Electronic Supplementary Information

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Chemicals and materials

Phenol, formaldehyde solution (36.5~38 % in H_2O), niobium(V) ethoxide ($Nb(OEt)_5$), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, bead) and concentrated HCl (35~37 %) were purchased from Samchun (Korea). Polystyrene-*b*-poly(ethyleneoixde) (PS-*b*-PEO) was synthesized by atomic transfer radical polymerization (ATRP).[1] All of the chemicals were used without further purification.

Synthesis of phenolic resin (resol)

5g of Phenol (53 mmol) was melted at 40 °C in a flask and mixed slowly with 1.1g of 20 wt% NaOH aqueous solution (5.3 mmol) under stirring. After 10 min, 8.6g of formaldehyde solution (106 mmol) was added to phenol solution. The molar ratio of phenol:formaldehyde:NaOH was 1:2:0.1. The solution reacted at 70 °C for 1 h with stirring, and the solution was cooled room temperature. The mixture was neutralized using 2 M HCl. Water was removed under vacuum condition below 50 °C, and THF was poured into resol to precipitate NaCl produced during neutralization. After NaCl removal by filtration, THF was removed by vacuum evaporation below 50 °C.

Preparation of functional macrodomain-embedded mesoporous Nb_2O_5 (FM-Nb_2O_5)

In a typical synthesis of FM-Nb_2O_5, 0.2 g of PS-*b*-PEO (34.6 kg/mol, 14.4 wt% of PEO, PDI of 1.39) was dissolved in 6 mL of THF, and 0.73 g of 20 wt% resol solution in THF was added into the polymeric solution. 0.55 g of $Nb(OEt)_5$ was added into the mixture under stirring. After 10 min, 0.44 g of concentrated HCl (35~37 wt%) was added dropwise to suppress formation of large size oligomers. After stirring for 1 h, the obtained clear solution was poured into a petri dish to evaporate THF and HCl slowly at 40 °C for 24 h, followed by sequential heating at 100 °C for 24 h in an oven. The as-made product was carbonized at 700 °C under Ar for 2 h with a heating rate of 1 °C min^{-1}, and subsequently heated at 450 °C under air for 5 h to remove carbon.

Preparation of mesoporous Nb_2O_5 (m-Nb_2O_5)

It was prepared using the same procedures for preparation of FM-Nb_2O_5 without resol. 0.2 g of PS-*b*-PEO was dissolved in 6 ml of THF. 0.88 g of $Nb(OEt)_5$ and 0.44 g of HCl were added in sequence. Since the mesostructure was affected by volume fraction of hydrophilic block,

$Nb(OEt)_5$ was added more instead of resol to prepare 2D-hexagonal structure. The remaining procedures are identical with those for FM-Nb_2O_5

Fabrication of Dye sensitized solar cell

For working electrodes of DSSCs, screen-printable paste was prepared by mixing 0.2 g FM-Nb_2O_5 power (or m-Nb_2O_5) with 0.175 g of binder solution (5 wt% ethyl cellulose dissolved in α-terpineol). The highly viscous paste was diluted by adding 0.13 g of α-terpineol and then thoroughly mixed. The obtained paste was deposited onto FTO glass using a doctor blade technique, followed by annealing at 500 °C for 30 min under air. The working electrodes were immersed in an ethanol solution containing 0.5 mM cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis-tetrabutylammonium (N719, Everlight) for 24 h. A platinum (Pt) counter electrode was prepared by dropping the 7 mM $H_2PtCl_6 \cdot 6H_2O$ in isopropanol and then annealing at 400 °C for 20 min. The working electrode was assembled with counter electrode using 60 µm thick Surlyn (DuPont 1702). The electrolyte was filled into the cell through hole drilled in the counter electrode. The electrolyte composed of 0.7 M 1-propyl-3-methylimidazolium iodide, 0.03 M I_2, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tertbutylpyridine in a mixed solution of acetonitrile and valeronitrile (85:15 v/v).

