Supporting information for

Efficient Electrochemical Reduction of Nitrobenzene by Defect-Engineered TiO_{2-x} Single Crystals

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This supporting information contains 15-page document, including 1-page description, 1 table, 11 figures, 1 scheme and this cover page.

Characterization

Morphology and structure were characterized by field-emission scanning electron microscope (FE-SEM, SIRION200, FEI Co., the Netherlands), high-resolution transmission electron microscope and selected-area electron diffraction (HRTEM/SAED, JEM-2100, JEOL Co., Japan). Surface area was measured with a Builder 4200 instrument (Tristar II 3020M, Micromeritics Co., USA). Crystal structure was analyzed by X-ray diffraction (XRD, X'Pert, PANalytical BV, the Netherlands). The electronic state were measured by electron spin-resonance spectroscopy (ESR, JES-FA200, JEOL Co., Japan). Diffuse reflectance spectra (DRS) were measured on a UV/Vis spectrophotometer (UV 2550, Shimadzu Co., Japan). Chemical compositions were measured by X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin-Elmer Inc., USA). The infrared spectra were recorded between 4000 and 400 cm^{-1} with a FTIR spectrometer (Magna-IR 750, Nicolet Instrument Co., USA) using a potassium bromide disc technique. Water contact angle was measured by a contact angle analyzer (JC2000A, Powereach Co., Shanghai, China).

Table S1 Comparison of HER specific activities of different TiO_2 catalysts in nitrogen-saturated 0.5 M KOH aqueous solution (scan rate: 50 mV s^{-1}, no stirring)

HER catalyst	specific activity (η, V/SCE)			
	-25 μA cm^{-2}	-50 μA cm^{-2}	-75 μA cm^{-2}	-100 μA cm^{-2}
TiO_2 SC	~ -0.32	~ -0.60	~ -1.02	~ -1.24
TiO_{2-x} SC@300°C	~ -0.32	~ -0.61	~ -0.97	~ -1.16
TiO_{2-x} SC@350°C	~ -0.44	~ -0.81	~ -1.16	~ -1.34
TiO_{2-x} SC@400°C	~ -0.44	~ -0.93	~ -1.24	~ -1.40
TiO_{2-x} SC@450°C	~ -0.47	~ -0.87	~ -1.24	~ -1.48
TiO_{2-x} SC@500°C	~ -0.43	~ -0.87	~ -1.22	~ -1.42
TiO_{2-x} SC@600°C	~ -0.34	~ -0.76	~ -1.19	~ -1.40
TiO_{2-x} SC@700°C	~ -0.35	~ -0.68	~ -1.14	~ -1.29
TiO_{2-x} SC@800°C	~ -0.40	~ -0.73	~ -1.18	~ -1.36

