

Supporting Information

Modulating the photocatalytic redox preferences between anatase TiO₂ {001} and {101} surfaces

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Materials synthesis

Anatase TiO₂ crystals coexposed with {001} and {101} facets were prepared by a typical hydrothermal method with Ti(SO₄)₂ as precursor and HF as morphology control agent. All of the reagents were of analytical grade and were used without further purification. Briefly, 0.21 g of Ti(SO₄)₂ was dissolved in 50 mL of HF aqueous solution (0.184 mol L⁻¹) under magnetic stirring. After 1 h of stirring, the mix solution was transferred to a Teflon-lined autoclave and the following hydrothermal reaction was carried out at 180 °C for 24 h. After the reaction, to inhibit the undesirable facet corrosion in natural cooling process, the Teflon-lined autoclave is rapidly cooled down to room temperature by water-cooling. Next, the white precipitate was separated by centrifugation and washed with deionized water for five times. To eliminate the surface F ions, the obtained product was calcinated at 450 °C for 2 h.^{1,2}

Photo-deposition

Photocatalytic oxidizing deposition of Fe₂O₃ and MnO_x. For the deposition of Fe₂O₃ by photooxidizing Fe²⁺ ions, 20 mg of TiO₂ powder, 0.5 g of NaIO₃ as electron acceptor and 1 mL of 17.8 mol L⁻¹ FeSO₄ aqueous solution as the precursor of Fe₂O₃ were mixed in 50 mL of deionized water under magnetic stirring for 30 min. The initial pH value of mixed solution containing FeSO₄ was 5.4. At ambient temperature, no reaction was observed under dark condition. However, when the mixed solution was irradiated by a 300 W Xe lamp equipped with infrared filter under continuous stirring, the color of the suspensions containing FeSO₄ were changed from aqua to yellow. After 3 h reaction, the yellow precipitate was separated by centrifugation and washed with deionized water for five times. Finally, the obtained product was dried at 60 °C for 6 h. The procedure for deposition of MnO_x by photooxidizing Mn²⁺ ions

was identical to that for Fe_2O_3 deposition, except that the FeSO_4 aqueous solution was replaced by 1 mL of 18.2 mol L^{-1} MnSO_4 aqueous solution as the precursor of MnO_x and the initial pH of the suspension in this case is 5.7. Brown powder was obtained after drying at $60 \text{ }^\circ\text{C}$.

For comparison, Fe^{2+} ions were directly thermally oxidized on TiO_2 . For this purpose, the mixed solution containing TiO_2 photocatalysts, FeSO_4 and NaIO_3 is heated to $90 \text{ }^\circ\text{C}$. The heating treatment can promote the direct reaction between Fe^{2+} ions and NaIO_3 in the absence of TiO_2 photoexcitation. After 3 h thermal reaction, the yellow precipitate was collected.

Photocatalytic reducing deposition of Fe_2O_3 and MnO_x . For the deposition of Fe_2O_3 by photoreducing FeO_4^{2-} ions, 20 mg of TiO_2 powder and 1 mL of 17.8 mol L^{-1} K_2FeO_4 aqueous solution were mixed in 50 mL of deionized water under magnetic stirring for 30 min. The initial pH value of mixed solution containing K_2FeO_4 was 10.2. For the photocatalytic reduction of FeO_4^{2-} ions, solvent H_2O acts as electron donor. Under Xe lamp irradiation, the color of the suspensions containing K_2FeO_4 was changed from carnation to yellow. After 3 h reaction, the precipitate was collected. To investigate the photocatalytic redox preferences of deprotonated TiO_2 {001} and {101} surfaces, 50 mL of deionized water in above experiments was replaced by 50 mL of 0.05 or 0.5 mol L^{-1} NaOH aqueous solution. The pH values of corresponding mixed solutions were 12.5 and 13.5, respectively. The following procedures were the same with above photocatalytic experiments. For the deposition of MnO_x by photoreducing MnO_4^- ions, the K_2FeO_4 aqueous solution were replaced by 1 mL of 18.2 mol L^{-1} KMnO_4 aqueous solution as the precursor of MnO_x , and the other precedures were identical to that for Fe_2O_3 deposition. In this experiment, the initial pH of the suspension is 5.6 and the color of the suspensions was changed from purple to brown during the irradiation.

For comparison, the thermodeposition of FeO_4^{2-} ions was also carried out by heating the reacting suspension at $90 \text{ }^\circ\text{C}$ for 3 h in deionized water or 0.5 mol L^{-1} NaOH aqueous solution.