Materials Characterization

Transmission electron microscopy (TEM) measurements were conducted on a JEOL JEM-1011 microscope operated at 200 kV. The samples for TEM measurements were microtomed and supported on Cu grids. Scanning electron microscopy (SEM) was performed on a Hitach S-4200 field emission SEM. Electron energy loss spectroscopy analysis was conducted on a JEOL JEM-2200FS transmission electron microscope. The small-angle X-ray scattering (SAXS) measurements were taken on a 4C SAXS beamline at the Pohang Light Source II. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-ray diffractometer (Cu Kα). Nitrogen physisorption isotherms were obtained at 77 K using a Micromeritics Tristar 3020 analyzer. Specific surface areas (S_{BET}) and pore diameter (D_P) were calculated by using BET and BJH models, respectively. The photocurrent–voltage (*J–V*) measurements were performed using a Keithly model 2400 source measurement unit. A class-A solar simulator (Yamashita Denso YSS-50A) was used and the light intensity was adjusted with an NREL-calibrated Si solar cell with KG-3 filter for AM 1.5G 1 sun light intensity. The

J-V measurement was performed with an aperture mask to prevent extra light coming through the lateral space. The incident photon-to-current conversion efficiency (IPCE) was measured using a K3100 EQX spectral IPCE measurement system (PV Measurements, Inc.). The active area of cell was measured by an image analysis program equipped with a digital microscope camera (Moticam 1000) and the thickness of electrode film was measured by an Alphastep IQ surface profiler (KLA Tencor).

