Supporting Information

Visible-light Driven Photoelectrochemical Water Oxidation on Nitrogen-modified TiO$_2$ Nanowires

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Experimental section

Material Characterization

Scanning electron microscopy (SEM) was performed on a Zeiss field-emission SEM using a 10 kV focus voltage and on a Hitachi S-5500 scanning transmission electron microscope (STEM) using a 30 kV focus voltage. Transmission electron microscopy (TEM) was performed on a JEOL 2010F field-emission TEM. The JEOL 2010F was also used to collect energy dispersive x-ray spectroscopy (EDX) spectra for elemental analysis. Grazing incidence X-ray diffraction (GIXRD) patterns were collected with a Bruker D8 diffractometer. UV−vis absorbance spectra were taken with a Cary 5000 spectrophotometer using a blank FTO substrate as a baseline standard. The transmittance spectra were collected using a Cary 500 UV-vis-NIR spectrophotometer attached to a Labsphere DRA-CA-5500 integrating sphere. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis X-ray photoelectron spectrometer. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as a reference. The elemental percentages were calculated from XPS spectra using the CasaXPS computer program with specific relative sensitivity factors for the Kratos Axis XPS (Ti 2p: 2.001, O 1s: 0.78, and N 1s: 0.47). CasaXPS was also used for peak fitting on XPS spectra. Ultraviolet photoemission spectroscopy (UPS) measurements were performed on the same Kratos Axis as for XPS measurements. UPS spectra were collected using the He (I) line (21.2 eV) with a negative bias voltage of -8.7 V applied to the samples in order to shift the spectra from the spectrometer threshold. The UPS spectrum for each sample was scanned 5 times to ensure that the uncertainty is smaller than the scan resolution (0.05 eV). The spectra were calibrated versus the Fermi edge of a polycrystalline Au foil.

Electrochemical and Photoelectrochemical (PEC) Characterization

The PEC measurements were performed using a three-electrode electrochemical cell with the FTO supported nanowire arrays as the working electrode, a Ag/AgCl (saturated KCl) reference electrode, a platinum wire counter electrode, and 1 M KOH electrolyte (pH = 13.5). The working electrode with exposed area of 0.16 cm^2 was illuminated from the back side (through the FTO substrate – TiO$_2$ nanowire interface) by a 100 W xenon lamp (Newport) through a UV/IR filter (Schott, KG3) to remove infrared (>800 nm) and short wavelength UV light (<300 nm). Using a Scientech calorimeter (Model 38-0101), the light intensity of the spectrum from 400 nm to 1.2 μm was measured as 37 mW/cm^2. The fraction of the total energy of the spectrum from 400 nm to 800 nm for our lamp is estimated to be 85% - 90 % of the total light energy, therefore, we estimate the energy flux in our PEC measurements to be ~ 41 – 43 mW/cm^2. A CHI 832 electrochemical station was used for linear sweep voltammetry (I-V) and amperometry (I-t) measurements. Incident photon to current conversion efficiencies (IPCEs) were calculated from amperometry measurements using a monochromator (Newport) in conjunction with a power meter and photodiode (Newport), given by:

$$IPCE = \frac{1240 \times j_{ph}}{\lambda \times I} \times 100\ \% \quad (1)$$

Where j_{ph} is the steady-state photocurrent density at a specific wavelength, λ is the wavelength of the incident light. I is the light power intensity of the wavelength at the film surface, I ranges from 80-300 μW/cm^2 over the spectrum of wavelengths studied (320 nm-550 nm). .

The measured potentials *vs.* the Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale *via* the Nernst equation