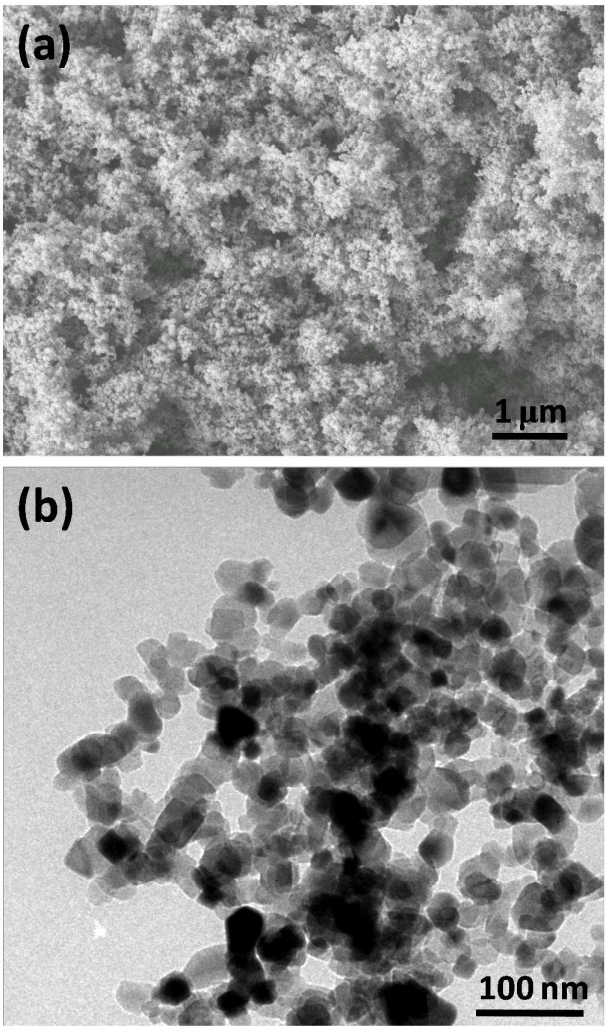


Fig. S1 SEM and TEM images (a and b) of commercial {101}-exposed TiO_2 PCs (Degussa P25 benchmark).

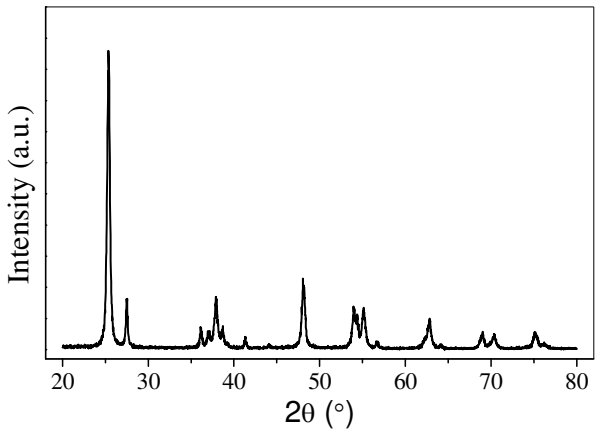


Fig. S2 XRD pattern of commercial {101}-exposed TiO_2 PCs (Degussa P25 benchmark).

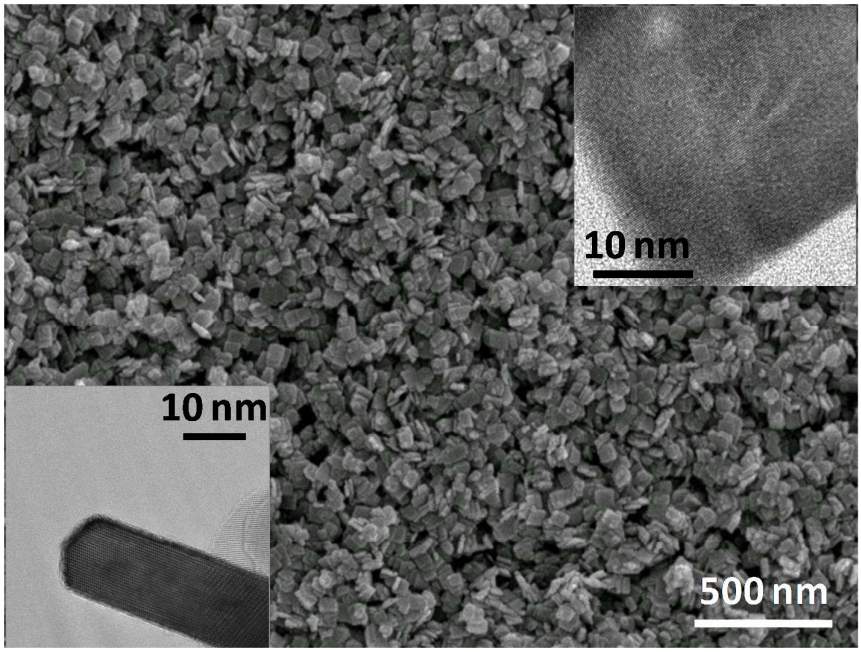


Fig. S3 SEM image of pristine {001}-exposed TiO_2 SCs. The insets show its corresponding TEM and HRTEM images, respectively.

