

Supporting Information

Photoelectrochemical Study of Oxygen Deficient TiO₂ Nanowire Arrays with CdS Quantum Dot Sensitization

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Experimental Section

Synthesis

1. Rutile TiO₂ nanowires. The synthesis of rutile TiO₂ nanowire arrays was based on a reported hydrothermal method with slight modification.¹ 15 mL concentrated hydrochloric acid (36.5-38% by weight) was mixed with 15 mL deionized water under stirring, follow by the addition of 0.475 mL titanium n-butoxide. This precursor solution was poured into a 40 mL autoclave with a Teflon liner. A fluorine-doped tin oxide (FTO) glass substrate was cleaned and transferred into the autoclave with conducting side facing down. The autoclave was then heated at 150 °C for 5 h. After cool down to room temperature, the substrate was covered with a white film of TiO₂ nanowire arrays. The substrate was washed with deionized water, and then air dried. To obtain crystalline TiO₂, the substrate was calcined at 550 °C for 3 h in the air.

2. CdS QD sensitized TiO₂ nanowires. CdS quantum dots were deposited on TiO₂ nanowire arrays by a chemical bath deposition method.² 5 mL of 40 mM Cd(acetate)₂ dihydrate aqueous solution, 5 mL of 40 mM thiourea aqueous solution and 10 mL deionized water were mixed in a 25 mL vial. Then 0.1 mL of concentrated ammonium hydroxide was added into the solution mixture. TiO₂ sample was submerged in the solution at 55 °C for 20 min.

Photoelectrochemical Measurements

Linear sweep voltammograms were measured in a three-electrode electrochemical cell with an Ag/AgCl reference electrode and a platinum wire as counter electrode, and TiO₂ nanowire samples as working electrode, at a scan rate of 20 mV/s. 0.5 M Na₂SO₄ aqueous solution (pH=7) was used as electrolyte. For CdS QDs sensitized TiO₂ nanowires (CdS-TiO₂, CdS-H:TiO₂,

H:CdS-TiO₂), linear sweep voltammograms measurements were made in a two-electrode electrochemical cell with a platinum wire as counter electrode and nanowire sample as working electrode at a scan rate of 20 mV/s. The electrolyte used was a mixture of 0.25 M Na₂S and 0.35 M Na₂SO₃ aqueous solution (pH = 11.5). All the TiO₂ photoanodes were fabricated by attaching a copper wire onto the bare edge of FTO glass substrate via soldering a small piece of indium metal, and then sealing the FTO glass substrate and metal contact region with insulating epoxy resin. The exposed effective area for the TiO₂ working electrode is around 0.15-0.2 cm². A 150 W Xe lamp (Newport 6255) coupled with an AM 1.5 global filter (Newport 81094) was used as the light source. The intensity of the incident light was measured with a digital power-meter and was controlled at 100 mW/cm². Incident-photon-to-current-conversion-efficiencies (IPCE) measurements were collected by a CHI 660D electrochemical station with a simulated solar light source (Newport 69920, 1000 W xenon lamp), coupled with an infrared water filter (Oriel 6127) and aligned with a monochromator (Oriel Cornerstone 130 1/8 m). All PEC measurement were carried out with front side illumination. Electrochemical impedance was measured on CHI 660D using Impedance-potential technique at a frequency of 10000Hz in 0.5M Na₂SO₄ solution under dark. Mott-Schottky plots were generated from capacitances of TiO₂ in a potential range of -0.2V to 0.5V Vs. RHE.

Material Characterization

X-ray diffraction (XRD) spectra were measured at room temperature on a Rigaku Americas Miniflex Plus powder diffractometer from a 2θ angle of 20 to 70 degree with a step size of 0.04 degree at a rate of 1 degree/min. Scanning electron microscopy (SEM) images were collected by

a field-emission SEM (Hitachi S-4800 II). X-ray Photoelectron Spectroscopy (XPS) analysis was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) using Mg-monochromatic X-ray at a power of 25 W with an X-ray-beam diameter of 10 mm, and a pass energy of 29.35 eV. The pressure of analyzer chamber was maintained below 5×10^{-8} Pa during the measurement. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.

