Assessing Effect of Surface States of Mesoporous NiO film on Charge Transport and Unveiling Unexpected Light Response Phenomenon in Tandem Dye-Sensitized Solar Cells

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Experimental Section

Materials: FTO glass is purchased from (Pilkington, TEC15); $NiCl_2$ (99.99%), H_2PtCl_6, ethanol, acetonitrile (ACN), tert-butyl-pyridine (TBP), I_2 and F108 polymer are purchased from Sigma-Aldrich. The P1[1] dye reported previously is used as a photosensitizer. The VG1-C8 dye is purchased from Dyenamo AB. TiO_2 paste (Dyesol, 30NR-T) is purchased from Dyesol. 1,2-dimethyl-3-propylimidazolium iodide (DMPII), Zirconium Dioxide (ZrO_2) pastes, Amosil 4R [Bisphenol-A-(epichlorhydrin) epoxy resin] and 4H (2,2'-iminodiethylamine)are purchased from Solaronix.

Preparation of electrolyte

The I^-/I_3^- based electrolyte is composed of I_2, DMPII and TBP with a molar ratio 0.05 M: 0.6 M: 0.05 M in acetonitrile.

Preparation of Pt electrode

The Pt based Counter electrode is fabricated according to pyrolysis method. In brief, 300 μL of H_2PtCl_6 (0.2 mM) in ethanol is drop-coated on FTO glass, followed by annealing at 450 °C for 30 minutes.

Preparation of ZrO_2 film

The ZrO_2 paste is deposited on clean FTO conductive substrate by doctor-blade method. And then annealing at 450 °C for 30 min.

Preparation of P1/ZrO_2/Pt film

The ZrO_2 paste is deposited on Pt/FTO conductive substrate by doctor-blade method. And then annealing at 450 °C for 30 min. And then, the ZrO_2/Pt film is dipped in 0.2 mM P1 in ACN solution for 16 h to form P1/ZrO_2/Pt film.

Preparation of Ni Sol−Gel and NiO film. Ni sol−gel is prepared according to previous reference [2]. In brief, 3 g of $NiCl_2$ and 3 g of F108 polymer are mixed with 9 g of deionized water and 18 g of ethanol, shaken until the solution become completely transparent. Then, the transparent solution is sonicated overnight (16 h). The obtained green gel is centrifuged at 10000 rpm/min for 30 min. Impurities at the bottom are removed and the gel on top is employed for the NiO precursor solution.

The NiO precursor is deposited on clean FTO conductive substrate by doctor-blade method. After drying in the air for 20 min and then transferred into the oven, calcined at 450 °C for 30 min and kept at 450 °C for another 30 min. Finally, cooled to the room temperature. And then repeated the above procedure once again. Finally, two layers of NiO film are obtained. The thickness of two-layer NiO film is about 1.5 μm.

Preparation of TiO_2 film and n-type DSSCs

The clean FTO conductive substrates are pretreated by immersion in a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and then washed with deionized water, dried up with flow N_2. The TiO_2 paste (Dyesol, 30 NR-T) is diluted to 50 wt% of the original paste with mixture containing 90 wt% terpineol and 10 wt% ethyl cellulose. And then the $TiCl_4$ treated FTO is screen printed with the diluted paste. The TiO_2 film are then treated by a heating process: 180 °C (10 min), 320 °C (10 min), 390 °C (10 min) and 500 °C (60 min) in an oven. The thickness of TiO_2 film is about 2 μm. For the TiO_2 film with thickness of 4 μm, the original TiO_2 paste (Dyesol, 30 NR-T) is printed with one layer. The other step is the same with above. After sintering, the samples are treated in 40 mM aqueous $TiCl_4$ by the above procedure once again. When the temperature is decreased to 120°C, the TiO_2 film is dipped into VG1-C8 dye solution (0.1 mM in ethanol) with 20 mM CDCA for 16 h [3]. And then washed with ethanol and dried with flow N_2. The TiO_2-VG1-C8 film is sealed together with a platinized FTO counter electrode by using a 25 μm thick Surlyn film (Solaronix). The electrolyte is injected through the edge of the cells and the edge is sealed with glue. The is consisted of mixed Amosil 4R and 4H (Scheme S1).