Reference

1 J. Hwang, J. Kim, E. Ramasamy, W. Choi, J. Lee, *Microporous Mesoporous Mater.* **2011**, *143*, 149

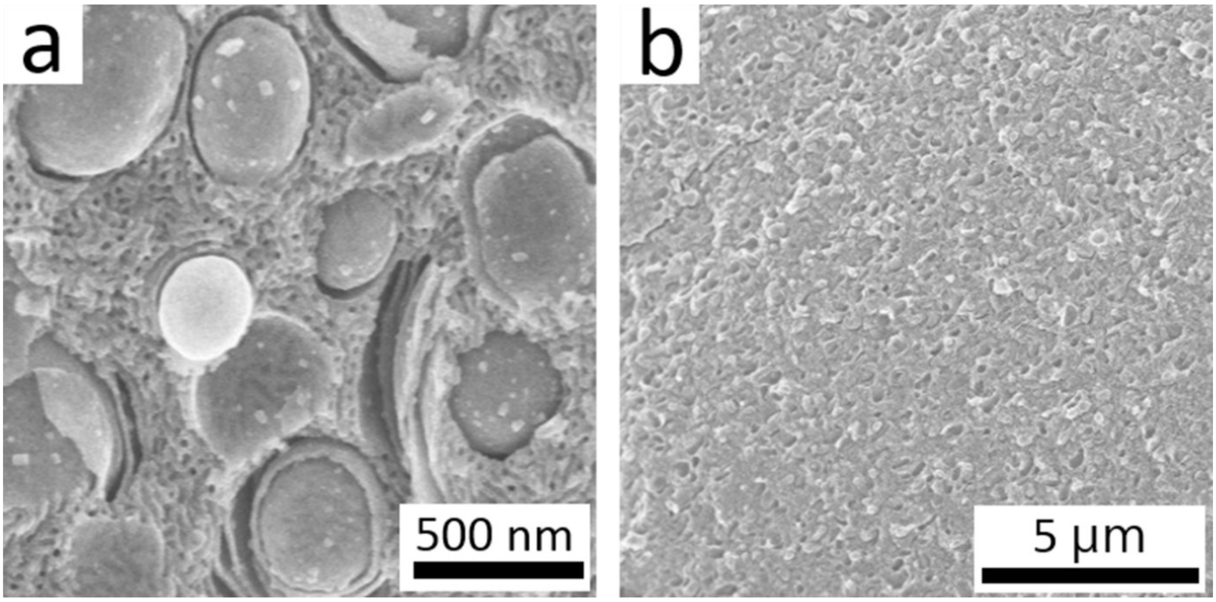


Fig S1. SEM images of FM-Nb_2O_5/C at difference length scales

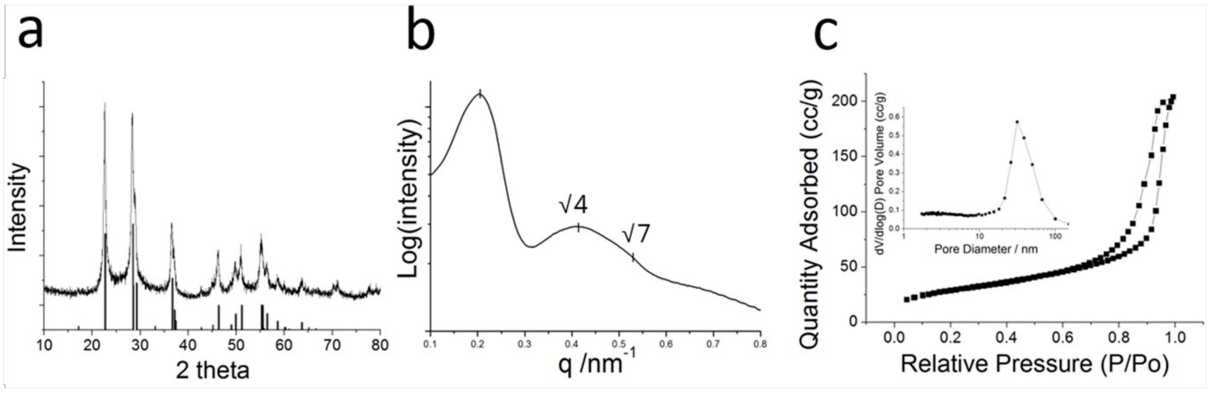


Fig S2. (a) XRD pattern corresponding to orthorhombic Nb_2O_5, (b) SAXS pattern of FM-Nb_2O_5 and (c) N_2 physisorption isotherm with (inset) the pore size distribution of FM-Nb_2O_5