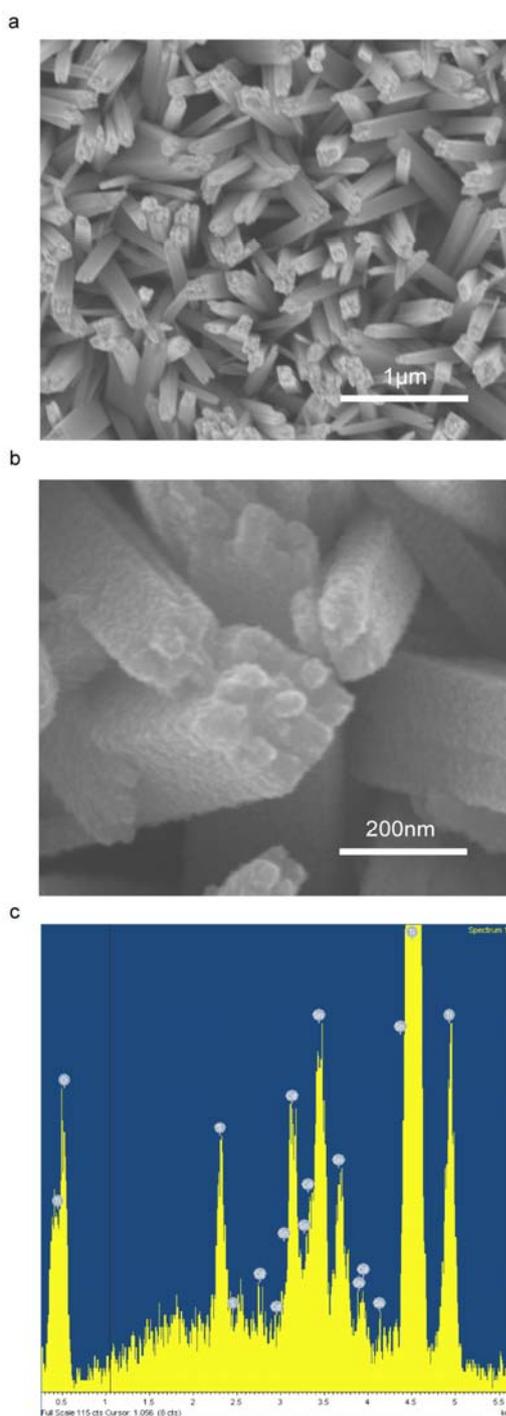


Figure S1. SEM images of (a) TiO₂ and (b) CdS QD sensitized TiO₂ nanowire arrays prepared on a FTO substrate. (c) EDX spectrum of CdS QD sensitized TiO₂ nanowire arrays.