Preparation of p-type DSSCs.

The NiO films are used to fabricate the p-type DSSCs. The NiO films are dipped in 0.2 mM P1 in ACN solution for 16 h. After washed with ACN and dried by N_2, the NiO-P1 film is sealed together with a platinized FTO counter electrode by using a 25 μm thick Surlyn film (Solaronix). The electrolyte is injected through the edge of the cells (Scheme S1).

Fabrication of Tandem DSSCs

The TiO_2-VG1-C8 film and the NiO-P1 film is sealed together with a 25 μm-thick Surlyn film. By adjusting different thickness of TiO_2 film, we can get the corresponding tandem DSSC. The electrolyte is injected through the side of the cells (Scheme S1).

UV and Fluorescence spectra

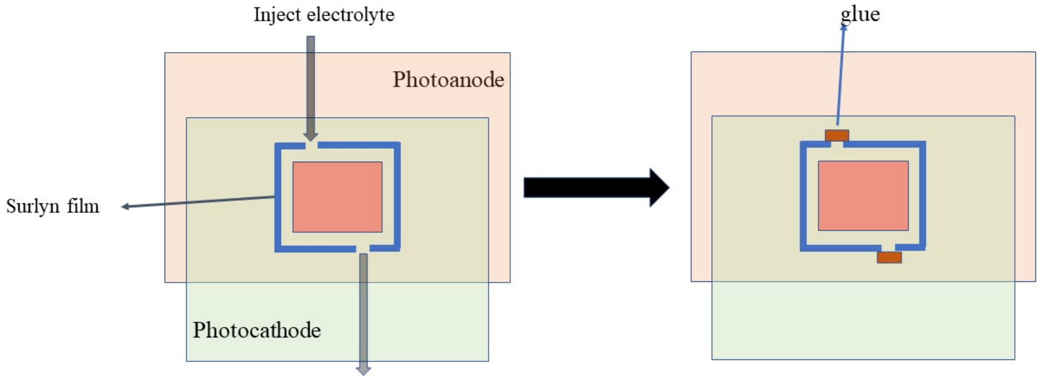
UV–vis measurements are analyzed by using a PerkinElmer Lambda 750 UV–vis spectrophotometer. Fluorescence spectra are analyzed by using a Fluorolog 3-222 emission spectrophotometer (Horiba Jobin-Yvon). The detail concentration of FRET experiment: emission spectrum: 0.2 mg of VG1-C8 (blue dye) is dissolved in 3 mL acetonitrile as the original solution for fluorescence spectra with excitation wavelength at 480 nm. And then 0.2 mM P1 based acetonitrile solution is prepared. Different volumes of P1 solution (50, 100, 150, 200, 250 μL) are added into the VG1-C8 based solution (3 mL) to observe the fluorescence intensity at 680 nm. The preparation of ZrO_2/VG1-C8/P1 film: the ZrO_2 film is dipped into VG1-C8 solution for 2 h and then transferred into P1 dye solution for 2 h.

Cyclic voltammetry and electrochemistry impendence spectra

Cyclic voltammetry (CV) was performed with a standard three-electrode electrochemical setup (Autolab). The reference electrode was $Ag/AgNO_3$ soaked in 1.0 mM $AgNO_3$ of acetonitrile (ACN) solution. Platinum (Pt) was used as the counter electrode. The electrolyte is composed of 5 mM I_2, 10 mM DMPII and 100 mM tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dry ACN. NiO film or Pt is used as working electrode. Electrochemistry impendence spectra (EIS) are performed for the dumpy cells in the dark, with use of AUTOLAB PGSTAT100 potentiostat. The frequency applied is in the range 100 kHz-0.1Hz.

Solar cells characterization

A Newport solar simulator (model 91160) equipped with a Keithley 2400 source meter, is applied for $J-V$ measurements. The solar simulator of model 91160A is used with one sun light intensity of 100 mW·cm^{-2}, AM 1.5 G, calibrated by a reference silicon solar cell. A black mask with an area of 0.16 cm^{-2} is used during the measurement. The IPCE spectra is measured with a computer-controlled set-up comprising a Xe light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a Keithley multimeter (model 2,700). The IPCE spectra is calibrated with a certified reference silicon solar cell (Fraunhofer ISE).



