Electronic Supplementary Information for

In-Fe mixed oxide as an oxygen-evolution photocatalyst for visible-light-driven Z-scheme water splitting

Yugo Miseki,[*a,b] Kana Fujita,[a,c] Shoji Iguchi,[a] Osamu Kitao,[a,b] Takahiro Gunji,[c] and Kazuhiro Sayama[*a,b,c]

[a]*Advanced Functional Materials Team, Research Center for Photovoltaics (RCPV) and* [b]*Global Zero Emission Research Center (GZR), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.*

[c]*Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan.*

*To whom the correspondence should be addressed.

E-mail: k. sayama@aist.go.jp and yugo-miseki@aist.go.jp

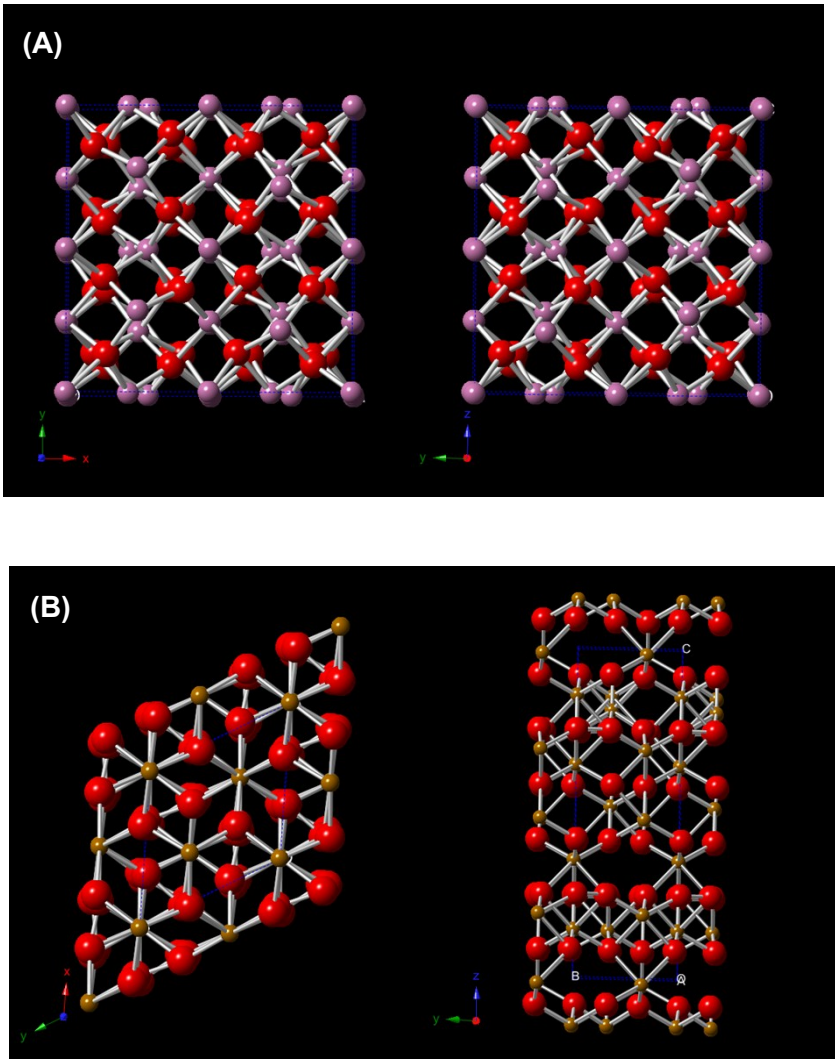

Figure S1 Crystal structure of (A) bixbyite-type structure (01-088-2160) and (B) corundum structure (01-076-8401).

XAFS Study.

Fe K-edge and In K-edge XAFS measurements were carried out using the BL01B1 beamline at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute. X-ray beam was monochromatized by a Si(111) and Si(311) double crystal monochromator for Fe K-edge and In K-edge measurements, respectively. Rh-coated mirror was used to cut the higher harmonic X-ray off. All samples were mixed with a proper amount of boron nitride and pressed into pellets.