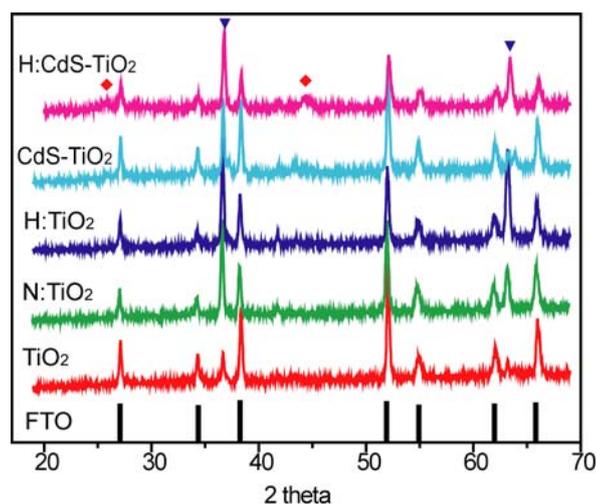


Figure S2. XRD spectra collected from pristine TiO₂, N-doped TiO₂ (N:TiO₂), hydrogen-treated TiO₂ (H:TiO₂), and CdS QD sensitized TiO₂ (CdS-TiO₂) nanowires. XRD peak positions of FTO substrate are provided as reference (black lines). The two diffraction peaks centered at 2θ angles of 36.5° and 63.2° (marked by ▼), are identified in the XRD spectra of all TiO₂ samples, which can be indexed as tetragonal rutile TiO₂ (JCPDS, No. 88-1175). Two diffraction peaks centered at 2θ angles of 26.4° and 44° (marked by ◆), are indexed as hexagonal CdS (JCPDS, No. 41-1049). The diffraction peaks of CdS are missing for CdS-TiO₂ nanowire sample possibly due to the poor crystallinity of CdS QDs on TiO₂ nanowires before thermal annealing.

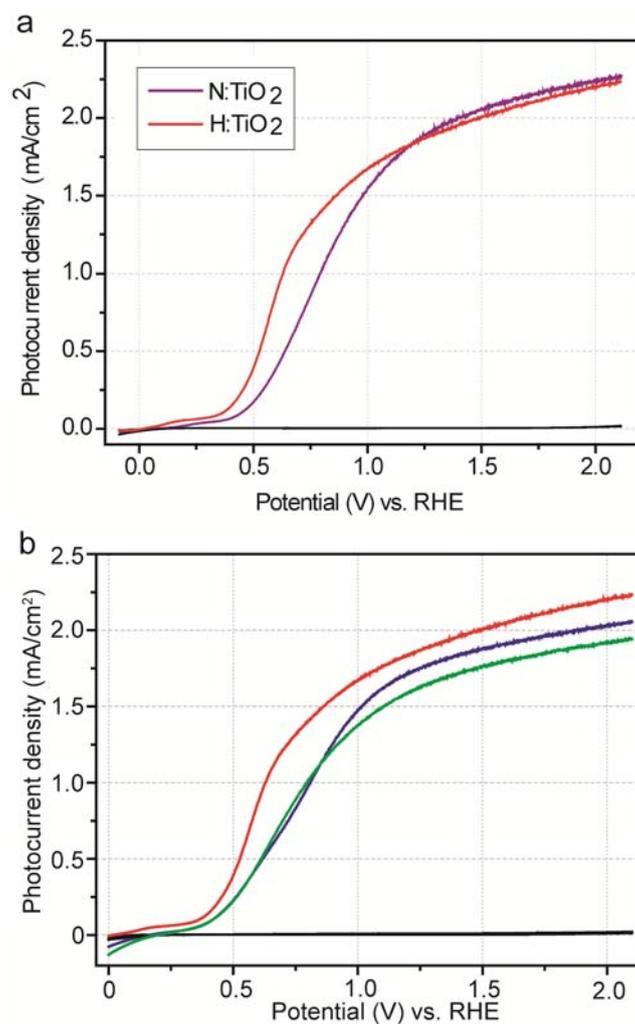


Figure S3. (a) Comparison of linear sweep voltammograms of optimized N:TiO₂ (annealed in ammonia for 50 min) and H:TiO₂ nanowires. (b) Linear sweep voltammograms of H:TiO₂ nanowires annealed in ammonia atmosphere for 0, 15 and 50 min, respectively. All linear sweeps were measured at a scan rate of 20 mV/s under 100 mW/cm² white light illumination.

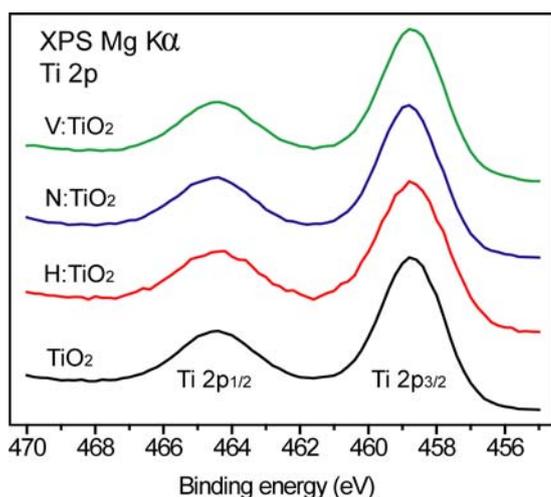


Figure S4. Ti 2p XPS spectra of pristine TiO₂, H:TiO₂, N:TiO₂ and V:TiO₂ nanowires.

