Supplementary Information

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

Yahya Alivov,1* Vivek Singh,1 Yuchen Ding,1 Logan Jerome Cerkovnik,1 Prashant Nagpal1,2,3*

1 Department of Chemical and Biological Engineering, University of Colorado, Boulder
2 Renewable and Sustainable Energy Institute, University of Colorado, Boulder
3 Materials Science and Engineering, University of Colorado, Boulder

Fig. S1 SEM images of the TiO₂ 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 TiO₂ 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 TiO$_2$ nanotube samples, with different Nb concentrations. Only reflection peaks corresponding to anatase TiO$_2$ was observed in all samples without any secondary phase peaks. Peaks marked “T” in the 20 patterns in this figure corresponds to the underlying Ti substrate from which TiO$_2$ nanotubes were grown; (b) Energy dispersive X-ray Spectrum (EDS) for Nb doped TiO$_2$ 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 TiO$_2$ NT samples, quantified using EDS, were determined to be 1.37%, 3.8%, 7.8%, and 11.8%, respectively, presenting nearly linear relationship between NbCl$_5$ content in electrolyte and EDS signal, as shown in (c).
Fig. S3. (a) EDS point scans taken from different points of individual Cu-doped TiO$_2$ 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 TiO$_2$ nanotubes crystal, rather than accumulating as clusters or secondary phase oxides. This data demonstrates that Cu dopants were uniformly incorporated in the TiO$_2$ crystal lattice. Similar scans for all dopants (cations and anions) were performed to ensure uniform doping in TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ 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 CS-AFM measurements. Alignment of the laser beam was done via the movement of the horizontal/vertical knobs to obtain the diffraction pattern from the gold coated cantilever.

![Au coated AFM tip](image)

**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).

<table>
<thead>
<tr>
<th>Type of doping</th>
<th>undoped</th>
<th>Nb</th>
<th>Cu</th>
<th>N</th>
<th>Cu-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shift in Fermi-level, using STM, meV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>n-type</td>
<td>100</td>
<td>-</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Estimated carrier concentration (from Fermi-level shifting), n, cm$^{-3}$</td>
<td>8.9 $\times 10^{17}$</td>
<td>4.9 $\times 10^{19}$</td>
<td>5.3 $\times 10^{16}$</td>
<td>2.38 $\times 10^{16}$</td>
<td>9.71 $\times 10^{14}$</td>
</tr>
</tbody>
</table>
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,

\[ n_i = N_s \exp\left(-\frac{E_g}{2k_B T}\right) \]

where \( n_i \) is the intrinsic carrier concentration, \( N_s \) 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 TiO\(_2\) 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:

\[ E_f - E_c = k_B T \ln\left(\frac{n_d}{n_i}\right) \]
\[ E_v - E_f = k_B T \ln\left(\frac{p_a}{n_i}\right) \]

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; b – 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 TiO$_2$ nanotube samples were calculated using equation:

\[
\ln(I) = \ln(S) + \left(\frac{e}{kT} - \frac{1}{E_0}\right)V + \ln J_s
\]

The slope for I-V is equal to: 
\[
\frac{q}{kT} - \frac{1}{E_0}, \text{ where } E_0 = E_{00} \coth(E_{00})
\]

\[
E_{00} = (\hbar q / 2)(n / m*)\varepsilon^{1/2}
\]

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, \(\varepsilon_0\) - vacuum permittivity, \(\varepsilon\) =31\(\varepsilon_0\) - dielectric constant for TiO$_2$, \(k\) – Boltzmann constant, \(m^* = m_0\) electron effective mass

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**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 TiO$_2$ 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 TiO$_2$ nanotubes; b) current sensing atomic force microscopy (CS-AFM) $I$-$V$ characteristics of n-type (Nb doped) and p-type (N doped) TiO$_2$ 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\(^5\),

$$I = V \exp\left( -\frac{q}{kT} \left( \frac{\phi}{V^{1/2}} - \frac{q}{\pi e_i} \right) \right)$$ (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 TiO\(_2\) nanotubes when irradiated with different monochromatic light wavelength ranging from 330 nm to 450 nm. We plotted $V \times \ln(I / V^2 \times P \times Abs)$ as a function of photon energy $h\nu$, 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 Agilent was equipped with a 6-ft silica gel capable to separate hydrocarbons. The column unfortunately was unable to separate carbon monoxide (CO), nitrogen (N$_2$) 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:

- Time = 0 min. P = 35 psi, T = 150°C.
- Time 3.15 min, temperature is ramped to 200°C at 40°C per minute
- Time 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,
\[ K_i = \frac{\text{Conc}_i \times \text{Pressure} \times \text{Volume}}{\text{Area}} \]

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

iii. **Summary**

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

**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.

<table>
<thead>
<tr>
<th>Photon, wavelength nm</th>
<th>Photon, energy eV</th>
<th>Irradiance up to photon in µmol cm(^{-2}) h(^{-1})</th>
<th>Spectrum photon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>3.20</td>
<td>25.92</td>
<td>1.44</td>
</tr>
</tbody>
</table>

**Example:**
The electron flux of 100 ppm of CH\(_4\) 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):
The molar concentration of CO$_2$/H$_2$O 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.

![Light spectrum of solar simulator (black curve) compared with AM1.5 solar spectrum (blue curve).](image-url)

**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 conduction band-valence band states with reduction potentials of different CO$_2$/H$_2$O redox reactions.

Supplemental References