

## Supporting Information

### Nitrogen-Doped Graphene/Pt Counter Electrodes for Dye-Sensitized Solar Cells

n-An Lin,<sup>a,b</sup> Chuan-Pei Lee,<sup>b</sup> Shu-Te Ho,<sup>a</sup> Tzu-Chiao Wei,<sup>b</sup> Yu-Wen Chi,<sup>c</sup> K. P. Huang,<sup>c</sup> and Jr-Hau He<sup>a,\*</sup>

Computer, Electrical and Mathematical Sciences and Engineering (CEMSE) Division, King Abdullah University of Science &

nology (KAUST), Thuwal 23955-6900, Saudi Arabia

stitute of Photonics and Optoelectronics, & Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, R

chanical and Systems Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, ROC

## Measurements and instruments:

The electronic structures of NGRs were confirmed by PHI Quantera XPS. Morphological study of NGR has been performed with a JEOL JSM-6500 field emission scanning electron microscopy and a JEOL JEM-3000F high-resolution transmission electron microscopy. The excitation source of Raman spectroscopy is a 532 nm laser beam (2.33 eV) with a power below 1 mW to avoid laser-induced heating. Optical reflectance spectroscopy was measured for wavelength region between 400 and 1100 nm under ambient conditions with a UV-vis-NIR spectrometer (JASCO ARN-733). IPCE measurement has also been carried out with a spectral response system (Hamamatsu Photonics Co., Ltd. R3011) for wavelength range from 400 to 850 nm. The Surface of the DSSC was covered by a mask with a circular illuminated area of 0.16 cm<sup>2</sup> and then illuminated under 1 sun intensity (AM1.5G). Incident light intensity (100 mW cm<sup>-2</sup>) was calibrated with a standard Si Cell (Hong-Ming tech. Co., Ltd.). Photocurrent-voltage curves of the DSSCs were obtained with a digital multimeter (2400, Keithley).

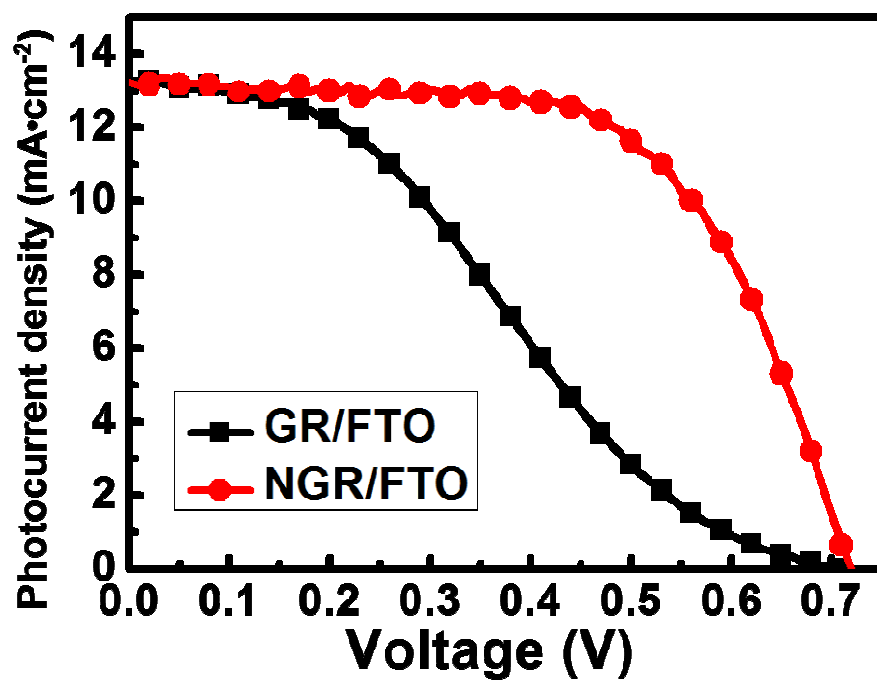


Figure S1 The  $J$ - $V$  curves of DSSCs with CEs using GR and NGR.