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E^o_{Ag/AgCl} \quad (2)$$

where E_{RHE} is the converted potential vs. RHE, $E_{Ag/AgCl}$ is the experimental potential measured against Ag/AgCl reference electrode, and $E^o_{Ag/AgCl}$ is the standard potential of Ag/AgCl at 25 ^{o}C (0.1976 V).
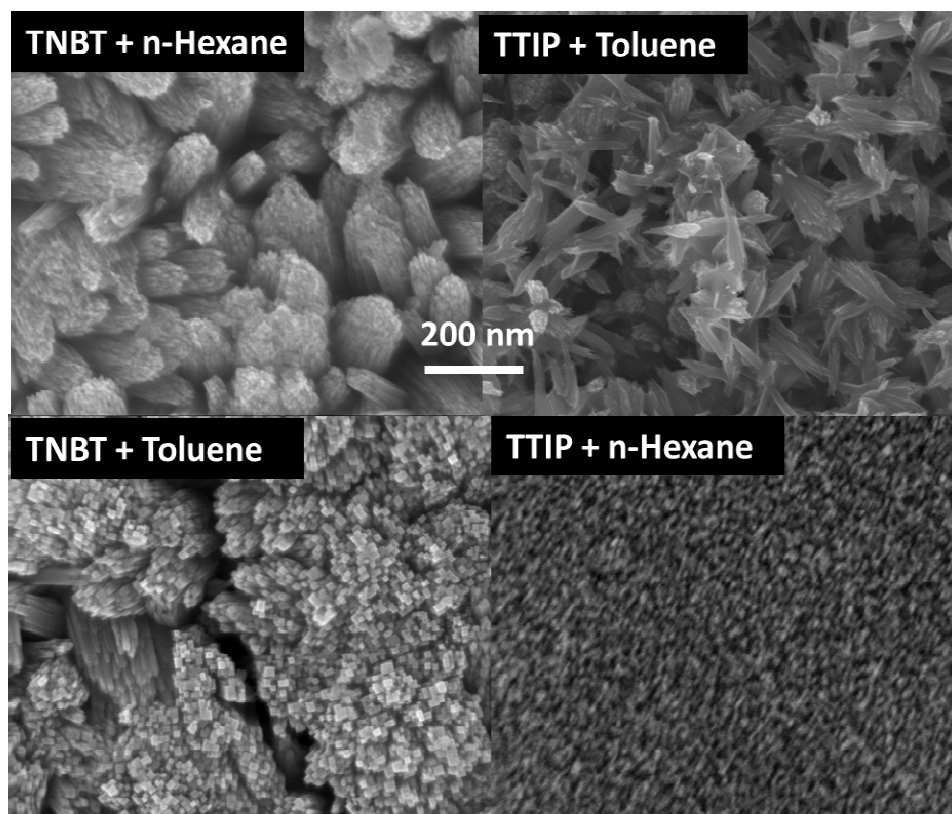
Figure S1. Morphology dependence of nanowire arrays on combinations of titanium precursors (*i.e.,* titanium tetra-isopropoxide (TTIP) and titanium (IV) tetra-n-butoxide (TNBT)) and non-polar solvents (*i.e.,* n-hexane and toluene). The scale bar applies to all the micrographs.
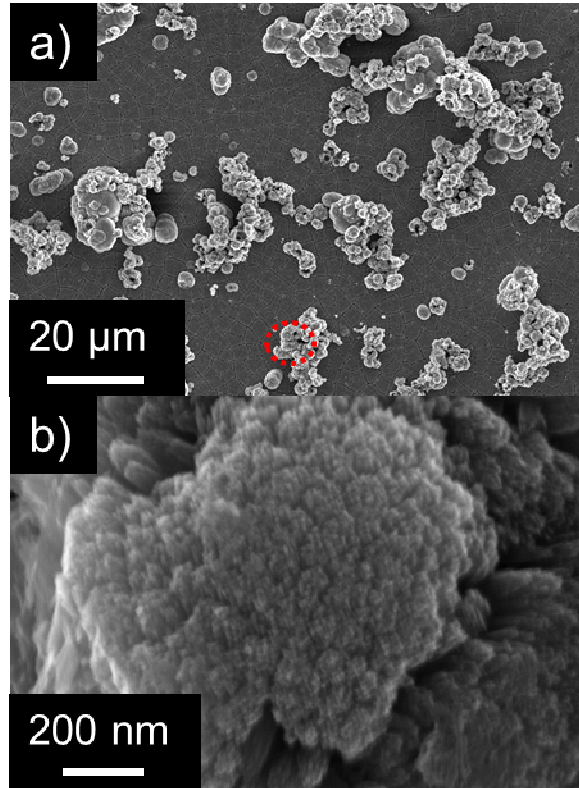
Figure S2. (a) Top-view SEM images of flower-like microparticles on top of the TiO$_2$ nanowire arrays and (b) the nanostructure of the flower-like particles (zoom-in view of the dotted circle in S2-a)
