introduction

In the past two decades, dye-sensitized solar cells (DSSCs) have attracted considerable interest owing to their low production cost, which makes them a suitable replacement for conventional solar cells.¹⁻¹¹ Each component of DSSCs, including sensitizers,^{2,4,10} electrodes,^{5,6,11} and electrolytes,^{8,9} has been extensively researched in order to enhance its performance. As a result, an energy-conversion efficiency of more than 12.3% has been demonstrated.7 Long-term stability and high efficiency are required for practical application of DSSCs. The stability of the liquid electrolytes commonly used in highly efficient DSSCs cannot be guaranteed because of solvent evaporation or leakage. All-solid-state DSSCs have emerged in an attempt to replace the liquid electrolytes with organic or inorganic hole conductors, such as p-type semiconductors,¹²⁻¹⁴ organic hole-transport materials,¹⁵⁻¹⁷ and solvent-free polymer electrolytes.¹⁸⁻²⁰ However, the photovoltaic performance of these types of all-solid-state DSSCs still lags behind that of the liquid type, possibly because highly viscous, solid electrolytes cannot easily penetrate the nanopores in photoelectrodes having the typical structure. Recent

Efficiency enhancement in solid dye-sensitized solar cell by three-dimensional photonic crystal[†]

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Dye-sensitized solar cells (DSSCs) offer an attractive alternative to conventional solar cells because of their lower production cost. However, the liquid electrolyte used in these cells is unstable because of solvent leakage or evaporation, and DSSCs that use a solid electrolyte do not perform as well. In this paper, we present a design in which a nanocrystal (nc)-TiO₂ underlayer is integrated with an optically active porous three dimensional photonic crystals (3D PCs) overlayer, and a sequential infiltration process is adopted to introduce additives to the solid electrolyte. This architecture allows effective dye sensitization, electrolyte infiltration, and charge collection from both the nc-TiO₂ and the PC layers, yielding enhanced absorption in a specific spectral region. We describe the fabrication process and demonstrate the improved performance of the fabricated DSSCs, which exhibited conversion efficiencies that were as much as 32% higher than those of a conventional DSSC. This approach should be useful in solid-state devices where pore infiltration is a limiting factor, as well as in weakly absorbing photovoltaic devices.

reports have described novel photoelectrode structures that use nanowires,^{21,22} nanotubes,^{23,24} hollow spheres,^{25,26} and three dimensional photonic crystals (3D PCs).^{27,28} In particular, the large porosity of 3D PC electrode structures provides good permeability for high-viscosity solid electrolytes. Moreover, electrodes containing a 3D PC have shown significant potential to yield an outstanding light-harvesting efficiency.27,28 Several theoretical and experimental approaches report a variety of possible effects, including the multiple scattering at disordered regions in the photonic crystal (PC),^{28,29} the formation of multiple resonant modes²⁷ and the faster electron transport and enhanced light harvesting using a novel three-dimensional (3D) self-assembled anatase TiO₂ fibrous network photoanode.³⁰ In doing so, the incident-photon-to-current conversion efficiency (IPCE) was shown to increase with respect to that a standard reference cell. However, the observation of a higher IPCE does not necessarily imply better performance. The formation of multiple resonant mode, which was predicted by a scalar wave approximation by Mihi and Míguez,²⁷ has generated interest because it promises significant enhancement over a large spectral range. According to these calculations, coupling a low-refractive-index 3D PC- TiO2 layer to a higher-index nanocrystal (nc)-TiO₂ layer should produce photon localization in the cell and thus greatly increase the probability of photon absorption.