Scheme S1 The fabrication process of DSSC.

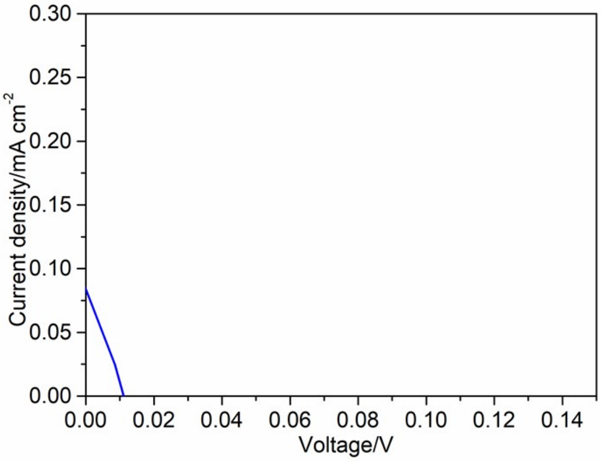


Figure S1 The *J-V* curve of NiO (Pt) based device without P1 dye.

Table S1 The photovoltaic parameters of DSSC with NiO (Pt) based device without P1 dye.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
NiO (Pt)	0.010	0.05	0.399	0.0002

In addition, NiO(Pt) based device without P1 dye is also fabricated to observe if the NiO film itself can be excited. The *J-V* curve of NiO/Pt based device is shown in Figure S1 and their photovoltaic parameters are summarized in Table S1. For NiO/Pt based device without P1 dye, a PCE of 0.0002% with a V_{oc} of 0.010 V, a J_{sc} of 0.05 mA.cm^{-2}, a FF of 0.399 is realized. The results indicate that the NiO itself can be excited and the electron can inject into the surface state of NiO [4].

Table S2 The photovoltaic parameters of DSSCs with TiO_2/VG1-C8 (P1/ZrO_2/Pt) based device.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
TiO_2/VG1-C8 (P1/ZrO2/Pt)-n-side	0.626	2.53	0.797	1.250
TiO_2/VG1-C8 (P1/ZrO2/Pt)-p-side	0.550	0.34	0.752	0.139

To prove the high IPCE of P1 in the tandem DSSC derived from FRET, a control experiment of TiO_2/VG1-C8 (P1/ZrO_2/Pt) based device is assembled. The ZrO_2 film is deposited on the surface of Pt/FTO. The *J-V* curve in Figure 8a shows that the TiO_2/VG1-C8 (P1/ZrO_2/Pt) based device can achieve a PCE of 1.250% with V_{oc} of 0. 626V, J_{sc} of 2.53 mA.cm^{-2}, a FF of 0.797 (Table S2) from n-side illumination. In such kind of devices, the P1 dye can't inject the hole into the ZrO_2 film under excitation because of the wide bandgap of ZrO_2 film. However, according to the IPCE spectrum (Figure 8b) of TiO_2/VG1-C8 (P1/ZrO_2/Pt), the characteristic peak of P1 dye can still be observed, which indicates that the energy of P1 has transferred to the VG1-C8 dye under excitation.

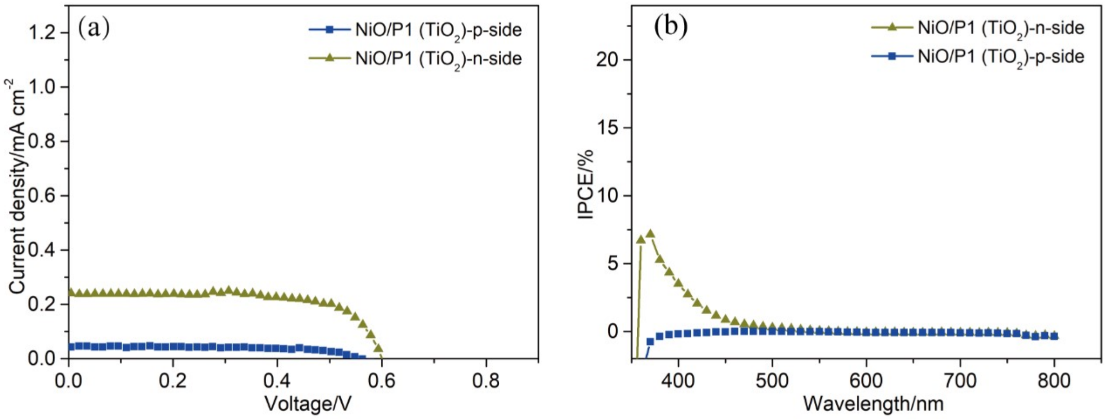


Figure S2 (a) The *J-V* curve and (b) IPCE curve of the NiO/P1(TiO_2) based device.