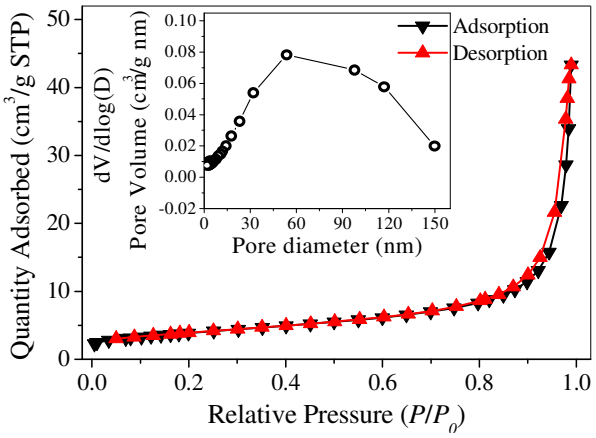


Fig. S4 Nitrogen sorption-desorption isotherms of the pristine {001}-exposed TiO_2 SCs.

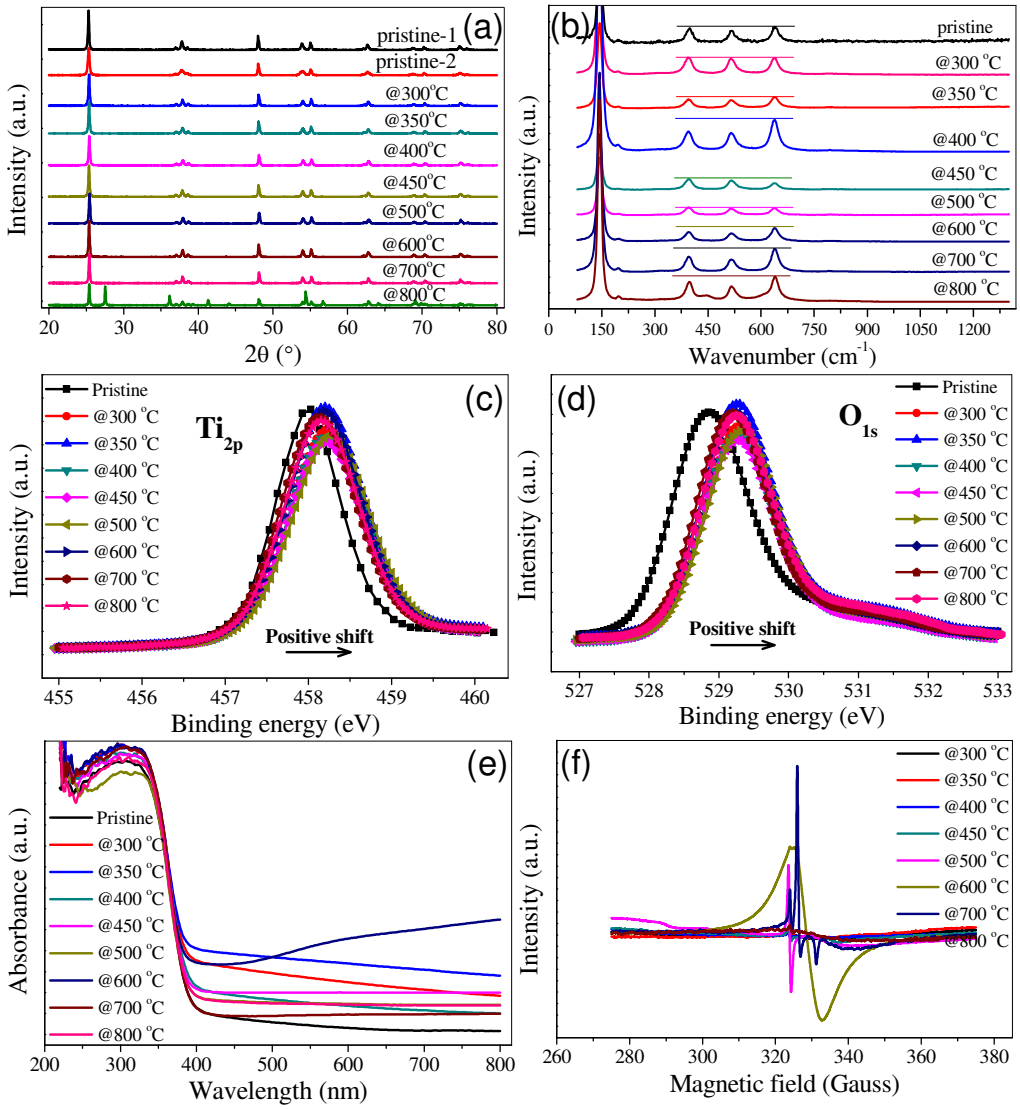


Fig. S5 Structural properties of the TiO_2 SCs and TiO_{2-x} SCs prepared at different reductive temperatures.

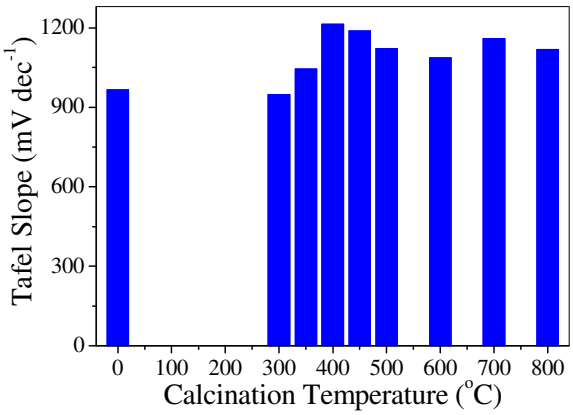