Catalyst characterization

The crystalline phase of the prepared sample was characterized by the X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer (Rigaku, Japan) using Cu K α radiation at a scan rate of 0.05° 2 θ s⁻¹. The high-resolution transmission electron microscopy (HRTEM) analysis were conducted by a JEM-2100F electron microscope (JEOL, Japan) with a 200 kV accelerating voltage. The morphology of samples was obtained from an S-4800 field emission scanning electron microscopy (FESEM) (Hitachi, Japan) at an acceleration voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi electron spectrometer with Mg K α (1253.6 eV) source. All binding energies are referenced to the C 1s peaks at 284.8 eV from the adventitious carbon.

Theoretical calculation

The surface chemical states of anatase TiO₂ {001} and {101} surfaces in aqueous solution were investigated by the density-functional-theory-based molecule dynamics (DFT-MD) method. All calculations were performed on the Vienna Ab-initio Simulation Package (VASP). 2 × 2 supercell with 9 O-Ti-O layers and 2 × 1 supercell with 8 O-Ti-O layers were used to simulate the TiO₂ {001} and {101} surfaces, respectively (Fig. S1). The interaction between adjacent atom slabs was eliminated by the vacuum slab with thickness of 20 Å. The vacuum slabs on TiO₂ {001} and {101} surfaces were filled with 34 and 48 of H₂O molecules, respectively (Fig. 1a and 1c). The density of H₂O molecules in the vacuum slabs is approximate to that of liquid water (1 g cm⁻³).

The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange-correlation function. The interaction between valence electrons and the ionic core was described by the PAW pseudo-potential. The plane-wave basis with energy cutoff of 450 eV was applied to the DFT-MD calculations. Considering the computational cost, the DFT-MD calculations were performed at the Γ -point only. The convergence threshold for total energy was set to 1.0 × 10⁻⁵ eV. The built models were equilibrated at a temperature of 300 K, similar to the common experimental conditions. The time step was set to 1 fs and 5000 steps was required. After the equilibration, the obtained models were used to calculate the projected density of state (PDOS) plots. The cutoff energy of 450 eV and the Monkhorst-Pack k-point mesh of 4 × 4 × 1 were adopted for the PDOS calculations of TiO₂ {001} and {101} surfaces. To simulate the surface deprotonation process, the 4 water molecules (as the same number as the surface Ti_{5c} sites) were replaced by OH⁻ ions, and the corresponding number of Na⁺ ions were also placed around the OH⁻ ions to keep the electroneutrality of the slabs. By this way, the water molecules are formally replaced by NaOH (Fig. 1b and 1d). The deprotonation energy (E_{deH}) of H₂O molecules adsorbed on TiO₂ {001} and {101} surfaces is calculated by following Equation (1).³

$$E_{\text{deH}} = E(\text{Ti-H}_2\text{O}) + n \times E(\text{NaOH-H}_2\text{O}) - E(\text{Ti-NaOH}) - E(\text{H}_2\text{O}) \quad (1)$$

where $E(\text{Ti-H}_2\text{O})$ is the total energy of H₂O-adsorbed TiO₂ surface, $E(\text{NaOH-H}_2\text{O})$ is

the total energy of NaOH-contained water group, $E(\text{Ti-NaOH})$ is the total energy of NaOH-adsorbed TiO_2 surface and $E(\text{H}_2\text{O})$ is the total energy of water group. The water group contains 30 H_2O molecules in the cubic box of $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$, close to a density of liquid water (1 g cm^{-3}). For NaOH-contained water group, 29 H_2O molecules, one Na^+ ion and one OH^- ion are located in one cubic box of $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$. The $E(\text{H}_2\text{O})$ and $E(\text{NaOH})$ were obtained from the DFT-MD simulations of pure and NaOH-contained water groups. The DFT-MD simulations of pure and NaOH-contained water groups share same parameter setting with those of TiO_2 surfaces above. After the equilibration, the obtained energies of models were used as the $E(\text{H}_2\text{O})$ of water group and the $E(\text{NaOH})$ of NaOH-contained water group, respectively.