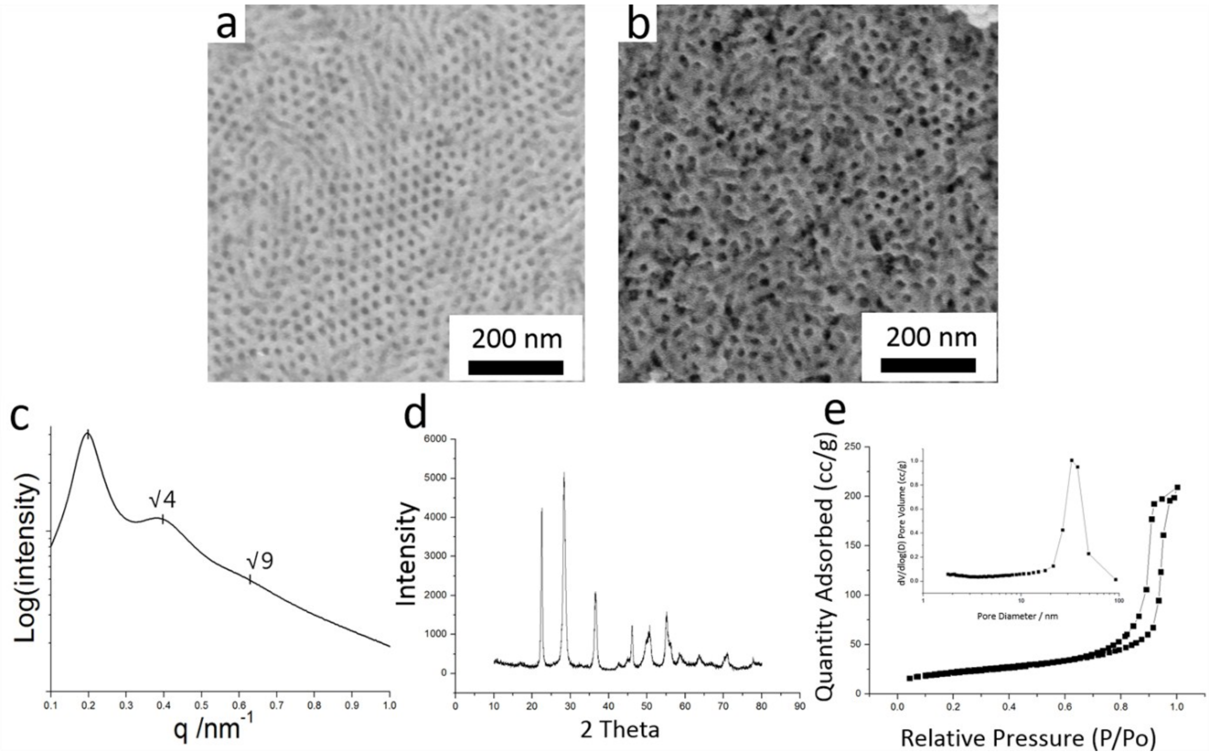


Fig S3. Structural characteristics of the mesoporous Nb_2O_5 (m-Nb_2O_5) synthesized without resol; SEM image after heat treatment (a) at 700 °C under Ar and (b) at 450 °C in the air, (c) SAXS pattern, (d) XRD pattern corresponding orthorhombic phase, and (e) N_2 physisorption isotherm, inset: pore size distribution.