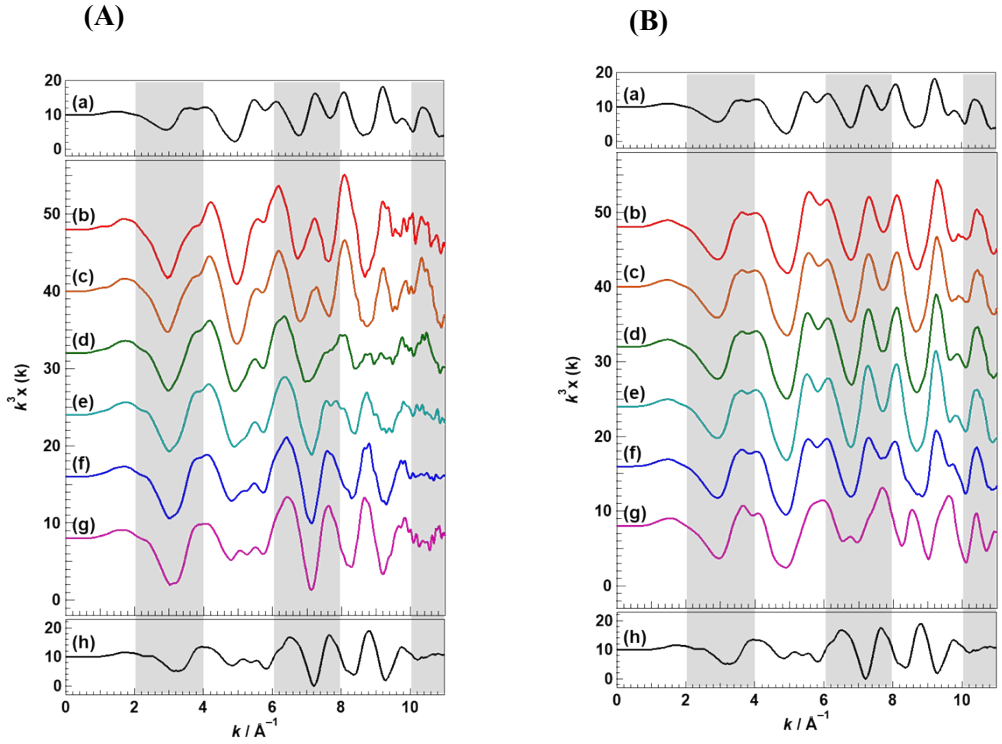

Figure S2 (A) EXAFS spectra of (a) In K-edge of In_2O_3, Fe K-edge of (b-g) In-Fe(15%) oxides calcined at different temperatures, and (h) Fe_2O_3, and (B) EXAFS spectra of (a) In K-edge of In_2O_3, (b-g) In-Fe(15%) oxides calcined at different temperatures, and (h) Fe K-edge of Fe_2O_3. Calcination temperature is (b) 1573 K, (c) 1373 K, (d) 1273 K, (e) 1173 K, (f) 1073 K, and (g) 973 K. All spectra excepting were recorded in the transmission mode using ionization chambers.

