Supporting information for

# Efficiency Enhancement in Solid Dye-Sensitized Solar Cell by Three-Dimensional Photonic Crystal

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**Contents:**

***Synthesis of nanocrystal(NC) $TiO_2$ particles and fabrication of solar cell:*** The 2-step autoclaving technique was applied to obtain high-purity anatase $TiO_2$ nanoparticles (NPs). A 30 wt.-% commercially available $TiO_2$ power (P25, Degussa) that consisted of ca. 30% rutile and 70% anatase phases in the crystalline phase was hydrothermally treated with 10 N NaOH in an autoclave at 130 $^oC$ for 20 h; this was followed by repeated washing with 0.1 N $HNO_3$ to obtain a pH value of ca. 1.5. Pure anatase colloidal $TiO_2$ NPs were obtained by autoclaving the low-pH titanate suspension at 240 $^oC$ for 12h. A paste of $TiO_2$ powder was prepared by stirring a mixture of 0.5 g of anatase-$TiO_2$ NPs, 100μL of Triton X-100, and 0.2 g of polyethylene glycol (PEG, Fluka, Mw=20,000) into 3 ml acetic acid (0.1 M). The $TiO_2$ paste was spread on a $SnO_2$:F coated glass substrate (Pilkington, TEC 8 glass, 8 Ω/□, 2.3 mm thick ) by the doctor-blade technique to give a flat and smooth surface using adhesive tape spacer. The film thickness was governed by the height of the adhesive tape. Finally, the $TiO_2$ coated electrode was gradually calcined to remove the polymer under sequential air flows at 150 $^oC$ for 15min, at 320 $^oC$ for 10min, and at 500 $^oC$ for 30min; in this manner, anatase $TiO_2$ NPs were produced. The particle size is about 25 nm as shown in SEM image. Further, post-treatment with the $TiCl_4$ aq. solution was applied to freshly sintered $TiO_2$ electrodes. An aqueous stock solution of 2 M $TiCl_4$ was diluted to 0.05 M in deionized water. Sintered electrodes were immersed into this solution and stored in an oven at 60°C for 1 h in a closed vessel. After flushing with deionized water and drying, the electrodes were sintered again at 500°C for 30 min. For photosensitization studies, the calcined $TiO_2$ NP electrode were immersed in an ethanol solution containing purified $3x10^{-4}$ M cis-di(thiocynato)-N,N′-bis(2,2′-bipyridyl-4-caboxylic acid-4′-tetrabutylammonium carboxy late) ruthenium (II) (N719, Solaronix) for 18 h at room temperature. The dye-adsorbed $TiO_2$ electrodes were rinsed with ethanol and dried under nitrogen flow. The liquid electrolyte was prepared by dissolving 0.6 M of 1- butyl-3-methylimidazolium iodide(BMII), 0.03 M iodine, 0.1M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine in acetonitrile and valeronitrile (85:15 v/v). The counter-electrode was produced by coating F:$SnO_2$ glass with a thin layer of a 5 mM solution of $H_2PtCl_6$ in isopropanol and heating at 400°C for 20 min. The two electrodes were sealed together with thermal melt polymer film (24 μm thick, DuPont). The typical active area of the cell was approximately 0.32 $cm^2$, and each exact area of the photoanode was calibrated by using an optical scanner with a resolution of 600 dot per inch (dpi).

***Synthesis and fabrication of 3dimensional photonic crystal**:* The opal spherical templates were prepared using a vertical deposition technique. Glass substrates with nc-$TiO_2$ film were placed in vials with deionized water containing between 0.1 and 0.3 vol % PS spheres in suspension, depending on the sphere size and intended opal film thickness. The water was then slowly evaporated at 50 °C in a drying oven. This method yields PS opal films with controllable thicknesses between 20 and 100 layers and large single crystalline domains, that can be oriented with the (111) planes of the fcc structure parallel to the substrate surface. $TiO_2$ was infiltrated into the opal templates by ALD using of titaniumtetrachloride ($TiCl_4$) and water ($H_2O$) as precursors. To avoid deformation or melting of the PS structures, the growth temperature was maintained at 85 °C, which is below the glass transition temperature of PS. The chamber pressure during the growth was maintained at 10 Torr and a relatively slow flow of $N_2$ carrier gas was maintained in the chamber. One ALD reaction cycle consisted of a 1 s exposure to $TiCl_4$ followed by a 20 s $N_2$ purge, and a 1 s exposure to $H_2O$ vapor, followed by another 20s $N_2$ purge. The PS spheres were then removed by firing the structure in air at 500 °C for 1 h, leaving an ordered fcc array of air holes in the $TiO_2$ layer.