Here, we present a design in which an $nc-TiO_2$ underlayer is integrated with an optically active porous 3D PC-TiO₂ overlayer, and a sequential infiltration process is adopted to introduce additives to the solid electrolyte. This design allows effective electrolyte infiltration, and enhances absorption in a

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 $[\]dagger$ Electronic supplementary information (ESI) available: Details of the sample fabrication procedure and the experimental method: Synthesis of nanocrystal (NC) TiO_2 particles and fabrication of solar cell, synthesis and fabrication of 3D photonic crystal, plastic-based electrolyte, characterization of 3D photonic crystal and solar cell. See DOI: 10.1039/c2ra22746k



Fig. 1 Schematic of procedure for preparing $FTO/nc-TiO_2/PC-TiO_2$ electrodes (a)–(e). FTO, $nc-TiO_2$ film, application of PC layer fabricated from PS spheres 370 nm in diameter, and final double-layered structure after ALD and calcinations. (f) Higher-magnification image of top of TiO_2 inverse opal layer fabricated from 370 nm PS spheres. (g) Cell configuration, (h) XRD pattern for TiO_2 inverse opal, (i) cross section image of $FTO/nc-TiO_2/PC-TiO_2$ electrodes which showed close contact between $nc-TiO_2$ and PC-TiO_2 (right corner inset) and the long range order of PC-TiO_2.

specific spectral region owing to the PC effect and PC-induced resonances. Application of the 3D PC electrode and the sequential infiltration process to DSSCs yields superior harvesting efficiency.

2. Experimental

To realize a PC-coupled DSSC (PC DSSC) that exhibits enhanced photocurrent over a large spectral region, we fabricated a fluorine-doped tin oxide (FTO)/nc-TiO₂/PC-TiO₂ double layer that can be illuminated from the anode side. Fig. 1 schematically illustrates the procedure for preparing FTO/nc-TiO₂/PC-TiO₂ electrodes for the DSSCs. To obtain the FTO/nc-TiO₂ structure for a conventional DSSC and the double-layered structure shown in Fig. 1g, nc-TiO₂ paste was applied to the FTO-glass slide by the doctor blade method; cellophane tape was used to control the film thickness. The nc-TiO₂ films were heated in air at 5 °C min⁻¹ to 500 °C and were then held for 30 min and subsequently cooled to room temperature (Fig. 1b). To produce the FTO/nc-TiO₂/PC-TiO₂ structure, an opal template composed of polystyrene (PS) spheres 370 nm in diameter was prepared onto the nc-TiO₂ film using a vertical deposition technique (Fig. 1c).³¹ The PS opal template was infiltrated by atomic layer deposition (ALD) using 150 cycles of titaniumtetrachloride (TiCl₄) and water (H_2O) (Fig. 1d). The growth rate during ALD growth is about 0.3 nm/cycle. The double layer was then heated to 500 $^{\circ}$ C (2 h, heat ramp 1 $^{\circ}$ C min⁻¹) to burn off the organic material from the PS colloidal template, crystallize the TiO₂, and leave a TiO₂ inverse opal (IO) on top of the nc-TiO₂ layer (Fig. 1e). The sample was exposed to reactive ion etching (CF₄, 5 min) to remove the top surface of deposited material on the TiO₂ IO (Fig. 1f). The X-ray diffraction (XRD) pattern of the highly crystalline anatase TiO₂ IO is shown in Fig. 1h. The thickness of the TiO₂ IO layer was typically 15 µm and can easily be adjusted by changing the concentration of PS spheres used for film growth. Fig. 1f and i shows the cross section image of $FTO/nc-TiO_2/PC-TiO_2$ electrode and the top surface of the (111) crystal plane of the inverted TiO2 PC layer obtained after the steps illustrated in Fig. 1a-e.