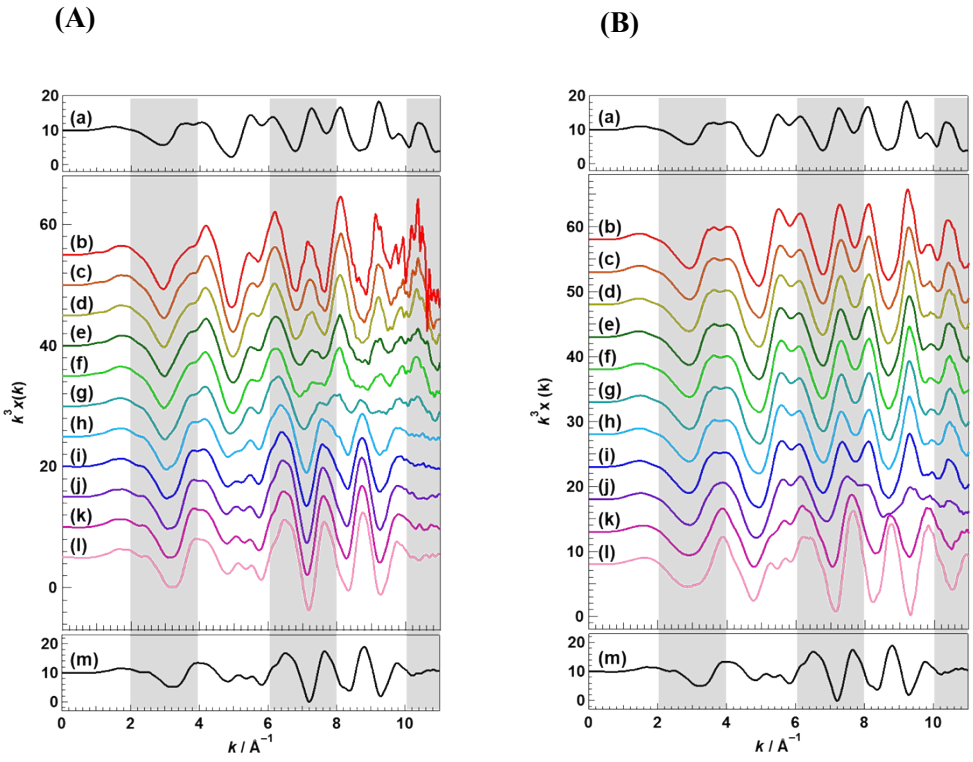

Figure S3 (A) EXAFS spectra of (a) In K-edge of In_2O_3, Fe K-edge of (b-l) In-Fe(x%) oxides, and (m) Fe_2O_3. x = (b) 5, (c) 13, (d) 15, (e) 18, (f) 20, (g) 25, (h) 40, (i) 50, (j) 75, (k) 87, and (l) 95. All spectra excepting (b) were recorded in the transmission mode using ionization chambers. The spectra (b) was obtained in the fluorescence mode using a Lytle detector, and (B) EXAFS spectra of (a) In K-edge of In_2O_3, (b-l) In-Fe(x%) oxides, and (m) Fe K-edge of Fe_2O_3. x = (b) 5, (c) 13, (d) 15, (e) 18, (f) 20, (g) 25, (h) 40, (i) 50, (j) 75, (k) 87, and (l) 95. All spectra were recorded in the transmission mode using ionization chambers.