***Plastic-Based Electrolyte***. For cell fabrication, a ($P_{1,4}I$)-doped succinonitrile plastic crystal electrolyte was used.[32, 33] This electrolyte has good performance for solid-state DSSCs, as reported in the literature.[34] Doping of ions into the plastic crystal phase of succinonitrile leads to enhanced diffusivity and high ionic conduction. Recently, Alarco et al and others have dissolved a large variety of salts in the highly polar medium based plastic crystals, such as succinonitrile, to fabricate solid-state ionic conductors. The plastic crystal electrolyte used in our experiment was prepared by mixing synthesized N-methyl-N-butylpyrrolidinium iodide ($P_{1,4}I$), $I_2$, and succinonitrile for the doped ions as the solid solvent in a mole ratio of 5:1:100, and the mixture was then heated to 70 °C. At room temperature, this compound electrolyte has a fast ionic conductivity of 3.0 ± 0.2 mS/cm. The observed fast ion transport in this solid material can be seen as a decoupling of diffusion and shear relaxation times, which probably originates from local defect rotations in the succinonitrile plastic crystal.[35-37] From the published literature and the authors' earlier work with liquid electrolytes, it was learned that, in addition to a redox mediator in the liquid system, two kinds of additives, such as 4-tertbutylpyridine (tBP) and guanidiniumthiocyanate (GSCN), can be used to improve the liquid cell performance. The addition of tBP into the electrolyte leads to a significant improvement of the open-circuit voltage (Voc), ascribed to either the suppression of dark current due to the blocking effect of tBP at the $TiO_2$/electrolyte interface or a shift of the titania conduction band. GSCN is another important and frequently used additive in electrolytes for DSSCs. It was reported that a combination of GSCN and tBP additives in the electrolyte results in a remarkable improvement of Voc and photocurrent because of the collective effect of a slower recombination reaction and a positive shift of the conduction band.[38, 39] However, for this solid-state system, when these additives were added to the iodide-doped succinonitrile, it had a solubility problem that tended to inhibit the formation of the plastic phase. It is believed that the additives were leading to a variation in the trans_gauche isomerization that accompanies the phase change.[40, 41] To avoid this problem, a two-step infiltration process was developed. We first injected the liquid-state electrolyte through pinholes of a sandwich cell along with the additives tBP and GSCN into the $TiO_2$ NP film and dried this electrolyte by putting the NP film in an oven at 80 °C for 12 h. By drying the liquid electrolyte, additives with a high boiling point remained entrapped in the $TiO_2$ pores while most of the solvent was evaporated. After that, the plastic electrolyte was injected into the cell at 80 °C. The cell was then cooled to room temperature to obtain a waxy solid electrolyte with the presence of additives. Using this two-step process, a room temperature ionic conductivity of 3.2 ± 0.2 mS/cm was obtained through the weak interaction between cations from additives and the nitriles of succinonitrile.

***Characterization of 3D photonic crystal and solar cell***: Optical property was 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. The conversion efficiency and *J*–*V* curve was characterized by the calibrated solar simulator with AM 1.5 G, 100 $mW/cm^2$. Anatase $TiO_2$ nanoparticles were investigated by using a field-emission scanning electron microscope (SEM, S4800, Hitachi), and an x-ray diffractometer (D/Max-A, Rigaku). The thickness of the $TiO_2$ film was measured by surface profiler (TENCOR. P-10). Impedance spectra were acquired with a computer-controlled potentiostat (IVIUMSTAT). The electrochemical impedance spectroscopy (EIS) of DSSC was performed under constant light illumination (100mWcm$^{-2}$) biased at open-circuit condition. The measured frequency range was 100 kHz to 100 mHz with perturbation amplitude of 10 mV. The obtained spectra were fitted using the Z-View software (v3.2c, Scribner Associates, Inc.).

We also measured J-V characteristics of conventional DSSC (4 μm nc-$TiO_2$) without PC-$TiO_2$ overlayer and PC-$TiO_2$ DSSC (14 μm PC-$TiO_2$) without nc-$TiO_2$ underlayer with a solid electrolyte in the supporting information (**Figure 1S** and **Table 1S**).