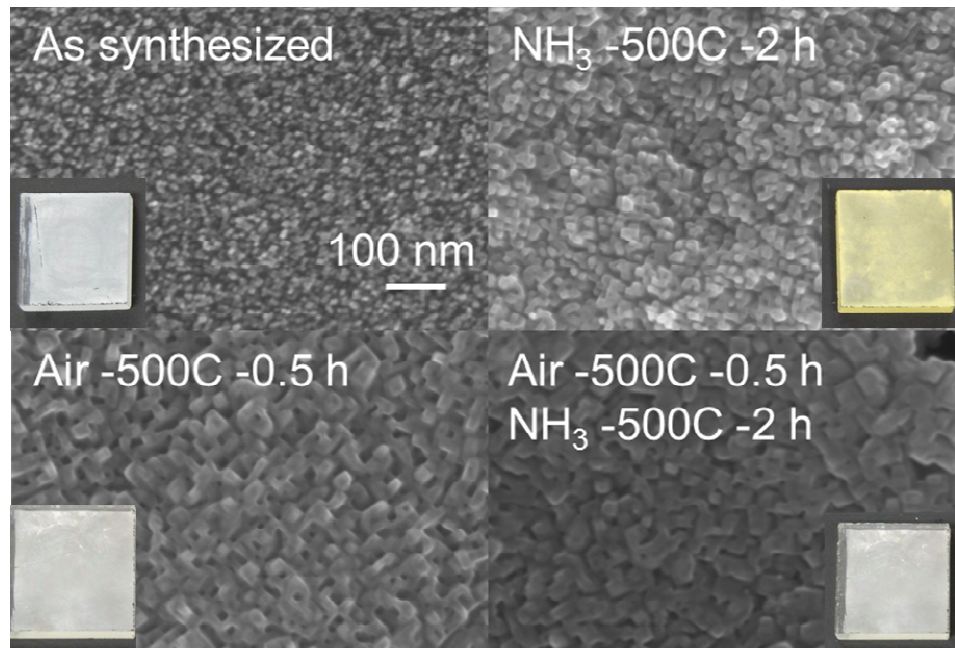
Figure S3. Top-view SEM image of TiO$_2$ nanowire arrays: as-synthesized film, film annealed in NH$_3$ at 500 ^{o}C for 2 hours, film annealed in air at 500 ^{o}C for 0.5 hours, and film annealed in air at 500 ^{o}C for 0.5 hours, followed by nitridation at 500 ^{o}C for 2 hours. The scale bar applies for all micrographs. The insets show the digital images of the corresponding films on FTO substrates (1.5 cm x 1.5 cm).
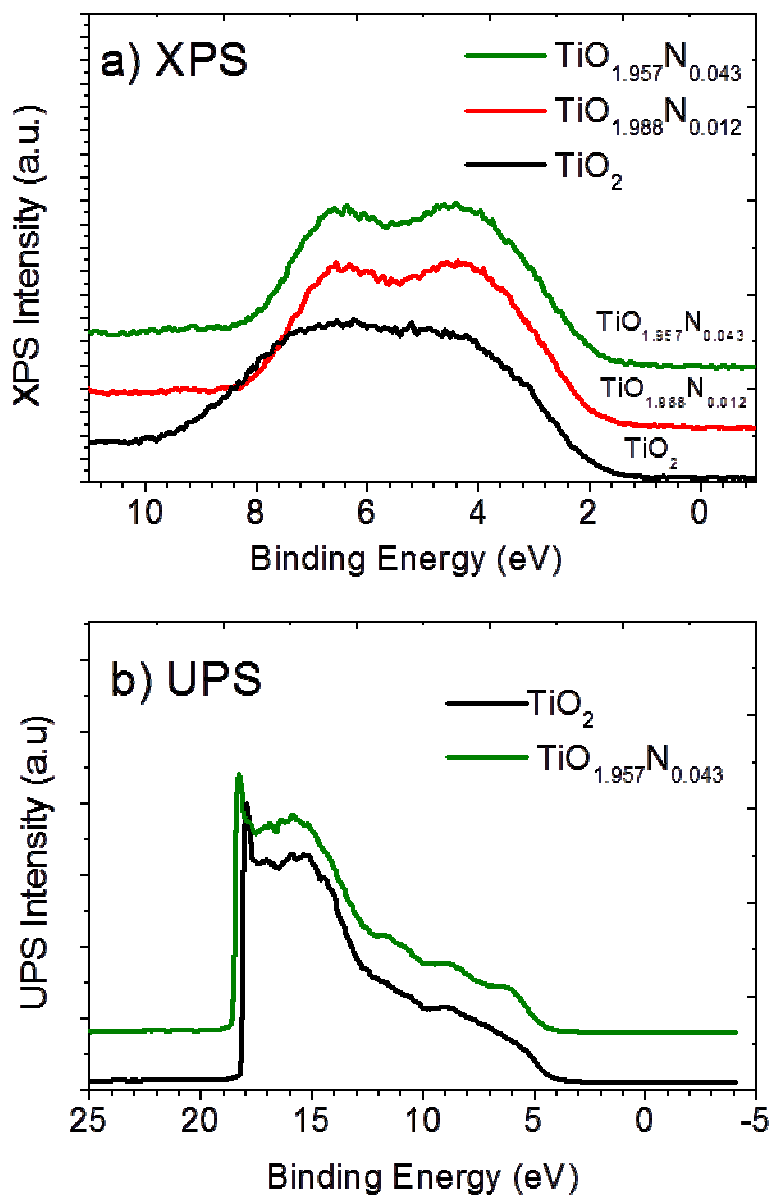
Figure S4. (a) XPS valence band spectra of the TiO_2, $TiO_{1.988}N_{0.012}$, and $TiO_{1.957}N_{0.043}$ samples and (b) UPS spectra of the TiO_2 and $TiO_{1.957}N_{0.043}$ samples. The UPS spectra were calibrated versus the Fermi edge of a polycrystalline Au foil.