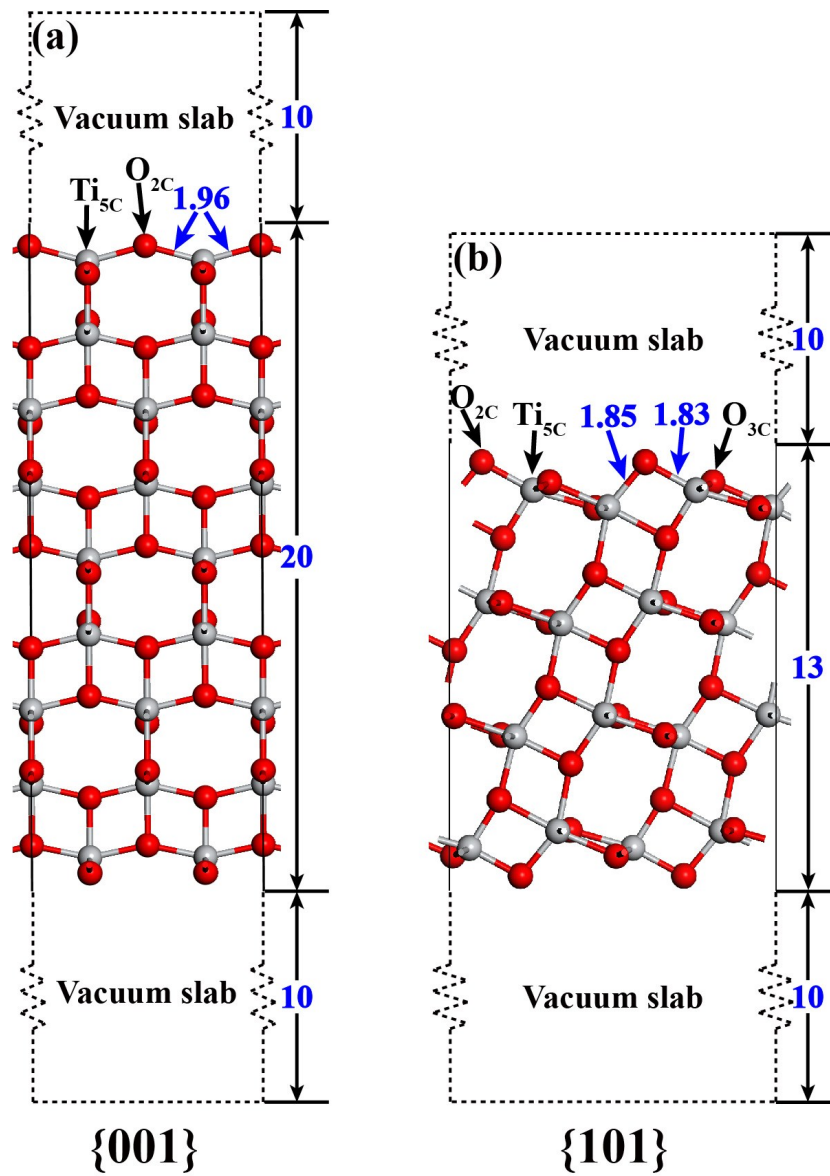


Fig. S1. Optimized geometry structures of TiO_2 (a) $\{001\}$ and (b) $\{101\}$ surfaces.

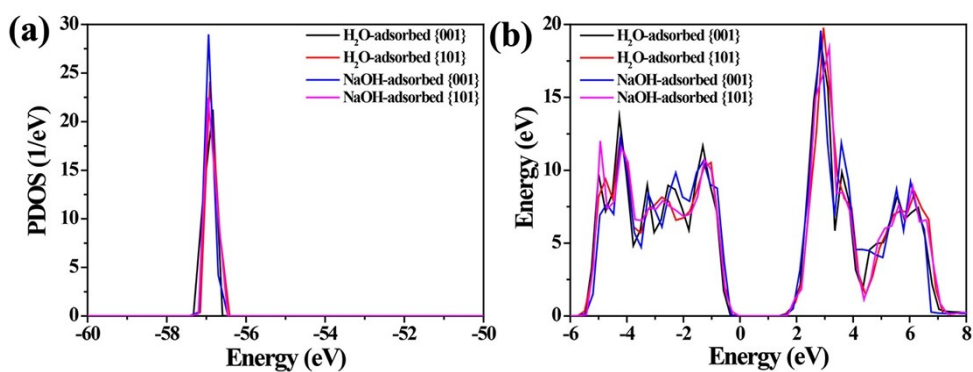


Fig. S2. The PDOS plots of middle O-Ti-O layer in H₂O/NaOH-adsorbed TiO₂ {001} and {101} surfaces: (a) Ti 3d states and (b) VB/CB states.

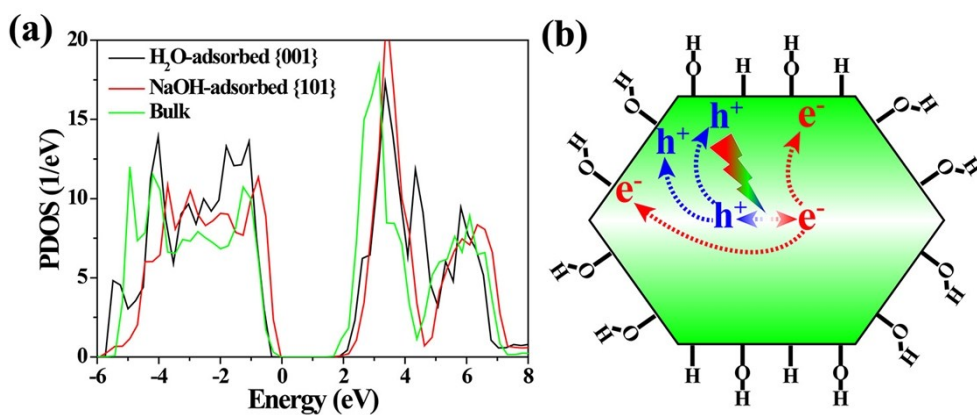


Fig. S3. (a) The PDOS plots of outmost O-Ti-O layer in H₂O-adsorbed TiO₂ {001} and NaOH-adsorbed TiO₂ {101} surfaces and (b) the corresponding charge-transfer mechanism.

