Electronic Supplementary Material (ESI) for Nanoscale.

α-Fe_2O_3/TiO_2 3D Hierarchical Nanostructures for enhanced Photoelectrochemical Water Splitting

Hyungkyu Han[1], Francesca Riboni[2], Frantisek Karlicky[1,3], Stepan Kment[1], Anandarup Goswami[1], P. Sudhagar[4], Jeongeun Yoo[2], Lei Wang[2], Ondrej Tomanec[1], Martin Petr[1], Ondrej Haderka[1], Chiaki Terashima[4], Akira Fujishima[4], Patrik Schmuki[2,5*] and Radek Zboril[1]*

[1] Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, Slechtitelu 11, 783 71 Olomouc, Czech Republic

[2] Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany

[3] Department of Physics, Faculty of Science, University of Ostrava, 30. dubna 22, 701 03 Ostrava, Czech Republic

[4] Photocatalysis International Research Center, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

[5] Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21569, Saudi Arabia

*Corresponding authors. Patrik Schmuki (E-mail: schmuki@ww.uni-erlangen.de), Radek Zboril (E-mail: radek.zboril@upol.cz)

S1. Theortical simulation

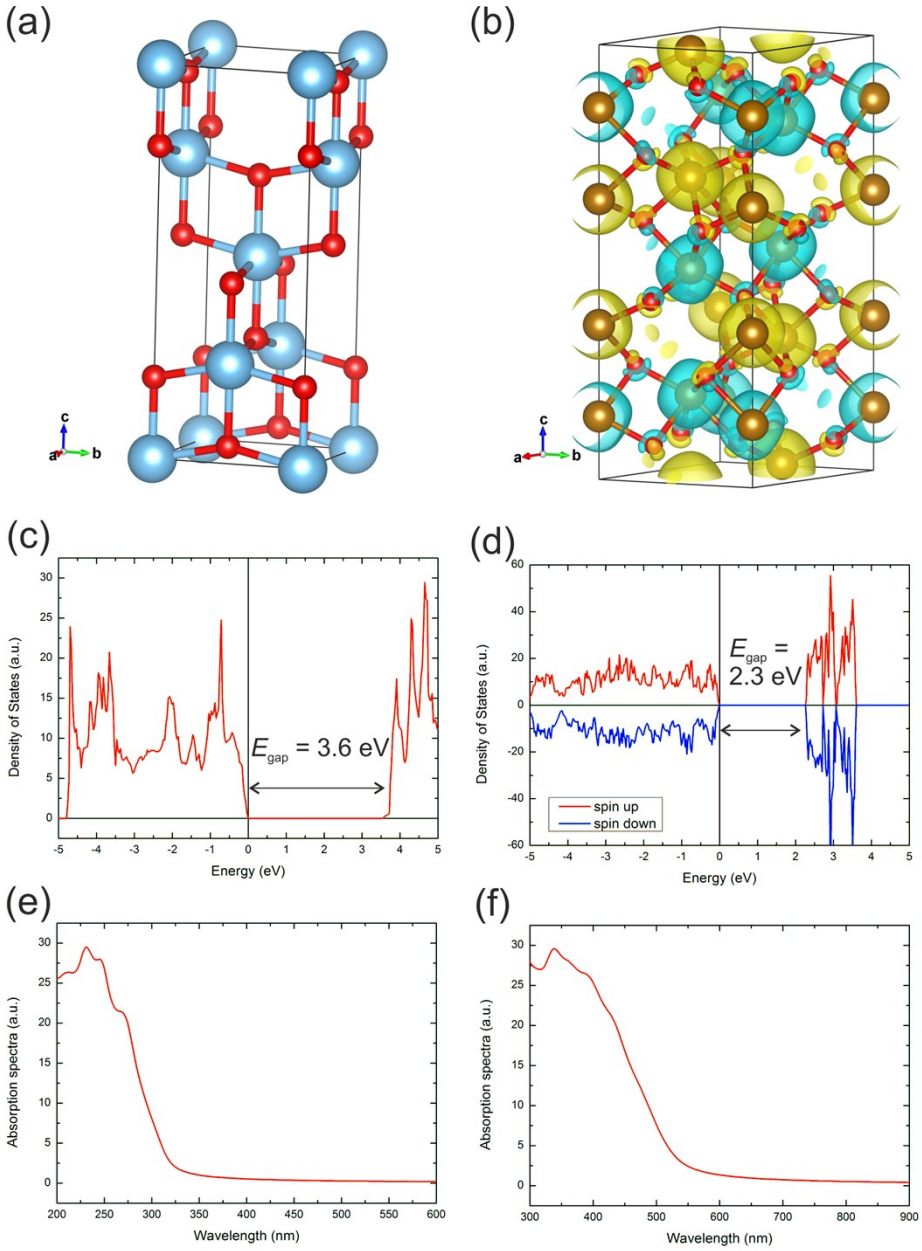