3. Results and discussion

A $(P_1 A)$ -doped succinonitrile solid electrolyte was used for cell fabrication.^{32,33} This electrolyte reportedly exhibits good performance in solid-state DSSCs.³⁴ Doping of ions into the solid phase of succinonitrile produces enhanced diffusivity and high ionic conduction. The solid electrolyte used in our experiment was prepared by mixing synthesized N-methyl-*N*-butylpyrrolidinium iodide $(P_{1,4}I)$, ^{32,34} I₂, and succinonitrile; the doped ions appear in the solid solvent in a molar ratio of 5:1:100. The mixture was then heated to 70 °C. At room temperature, this compound electrolyte has a fast ionic conductivity of 3.0 \pm 0.2 mS cm⁻¹. The observed fast ion transport in this solid material can be viewed as a decoupling of the diffusion and shear relaxation times, which probably originates in local defect rotations in the succinonitrile solid crystal.35-37 Although this solid-electrolyte-based DSSC with high ion conductivity exhibited the highest efficiency among cells using competing electrolyte materials, its photovoltaic characteristics still lag behind those of liquid-type DSSCs. A combination of guanidiniumthiocyanate (GSCN), and 4-tertbutylpyridine (tBP) additives in the electrolyte reportedly improve the open circuit voltage $V_{\rm oc}$ and the photocurrent remarkably because of the collective effect of a slower recombination reaction and a positive shift in the conduction band.^{38,39} However, when we introduced these additives to the iodide-doped succinonitrile in this solid-state system, a solubility problem occurred that tended to inhibit the formation of the solid phase. The additives are believed to cause variations in the trans-gauche isomerization that accompanies the phase change.^{40,41} To avoid this problem, we developed a two-step infiltration process. We first injected the liquid-electrolyte along with the tBP and GSCN into the DSSCs and then dried the resulting electrolyte by placing the DSSCs in an oven at 80 °C for 12 h. During drying the additives, which have high boiling points and remained entrapped in the nc-TiO₂/PC-TiO₂ double layer, while most of the solvent evaporated. Finally, the solid electrolyte was injected into the cell at 80 °C. More detailed experiment procedures are available in the ESI.†

Fig. 2 (a) shows the optical reflection and absorbance spectrum through the self-assembled fcc-TiO₂ PC fabricated with 370 nm spheres in this study. Optical properties were measured by UV/VIS/NIR Spectrometer (Perkin Elmer LAMBDA 1050) with wavelength range 185–3300 nm. The sample mount had two settings for measuring diffuse (scattered) reflectivity and total (diffuse and specular) reflectivity. Specularly reflected light was tightly reflected around the angle of incidence. Diffusely reflected light result from roughness, defects, *etc.* and was collected by an integrating sphere. The inverse opals were mounted to the diffuse reflectance accessory (DRA) sphere such that the [111] direction was pointing almost directly inwards. Specular reflectivity spectra were taken by subtracting the diffuse reflectivity from the total reflectivity.



Fig. 2 (a) Normal-incidence reflection and absorbance spectrum of 3D PC fabricated with 370 nm PS spheres: total, diffuse and specular reflection, (b) IPCE of PC DSSC compared to that of conventional DSSC and (c) IPCE (PC-DSSC)/ IPCE (conventional DSSC).