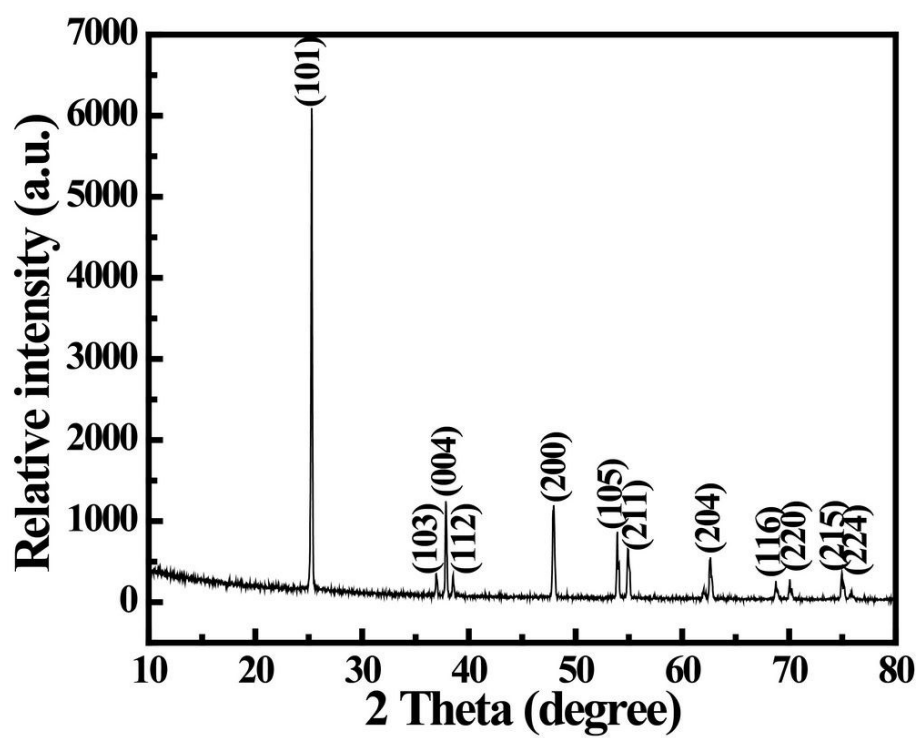


Fig. S4. XRD pattern of prepared sample. The XRD pattern of prepared sample is assigned to anatase TiO₂ (JCPDS standard card #71-1167).

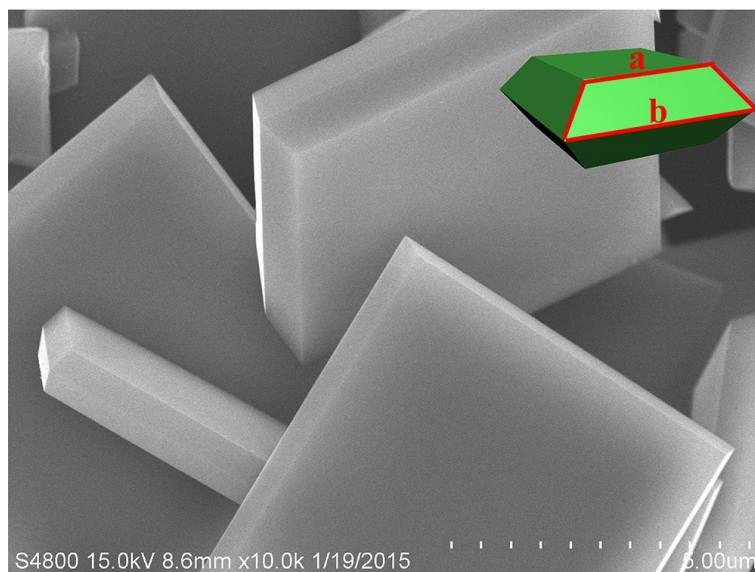


Fig. S5. FESEM image of prepared TiO₂ exposed with {001} and {101} facets. The area percentage of {001} facets on prepared TiO₂ ranges from 69.8% to 73.9% with average percentage of 71.7%, which are calculated by formulas: $S_{001}\% = \cos\theta / (\cos\theta + b^2/a^2 - 1)$ and $S_{101}\% = 1 - S_{001}\%$.⁴ Here θ is the theoretical value (68.3°) of angle between the {001} and {101} facets of anatase TiO₂. As shown in the inset above, two independent parameters a and b represent the lengths of the side of the square {001} truncation facets and the side of the bipyramid, respectively.