Figure S1. Calibration of the computational setup. (a-b) Atomic structure of the unit cell (Ti – blue, Fe – gold, O - red) and spin density surface (blue and yellow for up and down spin, respectively) for isovalue of 0.01 a.u., (c-d) density of electronic states and (e-f) optical spectra of bulk anatase TiO_2 (left column) and bulk hematite α-Fe_2O_3 (right column) calculated by PBE+U DFT. The choice of U = 7.5 eV for Ti atoms and U = 4.3 eV for Fe atoms provides fine agreement with literature data: E_{gap} ~ 3.6 eV of TiO_2 is close to experimental value (electronic band gap unknown, indirect optical gap of 3.2 eV[1]) and reproduces calculated benchmark G_0W_0 electronic band gap of 3.7 eV[2]. Magnetic moment $\mu \approx 4.2$ μ_B on Fe in antiferromagnetic α-Fe_2O_3 is close to experimental value of 4.9 μ_B; E_{gap} ~ 2.3 eV is close to experimental value (2.2 eV[3], 2.0-2.7 eV[4]).

[1] J. Am. Chem. Soc. 118 (1996) 6716; [2] J. Phys.-Condens. Mater. 24 (2012) 202201; [3] J. Solid State Chem. 27 (1979) 307; [4] Phys. Rev. B 34 (1986) 7318)

S2. Surface morphology results

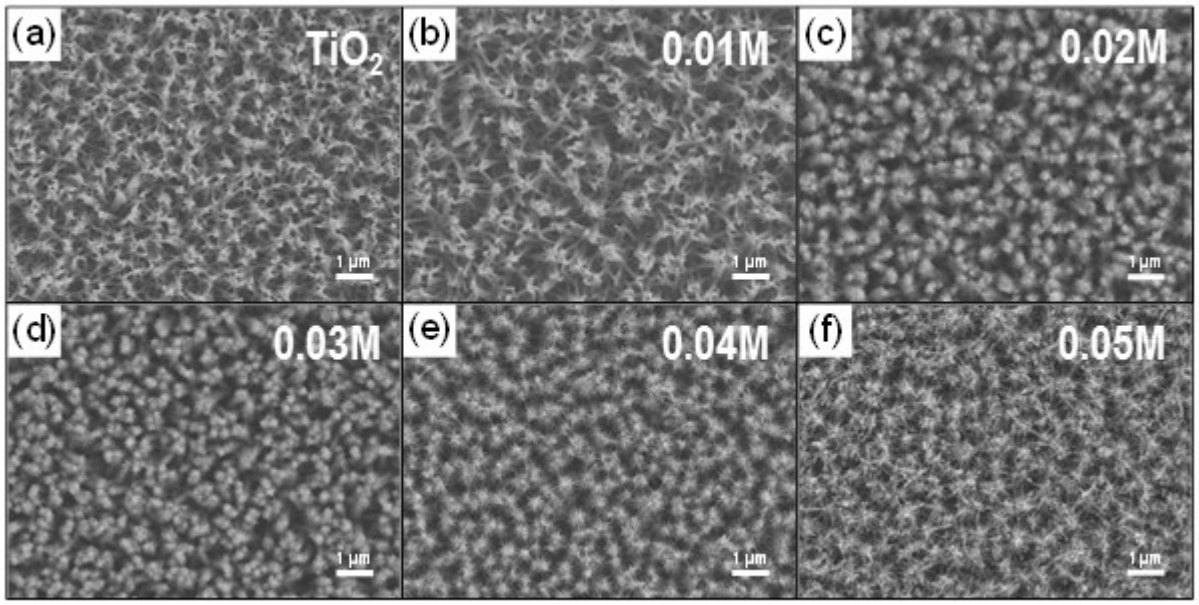

Figure S2. Top view SEM images of (a) TiO_2 NTs and (b–f) α-Fe_2O_3/TiO_2 NT composites prepared starting from Fe(III) precursor solutions with different concentrations (*i.e.*, 0.01–0.05 M).