Fig. S6 Tafel slopes of the different TiO_2 catalysts calculated from their corresponding HER curves in nitrogen-saturated 0.5 M KOH aqueous solution (scan rate: 50 mV s^{-1}, no stirring).

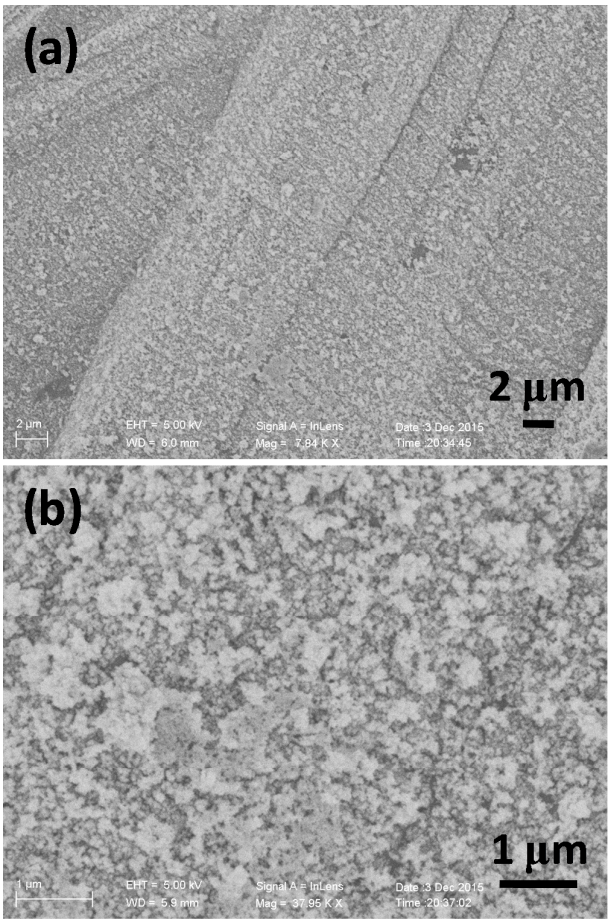


Fig. S7 SEM images of noble metallic Pd reference on carbon substrate.