Table S3 The photovoltaic parameters of DSSCs with NiO/P1(TiO_2) based device.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
NiO/P1(TiO_2)-p-side	0.560	0.04	0.702	0.017
NiO/P1(TiO_2)-n-side	0.600	0.24	0.709	0.101

The P1 dye can desorb from NiO as proved in Figure S3 and should be able to re-sensitize TiO2 as well. But no obvious P1 IPCE (Figure S2b) is observed from this solar cell, that is because P1 does not work well TiO_2 (see Figure 10), particularly considering with low dye-loading.

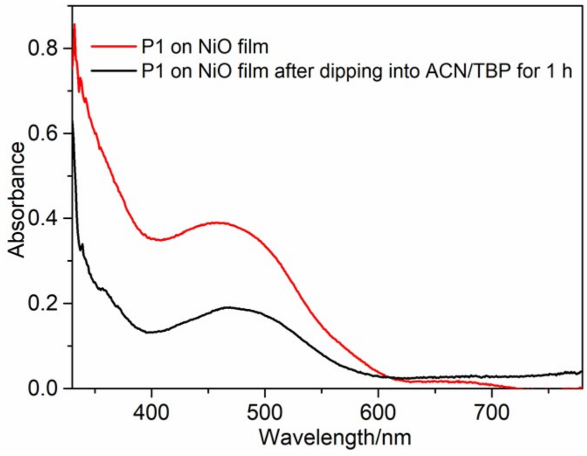


Figure S3 The UV-vis absorption spectrum of NiO/P1 film.

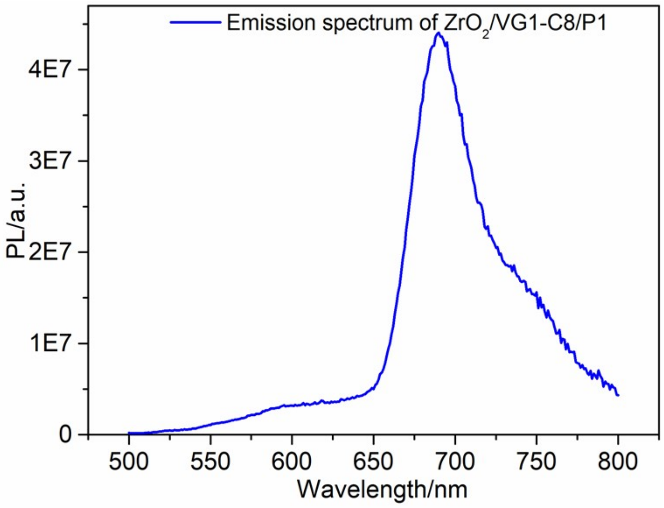


Figure S4 The fluorescence emission spectrum of ZrO_2/VG1-C8/P1 film (excitation wavelength: 480 nm).

Table S4 The photovoltaic parameters of DSSCs with TiO_2 film sensitized VG1-C8 or P1 dye.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
TiO_2/VG1-C8/P1 (Pt)	0.589	1.90	0.748	0.837
TiO_2/VG1-C8/P1 in electrolyte (Pt)	0.573	1.26	0.734	0.530