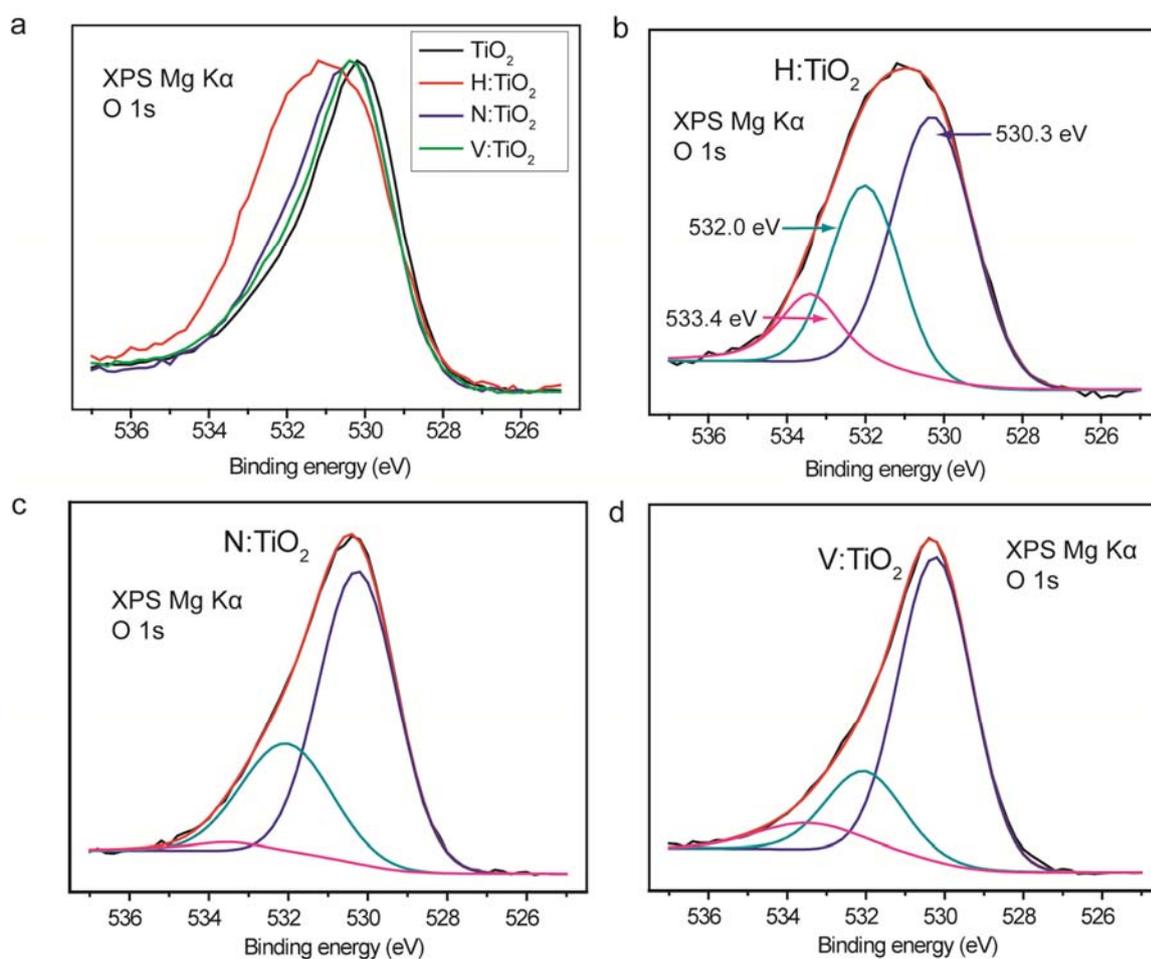


Figure S5. (a) Normalized O 1s XPS spectra of the pristine TiO₂, H:TiO₂, N:TiO₂ and V:TiO₂ nanowires. O 1s XPS spectra of (b) H:TiO₂ nanowires, (c) N:TiO₂ nanowires, and (d)

V:TiO₂ nanowires. (b-d) The broad peaks are deconvoluted into three peaks. The black curve is the experimental result. The red curve is the summation of the synthetic peaks centered at 530.3 (blue curve), 532.0 (green curve) and 533.4 eV (purple curve).