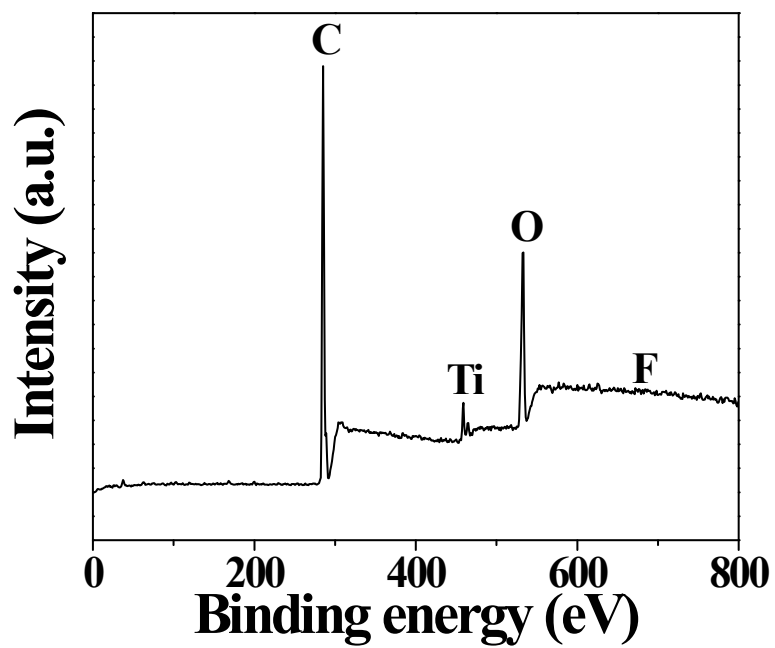


Fig. S6. XPS spectra of prepared TiO_2 . The XPS spectrum shows no peaks at the region of F element, confirming that the surface F species on TiO_2 surface are effectively removed by 450 °C calcination treatment

