Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Titanium dioxide nanotube membranes for solar energy conversion: effect of deep and shallow dopants

Yuchen Ding[a,b], *Prashant Nagpal*[b,c,d]

[a] Chemistry and Biochemistry, University of Colorado Boulder

[b] Renewable and Sustainable Energy Institute, University of Colorado Boulder

[c] Chemical and Biological Engineering, University of Colorado Boulder

[d] Materials Science and Engineering, University of Colorado Boulder, Boulder, CO 80303

TiO_2 nanotubes (NTs) growth

TiO_2 nanotubes were grown with electrochemical oxidation (anodization) using titanium metal sheets (0.5" x 0.5") as anode (working electrode) and platinum coated electrode as cathode. Ethylene glycol (EG) containing 1% wt. NH_4F (etchant) and 2% wt. was used as electrolyte. The growing was processed for 5 hours with applied 30 V DC voltage. Doping with different elements can be easily done with correspondent precursors. For anion (nitrogen here) doping, 5% wt. hexamethylenetetramine was directly added to the electrolyte as the nitrogen precursor. For cation (niobium and copper) doping, 1% wt. $NbCl_5$ and $CuSO_4 \cdot 5H_2O$ solution were used, respectively, with applied -15V DC voltage (by changing the polarity), with the period cycle of growing/doping = 1h/1min. The as-synthesized samples were annealed under 500 ^oC for 2 hours (with a ramping rate of 4 ^oC/min) to improve the crystallinity. Dopant levels can be measured by Energy Disperse X-ray Spectroscopy (EDS). As a result, dopant level show linear relationship with the weight amount of correspond precursors used in the doping process (with fixed time and doping applied voltage). Stand-alone TiO_2 nanotube thin film can be delaminated from the titanium substrate with a second electrochemical anodization technique. Using annealed sample and platinum coated electrode as anode and cathode, respectively, the delamination was carried out in the same electrolyte for growing TiO_2 NTs with applied 60 V DC bias for about 30 minutes.

The thin film was carefully washed with ethanol to remove the electrolyte and transferred to the clean glass slides.

Ultraviolet-Visible (UV-VIS) Spectroscopy

UV-VIS Spectrum was measured using VWR UV-1600PC spectrophotometer (with the wavelength ranging from 200 nm to 1100 nm). The samples (delaminated thin films) were sandwiched between two clean glass slides for measuring.

Electrochemical Characterization

Electrochemical properties of these electrodes were measured using a Bio-logic SP-200 potentiostat/galvanostat. Potentiodynamic characters (dark and light linear sweep voltammetry, LSV) of Ti/TiO_2 NTs electrode was performed in 0.5 M (pH = 6.5) Na_2SO_4 solution at a scan rate of 10 mV/s from -1.0 ~ 2.5 V (vs. reference). A three-electrode configuration with platinum wire as counter electrode, and Ag/AgCl (filled with 1 M KCl solution) electrode as reference electrode was used. Photodynamic evaluation was carried out under 1 SUN illumination using a 300 W xenon lamp (adjusted to 100 mW/cm^2 light intensity). Chronoamperometry (CA) technique was used to evaluate the generation of photocurrent, under +0.0 V vs Ag/AgCl reference. Two-electrode measurements were used to evaluate the efficiency of these nanotubes as a photoanode for water oxidation. The setup is similar to the three-electrode configuration, with the elimination of the Ag/AgCl reference electrode.

The efficiency of these TiO_2 nanotube photoanode can be evaluate from the applied bias photon-to-current efficiency (ABPE), calculated from the photocurrent-applied bias relationship measured from two-electrode measurement.

Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the kinetic properties of these photocatalysts under AC polarization. Using the same conditions for LSV measurement, the experiments were conducted in a frequency range from 100 kHz to 100mHz, with an amplitude of 10mV AC polarization on a +0.2 V vs reference DC bias, after a 10 min delay. Both dark and light characters were studied. In the light measurement, a 4 W, 365 nm (with an approximate intensity of around 5.1 mW/cm^2)

UV lamp was used as light source. Bode plot and Nyquist plot were extracted from the measurements and fitted to suggested equivalent circuit using the Zfit function in EC-lab software (Bio-logic).