S3. Cross section SEM results

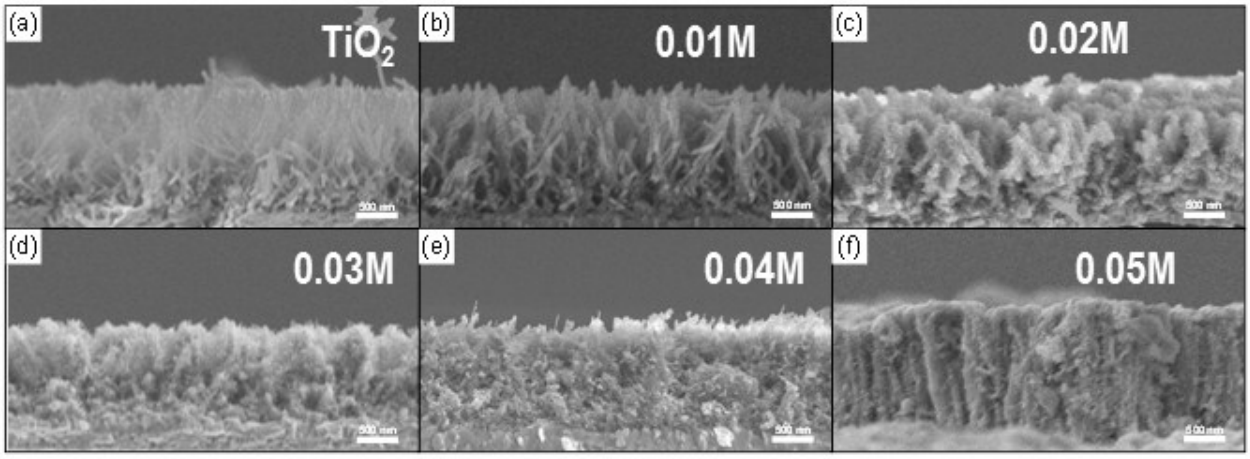

Figure S3. Cross sectional view SEM images of (a) TiO_2 NTs and (b–f) α-Fe_2O_3/TiO_2 NT composites prepared starting from Fe(III) precursor solutions with different concentrations (*i.e.*, 0.01–0.05 M).

S4. Composition analysis

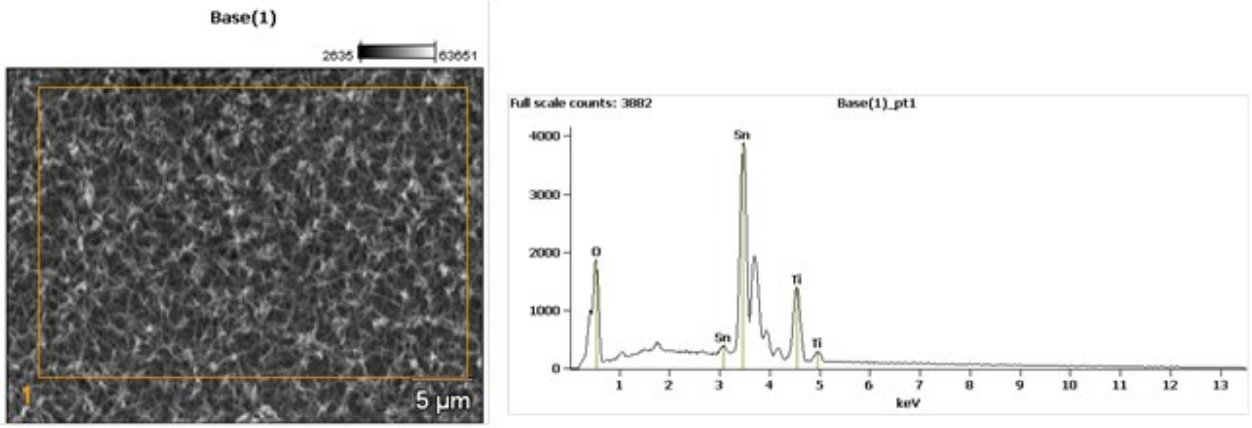

Figure S4. SEM image and corresponding EDX spectrum of pure TiO_2 NTs.