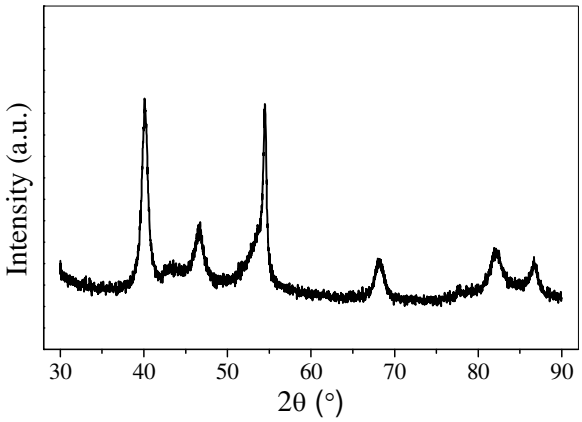


Fig. S8 XRD pattern of noble metallic Pd reference on carbon substrate.

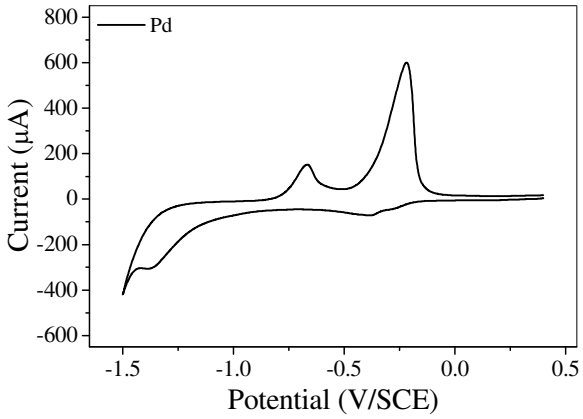


Fig. S9 CV curve of NB on noble metallic Pd reference on carbon substrate.

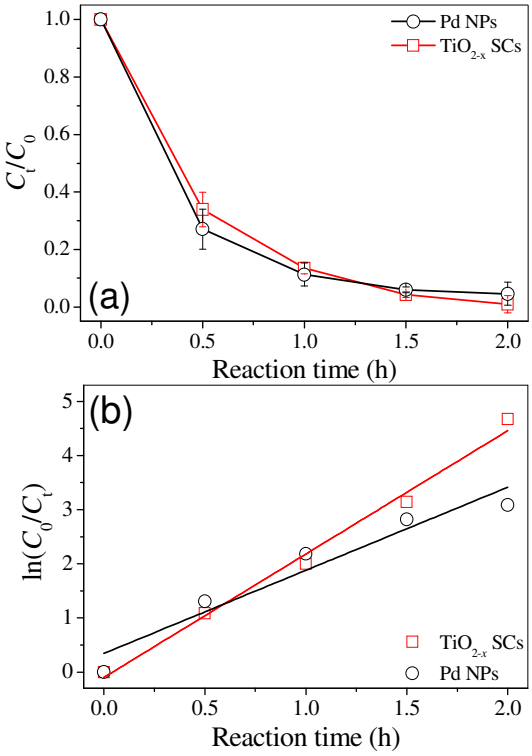


Fig. S10 Electrochemical reduction of NB on defective TiO_{2-x} SCs at 400 °C and Pd reference on carbon substrate under identical conditions. Electrolysis conditions: cathodic bias (-1.2 V/SCE), NB concentration (300 mg L^{-1}), NB solution volume (80 ml), stirring rate (500 rpm) and electrolysis time (2.0 h).