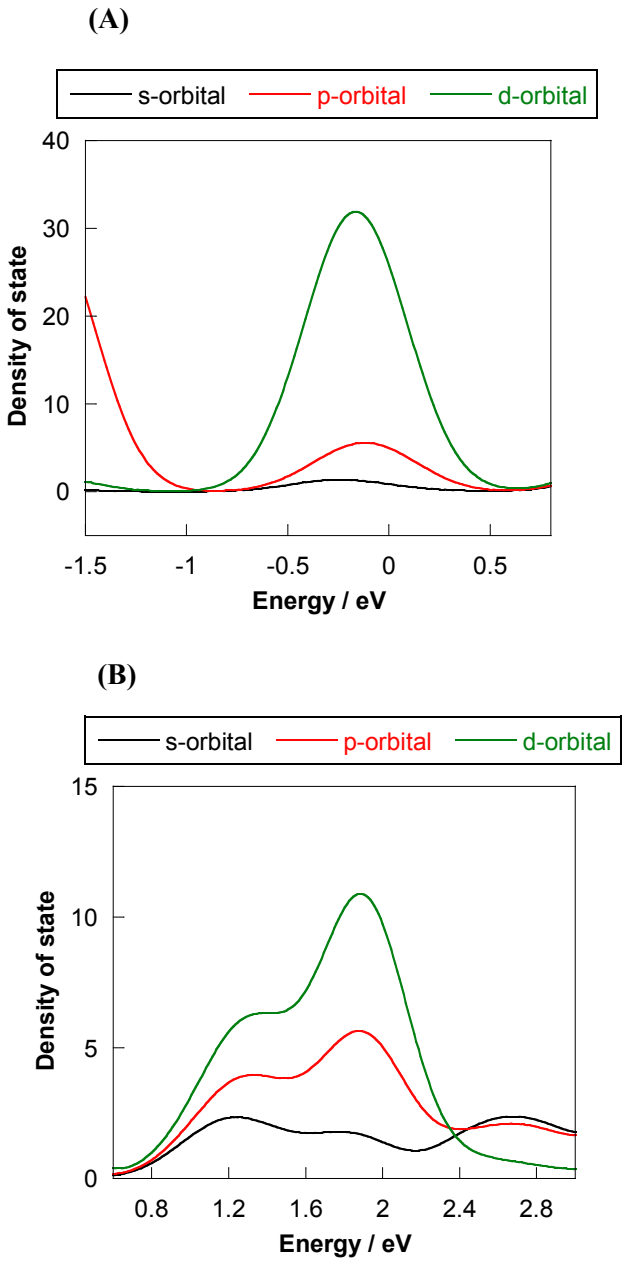

Figure S4 Calculation result which was performed with density functional theory (DFT) (CASTEP) based on the optimized structure using the structural parameters from ICDD (01-088-2160) as the initial guess.