S5. Elemental mapping result

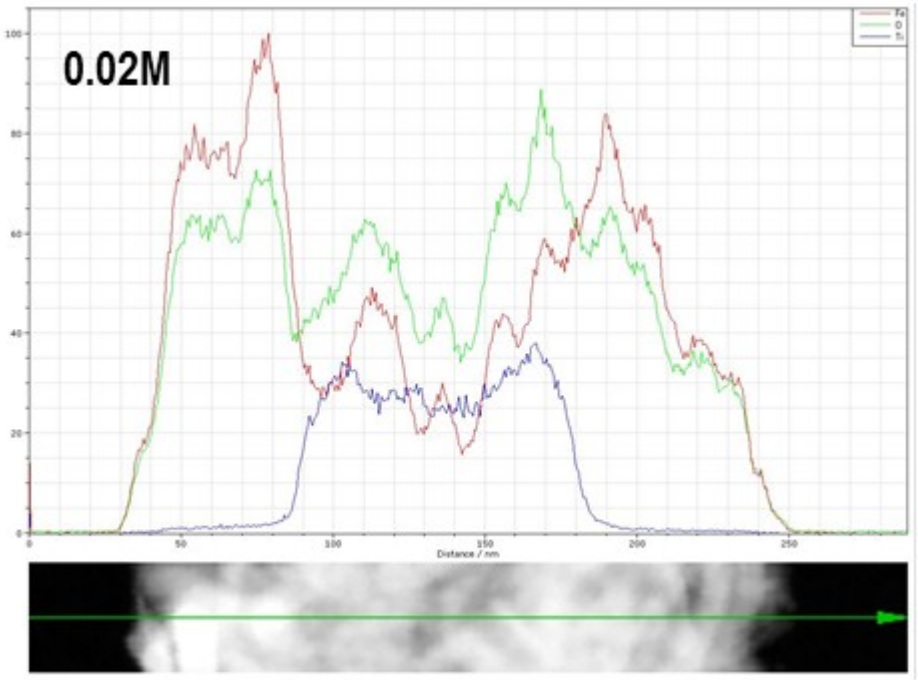

Figure S5. Auger Electron Spectroscopy (AES) horizontal mapping across the 0.02 α-Fe_2O_3/TiO_2 layer.