**Table S1** Photovoltaic parameters of DSSCs with CEs using GR and NGR alone, measured under  $100 \text{ mW}\cdot\text{cm}^{-2}$  of AM 1.5G illumination.

CEs	$V_{\text{OC}}$ (mV)	$J_{\text{SC}}$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	$FF$	$\eta$ (%)
GR/FTO	710	13.24	0.31	2.94
NGR/FTO	718	13.26	0.61	5.84

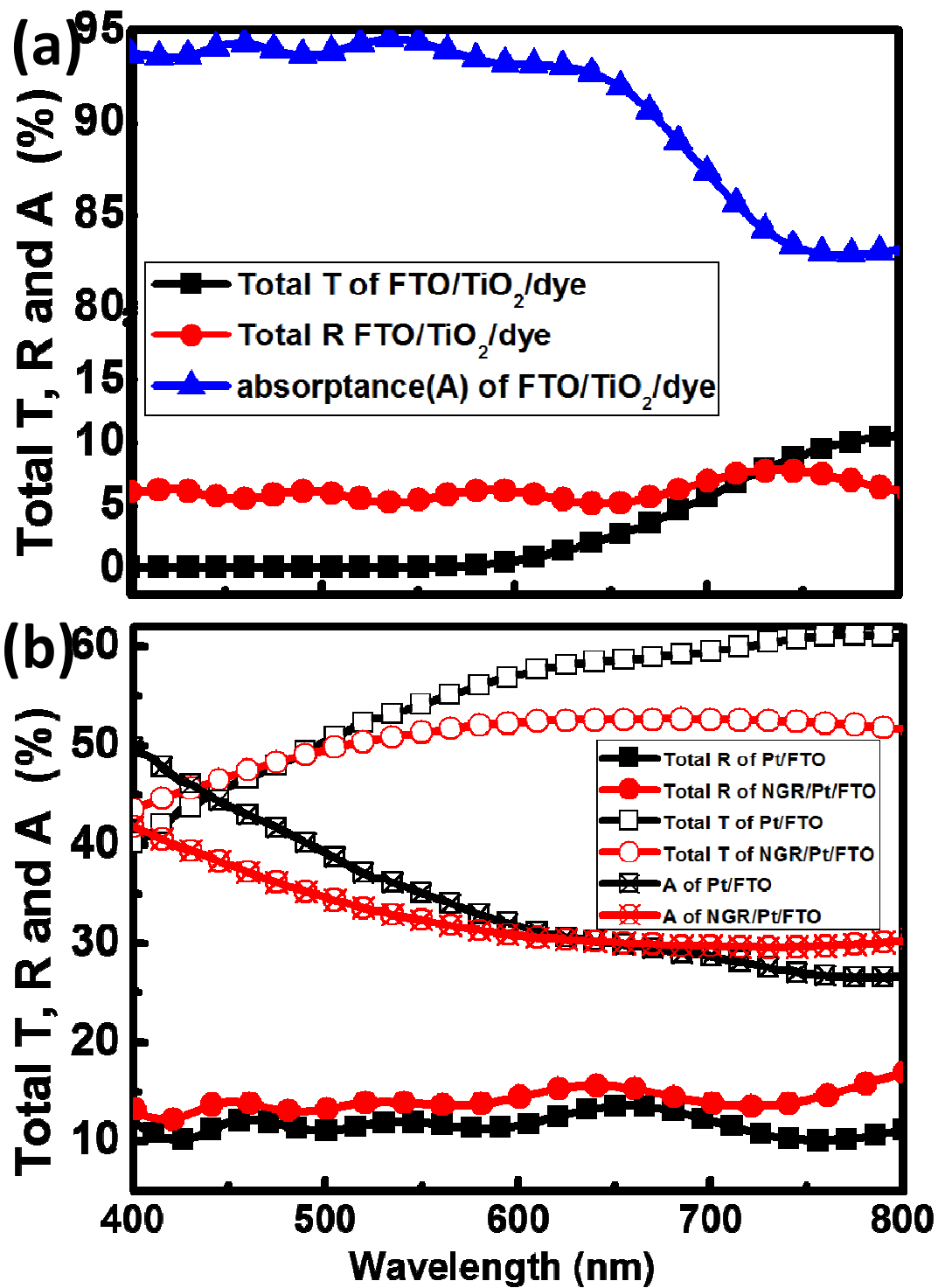


Figure S2 (a) Total reflectance (R), total transmittance (T) and absorptance (A) spectra of FTO/TiO<sub>2</sub>/dye electrodes. (b) Total R, to  
A spectra of Pt/FTO and NGR/Pt/FTO CEs.

