Supplementary Information

Doping wide-bandgap titanium-dioxide nanotubes: optical, electronic and magnetic properties

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Fig. S1 SEM images of the TiO_2 nanotubes with different diameters grown at different anodization conditions: **a** and **b** correspond to nanotubes with 18 nm diameter (grown at 7 V), **a** shows nanotubes at early stage of the growth when nanotubes start forming. **c**, **d**, **e**, **f**, and **g** correspond to nanotubes with diameters 43 nm (grown at 15 V), 86 nm (30 V), 170 nm (60 V), and 322 nm (120 V), and 550 nm (200 V).Scanning electron microscopy (SEM) analysis showed that the morphology of TiO_2 nanotubes did not change after doping and well-defined tubular structure as typical to undoped samples was observed.



Fig.S2 XRD (a) patterns for undoped and Nb doped TiO₂ nanotube samples, with different Nb concentrations. Only reflection peaks corresponding to anatase TiO₂ was observed in all samples without any secondary phase peaks. Peaks marked "T" in the 2 θ patterns in this figure corresponds to the underlying Ti substrate from which TiO₂ nanotubes were grown; (b) Energy dispersive X-ray Spectrum (EDS) for Nb doped TiO₂ nanotubes with different concentrations of Nb precursor: a) 0.1%, b) 0.4%, c) 0.8%, and d) 1.2 %. The corresponding Nb concentration in TiO₂ NT samples, quantified using EDS, were determined to be 1.37%, 3.8%, 7.8%, and 11.8%, respectively, presenting nearly linear relationship between NbCl₅ content in electrolyte and EDS signal, as shown in (c).



Fig. S3. (a) EDS point scans taken from different points of individual Cu-doped TiO₂ nanotubes (we show two representative points). This scan was performed by pointing focused electron beam onto the surface of single nanotube (or mapping the elemental distribution over a large area). Highly pronounced Cu peaks seen at different points (we are showing two points for clarity), indicate Cu is uniformly incorporated in TiO₂ nanotubes crystal, rather than accumulating as clusters or secondary phase oxides. This data demonstrates that Cu dopants were uniformly incorporated in the TiO₂ crystal lattice. Similar scans for all dopants (cations and anions) were performed to ensure uniform doping in TiO₂ nanotubes. **b**, EDS elemental maps over large areas, showing uniform incorporation of the dopant (copper here). Such elemental maps were used to ensure uniform doping in wide-bandgap nanotubes. **c**, Schematic showing EDS elemental mapping using characteristic X-rays emitted on irradiation with electron beam.

Methods and instruments used for characterization of doped TiO₂ nanotubes

Current sensing AFM (CS-AFM) measurements: CSAFM measurements were performed 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 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 current scans were taken at different bias voltage ranging from -5 to +5 V with steps of 50 mV. The measurements were performed by contacting top of vertically aligned TiO₂ nanotubes and the open area of Ti sheet as the second contact to form complete circuit. **Fig. S4** illustrates the experimental configuration used for the horizontal/vertical knobs to obtain the diffraction pattern from the gold coated cantilever.



Fig. S4 A schematic showing electrical circuit during CS-AFM measurements

STM/STS sample preparation: Scanning Tunneling Microscope/Spectroscopy was done on cleaned ITO substrate, or fresh template stripped Au (111) substrates. For single nanoparticle optical-electronic measurements, Indium-tin-oxide (ITO) substrates were sonicated in a 1:1:1 mixture of methanol, acetone and water for 15 minutes, dried in pure nitrogen and used immediately. For other STS/STS measurements, 100-150nm evaporated gold on a clean silicon substrate was flame annealed and template stripped using cured epoxy (EPOTEK 377, Epoxy Technologies) substrate. Freshly cleaved samples were immediately used for STM/STS analysis. For doped widebandgap nanotube samples (high conductivity), as-prepared nanotubes can also be used and contacted using thin titanium metal foil at the bottom. However, for comparison, only nanotubes measured on the same substrates are shown here. Each sample was measured several times along the nanotube (line scans), and representative data (averaged) has been

shown in the main and supplemental text. The n- to p-type doping was verified both using tunneling spectroscopy (STS), and using electronic I-V and I-V-T measurements on single nanotube and ensembles. On analysis of the data obtained by tunneling and direct electronic measurements, the mobility, carrier concentration were found to be well matched to the observed shifts in electronic energy levels (see comparisons shown in Table I and SI below).

	undoped	Nb	Cu	N	Cu-N
Type of doping	n-type	n-type	p-type	p-type	p-type
Shift in Fermi-level, using STM, meV	-	100	-	20	100
Estimated carrier concentration (from Fermi- level shifting), n, cm ⁻³	8.9 ×10 ¹⁷	4.9 ×10 ¹⁹	5.3 ×10 ¹⁶	2.38 ×10 ¹⁶	9.71 ×10 ¹⁴

Correlating the shifts in Fermi-level (using STM measurements) with the measured carrier densities