S6. Elemental mapping result

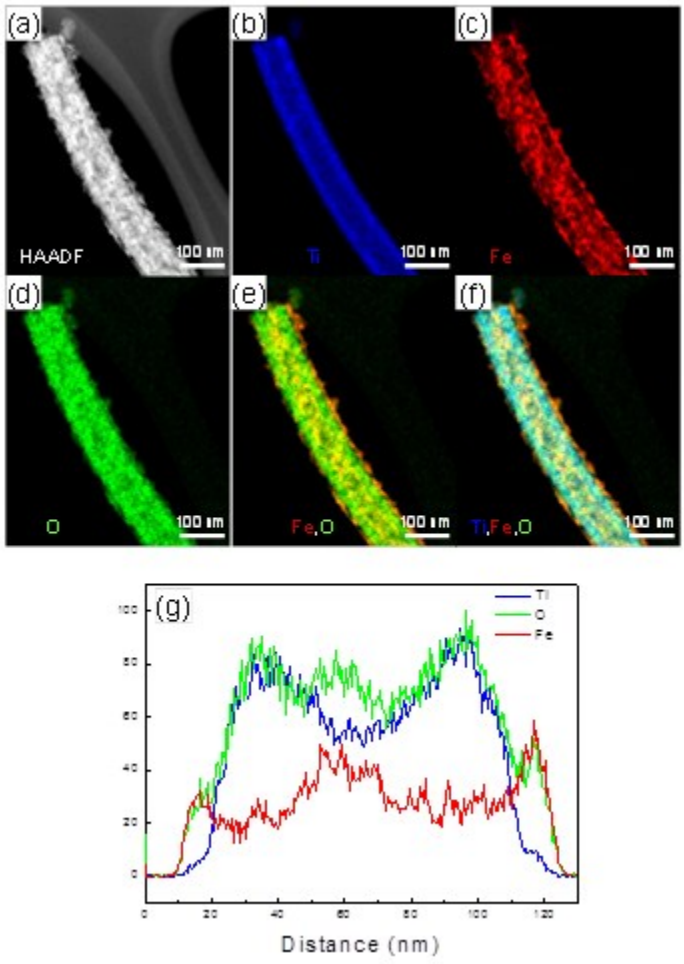

Figure S6. 0.01 α-Fe_2O_3/TiO_2 NT composite layer: (a) HAADF image and (b–f) Ti, Fe, O, Fe+O and Ti+Fe+O elemental mapping of the 0.02 Fe_2O_3/TiO_2 NT sample. (g) AES horizontal mapping.

S7. Elemental mapping result

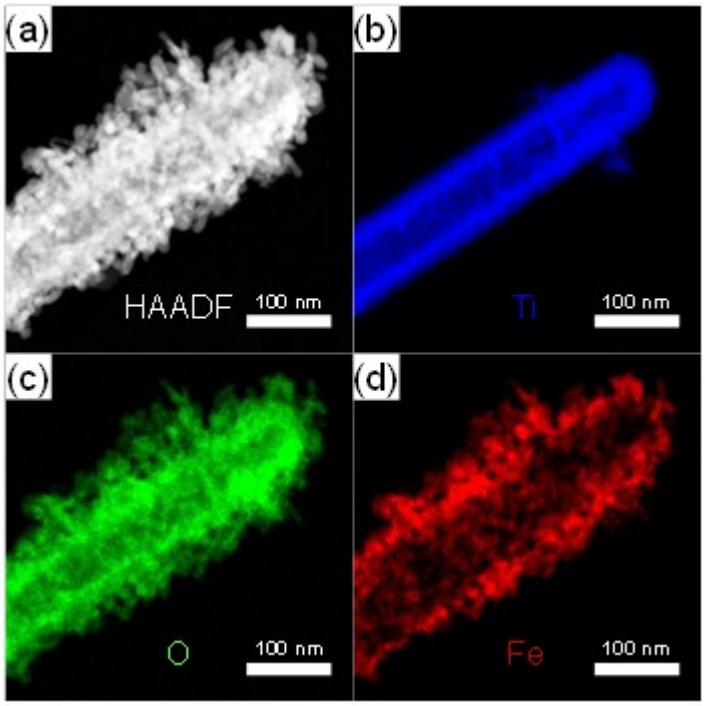

Figure S7. 0.03 α-Fe_2O_3/TiO_2 NT composite layer: (a) HAADF and (b–d) Ti, O and Fe elemental mapping.