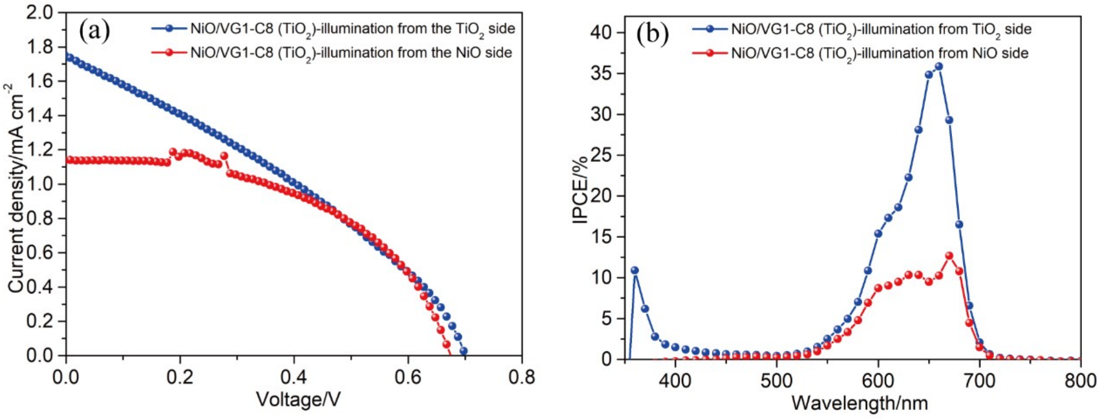


Figure S5 (a) *J-V* curve (b) IPCE curve of NiO film sensitized VG1-C8 with bare TiO_2 film as counter electrode.

Table S5 The photovoltaic parameters of DSSCs with NiO/VG1-C8 (TiO_2) based device.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
NiO/VG1-C8(TiO_2)-n-side	0.701	1.75	0.330	0.405
NiO/VG1-C8(TiO_2)-p-side	0.675	1.14	0.531	0.408

If NiO/VG1-C8 electrode is used to make solar cell with bare TiO_2 electrode, then one can see that the solar cell work well (Figure S5a). As TiO_2 is inert to catalyze I^-/I_3^-, it must be from VG1-C8 re-sensitizes TiO_2 and NiO acts a counter electrode (poor fill factor). This can be further proved from that the solar cell shows much higher photocurrent and IPCE from n-side illumination (Figure S5b). VG1-C8 has very high extinction coefficient, low dye-loading is still good to harvest enough light.

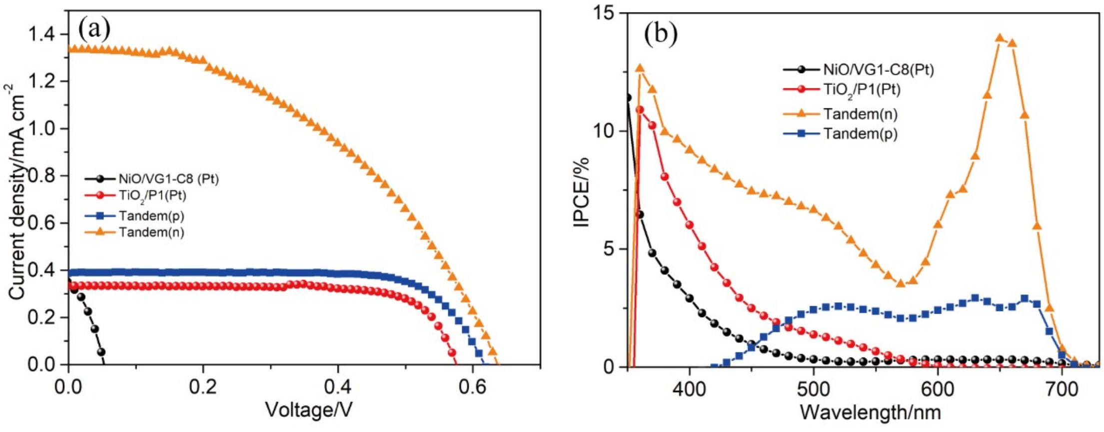


Figure S6 (a) *J-V* curve of NiO/VG1-C8 and TiO_2/P1 based device. (b) IPCE curve of NiO/VG1-C8 and TiO_2/P1 based device.

When P1 and VG1-C8 dyes are switched, P1 on TiO_2 and VG1-C8 on NiO, one can see actually both individual solar cells do not work well (Figure S6a, Table S6). From IPCE (Figure S6b), P1 on TiO_2 gives an IPCE value less than 2% at 520 nm and VG1-C8 on NiO renders an IPCE value less than 0.5% at 700 nm. But in tandem solar cells with these two electrodes, obvious IPCE (Figure S6b) response from both dyes are observed, particularly when it is illuminated from n-side. This is therefore attributed to the desorption of VG1-C8 from NiO and re-sensitization of TiO_2 (Figure S5) and consequent FRET between two dyes.