It consists of a broad reflection peak at 741 nm corresponding to the fundamental PBG and additional reflection spectra peaks at 543 and 434 nm and this is consistent with the absorbance spectrum. This spectrum reveals that the proposed fabrication method produces high-quality PC structures with the expected optical characteristics. We have integrated the total and diffuse reflectivity spectra for 370 nm 3D PC. The integration of the total and diffuse reflectivity spectra are 19 685 and 7748, respectively, for 370 nm 3D PC. Therefore, the integration of specular reflection is 11 937. Dye desorption experiments were carried out using nc-TiO₂ films coated with the N719 dye prepared from a 0.3 mM ethanolic solution. For each sample, the dye was desorbed from the nc-TiO₂ electrodes 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 (Hewlett Packard 8453). The number of molecules was calculated from UV-vis absorption spectra of desorbed sensitizers using the extinction coefficient of the N719 sensitizer ($\varepsilon = 3748 \text{ cm}^{-1} \text{ M}^{-1}$ at 535 nm). The total amount of adsorbed dye on the 8 μ m nc-TiO₂ and 4 μ m nc-TiO₂/14 μ m PC-TiO₂ double layer were 7.05 \times 10⁻⁸ mol cm $^{-2}$ and 6.95 $\,\times\,$ 10 $^{-8}$ mol cm $^{-2}$, respectively. It is confirmed that the enhancement of photocurrent is not attributed to the different amount of the adsorbed dye on both samples. It was determined that 5.97×10^{-5} mol g⁻¹ of sensitizer molecules were attached to the surface of 8 µm nc-TiO₂ compared to 3.92×10^{-5} mol g⁻¹ for 4 µm nc-TiO₂/14 µm PC-TiO₂ double layer. To determine the significance of the PC top layer for light harvesting, the incident-photon-to-current efficiency (IPCE) of the PC DSSC was compared to that of a conventional DSSC. IPCE was measured as a function of wavelength from 400 nm to 800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV Measurement, Inc.). A 75-W xenon lamp was used as the light source for generating a monochromatic beam. Calibration was performed using a silicon photodiode (NIST-calibrated photodiode G425) as a standard, and IPCE values were collected at a low chopping speed of 10 Hz. The IPCE characteristics of the PC DSSC are shown in Fig. 2 (b). Two main characteristics are apparent in the IPCE spectra. First, a PC DSSC with a surface area comparable to that of the conventional DSSC exhibits comparable peak absorption values in the measured spectral range. The fact that the IPCE increased supports our assertion that the PC top layer is electrically connected and contributes to light harvesting over the entire measured spectrum. Second, the IPCE maxima reveal the significance of a PC top layer for spectrally selective light harvesting. From the observed pore sizes (295 nm) of the IO structures fabricated from 370 nm PS, we calculated their respective Bragg peak positions in the electrolyte at about 841, 643 and 534 nm, respectively. The theoretical work by Usami showed that random scattering in DSSCs should occur most efficiently at $\lambda = 1.33d$, where *d* is the diameter of the scattering object.42 For our feature sizes, random scattering would therefore occur in the ultraviolet. The PC DSSC's substantially increased IPCE in the green (around 524 nm) and red (around 670 nm) in Fig. 2 (b), on the other hand, arises from PC back reflection at 534 and 643 nm, respectively. The PC DSSC shows a relative increase in absorption in the blue, which suggests that multidirectional scattering from defects in the PC layer contributes to the absorption enhancement.^{28,29} However, the shape of the IPCE spectra for PC DSSC is red-shifted compared to that of the

conventional DSSC. Increased absorption appears near the calculated T-L pseudo-band-gap of the PC and cannot be attributed solely to multidirectional scattering. The enhancement occurs in a wider spectral region than expected for PC back reflection at the green and red edges of the PBG. The results of IPCE (PC-DSSC)/IPCE (conventional DSSC) also showed improvement of IPCE over a large spectral range as shown in Fig. 2(c) and in particular, it showed high improvement in blue and red region. Three effects may contribute to the increase in photocurrent: (1) back reflection of light in the stop-band region of the PC that occurs because the PC layer acts as a dielectric mirror as shown in Fig. 2. (specular reflection), (2) multidirectional scattering from defects in the PC layer in the blue spectral region as shown in Fig. 2 (diffuse reflection), and (3) broader absorption enhancement of the stop band caused by resonant modes as predicted by Mihi and Míguez.²⁷ Our straightforward fabrication method allows close contact between the nc-TiO₂ and the PC-TiO₂. This enables significant enhancement in specific regions of the action spectrum as well as additional charge carrier generation arising from the photoactive material of the PC-TiO₂, which is now a functional part of the DSSC.