Open-circuit potential (OCP) decay/relaxation was conducted using the same three-electrode setup to evaluate the charge transfer characters on the nanotube-electrolyte surface. The measurements were firstly taken in dark for at least 25 min (to stabilize the OCP) and then under UV irradiation until the change of OCP were small (~35 min). The UV irradiation was then turned off and the relaxation measurements were taken for about 1 hour.

Table S1 Parameters extracted from the equivalent circuit fit

	Undoped	**Nb-doped**	**Cu-doped**
$\mathbf{R_s}$ $(k\Omega \cdot cm^2)$	0.0170 ± 0.0008	0.0175 ± 0.0007	0.0174 ± 0.0009
$\mathbf{R_{ct}}$ $(k\Omega \cdot cm^2)$	4.96 ± 0.20	3.73 ± 0.18	6.07 ± 0.29
$\mathbf{C_{dl}}$ $(\mu F/cm^2)$	424 ± 22	328 ± 16	317 ± 14
$\mathbf{R_{sc}}$ $(k\Omega \cdot cm^2)$	0.593 ± 0.029	3.84 ± 0.19	6.44 ± 0.30
$\mathbf{C_{sc}}$ $(\mu F/cm^2)$	1.75 ± 0.070	8.99 ± 0.36	12.3 ± 0.55
$\mathbf{R_1}$ $(k\Omega \cdot cm^2)$	0.720 ± 0.036	0.400 ± 0.020	4.26 ± 0.16
$\mathbf{C_1}$ $(\mu F/cm^2)$	69.2 ± 3.5	68.8 ± 2.1	82.4 ± 3.9
$\mathbf{R_2}$ $(k\Omega \cdot cm^2)$	0.375 ± 0.022	0.005 ± 0.0003	12.4 ± 0.50
$\mathbf{C_2}$ $(\mu F/cm^2)$	2.31 ± 0.14	49.8 ± 2.5	431 ± 20
$\mathbf{R_3}$ $(k\Omega \cdot cm^2)$	0.212 ± 0.009	0.027 ± 0.001	0.759 ± 0.039
$\mathbf{C_3}$ $(\mu F/cm^2)$	27.3 ± 1.4	112 ± 4.72	146 ± 6.30

Photocatalytic Methylene Blue degradation test

Photocatalytic degradation of Methylene Blue (MB) was carried out in a capped quartz cuvette containing 3 ml 0.05 mM (150nmol) methylene blue solution and wireless Ti/TiO_2 electrode, with an exposed surface area of about 1 cm^2. The whole system was irradiated with 365 nm monochromatic light (5.1 mW/cm^2) using a 4W UV lamp. The absorption of the solution was taken at 0, 10, 40, 80 and 120 min using a calibrated UV spectrometer, the decrease of absorption and the fating of blue color indicates the degradation of methylene blue dyes. The decease of the absorption peak around 670 nm was used to calculate the kinetic constant of reaction and the quantum yield of photocarrier generation.

Current sensing AFM (CSAFM) measurements

CSAFM measurements were done using modified Molecular Imaging PicoSPM II setup. The CSAFM tips used were coated in-house using thermal evaporator with 5nm of 99.99% Cr and 15 nm of 99.99% Au, both purchased from Kurt J. Lesker Company. The silicon nitride tips for contact mode imaging and spectroscopy were obtained from NanoDevices Inc. Contact force was set to soft contact (deflection set point between -1 and -3V). Multiple topography and current scans were taken at different bias voltage ranging from -200 to +200 mV with steps of 50 mV. The scan area was set to 1 μm^2 at a scan rate of 1 line per second and 512 points/line. TiO_2 NTs were scratched from titanium substrate and dispersed in little amount of ethanol. A thin layer of TiO_2 NTs were formed on ITO coated glass by drop casting. The sample placed on a transparent ITO substrate was connected using a wire attached to the ITO using conductive silver paste.