Table S6 The photovoltaic parameters of DSSCs with TiO_2 film sensitized P1 dye and NiO sensitized VG1-C8.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
TiO_2/P1 (Pt)	0.576	0.33	0.742	0.141
NiO/VG1-C8 (Pt)	0.036	0.36	0.355	0.005
Tandem (p)	0.637	1.33	0.441	0.374
Tandem (n)	0.617	0.39	0.734	0.177

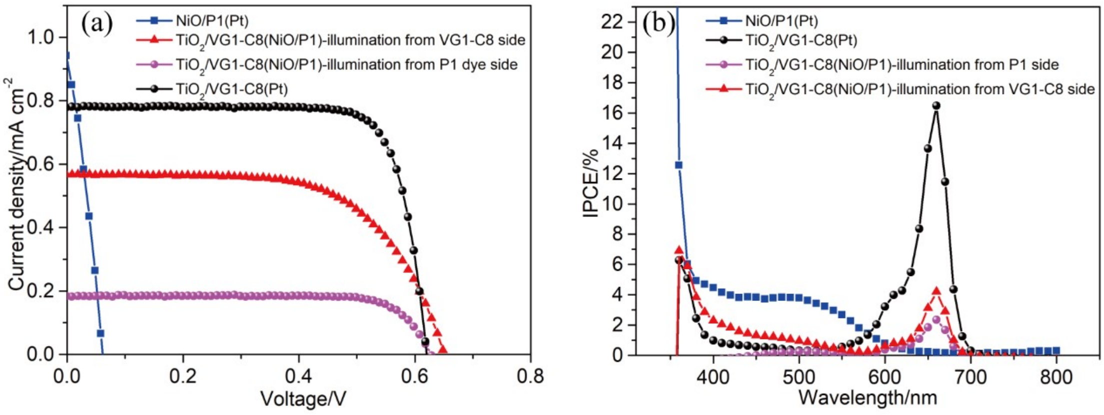


Figure S7 (a) *J-V* curve of the solar cells with blocking layers for TiO_2 and NiO and (b) *IPCE* curve of the solar cells with blocking layers for TiO_2 and NiO.

Table S7 The photovoltaic parameters of DSSCs with NiO and TiO_2 blocking layers.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	*PCE* (%)
TiO_2/VG1-C8 (Pt)	0.620	0.78	0.742	0.359
NiO/P1 (Pt)	0.061	0.89	0.308	0.017
Tandem (n)	0.651	0.57	0.627	0.233
Tandem (p)	0.628	0.18	0.782	0.088

As we proved NiO surface states can be catalyst for electrolyte reduction, then preventing electrons from reaching NiO surface states should significantly decrease the IPCE response from both dyes. Therefore, a compact NiO layer (ca. 80 nm) underneath mesoporous NiO is added. One can see that the photocurrent (Figure S7a) values of solar cells are slightly decreased, but the IPCE (Figure S7b) response from both dyes in tandem solar cell are indeed decreased significantly, as compared to Figure 5 in main text.

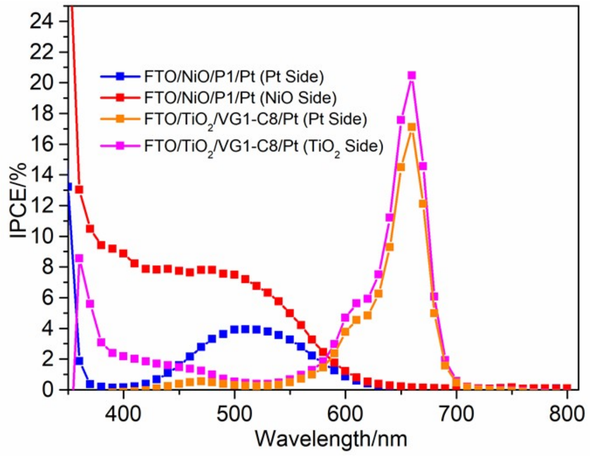


Figure S8 The IPCE curve of n-type or p-type cells illuminated from the Pt side.

Reference:

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