Supporting Information

Chemicals

Fluorine-doped tin oxide (FTO, TEC 15, Hartford Glass Co.) coated glass was used for all experiments. The glass was cleaned by hand with soapy water and ethanol, and then sonicated in an aqueous solution of 2% deconex, rinsed with DI water and finally sonicated in isopropanol. Just before use, the glass was blown dry of isopropanol and then heated to 500 °C for 20 min. The ALD niobium source, (t-butylimido) tris(diethylamido) niobium(V) (TBTDEN, Digital Specialty Chemicals, 99.8%), and tin source, Tetrakis(dimethylamino)tin(IV) (TDMASn, AB111631, ABCR) were used as-received.

The porous template was prepared from a paste based on commercial TiO_2 particles (Huntsman Tioxide A-HR, 99%), ethyl cellulose, and terpineol according to published procedures[1]. The viscosity was adjusted with additional terpineol and films were prepared by spin coating followed by drying and calcination[1].

ALD

A Savannah 100 ALD (Cambridge NanoTech) was used in conjunction with an UV ozone generator (Yanco industries LTD) using ultrapure oxygen. Ultra pure nitrogen was used as the carrier gas with a constant flow rate of 20 sccm. The precursor reservoirs for TDMASn and TBTDEN were held at 55 and 110 °C, respectively. The manifold between the precursors and reactor chamber was maintained at 150 °C. The reactor chamber was maintained at 120 °C. The ALD protocols were adapted upon those previously reported for tin oxide[2] and niobium oxide[3]. An "exposure mode" deposition was used to allow time for precursor diffusion into and out of the porous templates. Exposure mode was performed by closing the valve between the reactor and the vacuum pump, followed by a precursor pulse and an infiltration delay, followed by opening the valve and another purge delay.

SnO_2 was deposited by a cycle with the following sequence: close, 0.5 s TDMASn pulse, 10 s delay, open, 15 s delay, close, 0.1 s O_3 pulse, 10 s delay, open, 15 s delay. This sequence corresponds to a single Sn cycle.

Nb_2O_5 was deposited by a similar cycle with the following sequence: close, 0.5 s TBTDEN pulse, 10 s delay, open, 35 s delay, close, 0.1 s O_3 pulse, 10 s delay, open, 45 s delay. The longer purge times are necessary to allow for slower surface desorption. This sequence corresponds to a single Nb cycle.

NTO was deposited by the repetition of a supercycle with a "sandwich" structure having a single Nb cycle at the middle of a series of Sn cycles. For example, NTO-2 was deposited with the following supercycle: 25 Sn cycles, 1 Nb cycle, 24 Sn cycles. Each such supercycle lead to 6.4 nm of NTO and the film thickness was adjustable with the number of supercycles. The as-deposited films were smooth before calcination (Figure S1). The films were calcined with a 30 minute ramp to 500 °C with a 30 minute hold before cooling naturally.

A niobia blocking layer was deposited similarly, but with the reactor chamber at 150 °C. The pulse sequence was: close, 0.5 s TBTDEN pulse, 10 s delay, open, 25 s delay, close, 0.015 s water pulse, 10 s delay, open, 35 s delay. This cycle was run 36 times to deposit an optimized 2 nm blocking layer as previously reported[4]. After deposition the sample was heated to 500 °C for 30-60 min.

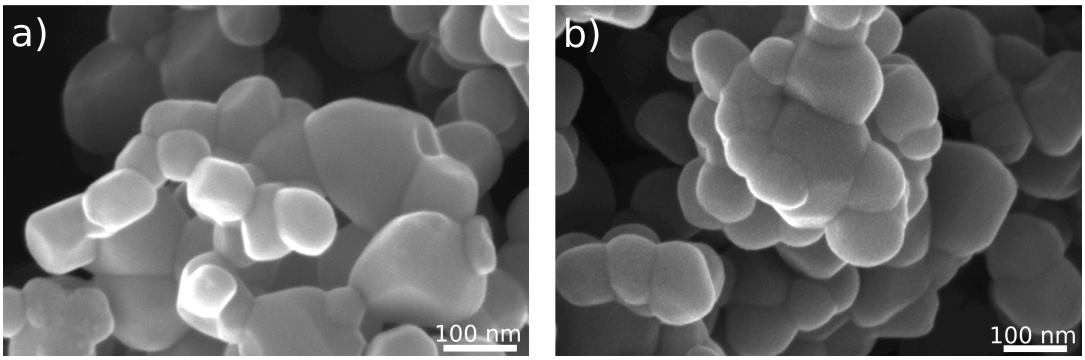

Figure S1. High magnification SEM images of the TiO_2 template before (a) and after (b) deposition of NTO-2.

APCVD

Atmospheric pressure chemical vapor deposition was performed in a custom-built reactor as previously reported in detail[5]. The deposition time was optimized with the photocurrent, leading to the highest photocurrents with 40-50 second exposures. Longer depostion times lead to cauliflower growth above of the host.