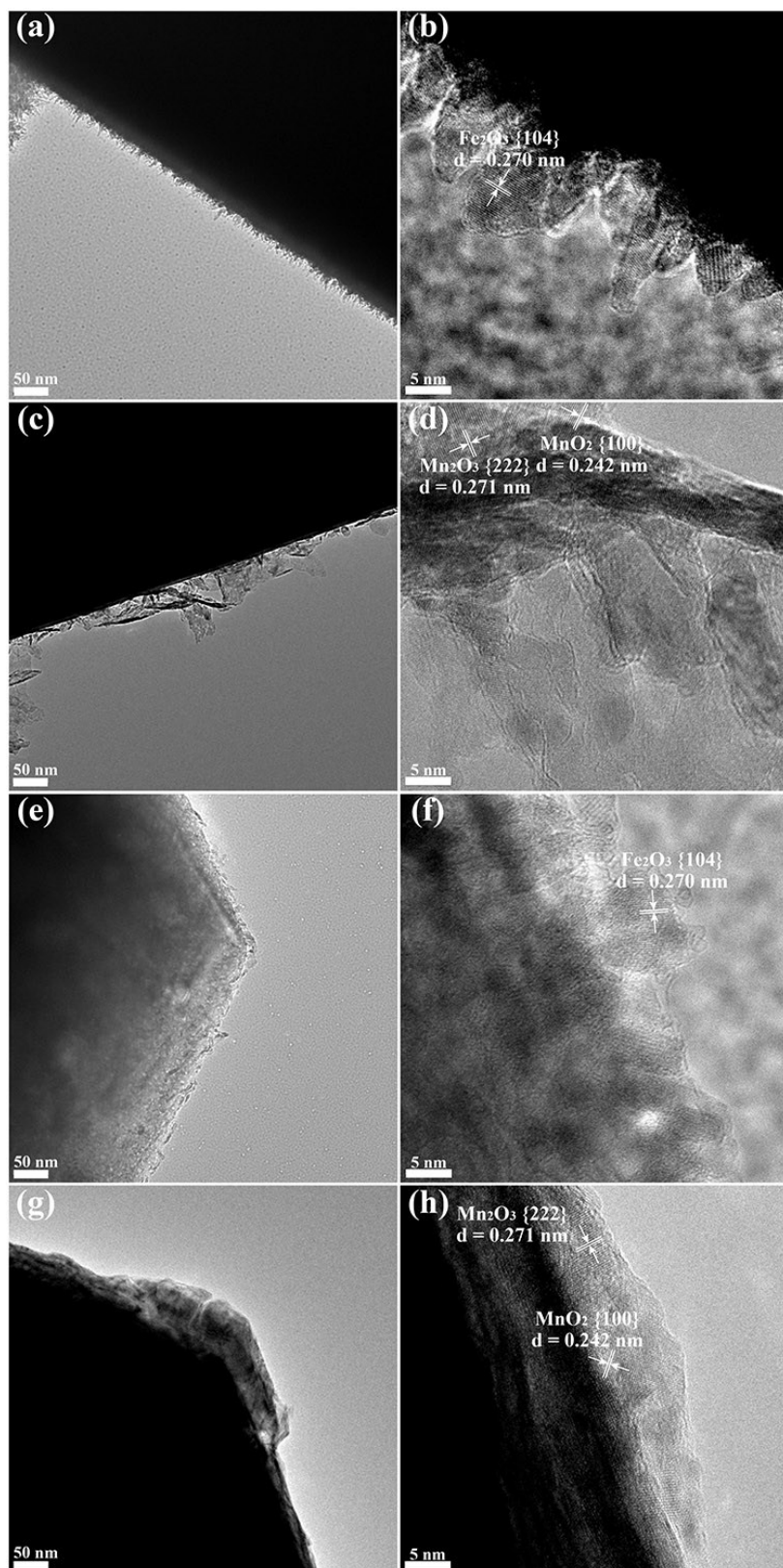


Fig. S7. HRTEM images of TiO_2 with metal oxides deposited: (a and b) $\text{Fe}_2\text{O}_3/\text{TiO}_2$ with Fe^{2+} ions as Fe source, (c and d) $\text{MnO}_x/\text{TiO}_2$ with Mn^{2+} ions as Mn source, (e and f) $\text{Fe}_2\text{O}_3/\text{TiO}_2$ with FeO_4^{2-} ions as Fe source and (g and h) $\text{MnO}_x/\text{TiO}_2$ with MnO_4^- ions as Mn source. HRTEM images confirm the formation of rhombohedral Fe_2O_3 and MnO_x (cubic Mn_2O_3 and hexagonal MnO_2).

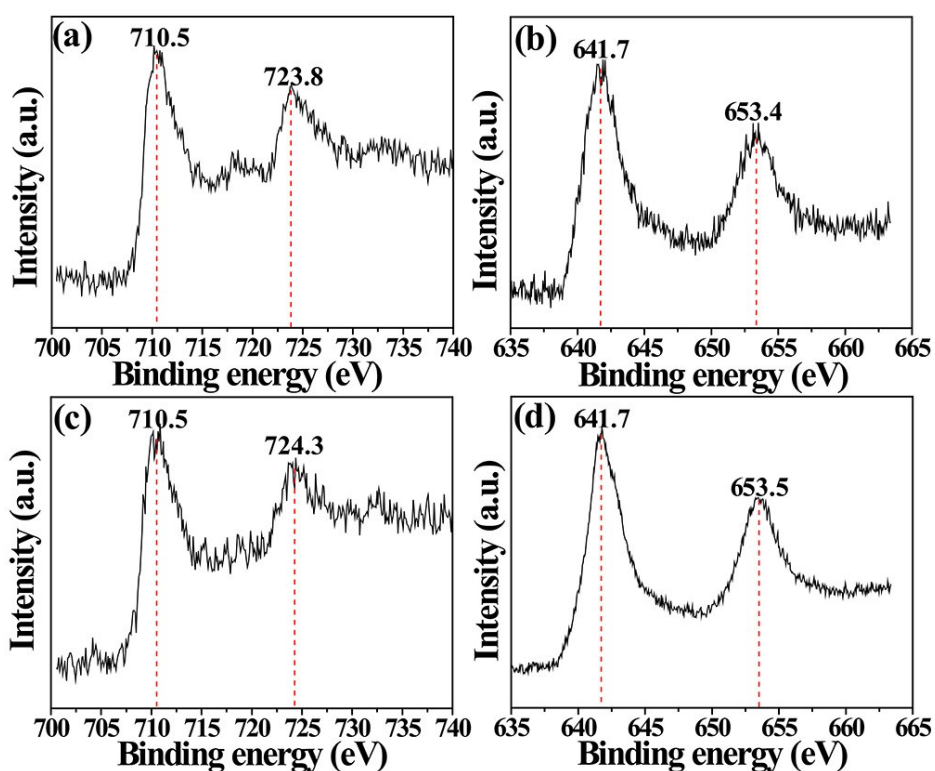


Fig. S8. XPS spectra of samples with metal oxide deposited: (a) Fe₂O₃/TiO₂ with Fe²⁺ ions as Fe source, (b) MnO_x/TiO₂ with Mn²⁺ ions as Mn source, (c) Fe₂O₃/TiO₂ with FeO₄²⁻ ions as Fe source and (d) MnO_x/TiO₂ with MnO₄⁻ ions as Mn source.