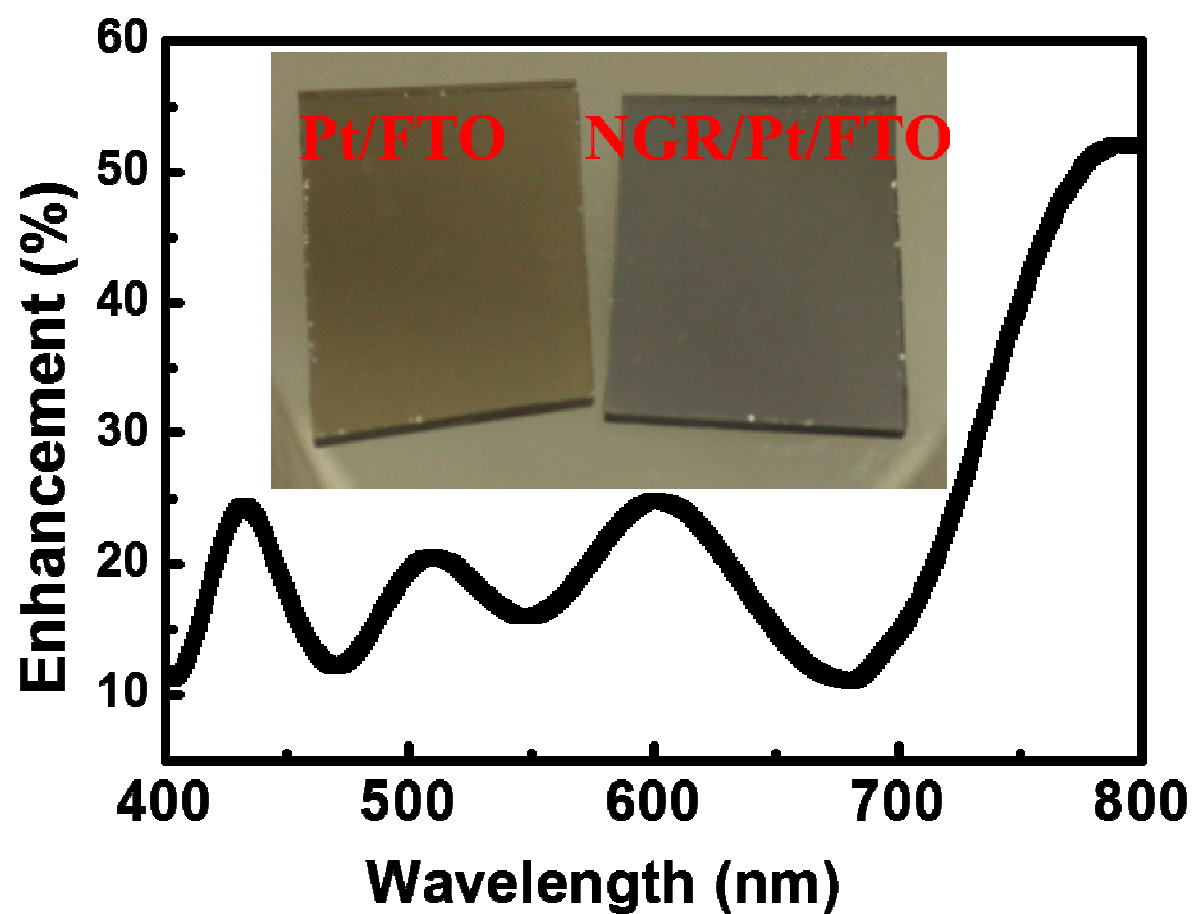


Figure S3. The enhancement of total R spectrum. The inset is the photoimage of Pt/FTO and NGR/Pt/FTO CEs.