Table II Summary of estimated carrier concentration from STM data

The intrinsic carrier concentration in wide-bandgap semiconductors is negligible,

$$n_i = N_s \exp(-\frac{E_g}{2k_BT})$$
 where n_i is the intrinsic carrier concentration, Ns is the number of available

states, E_g is the bandgap, and k_B is the Boltzmann constant. Therefore, the doped carrier concentrations can be estimated using the shifts in Fermi-energy (monitored by the STM data, Fig.1c). As shown in Table II, we used the undoped and copper-doped TiO₂ nanotubes as n- and p- "standards" respectively, and estimated the carrier concentrations of Nb, N and Cu-N co-doped nanotubes, using the STM data. The shift in Fermi-energies is given as:

$$E_f - E_c = k_B T \ln(\frac{n_d}{n_i})$$
$$E_v - E_f = k_B T \ln(\frac{p_a}{n_i})$$

for n-type donor and p-type acceptors respectively. These values obtained are in reasonable agreement with the estimates obtained from current-voltage CS-AFM spectroscopy, as summarized in Table I.



Fig. S5. a, Temperature dependent current-voltage characteristics presented in 3D mode; $\mathbf{b} - \mathbf{e}$ Richardson for doped and undoped samples; the activation energies were derived to be 0.027 eV, 0.014 eV, 0.097 eV, and 0.502 eV, respectively, for undoped, Nb-doped, Fe-doped, and Cu-doped samples.

Charge carrier concentration in TiO₂ nanotube samples were calculated using equation:

$$\ln(I) = \ln(S) + (\frac{e}{kT} - \frac{1}{E_0})V + \ln J_s$$

The slope for I-V is equal to: $\frac{q}{kT} - \frac{1}{E_0}$, where $E_0 = E_{00} \operatorname{coth}(E_{00}/kT)$, and $E_{00} = (\hbar q/2)(n/m * \varepsilon)^{1/2}$

Thus, from the slope of the ln(I) vs V plot at higher voltages carrier concentration was calculated using equation $slope = \frac{q}{kT} - \frac{1}{E_0}$ where q –elementary charge, h - plank constant, ε_0 - vacuum permittivity, ε =31 ε_0 - dielectric constant for TiO₂, k – Boltzmann constant, m*=m₀ electron effective mass



Fig. S6 CS-AFM current-voltage (*I-V*) characteristics and corresponding ln(I) vs V plots of single nanotubes of (**a**) undoped, (**b**) Fe-doped, (**c**) Nb-doped, and (**d**) Cu-doped TiO₂ nanotube samples. This data was analyzed to extract carrier concentration (described above).



Fig.S7 a) Dependence of doped nitrogen (N) and N precursor (hexamethylenetetramine) concentration in electrolyte; linear relationship between amount of N precursor in electrolyte and detected N in TiO₂ nanotubes; b) current sensing atomic force microscopy (CS-AFM) *I-V* characteristics of n-type (Nb doped) and p-type (N doped) TiO₂ nanotubes.

The new Figure of Merit

For a more detailed analysis of photoconductance data, instead of the simple $\ln(I/V^2)$ vs (1/V)functional form used in F-N plots, we developed a new figure of merit for photogenerated charges. Using the functional form of the Fowler-Nordheim equation^{S1},

$$I = V \exp\left[-\frac{q}{kT}\left(\phi - V^{1/2}\sqrt{\frac{q}{\pi\varepsilon_i}}\right)\right]$$
(Fowler-Nordheim equation)

 $V \times \ln(I/V^2)$ is proportional to the activation barrier for charge transport. However, this equation was developed for electrically injected charges, where for the same applied bias, same number of charges can be injected for a given barrier. Since we wanted to analyze optically injected charge carriers, we normalized the number of charges by the incident light intensity, and the absorbance in single nanoparticle constructs or thin films. We plotted $V \times \ln\left(\frac{I_{PR}}{V^2 \times P \times Abs}\right)$ vs. photon energy, to understand

the conduction pathway for photogenerated charges (Fig.3b). This new figure of merit represents the activation energy for charge transport of photogenerated charges, as a function of incident photon energy (Fig.3b). The step-like change at the bandedge gives a clear threshold for energy states (donor and acceptor states) involved in photogeneration and charge conduction in these indirect bandgap semiconductors. This data, along with the STM measurements, was used to study doping in these wide-bandgap nanotubes (Rayleigh scattering and indirect bandgap of anatase TiO_2 makes exact determination of bandgap and energy states difficult using simple optical measurements),



Fig. S8 Fowler – Nordheim (I/V^2) vs I/V plot for Cu doped TiO₂ nanotubes when irradiated with different monochromatic light wavelength ranging from 330 nm to 450 nm. We plotted $V*ln(I / V^2*P*Abs)$ as a function of photon energy hv, where P is the power of incident light, and Abs is absorption coefficient, (see Fig. 3b in the article).



Figure S9 Carrier concentration (blue) and mobility (green) of 1 wt% Nb doped TCO nanotubes, as a function of temperature. Temperature was varied in the range 20 - 300 K.