STM and STS measurements

Scanning Tunneling Microscope images were obtained using a customized Molecular Imaging PicoScan 2500 setup (with PicoSPM II controller). An STM nosecone (N9533A series, Agilent Technologies) was used for scanning and spectroscopy using chemically etched Pt-Ir tips (80:20) purchased from Agilent Technologies, USA. The measurements were done at room temperature under atmospheric conditions. Tunneling junction parameters were set at tunneling currents ranging between 100 and 500 pA and sample bias voltage between -5 and +5 V.

Spectroscopy measurements were obtained at a scan rate of 1V/s with previous junction parameters. For STM measurements, the pre-amp sensitivity set to 1nA/V. The tunneling current as a function of applied bias voltage (STS) was recorded at multiple positions on the sample at room temperature and atmospheric pressure. The samples were prepared using the same procedure as in the CSAFM measurement.

Gas-phase reduction of CO_2 and H_2O

20 mg of the nanotube scratched from metal sheet was deposited in a rounded glass vial cut in half with a 0.64 cm^2 cross sectional area. The vial was then enclosed in a 48-mL reactor and purged for 45 minutes with CO_2 (75 cm^3 min^{-1}) humidified in a bubbler filled with D.I. water. After purging, the reactor was closed and irradiated with 1 SUN (100 mW cm^{-2}) through a glass window using a solar simulator (ABET Technologies). One-milliliter samples were extracted from the reactor and injected into a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) for measuring concentrations. Separation of the hydrocarbons was done with a Hayesep D column or with Silica-gel column. Reported data of photocatalytic rate and quantum yield were calculated based on the electron flux (μmol cm^{-2} h^{-1}) used to form CH_4.

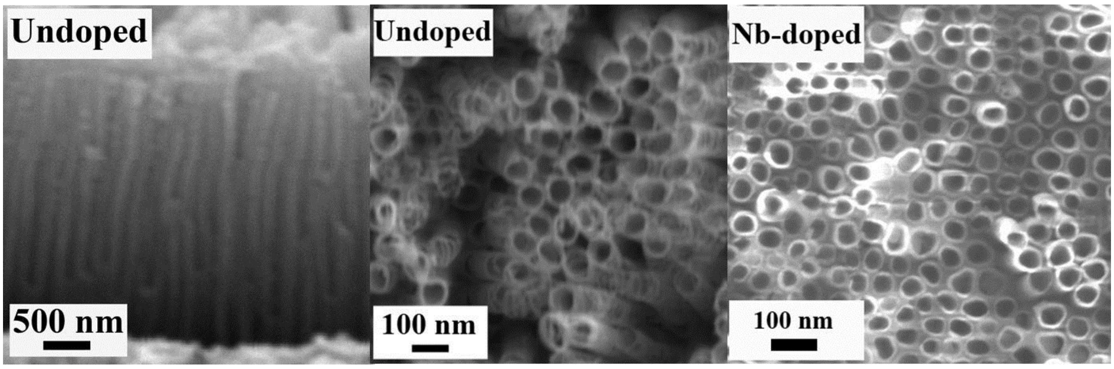

Figure S1 Field Emission Scanning Electron Microscopy (FESEM) of undoped and Nb-doped TiO_2 nanotubes.