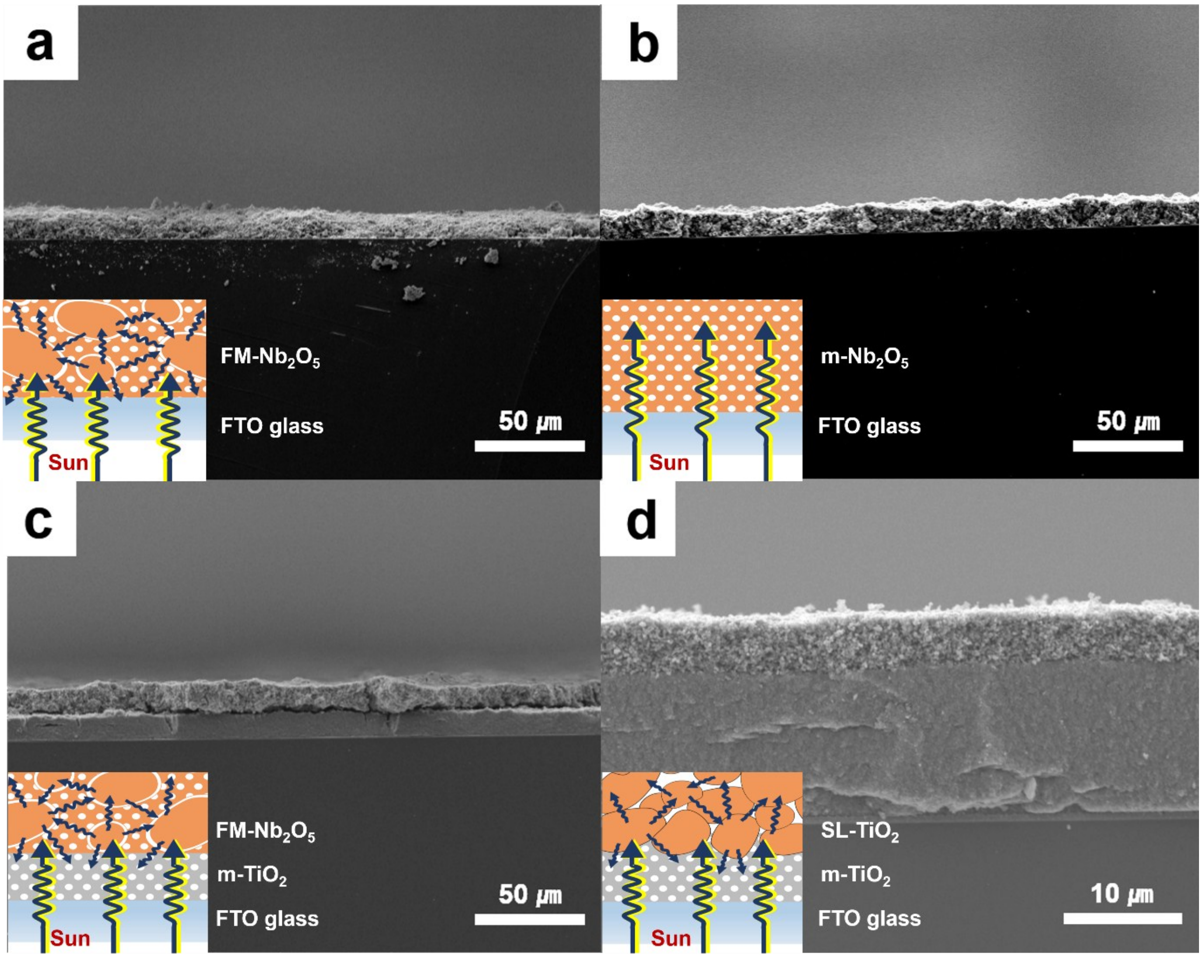


Fig S4. Cross-sectional SEM images of (a) FM-Nb_2O_5, (b) m-Nb_2O_5, (c) m-TiO_2+FM-Nb_2O_5 and (d) m-TiO_2+SL-TiO_2 bilayer films. Insets are schematic representations of the four electrodes with different light pathway caused by light scattering effect.