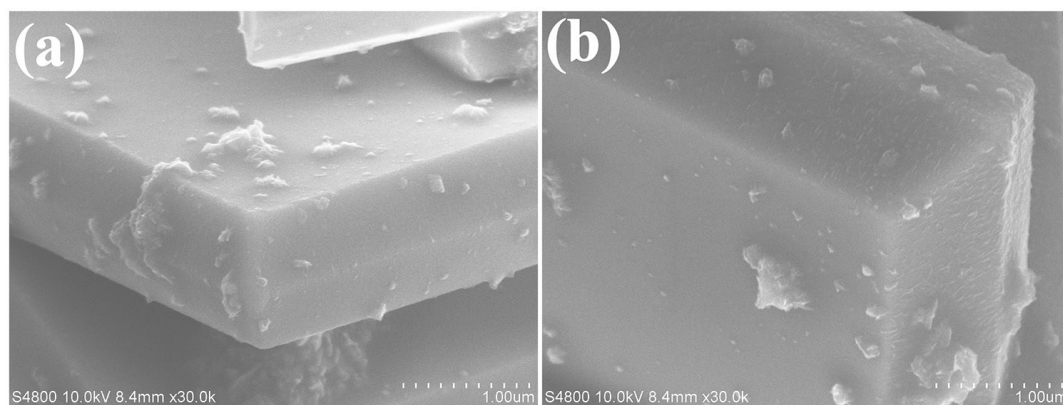


Fig. S9. FESEM images of TiO₂ with metal oxides deposited by conventional chemical reaction: (a) Fe₂O₃/TiO₂ with Fe²⁺ ions as Fe source and (b) Fe₂O₃/TiO₂ with FeO₄²⁻ ions as Fe source.

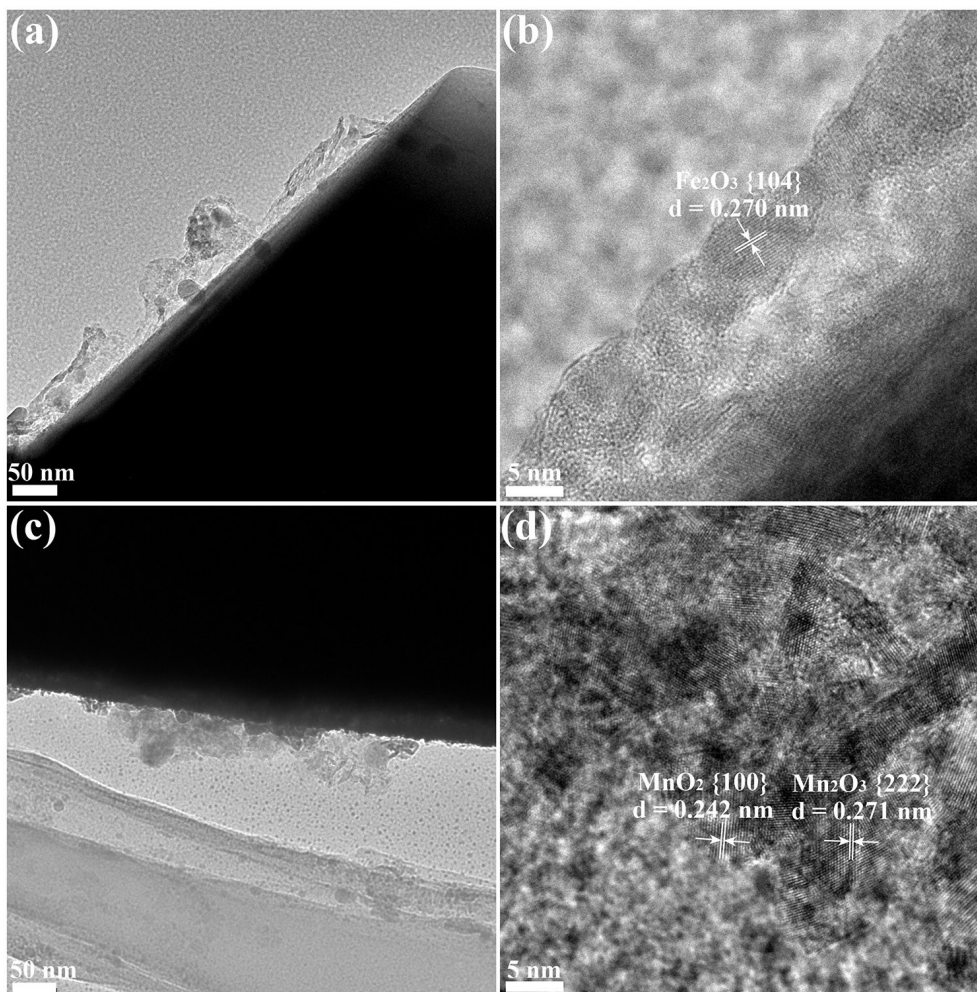


Fig. S10. HRTEM images of the Fe₂O₃/TiO₂ and MnO_x/TiO₂ samples prepared by photo-reduction at pH = 13.5.