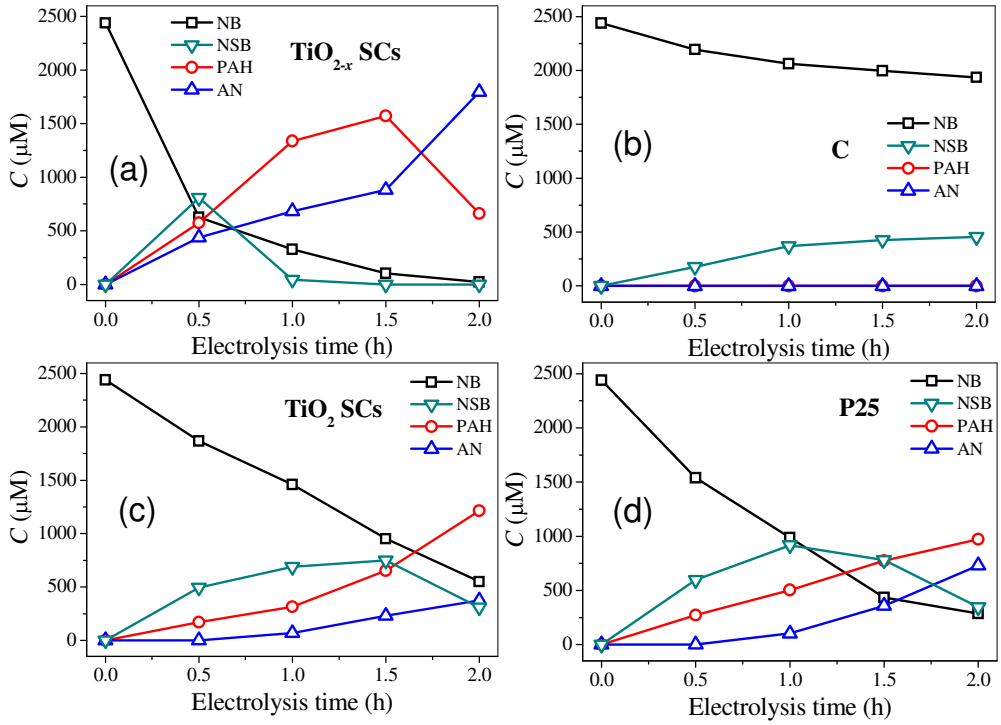
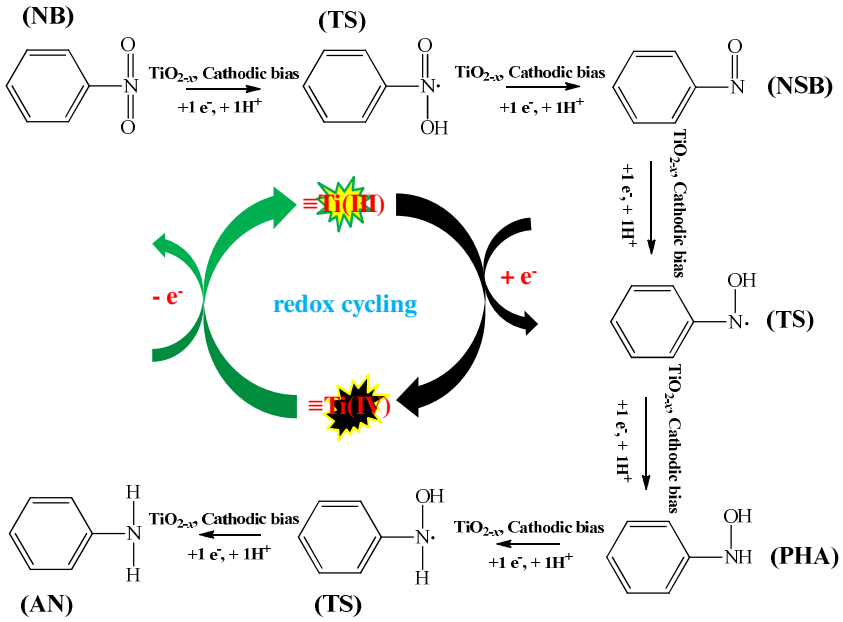


Fig. S11 Conversion of the main intermediates from the electrochemical reduction of NB on the TiO_{2-x} SCs prepared at 400 °C and three different references. Electrolysis conditions: cathodic bias (-1.2 V/SCE), NB concentration (300 mg L^{-1}), NB solution volume (80 ml), stirring rate (500 rpm) and electrolysis time (2.0 h).



Scheme S1 Defect-centered NB reduction pathway on the defective TiO_{2-x} SCs. The mixed-valence Ti species cycling between +3 and +4 states at oxygen vacancy sites provide as an efficient electron shuttle and transport route for reductive electrons migrated from carbon cathode to TiO_{2-x} SCs and then to protons to generate active hydrogen ($\cdot H/\cdot H^-$). TS represents transition state.