S8. Crystallite structure analysis

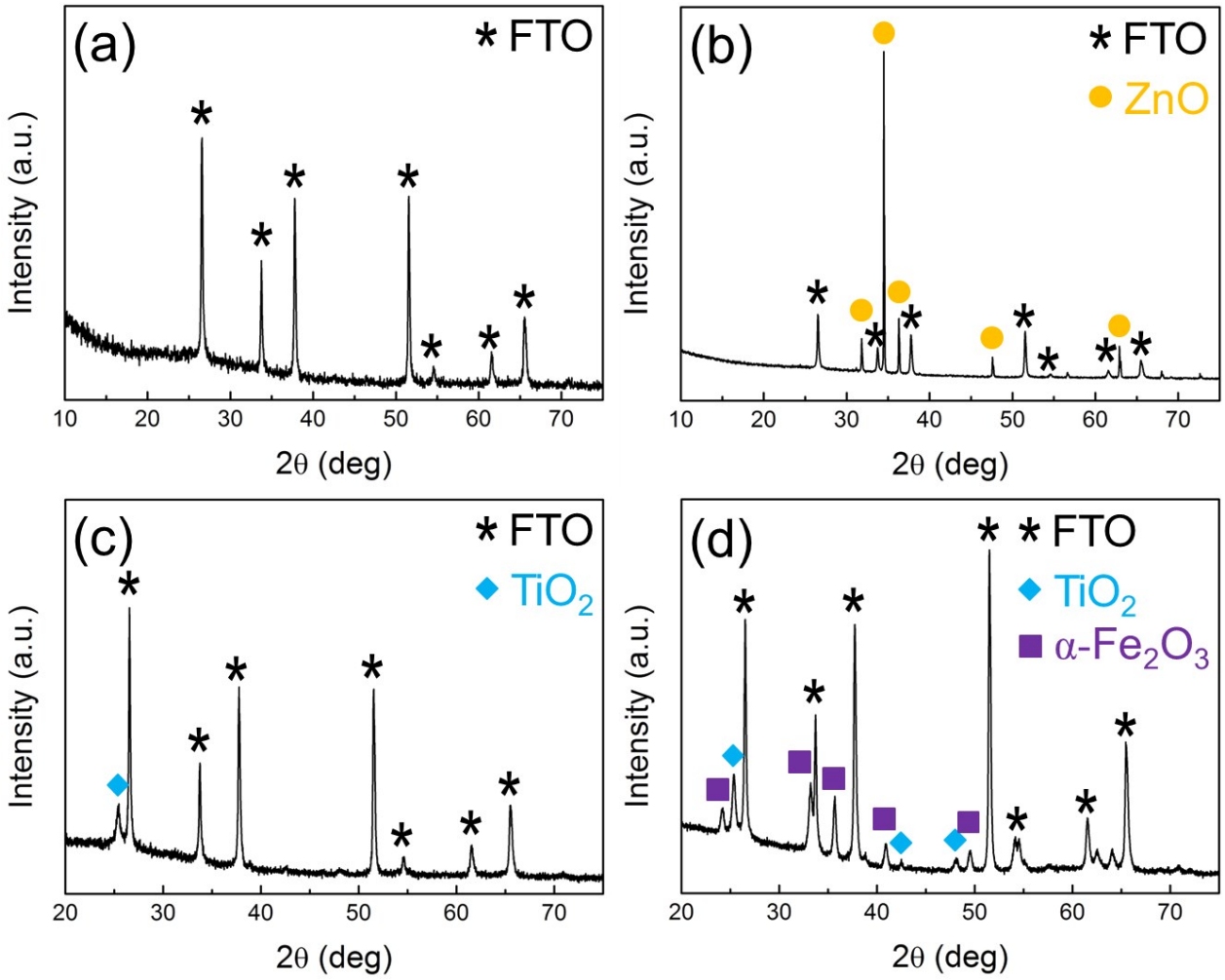

Figure S8. XRD patterns of (a) FTO layer, (b) ZnO nanorods on FTO, (c) TiO_2 nanotubes on FTO and (d) α-Fe_2O_3/TiO_2 NT composite on FTO.