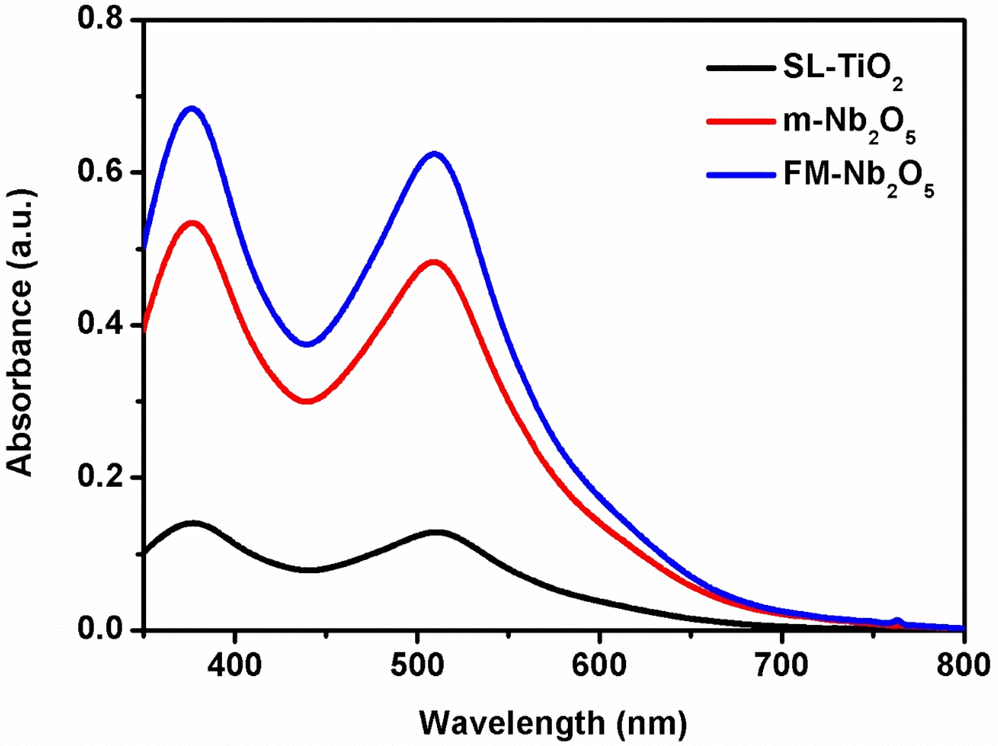


Fig S5. Absorbance spectra of the solution containing the dye molecules detached from the films made of SL-TiO_2, m-Nb_2O_5 and FM-Nb_2O_5.

Table S1. Photovoltaic characteristics and dye loading of SL-TiO_2, m-Nb_2O_5, and FM-Nb_2O_5 based DSSCs.

Sample	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF**	**η (%)**	**Dye loading (× 10^{-8} mol cm^{-2} μm^{-1})**
SL-TiO_2	0.80	0.58	0.62	0.28	0.76
m-Nb_2O_5	0.74	2.67	0.82	1.63	3.46
FM-Nb_2O_5	0.73	4.57	0.82	2.75	4.48

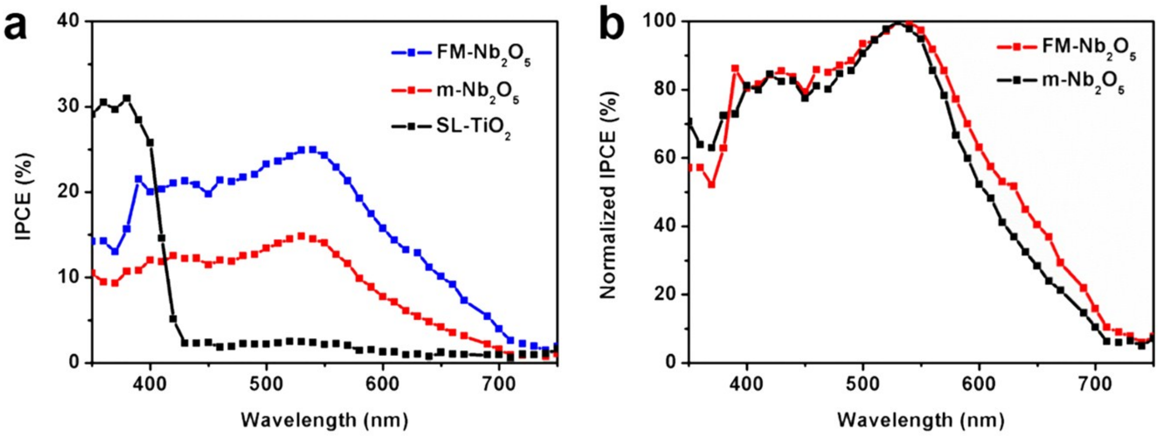


Fig S6. (a) IPCE spectra of DSSCs made from FM-Nb_2O_5, m-Nb_2O_5 and SL-TiO_2, (b) Normalized IPCE of (a) corresponding to FM-Nb_2O_5 and m-Nb_2O_5 based devices.