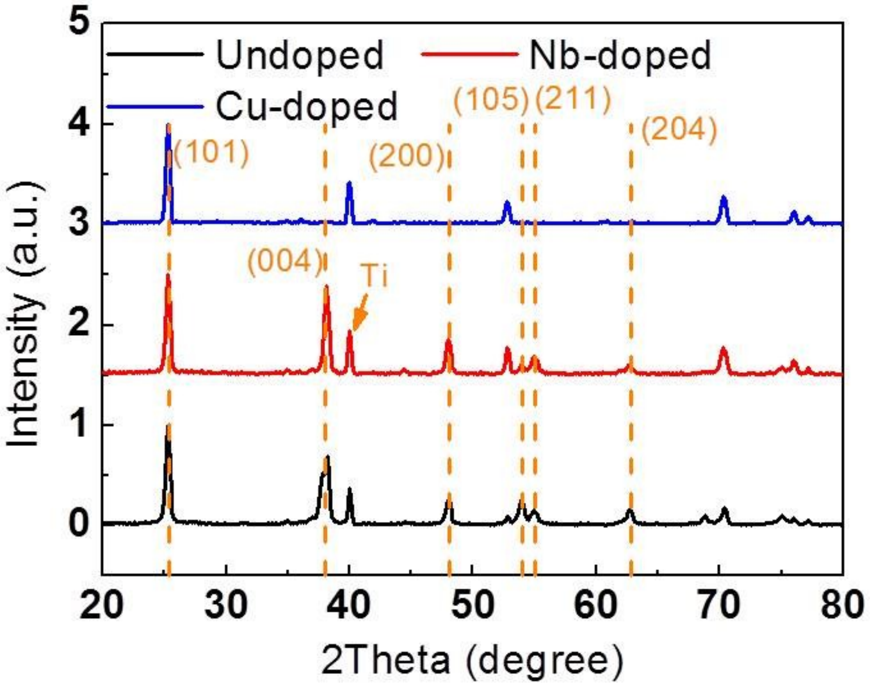

Figure S2 X-ray powder diffraction (XRD) of undoped and doped TiO_2 nanotubes, with labeled Miller index for different crystal surface.

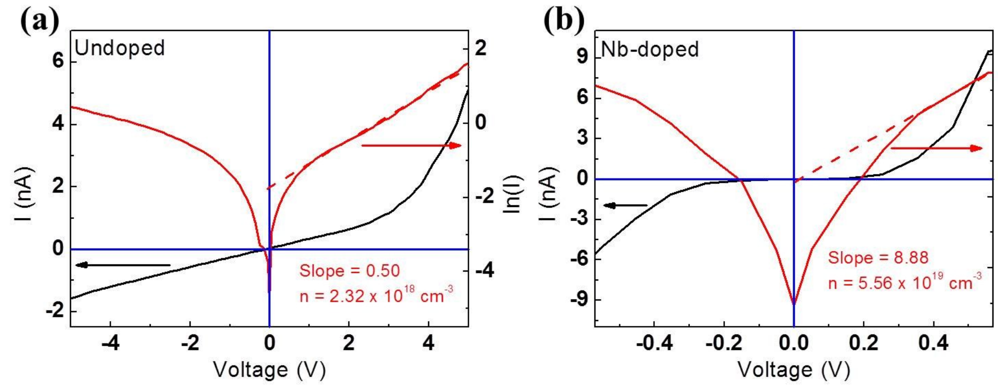

Figure S3 Current-sensing atomic force microscopy (CSAFM) measurement of (a) undoped and (b) Nb-doped TiO_2 nanotubes, showing both the I~V and ln(I)~V characters.

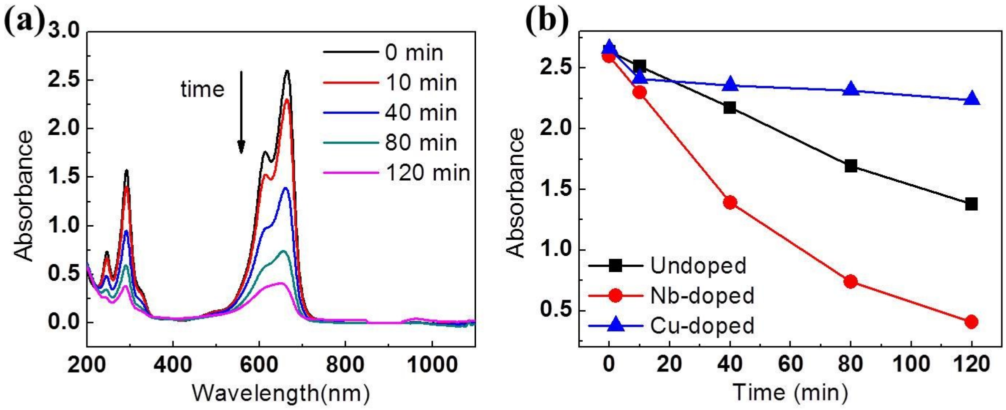

Figure S4 (a) The UV-VIS spectrum of methylene blue, showing the decrease of absorption with time under photocatalytic degradation of Nb-doped TiO_2 nanotubes. (b) The change of 670 nm peak absorbance with time under photocatalytic degradation of undoped and doped TiO_2 nanotubes.