I-V measurements of the DSSCs were conducted under a standard AM1.5 illumination of 100 mW cm⁻² (active area 0.32 cm²). We measured the *J*-V characteristics using the shading mask method of Ito et al.44 that has been used to limit photocurrent overestimation arising from light-guiding effects that occur as light passes through the conduction glass electrode. Fig. 3 shows the J-V curves for the PC DSSC with solid and liquid electrolytes and that of a conventional DSSC for comparison. The PC DSSC with the solid electrolyte exhibits a 21% increase in photocurrent ($J_{sc} = 13.9 \text{ mA cm}^{-2}$) compared to the conventional DSSC (11.5 mA cm^{-2}) owing to the PC effect, which is consistent with the relative increase of IPCE (20%) measurements in Fig. 2 (b). The easy penetration of the solid electrolyte into the PC DSSC via the porous 3D PC-TiO₂ overlayer reduces charge transfer resistance at the photoelectrode/solid electrolyte. PC DSSC (solid electrolyte) exhibited conversion efficiencies 32% higher than that of a conventional DSSC (solid electrolyte). The photocurrent of the PC DSSC with the liquid electrolyte ($J_{sc} = 16.1 \text{ mA cm}^{-2}$) is also increased compared to that of a conventional DSSC (J_{sc} = 13.2 mA cm⁻²) due to the 3D PC effect. The influence of TiO₂ thickness on DSSC performance was studied using a solid electrolyte. J-V characteristics of solar cells fabricated with different TiO₂ film thickness (8 µm nc-TiO₂, 12 µm nc-TiO₂, and 24 µm: 4 µm nc-TiO₂/14 µm PC-TiO₂) and structure (PC DSSC and conventional DSSC) with a solid electrolyte are shown in Fig. 3 (b). As shown in Fig. 3 (b), the conventional DSSC with film thickness of 8 μ m showed a J_{sc} of 11.5 mA cm^{-2} , V_{oc} of 0.713 mV, and fill factor of 66.8% resulting in a conversion efficiency of 5.48%. An increase in the TiO_2 film thickness to 12 μ m resulted in a slightly improved J_{sc} (12.3 mA cm⁻²) but simultaneously decreased V_{oc} (0.69 mV) and fill factor (57%), resulting in a decrease of the conversion efficiency to a value of 4.83%. The penetration of the solid



Fig. 3 *J*–*V* characteristics of solar cells fabricated with different structure (a) PC DSSC (4 μ m nc-TiO₂/14 μ m PC-TiO₂) and conventional DSSC (8 μ m nc-TiO₂) and (b) different TiO₂ film thickness (8 μ m nc-TiO₂, 12 μ m nc-TiO₂, and 24 μ m: 4 μ m nc-TiO₂/20 μ m PC-TiO₂) with liquid and solid electrolyte.

electrolyte into conventional nc-TiO₂ electrodes is problematic due to their small pores.⁴³ However, the PC DSSC consisting of a 4 µm nc-TiO₂ electrode and a 20 µm PC-TiO₂ top layer showed an enhanced J_{sc} of 16.9 mA cm⁻², V_{oc} of 0.76 mV, and fill factor of 64%, resulting in an increased conversion efficiency of 8.2%. This enhancement can be explained by effective electrolyte infiltration, and improved absorption in a specific spectral region owing to the PC effect. From Table 1, it is seen that the efficiencies of PC DSSC for the liquid electrolyte and the solid electrolyte are 8.58% and 7.22%, respectively. We also measured J-V characteristics of conventional DSSC (4 µm nc-TiO₂) without PC-TiO₂ overlayer and PC-



Fig. 4 Electrochemical impedance spectroscopy (EIS) results of the convention DSSC and PC DSSC with liquid and solid electrolyte at open-circuit conditions under AM 1.5 illumination. The left top image (inset) shows the equivalent circuit diagram used to fit the observed impedance spectra in this figure.

 $TiO_2 DSSC (14 \ \mu m PC-TiO_2)$ without nc- TiO_2 underlayer with a solid electrolyte in the ESI (Fig. 1S and Table 1S[†]). In order to prove PC-TiO_2 effect in the DSSC, DSSCs with different amounts of absorbed dye were fabricated and characterized in the ESI (Fig. 2S and Table 2S[†]). The conventional DSSC without PC-TiO_2 overlayer and PC-TiO_2 DSSC without nc-TiO_2 underlayer with solid electrolyte showed conversion efficiency of 3.5% and 2.5%, respectively. From these results, we can also confirm the PC effect in the PC DSSC.