S9. DFT analysis

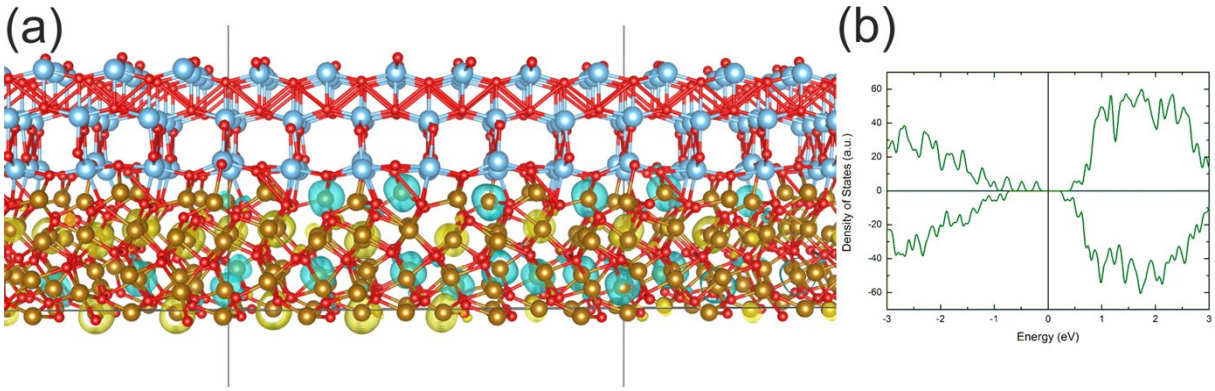

Figure S9. (a) Example of the α-Fe_2O_3/TiO_2 heterocomposite (Ti – blue, Fe – gold, O - red) used in DFT simulations with highlighted 15.14 Å × 38.04 Å computational supercell (black line) containing 81 atoms (18 Fe, 51 O, 12 Ti) and spin density (blue and yellow for up and down spin, respectively) for isovalue of 0.01 a.u. (b) Density of electronic states corresponding to the structure from (a).

S10. Steady-state photocurrent of 0.02 Fe_2O_3/TiO_2

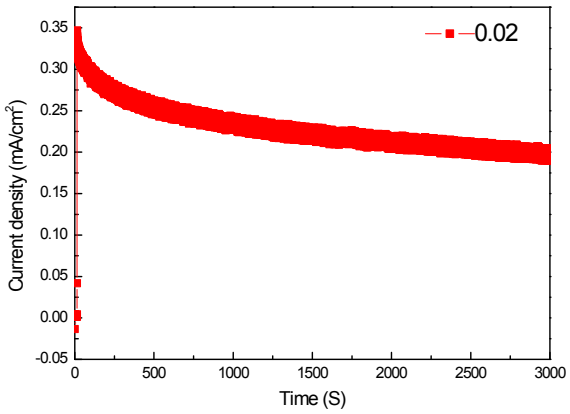

Figure S10. Steady-state photocurrent of the 0.02 Fe_2O_3/TiO_2 layer measured in 1 M NaOH at 0.8 V *vs* Ag/AgCl under AM 1.5G simulated sun light (100 mW cm^{-2}).

S11. Photoelectrochemical water splitting with pure α-Fe_2O_3 layers

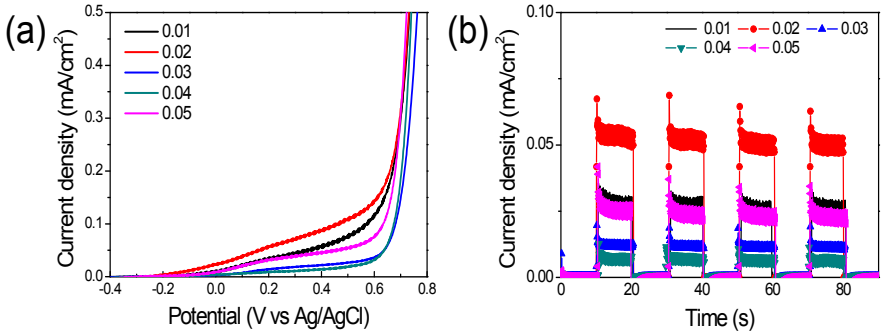

Figure S11. (a) Current-potential characteristics of α-Fe_2O_3 on FTO, measured in 1 M NaOH at 10 mV s^{-1} scan rate, under AM 1.5G illumination. (b) Photo-transient characteristics of α-Fe_2O_3 on FTO, measured in 1 M NaOH at +0.26 V vs Ag/AgCl and under AM 1.5G chopped light illumination.

S12. Nyquist plots of electrochemical impedance measurements of α-Fe_2O_3 layers

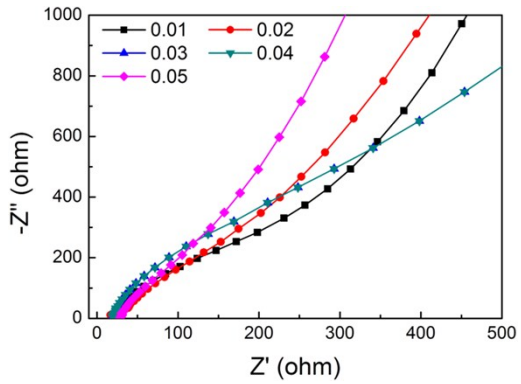

Figure S12. Nyquist plots of electrochemical impedance of α-Fe_2O_3 on FTO, measured at +0.26 V (vs Ag/AgCl (3 M KCl)), in 1 M NaOH, under AM 1.5G illumination.