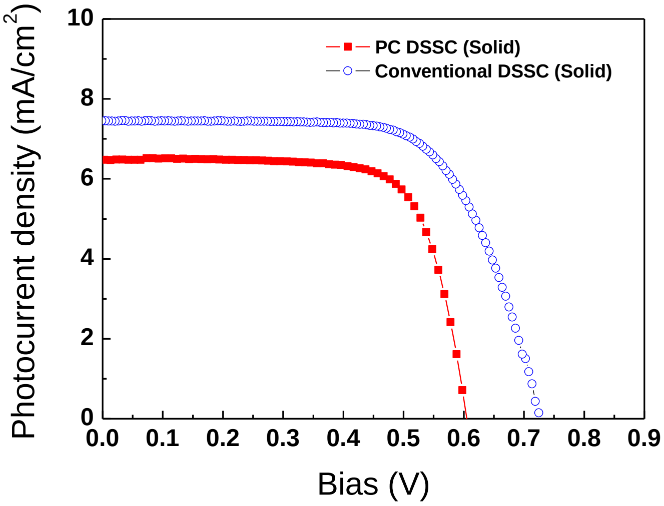

**Figure 1S**. J-V characteristics of PC DSSC (14μm PC-$TiO_2$) and conventional DSSC (4 μm nc-$TiO_2$) with solid electrolyte.

| Sample structure | Electrolyte | JV characteristics | | | |
|---|---|---|---|---|---|
| | | $V_{OC}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | EFF (%) |
| Conventional DSSC (4 μm nc-$TiO_2$) | Solid | 0.71 | 7.5 | 67 | 3.5 |
| PC DSSC (14 μm PC-$TiO_2$) | Solid | 0.6 | 6.2 | 72 | 2.5 |

**Table 1S.** J-V characteristics of PC DSSC and conventional DSSC with solid electrolyte.

In order to prove PC-$TiO_2$ effect in the DSSC, DSSCs with different amount of absorbed dye were fabricated and characterized in the supporting information (**Figure 2S** and **Table 2S**).

When the amount of absorbed dye on the cell is decreased from $7.05\times10^{-8}$ to $5.91\times10^{-8}$ mol/cm$^2$ by 16%, the efficiency of cells is still improved by 15% from 5.48 to 6.35 % owing to PC effect. Even though, the amount of absorbed dye on the cell is further decreased to $4.85\times10^{-8}$ mol/cm$^2$ by 31%, the efficiency of cells is only decreased by 12% from 5.48 to 4.81%. From these results, we can confirm the PC-$TiO_2$ effect in the PC DSSC.

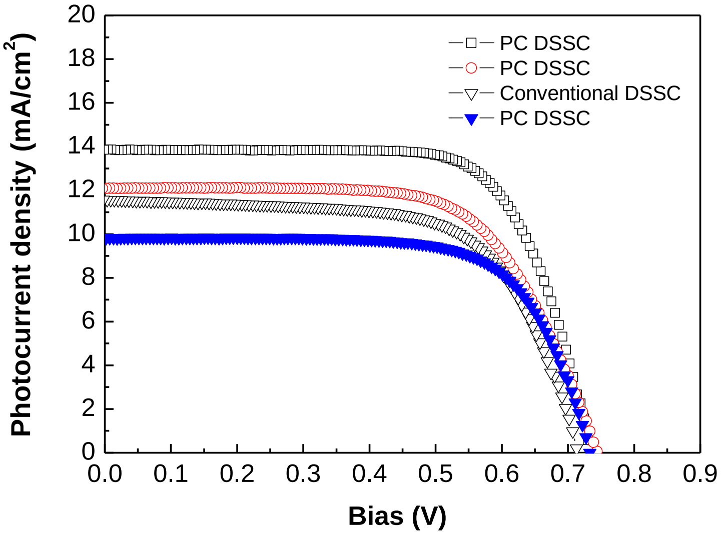

**Figure 2S**. J-V characteristics of PC DSSC (nc-$TiO_2$/ PC-$TiO_2$) and conventional DSSC (nc-$TiO_2$) with different amount of absorbed dye.

| **Sample structure** | **Absorbed dye (mol/cm$^2$)** | **JV characteristics** | | | |
|---|---|---|---|---|---|
| | | **$V_{OC}$ (V)** | **$J_{sc}$ (mA/cm$^2$)** | **FF (%)** | **EFF (%)** |
| PC DSSC(nc-$TiO_2$/ PC-$TiO_2$) | $6.95\times10^{-8}$ | 0.735 | 13.9 | 70.9 | 7.22 |
| PC DSSC(nc-$TiO_2$/ PC-$TiO_2$) | $5.91\times10^{-8}$ | 0.74 | 12.1 | 71 | 6.35 |
| PC DSSC(nc-$TiO_2$/ PC-$TiO_2$) | $4.85\times10^{-8}$ | 0.734 | 9.8 | 67 | 4.81 |
| Conventional DSSC (nc-$TiO_2$) | $7.05\times10^{-8}$ | 0.713 | 11.5 | 66.8 | 5.48 |

**Table 2S.** J-V characteristics of PC DSSC (nc-$TiO_2$/ PC-$TiO_2$) and conventional DSSC (nc-$TiO_2$) with different amount of absorbed dye.