Stability

Stability tests were performed using aqueous solutions between pH 1-13.6. The solutions were prepared from deionized water and the pH was adjusted using either NaOH or HCl and a calibrated Knick pH-Meter 761 Calimatic. Calcined 1 cm^2 pieces of NTO-2 on quartz were placed in ~20 mL of each solution to test for stability. After one week, the pH was checked again before conductivity and absorbance measurements.

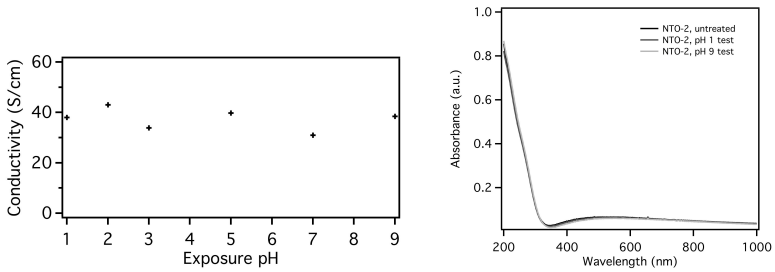

Figure S2. Samples of NTO-2 maintained high conductivity after extended exposure to pHs from 1 to 9 (left). The optical transparency was similarly undisturbed by pH exposures between 1 and 9 (right).

Characterization

UV Vis absorption and transmission measurements were made with a Hewlett-Packard 8452A diode array spectrophotometer. Quartz substrates were used for NTO deposition and as the baseline reference.

ALD growth rates were determined by ellipsometry (Sopra GES 5E) measurements on relatively thick ~100 nm samples grown on Si wafers under identical ALD conditions. The obtained spectra (1-6 eV photons) were fitted using modified-Cauchy dispersion law to extract the thickness.

XPS data were collected with an Axis Ultra (Kratos Analytical) using a monochromatic Al K-alpha X-ray source (1,486.6 eV).

Hall Probe measurements were obtained with a HMS-3000 (Ecopia) using ~100 nm thick films on quartz substrates and a 0.54 T magnet. Contact points were made with ultrasonic soldering. Multiple measurements were made for each deposition condition and averages were reported with the standard deviation (Fig 2a).

A Bruker D8 Discover diffractometer was used to acquire XRD spectra. Monochromatic Cu Kα1 radiation (1.540598 Å) was used as the X-ray source with an incident angle of 1° to enhance the signal from the thin ALD films. The spectra were acquired by moving the linear silicon strip "Lynx Eye" detector between 2θ = 10-90°.

SEM was performed with a field emission source, an accelerating voltage of 5 kV, and an in-lens secondary electron detector (FEI XLF30-SFEG and also a Zeiss Merlin). All measurements reported from electron microscopy were based upon numerous measurements from multiple images and were reported with the standard deviation.

PEC water splitting measurements were made using a 1 M NaOH electrolyte (pH 13.6), a platinum counter electrode, and an Ag/AgCl reference electrode in a saturated KCl solution. Current-potential measurements were made with a Princeton Applied Research potentiostat model 273A scanning at 50 mV/s from cathodic to anodic potentials. The AM 1.5 light source was a 450 W Xenon lamp (Osram, ozone free) equipped with a KG3 filter and with an intensity of 100 mW/cm^2. The sample face was irradiated through a window with a 0.5 cm^2 mask. IPCE measurements were performed using a 300 W Xenon lamp with a Bausch and Lomb (10 nm bandwidth) monochromator. The photons were measured with a Si photodiode.

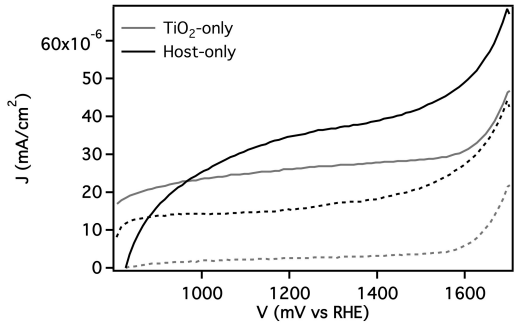

Figure S3. Negligible photocurrent was found for TiO_2-only (gray) and Host-only (black) samples as determined by current-voltage measurements under AM 1.5 simulated light in 1 M NaOH. Dark currents are shown as dashed lines.

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2. Elam, J. W.; Baker, D. A.; Hryn, A. J.; Martinson, A. B. F.; Pellin, M. J.; Hupp, J. T., Atomic layer deposition of tin oxide films using tetrakis(dimethylamino) tin. *J. Vac. Sci. Technol. A* **2008,** *26* (2), 244-252.
3. Blanquart, T.; Niinisto, J.; Heikkila, M.; Sajavaara, T.; Kukli, K.; Puukilainen, E.; Xu, C. Y.; Hunks, W.; Ritala, M.; Leskela, M., Evaluation and Comparison of Novel Precursors for Atomic Layer Deposition of Nb2O5 Thin Films. *Chem. Mat.* **2012,** *24* (6), 975-980.
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