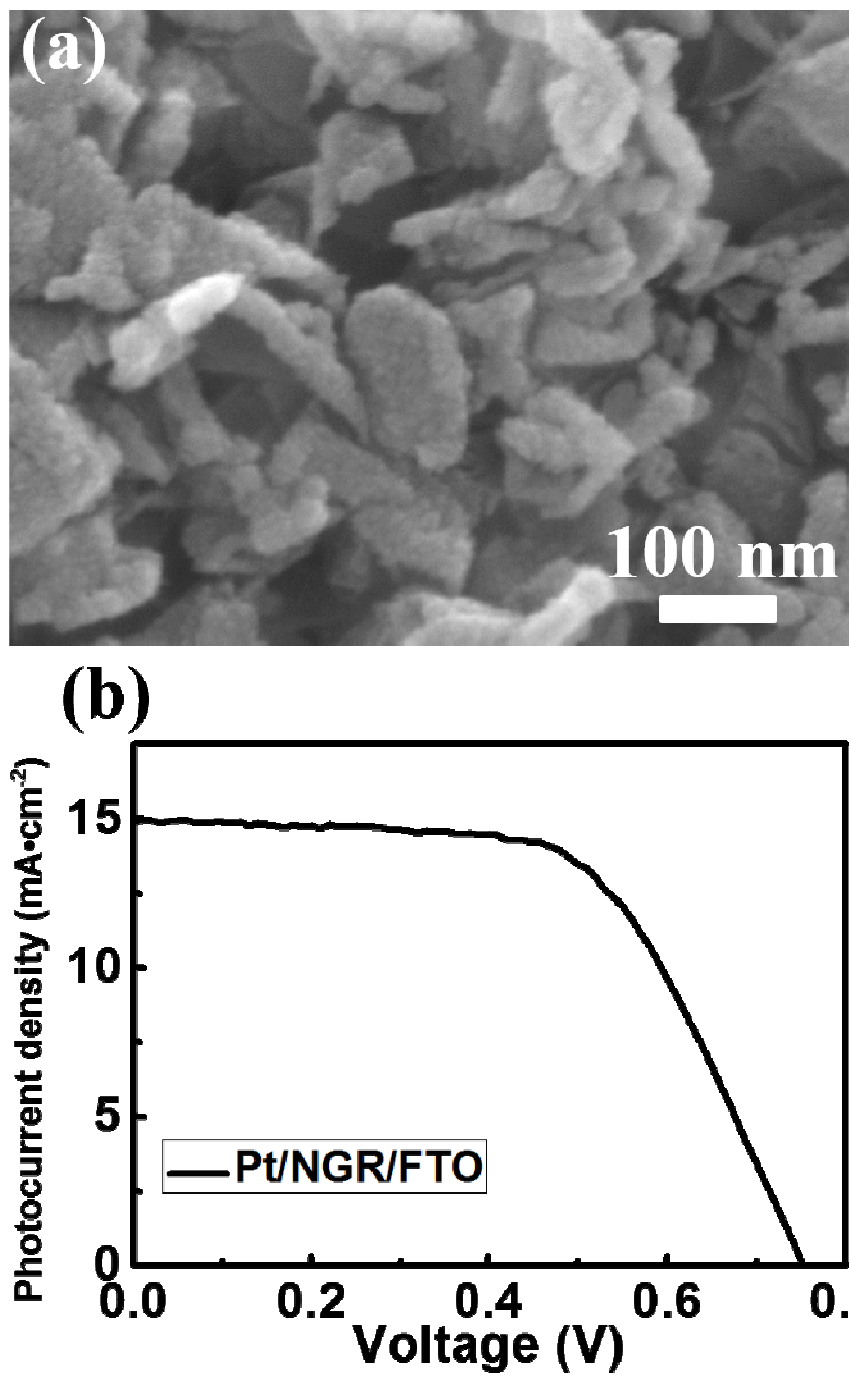


Figure S4. (a) The SEM image of Pt/NGR/FTO and (b) the  $J$ - $V$  curve of the DSSC with Pt/NGR/FTO CEs.

In the case of the DSSC with CE using a reverse bi-layer structure, Pt/NGR/FTO, shows a  $\eta$  of 6.81%, and its  $J_{SC}$ ,  $V_{OC}$ , and  $FF$  are 14.92 mA·cm<sup>-2</sup>, 745 mV, and 0.61, respectively

According to reported literatures, the conduction band minimum (CBM, -4.4 eV)<sup>S1</sup> and Fermi level ( $E_F$ , -5.1 eV)<sup>S2</sup> of TiO<sub>2</sub> film, the ground/excited state oxidation potentials (GSOP/ESOP, -0.6/1.12 V *vs.* NHE) of N719 dye<sup>S3</sup>, the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> (0.5 V *vs.* NHE)<sup>S1</sup>, and the  $E_F$  of FTO (-4.9 eV)<sup>S2</sup> and Pt (-4.95 eV)<sup>S4</sup> in the dark without  $E_F$  alignment have been schematically shown in Figure S5. In Figure S5, the VBM of TiO<sub>2</sub> is not shown because it is much deeper than GSOP of dye and thus it does not participate in photochemical reaction. Obviously, the  $E_F$  of Pt (0.45 V *vs.* NHE) is slightly higher than the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> (0.5 V *vs.* NHE)<sup>S1</sup> under dark condition before  $E_F$  alignment.