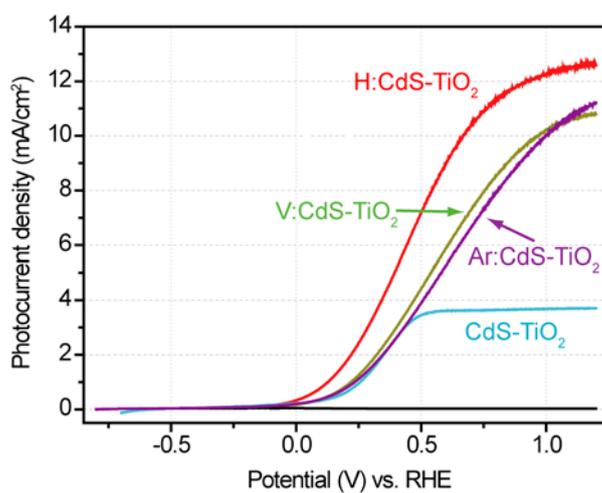


Figure S6. Linear sweep voltammograms of the pristine CdS-TiO₂, V:CdS-TiO₂, Ar:CdS-TiO₂, and H:CdS-TiO₂ nanowires, measured at a scan rate of 20 mV/s under 100 mW/cm² white light illumination.

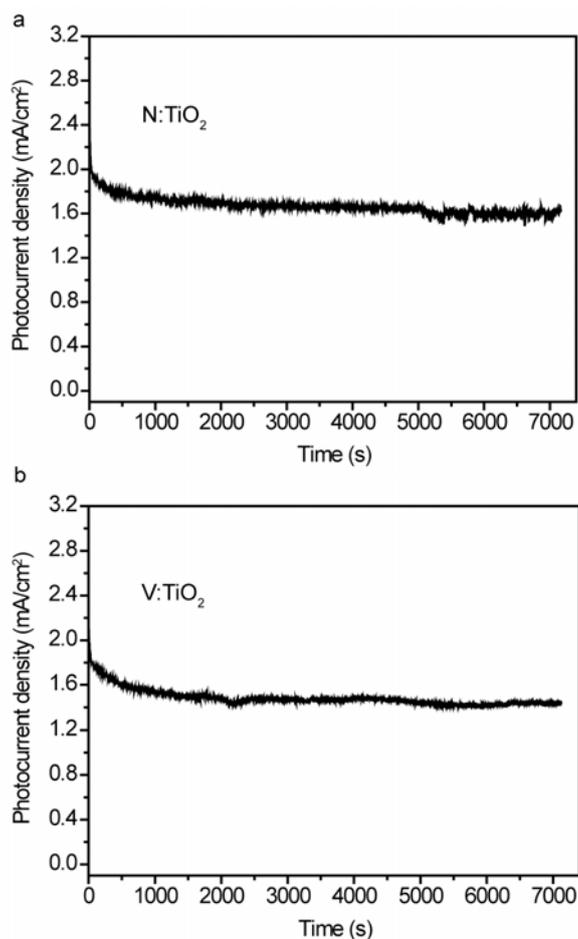


Figure S7. The photocurrent-time profiles of (a) N:TiO₂ and (b) V:TiO₂ nanowire samples, measured at a potential of 1.23 V vs. RHE under 100 mW/cm² white light illumination.

References

1. B. Liu and E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985-3990.
2. R. B. Kale and C. D. Lokhande, *J. Phys. Chem. B*, 2005, **109**, 20288-20294