Measuring Photocatalytic Activity

Gas chromatography

- i. **Identification and separation**. Two 14 L gas samples were bought from MATHESON TRI•GAS. Gas cylinder 1 presented a composition of 1000 ppm for each saturated hydrocarbon methane, ethane, propane, butane, pentane and hexane, and was balanced with Helium (He) gas. A second sample, also balanced with He, had a concentration of 1000 ppm of unsaturated hydrocarbons ethylene, propylene, 1-butene, 1-pentene and 1-Hexene. A gas chromatography G1540 Agilient was equipped with a 6-ft silica gel capable to separate hydrocarbons. The column unfortunately was unable to separate carbon monoxide (CO), nitrogen (N₂) and oxygen, nonetheless, former experiments using a 6ft-Hayesep D column did not report the formation of CO. Variation of the temperature and pressure was employed for separation. The final ramping program for separation was:
 - \circ Time = 0 min. P = 35 psi, T = 150°C.
 - Time 3.15 min, temperature is ramped to 200°C at 40°C per minute
 - Tim 25 min, program stops and return to initial conditions
- ii. Calibration. Measurement of species concentration was done by purging and filling up the reactor volume with a gas mixture of known concentration. Constant (K_i) values based on variables expected effect and area measured were calculated. Since we work at low concentrations, below 1000 ppm, the area signal measured is expected to be linear with variables that increase the amount of material, for instance, pressure, concentration and volume. Thus,

ν	$Conc_i \times Pressure \times Volume$
$\Lambda_i =$	Area

unit used were, Torr for pressure, ppm for concentration and μL for volume.

iii. Summary

Species	Retention time min	Constant ppm·torr·µL area ⁻¹	Detector used
Hydrogen	0.48	8,411,645	TCD
Methane	0.78	97,414	FID
Ethane	0.93	50,541	FID
Ethylene	1.38	45,252	FID
Propylene	2.08	30,173	FID
Propane	2.73	34,219	FID
1-Butene	3.88	23,392	FID
Butane	4.43	35,843	FID
1-Pentene	5.42	19,267	FID
Pentane	6.23	20,740	FID
1-Hexene	6.23	17,079	FID
Hexane	7.93	19,306	FID
Acetaldehyde	16.2	56,261	FID
Methanol	>30min	NA	FID
Ethanol	>30min	NA	FID

Irradiance measurement and calibration

A solar simulator (ABET technologies) was used for measurements of photocatalysis using simulated sunlight irradiation. The light source (especially for high sun measurements) was measured using a calibrated power meter (1918-R, Newport Corporation) equipped with a 818-UV silicon detector. A rough calibration of the light source was done using a silicon photodiode (S1787-12, Hamamatsu Photonics). Since the photodiodes are linear with light intensity (under this illumination intensity), high sun light intensities were measured using our calibrated silicon photodiodes.

Photon _i wavelength nm	$\begin{array}{l} Photon_i \ energy \\ eV \end{array}$	Irradiance up to photon in μ mol cm ⁻² h ⁻¹	Spectrum photon %
400	3.20	25.92	1.44

Example:

The electron flux of 100 ppm of CH₄ produced in 30 minutes in our reactor is measured as follow:

Sampling port pressure = 760 Torr.

Reactor volume = 48.2 mL.

Reactor Temperature = 25° C, the change in reactor temperature was negligible, even under high sun illumination.

First we determine the number of nanomols produced (S stands for sample and R for reactor):

$$n = \frac{P_{s}V_{R}}{RT_{R}} = \frac{\frac{100 \ ppm \ \times (1/_{10^{6}}) \times 760(torr) \times (1 \ (atm)/_{760(torr)} \times 0.048(L))}{0.08206 \ atm \ L/_{mol \ K} \times 298K} \times \frac{(10^{9} nanomol)}{1 \ mol}$$

1.971 nanomol of CH₄

$$e^{-flux} = 1.971 \times \left(\frac{8 \ electron}{1 \ nanomol \ CH_4}\right) \times \left(\frac{1\mu mol}{10 \ nanomol}\right) \times \left(\frac{1}{30min}\right)$$

 $\times \left(\frac{60min}{1h}\right) \times \left(\frac{1}{0.78cm^2}\right) = 4.043 \ e^{-\mu mol \ cm^{-2}h^{-1}}$

The molar concentration of CO₂/H₂O was 31, and the vapor pressure of water was 23.8 mm of Hg.

Quantum yield

The quantum yield is determined by dividing the total sum of electron used to produce hydrogen and hydrocarbons, by the photon irradiation. The photon irradiation threshold is defined by the Titanium dioxide energy bandgap.

Calibration of acetaldehyde: Pure acetaldehyde sample were diluted to a 15,265 ppm concentration using chloroform as balance, and 1 microLiter was injected and followed a similar method as with gas species.



Figure S10 Light spectrum of solar simulator (black curve) compared with AM1.5 solar spectrum (blue curve).



Figure S11 STS measurements of alignment of TiO_2 nanotube conductions band-valence band states with reduction potentials of different CO_2/H_2O redox reactions.

Supplemental References

S1. Fowler R.H.; Nordheim L. Proceedings of the Royal Society of London 1928, 119, 173–181.