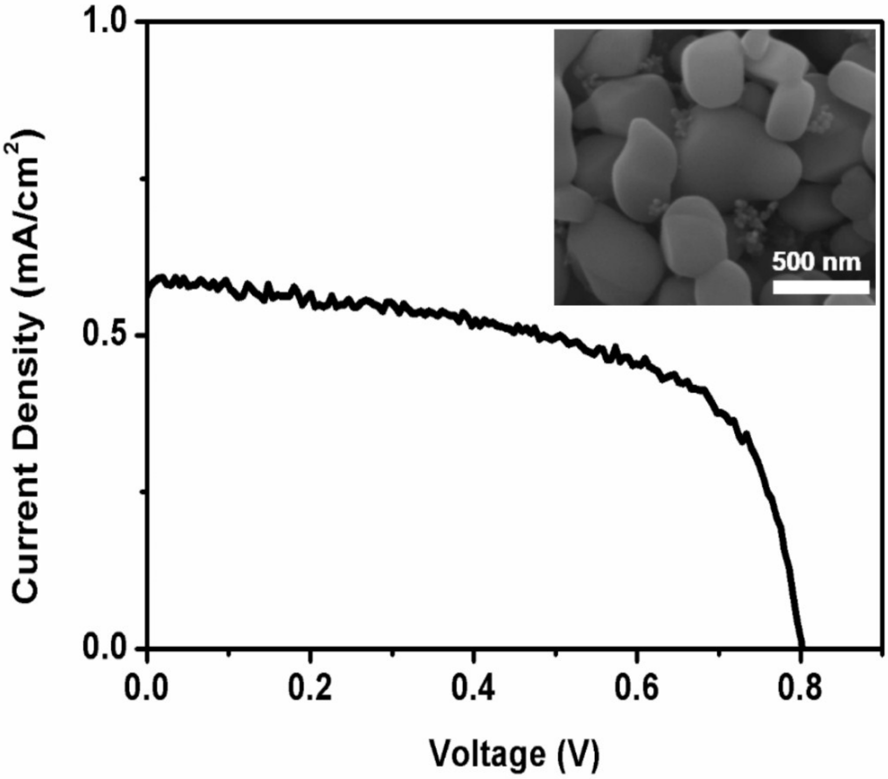


Fig S7. *J-V* curve of DSSC made with SL-TiO_2 WE with thickness of 12 μm. Inset shows submicron large TiO_2 particles consisting the SL-TiO_2 film.