While the DSSC is illuminated by solar light, the band diagram would be changed as shown in Figure S6. Under illumination, the conduction band of TiO<sub>2</sub> film (-4.0 eV)<sup>S6</sup>, the GSOP/ESOP (-0.6/1.12 V, *vs.* NHE)<sup>S3</sup> of N719 dye, the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> (0.5 V *vs.* NHE)<sup>S1</sup> have been schematically shown in Figure S6. Note that, under illumination, the  $E_F$  alignment of FTO, TiO<sub>2</sub> and Pt is achieved due to photo-carrier injection, and thus the  $E_F$  is called quasi-Fermi level (quasi- $E_F$ ).<sup>S7-S9</sup> Zhang *et al.* have been reported the quasi- $E_F$  of TiO<sub>2</sub> by measuring the potential difference between the Ti electrode on the top of TiO<sub>2</sub> and the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> under illumination.<sup>S8,S9</sup> The minimum of quasi- $E_F$  is higher than the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> at short-circuit (without applying voltage) by 0.1 V. The quasi- $E_F$  will be raised by applying voltage to measure the  $J$ - $V$  curves of DSSCs.<sup>S8,S9</sup> While the measured photocurrent is zero (under open-circuit condition), the potential difference of quasi- $E_F$  and redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> is open-circuit voltage.<sup>S8,S9</sup> Thus, under illumination, the  $E_F$  of Pt is much higher than the redox potential of I<sub>3</sub><sup>-</sup>/I<sup>-</sup>.



