[S-1] Synthesis of Nb-doped TiO\textsubscript{2} nanoparticles

In a typical reaction, 3ml of Titanium isopropoxide (Ti(i-PrO)\textsubscript{4}, TCI) was added dropwise in 54mL of DI water. After the mixture was stirred for 1h, the precipitate was washed with DI water three times, and the white sediment was mixed with 15mL DI water, 30mg of Nb Oxalate (NbOXL, Alfa Aesar) or NbCl\textsubscript{2} (Alfa Aesar), and 1mL tetramethylammonium hydroxide (TMNOH, 25% in water, TCI). The turbid dispersion was stirred for 24 hours at 85 °C. 20mL of translucent TiO\textsubscript{2} dispersion in water was added in 40mL Teflon liner, which was tightly sealed in a stainless steel bomb reactor (4744, Parr instrument). Mild hydrothermal reaction was carried out at 180 °C in a temperature stabilized oven for 1h, and the final dispersion was centrifuged at 10000rpm. The sediments were redispersed in DI water. The washing process for TiO\textsubscript{2} nanoparticle was repeated three times.

Opaqueness changes of aqueous TiO\textsubscript{2} and Nb-doped TiO\textsubscript{2} disersions as the subsequent reactions proceed.
[S-2] Fabrication procedure of Nb-TiO\(_2\) IO Photo-electrode

Equal volumes of respective PS and Nb-TiO\(_2\) aqueous dispersions were mixed, and about 300\(\mu\)L aliquot of the mixed dispersion was introduced to a top cell of the coating apparatus where 100\(\mu\)m-space between the top cell and the bottom FTO substrate was formed by scotch\textsuperscript{®} tape spacers between two substrates. The top cell was then pulled by syringe pump (KD scientific) with a line velocity of 1mm/min, and colloidal self-assembly took place at the drying meniscus while hot air was blown from the top to accelerate water evaporation. Then the substrate with the hybrid film was subjected to the thermal calcinations at 450 \(^{\circ}\)C for 2 hours respectively in a furnace (heating rate = 2 \(^{\circ}\)C/min) to remove PS \(\mu\)-particles.

[S-3] Fabrication procedure of DSSC single cell

The Nb-TiO\(_2\) photoelectrode was immersed in 0.5mM N719 dye (cis-bis(isothiocyanato)-bis(2,20-bipyridyl-4,40-dicarboxylate) ruthenium(II) bis (tetrabutylammonium), solaronix) in ethanol for 1 day. The excess dye was washed away with ethanol. Pt counter electrode was fabricated by spin coating 0.7mM H\(_2\)PtCl\(_6\) in 2-propanol on an FTO glass followed by thermal sintering at 450 \(^{\circ}\)C for 2 hours. A photoelectrode and a Pt counter electrode were sandwiched using 25\(\mu\)m Surlyn\textsuperscript{®} sheet (1702 DuPont) as spacer. Liquid electrolyte was inserted through a hole at the counter electrode, and the single cell was completed by sealing the hole with Surlyn\textsuperscript{®}. The liquid electrolyte used in this study was composed of 0.7M 1-butyl-3-methylimidazolium iodide (BMII), 0.03M Iodine (I\(_2\)), 0.1M Guanidium thiocyanate (GSCN), and 0.5M 4-tert-butylpyridine (TBP) in a mixed solvent of acetonitrile and valeronitril by 85:15 volume ratio.

[S-4] Characterization of nanoparticles and IO films

For transmission electron microscopic (TEM) analysis of an Nb-doped TiO\(_2\) nanoparticle, 10\(^{-3}\) wt% dispersion in water was cast on the carbon-coated Cu grid. After vacuum-drying at room temperature (r.t.), the nanoparticles were imaged by high resolution (HR) TEM (tecnai F20, FEI). Overall crystalline structures and average particle size of the powder product were characterized using X-ray diffractometer (XRD, Rigaku D/Max-2500) with Cu-K radiation as light source. The beam size of XRD was 1.7x10 mm\(^2\), and the measurement was done within 10-80\(^{\circ}\) angular range at 1 deg/min scan rate. IO structure of each photoelectrode was imaged by scanning electron microscopy (SEM, S-4700, HITACHI). The photographs of opal films were obtained using a digital single lens reflex (DSLR) camera (DSLR-A550, SONY).
HR-TEM images of Nb-doped TiO$_2$ nanoparticles from (a) NbCl$_2$ precursor, (b) NbOXL precursor. It is obvious that NbCl$_2$ precursor resulted in relatively smaller particles compared to NbOXL. Inset figures are the selected area electron diffraction (SAED) patterns for each particle showing anatase morphologies respectively.
[S-6] Photographs of Nb-doped TiO$_2$ IO films with (a) 1%, (b) 4% doping from NbOXL before and after calcinations showing red to violet color changes. The reflective colors originate from the ordered IO structures.
Cross-section SEM images of IO films of (a) bare TiO₂ IO, (b) Nb-TiO₂ 2% by NbCl₂, (c) Nb-TiO₂ 2% by Nb OXL, (d) Nb-TiO₂ 4% by Nb OXL, respectively showing well ordered IO structures near top surface and randomly oriented structures near FTO glass.