The electrochemical impedance spectroscopy (EIS) analysis was used to investigate the interfacial properties, internal resistance and charge-transfer kinetics of nc-TiO₂ layers in DSSCs.45,46 Impedance spectra were acquired with a computercontrolled potentiostat (IVIUMSTAT). The EIS of DSSC was performed under constant light illumination (100 mW cm⁻²) biased at open-circuit condition. The measured frequency range was 100 kHz to 100 mHz with perturbation amplitude of 10 mV. Fig. 4 shows the Nyquist plots of conventional and PC DSSCs with liquid and solid electrolytes. The impedance spectra can be interpreted and modeled using equivalent circuits, with each component explained below. Each equivalent circuit consisted of several components as shown in Fig. 4 (inset): ohmic resistance (R_S), charge transfer resistance at the counter-electrode/electrolyte (R_1) , charge transfer resistance at the photoelectrode/electrolyte (R_2) , resistance at the Warburg



Sample structure	Electrolyte	<i>J–V</i> characteristics			
		$V_{\rm OC}$ (V)	$J_{\rm sc}~({ m mA~cm}^{-2})$	FF (%)	EFF (%)
PC DSSC (4 µm nc-TiO ₂ /14 µm PC-TiO ₂)	Liquid	0.827	16.1	64.6	8.58
PC DSSC (4 µm nc-TiO ₂ /14 µm PC-TiO ₂)	Solid	0.735	13.9	70.9	7.22
Conventional DSSC (8 μ m nc-TiO ₂)	Liquid	0.82	13.2	66	7.15
Conventional DSSC $(8 \ \mu m \ nc-TiO_2)$	Solid	0.713	11.5	66.8	5.48
PC DSSC (4 µm nc-TiO ₂ /20 µm PC-TiO ₂)	Solid	0.76	16.9	64	8.2
Conventional DSSC (12 μ m nc-TiO ₂)	Solid	0.69	12.3	57	4.83

PC DSSC (4 µm nc-TiO₂/14 µm PC-TiO₂)

PC DSSC (4 µm nc-TiO₂/14 µm PC-TiO₂)

Conventional DSSC (8 μ m nc-TiO₂)

Conventional DSSC (8 µm nc-TiO₂)

9.4

10.2

9.6

14.8

 $W_{\rm s}/\Omega$

4

5

5.1

9.1

Sample structure	Electrolyte	$R_{ m s/}\Omega$	R_1/Ω	R_2/Ω			

Liquid

Liquid

Solid

Solid

Table 2 Electrochemical parameters of PC DSSC and conventional DSSC with liquid and solid electrolyte

diffusion of the redox I/I_3 couple in electrolyte (W_s), the constant phase element of capacitance corresponding to R_1 (CPE1), and the constant phase element of capacitance corresponding to R_2 (CPE2).⁴⁷ In Fig. 4, the Nyquist spectra of the DSSCs showed three semicircles: the first semicircle, in the high-frequency region, represents R_1 ; the second semicircle, in the middle-frequency region, represents R_2 ; the third semicircle, in the low-frequency region, represents $W_{\rm S}$, and the curve from the origin to first semicircle starting point on the left represents $R_{\rm S}$. These four internal impedances have a direct effect on the electron transport mechanism in DSSCs. As a consequence, the cell performance of the DSSCs is improved when the sum of the resistance components (R_S , R_1 , R_2 , and $W_{\rm S}$) is small. As seen in Table 2, $R_{\rm S}$ of the DSSCs without a PC overlayer was not significantly different from that of DSSCs with a PC overlayer, indicating that the introduction of a PC overlayer has little effect on FTO glass resistance in both liquid and solid electrolytes. However, both R_2 and W_S were decreased by the introduction of the PC overlayer into the solid electrolyte, indicating a decrease in charge transfer resistance at the photoelectrode/electrolyte and the resistance related to Warburg diffusion of the I/I3 redox couple in the solid electrolyte. In particular, R_2 and W_5 decreased from 14.8 Ω to 10.2 Ω and from 9.1 Ω to 5.1 $\Omega,$ respectively. This is attributed to the enhanced infiltration of solid electrolyte into PC DSSC containing a significant portion of macropores facilitating efficient hole transport and dye regeneration.