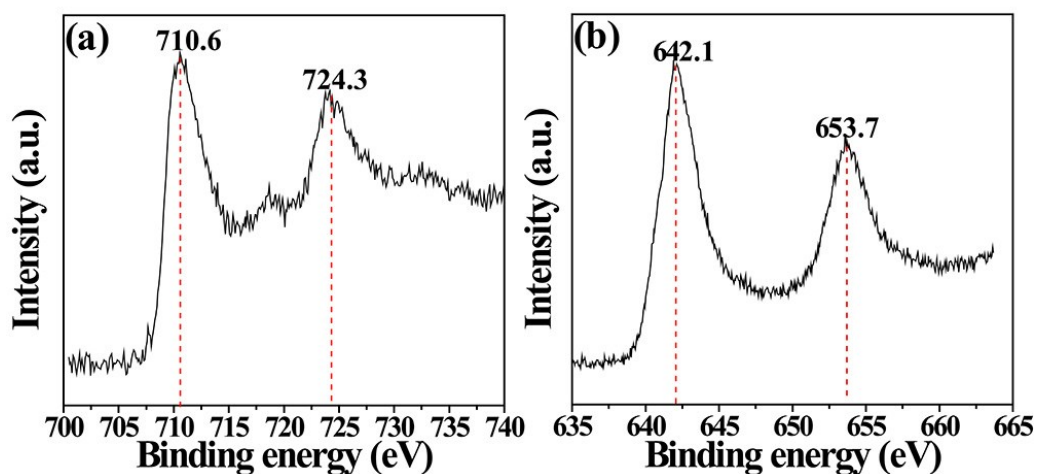


Fig. S11. XPS spectra of samples with metal oxide deposited: (a) $\text{Fe}_2\text{O}_3/\text{TiO}_2$ with FeO_4^{2-} ions as Fe source at pH = 13.5 and (b) $\text{MnO}_x/\text{TiO}_2$ with MnO_4^- ions as Mn source at pH = 13.5.

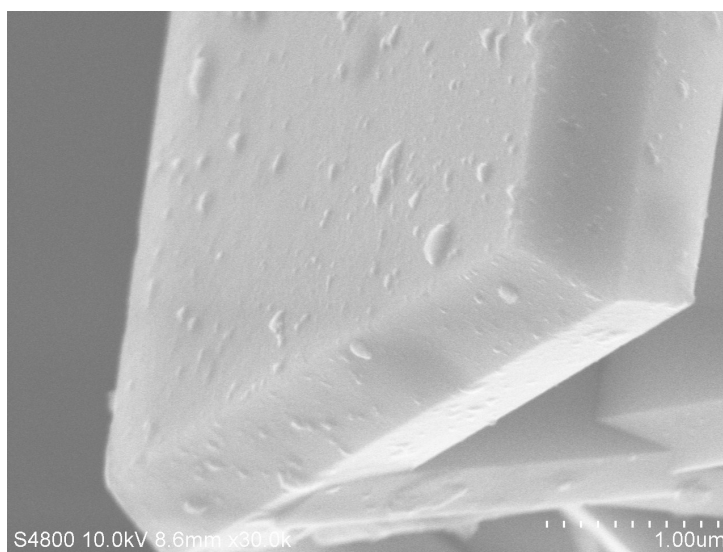


Fig. S12. FESEM images of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples FeO_4^{2-} ions as Fe source prepared by conventional chemical reaction at pH = 13.5.

- (1) J. Pan, G. Liu, G. Q. Lu and H. M. Cheng, *Angew. Chem. Int. Ed.*, 2011, **50**, 2133–2137.
- (2) G. Liu, C. Sun, H. G. Yang, S. C. Smith, L. Wang, G. Q. Lu and H. M. Cheng, *Chem. Commun.*, 2010, **46**, 755-757.
- (3) J. Cheng and M. Sprik, *J. Chem. Theory Comput.* 2010, 6, 880–889.
- (4) J. G. Yu, J. X. Low, W. Xiao, P. Zhou and M. Jaroniec, *J. Am. Chem. Soc.*, 2014, 136, 8839–8842.