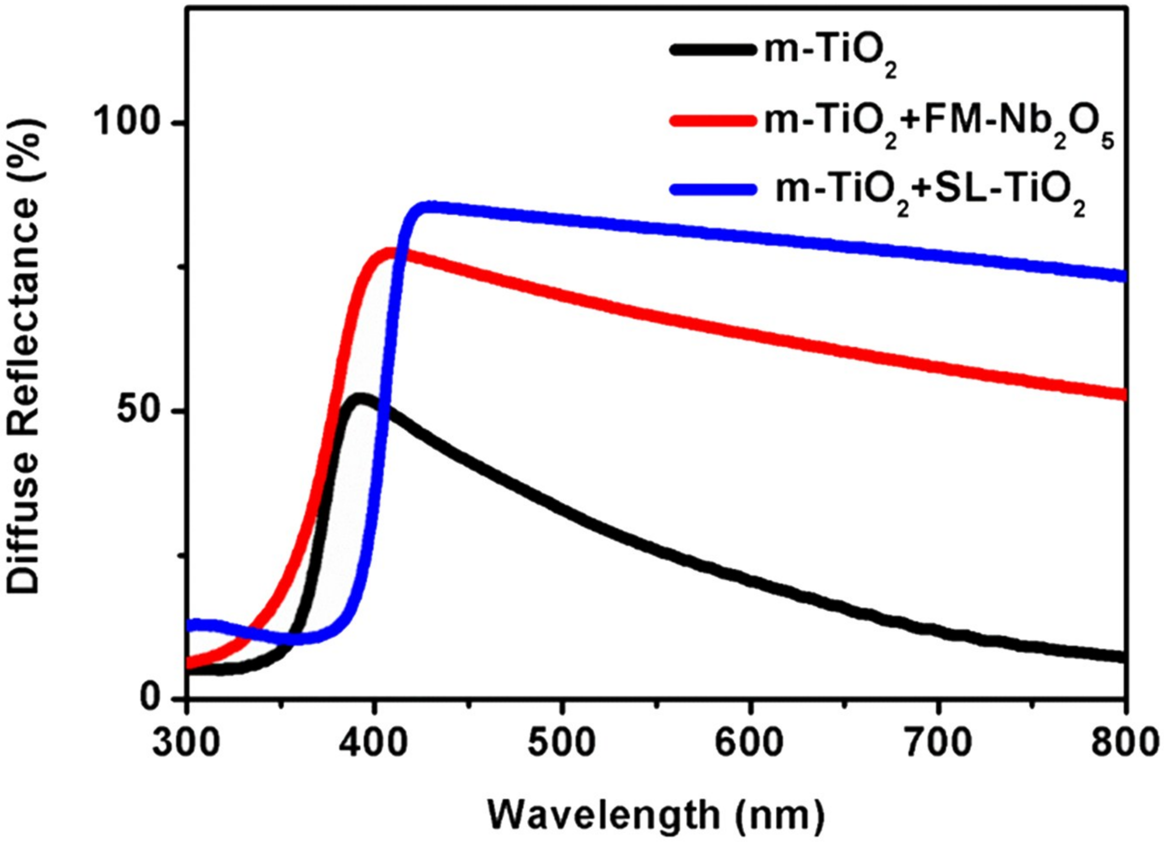
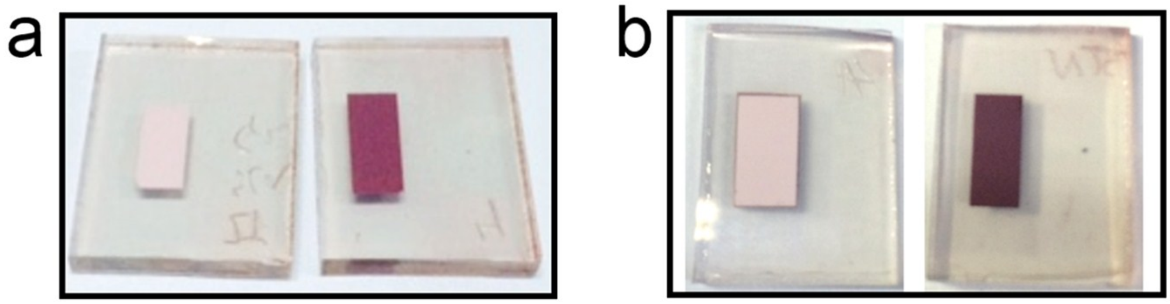


Fig S8. Diffuse reflectance spectra of the three films made of m-TiO_2 only, m-TiO_2+FM-Nb_2O_5, and m-TiO_2+SL-TiO_2 bilayer films before dye adsorption.



$SL\text{-}TiO_2$ $FM\text{-}Nb_2O_5$

$m\text{-}TiO_2$ $+SL\text{-}TiO_2$ $m\text{-}TiO_2$ $+FM\text{-}Nb_2O_5$

Fig S9. Optical images of (a) $SL\text{-}TiO_2$ and $FM\text{-}Nb_2O_5$ single films with same thickness of 12 μm, (b) $m\text{-}TiO_2$+$SL\text{-}TiO_2$ and $m\text{-}TiO_2$+$FM\text{-}Nb_2O_5$ bilayer films after N719 dye adsorption. $FM\text{-}Nb_2O_5$ film showed deep purple color meaning the high loading of N719 dye due to its high surface area, while $SL\text{-}TiO_2$ film has very pale purple color nearly close to its pristine white film. The images of bilayers as shown in figure S9b highlight that upper $FM\text{-}Nb_2O_5$ layer plays roles in light absorption as well as light scattering, leading to improved light harvesting capability.

Table S2. Photovoltaic performances of DSSCs made of m-TiO_2 film only and m-TiO_2 with FM-Nb_2O_5 or SL-TiO_2 bilayer films.

Sample	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF**	**η (%)**
m-TiO_2	0.75	12.96	0.71	6.95
m-TiO_2+SL-TiO_2	0.75	14.24	0.71	7.56
m-TiO_2+FM-Nb_2O_5	0.75	14.91	0.72	7.99