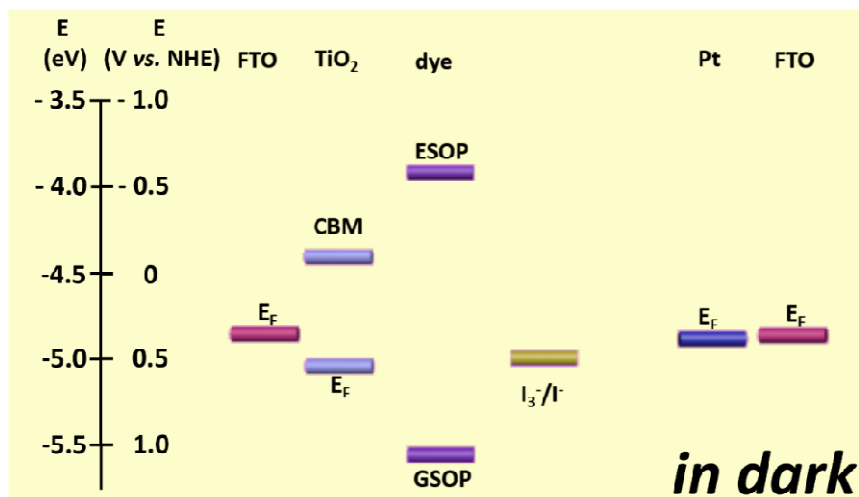


Figure S5. Schematics of the energy diagram of a DSSC with Pt/FTO CE in the dark before  $E_F$  alignment.

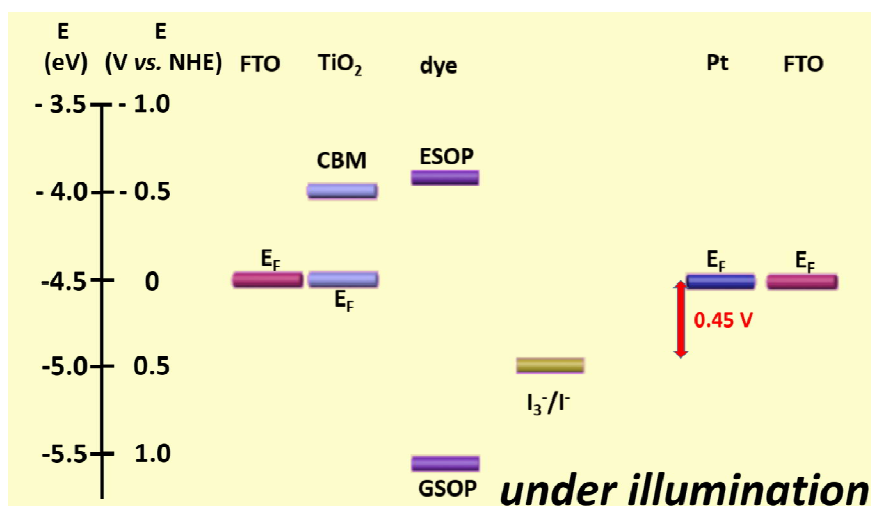


Figure S6. Schematics of the energy diagram of a DSSC with Pt/FTO CEs under light illumination.

Song *et al.* have reported that the work function of graphene can be determined by the work function of the contact materials.<sup>S10</sup> In addition, Rani *et al.* have been reported that the bandgap of NGR is *ca.* 0.38 eV.<sup>S11</sup> Thus, we can estimate that the V<sub>GR</sub> of NGR should be located between the redox potential of  $I_3^-/I^-$  and the  $E_F$  of Pt/FTO CEs. The energy diagram of a DSSC with NGR/Pt/FTO CE under light illumination is shown in Figure S7. Therefore, in our work, the mechanism of cascade-hole transfer between electrolyte and NGR/Pt/FTO CEs is confirmed.