To illustrate the stability of the solid electrolyte as mentioned in the introduction *i.e.* solvent evaporation or leakage, a comparison is carried out: two cells prepared and



Fig. 5 Parameters J_{sc} , V_{oc} , FF, and cell efficiency as a function of time.

sealed in the same way, except one was filled with liquid electrolyte and the other with our solid electrolyte. It is noted that, after 2 weeks, the liquid cell showed that most of its electrolyte in the device was evaporated, whereas the solid cell retained its electrolyte and the conversion efficiency was pretty much unchanged. Fig. 5 displays the parameters J_{sc} , V_{oc} , fill factor, and cell efficiency as a function of time. For a period of 60 days, it is found that the cell parameters are more or less unchanged.

2.1

3.2

2.3

6.1

4. Conclusion

4.9

4.9

4.8

5.1

In conclusion, we present a fabrication method for a DSSC architecture in which an nc-TiO₂ anatase underlayer is coupled with an optically and electrically active 3D periodic TiO₂ PC overlayer. This design enables effective dye sensitization, electrolyte infiltration and charge collection from both the nc-TiO₂ and PC-TiO₂ layers. Because the layers are in direct physical and electronic contact, light harvesting in specific spectral regions was significantly increased by the 3D PC effect and PC-induced resonances. We also developed a two-step process whereby additives are incorporated into the solid electrolyte to increase the cell efficiency. Finally, since the integration of an electrically and optically active PC increases the absolute IPCE and broadens the light harvesting capability of DSSCs, the conversion efficiencies of the solid-state cells were improved by as much as 32%. This approach should be useful in solid-state devices where pore infiltration is a limiting factor as well as in weakly absorbing photovoltaic devices.

Acknowledgements

This work was supported by the DGIST R&D Program of the Ministry of Education, Science and Technology of Korea (13-ES-04).

References

- 1 B. O'Regan and M. Gratzel, Nature, 1991, 353, 737.
- 2 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Gratzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
- 3 B. Lee, D. B. Buchholz and R. P. H. Chang, *Energy Environ. Sci.*, 2012, 5, 6941.

- 4 M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Cointe, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Gratzel, *J. Am. Chem. Soc.*, 2001, 123, 1613.
- 5 J. R. Durrant, S. A. Haque and E. Palomares, *Coord. Chem. Rev.*, 2004, **248**, 1247.
- 6 A. J. Frank, N. Kopidakis and J. V. D. Lagemaat, *Coord. Chem. Rev.*, 2004, **248**, 1165.
- 7 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, 334, 629.
- 8 I. Chang, B. Lee, J. He, R. P. H. Chang and M. G. Kanatzidis, *Nature*, 2012, **485**, 486.
- 9 A. F. Nogueira, C. Longo and M. A. De Paoli, *Coord. Chem. Rev.*, 2004, **248**, 1455.
- 10 N. Robertson, Angew. Chem., Int. Ed., 2006, 45, 2338.
- 11 M. Quintana, T. Edvinsson, A. Hagfeldt and G. Boschloo, *J. Phys. Chem. C*, 2007, **111**, 1035.
- 12 B. O'Regan, D. T. Schwartz, S. M. Zakeeruddin and M. Gratzel, *Adv. Mater.*, 2000, **12**, 1263.
- 13 J. Bandara and J. P. Yasomanee, *Semicond. Sci. Technol.*, 2007, 22, 20.
- 14 A. Morandeira, J. Fortage, T. Edvinsson, L. L. Pleux,
 E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarstrom and
 F. Odobel, *J. Phys. Chem. C*, 2008, 112, 1721.
- 15 L. Schmidt-Mende, S. M. Zakeeruddin and M. Gratzel, *Appl. Phys. Lett.*, 2005, **86**, 013504.
- 16 R. Senadeera, N. Fukuri, Y. Saito, T. Kitamura, Y. Wada and S. Yanagida, *Chem. Commun.*, 2005, 2259.
- 17 J. E. Kroeze, N. Hirata, L. Schmidt-Mende, C. Orizu, S. D. Ogier, K. Carr, M. Gratzel and J. R. Durrant, *Adv. Funct. Mater.*, 2006, 16, 1832.
- 18 A. F. Nogueira, J. R. Durrant and M. A. De Paoli, *Adv. Mater.*, 2001, 13, 826.
- 19 T. Stergiopoulos, I. M. Arabatzis, G. Katsaros and P. Falaras, *Nano Lett.*, 2002, **2**, 1259.
- 20 J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Huang, P. Li, S. Yin and T. Sato, *J. Am. Chem. Soc.*, 2008, **130**, 11568.
- 21 J. B. Baxter and E. S. Aydil, *Appl. Phys. Lett.*, 2005, 86, 053114.
- 22 M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, 4, 455.
- 23 G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2006, 6, 215.
- 24 D. Kuang, J. Brillet, P. Chen, M. Takata, S. Uchida, H. Miura, K. Sumioka, S. M. Zakeeruddin and M. Gratzel, *ACS Nano*, 2008, 2, 1113.