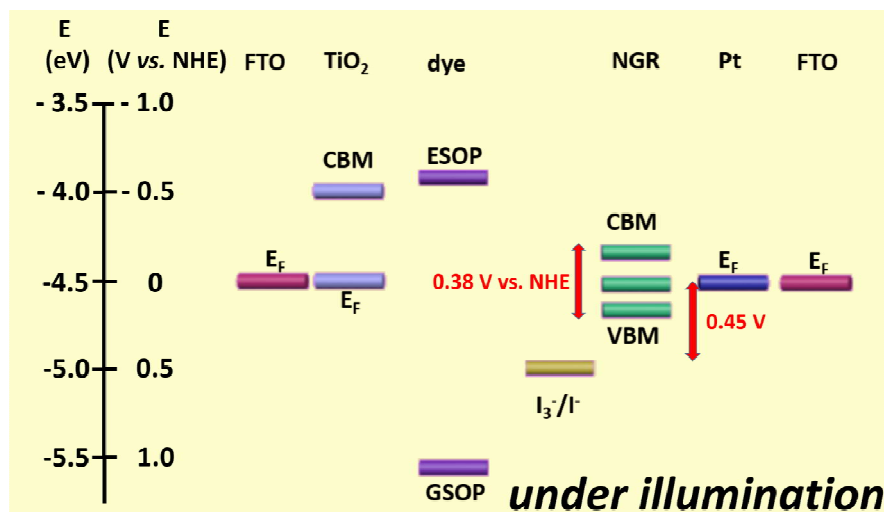


Figure S7. Schematics of the energy diagram of a DSSC with NGR/Pt/FTO CE under light illumination.

## erence

- Dai, F. R.; Wu, W. J.; Wang, Q. W.; Tian, H.; Wong, W. Y. Heteroleptic ruthenium complexes containing uncommon 2,2'-bipyridine chromophores for dye-sensitized solar cells. *DaltonTrans.* **2011**, 40, 2314–2323.
- Wei, X.; Xie, T.; Xu, D.; Zhao, Q.; Pang, S.; Wang, D. A study of the dynamic properties of photo-induced charge carriers in porous TiO<sub>2</sub>/conductive substrate interfaces by the transient photovoltage technique. *Nanotechnology* **19**, 2008, 275707-6.
- Daeneke, T.; Kwon, T. H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. High-efficiency dye-sensitized solar cells with ionic liquid-based electrolytes. *Nat. Chem.* **2011**, 3, 211-215.
- Sim, k.; Sung, S. J.; Jo, H. J.; Jeon, D. H.; Kim, D. H.; Kang, J. K. Electrochemical investigation of high-performance dye-sensitized solar cells based on molybdenum for preparation of counter electrode. *Int. J. Electrochem. Sci.* **2013**, 8, 8272-8281.
- Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. *Chem. Rev.*, 2010, 110, 6595-6663.
- De Angelis, F.; Fantacci, S.; Selloni, A. Alignment of the dye's molecular levels with the TiO<sub>2</sub> band edges in dye-sensitized solar cells: a DFT–TDDFT study. *Nanotechnology* **2008**, 19, 424002-7.
- Grätzel, M. Photoelectrochemical cells. *Nature* **2001**, 414, 338-344.
- Zhang, S.; Yanagida, M.; Yang, X.; Han, L. Effect of 4-tert-butylpyridine on the quasi-fermi level of dye-sensitized TiO<sub>2</sub> film. *J. Phys. Express* **2011**, 4, 042301-3.
- Zhang, S.; Yang, X.; Zhang, K.; Chen, H.; Yanagida, M.; Han, L. Effects of 4-tert-butylpyridine on the quasi-Fermi levels of TiO<sub>2</sub> in the presence of different cations in dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* **2011**, 13, 19310-19313.
- 0) Song, S. M.; Park, J. K.; Sul, O. J.; Jin, Cho, B. J. Determination of work function of graphene under a metal electrode and its effect on contact resistance. *Nano lett.* **2012**, 12, 3887-3892.

) Rani, P.; Jindal, V. K. Designing band gap of graphene by B and N dopant atoms. *Rsc Adv.* **2013**, 3, 802-812.