- 25 Y. Kondo, H. Yoshikawa, K. Awaga, M. Murayama, T. Mori,
 K. Sunada, S. Bandow and S. Iijima, *Langmuir*, 2008, 24, 547.
- 26 H. J. Koo, Y. J. Kim, Y. H. Lee, W. I. Lee, K. Kim and N. G. Park, *Adv. Mater.*, 2008, **20**, 195.
- 27 A. Mihi and H. Míguez, J. Phys. Chem. B, 2005, 109, 15968.
- 28 L. Halaoui, N. Abrams and T. Mallouk, J. Phys. Chem. B, 2005, 109, 6334.
- 29 R. Rengarajan, D. Mittleman, C. Rich and V. Colvin, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **71**, 15968.
- 30 N. Tetreault, E. Arsenault, L.-P. Heiniger, N. Soheilnia, J. Brillet, T. Moehl, S. Zakeeruddin, G. A. Ozin and M. Gratzel, *Nano Lett.*, 2011, **11**, 4579.
- 31 D. K. Hwang, H. Noh, H. Cao and R. P. H. Chang, *Appl. Phys. Lett.*, 2009, **95**.
- 32 D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164.
- 33 Q. Dai, D. R. MacFarlane and M. Forsyth, *Solid State Ionics*, 2006, 177, 395.
- 34 P. Wang, Q. Dai, S. M. Zakeeruddin, M. Forsyth, D. R. MacFarlane and M. Gratzel, *J. Am. Chem. Soc.*, 2004, **126**, 13590.
- 35 H. M. Hawthorne and J. N. Sherwood, *Trans. Faraday Soc.*, 1970, **66**, 1792.
- 36 G. Cardini, R. Righini and S. Califano, *Chem. Phys.*, 1991, 95, 679.
- 37 Q. Dai, D. R. MacFarlane, P. C. Howlett and M. Forsyth, *Angew. Chem.*, 2005, 117, 317.
- 38 N. Kopidakis, N. R. Neale and A. J. Frank, J. Phys. Chem. B, 2006, 110, 12485.
- 39 C. Zhang, Y. Huang, Z. Huo, S. Chen and S. Dai, *J. Phys. Chem. C*, 2009, **113**, 21779.
- 40 S. Long, D. R. MacFarlane and M. Forsyth, *Solid State Ionics*, 2003, **161**, 105.
- 41 P. J. Alarco, Y. Abu-Lebdeh, A. Abouimrane and M. Armand, *Nat. Mater.*, 2004, **3**, 476.
- 42 A. Usami, Chem. Phys. Lett., 1997, 277, 105.
- 43 B. O'Regan, F. Lenzmann, R. Muis and J. Wienke, *Chem. Mater.*, 2002, **14**, 5023.
- 44 S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, M. S. Zakeeruddin and M. Grätzel, *Progr. Photovolt.: Res. Appl.*, 2006, 14, 589.
- 45 P.-Y. Chen, C.-P. Lee, R. Vittal and K.-C. Ho, *J. Power Sources*, 2010, **195**, 3933.
- 46 B. Lee, D.-K. Hwang, P. Guo, S.-T. Ho, D. B. Buchholtz, C.-Y. Wang and R. P. H. Chang, *J. Phys. Chem. B*, 2010, 114, 14582.
- 47 L. Y. Han, N. Koide, Y. Chiba and T. Mitate, *Appl. Phys. Lett.*, 2004, 84, 2433.