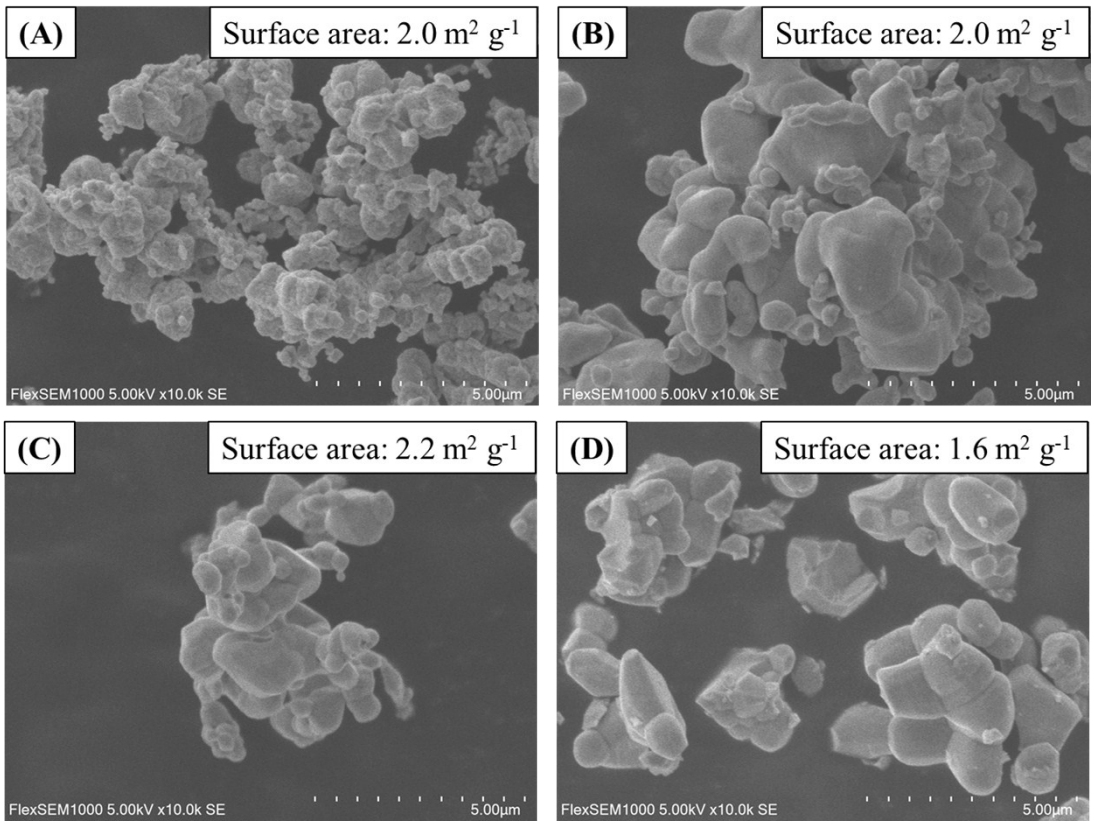

Figure S5 SEM images and BET surface area of In-Fe(x%) oxides prepared at 1373 K with various x values. (A): In-Fe(0%) oxide, (B): In-Fe(13%) oxide, (C): In-Fe(25%) oxide, and (D): In-Fe(87%) oxide.

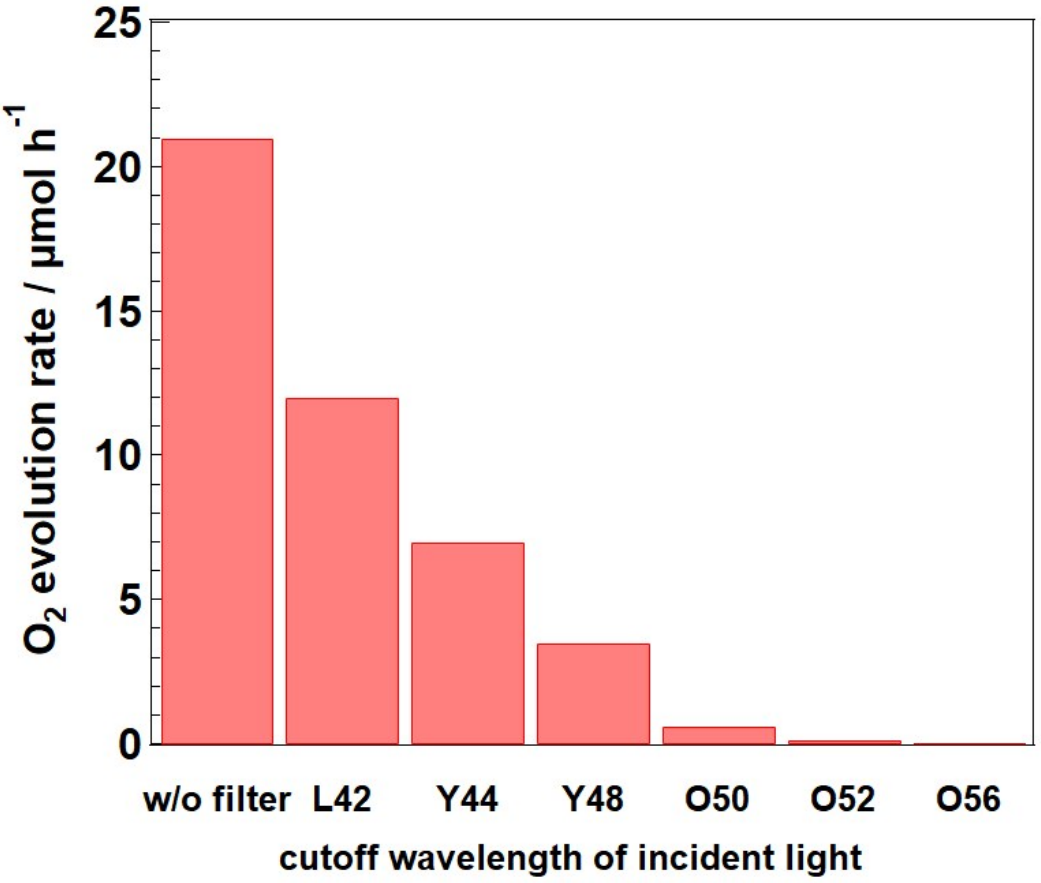

Figure S6 Dependence of the initial oxygen evolution rate of In-Fe(15%) oxide on the cutoff wavelength of the incident light. Catalyst: 100 mg, 20 mM $AgNO_3$: 300 mL, light source: 300 W Xe arc lamp attached with cut off filters.

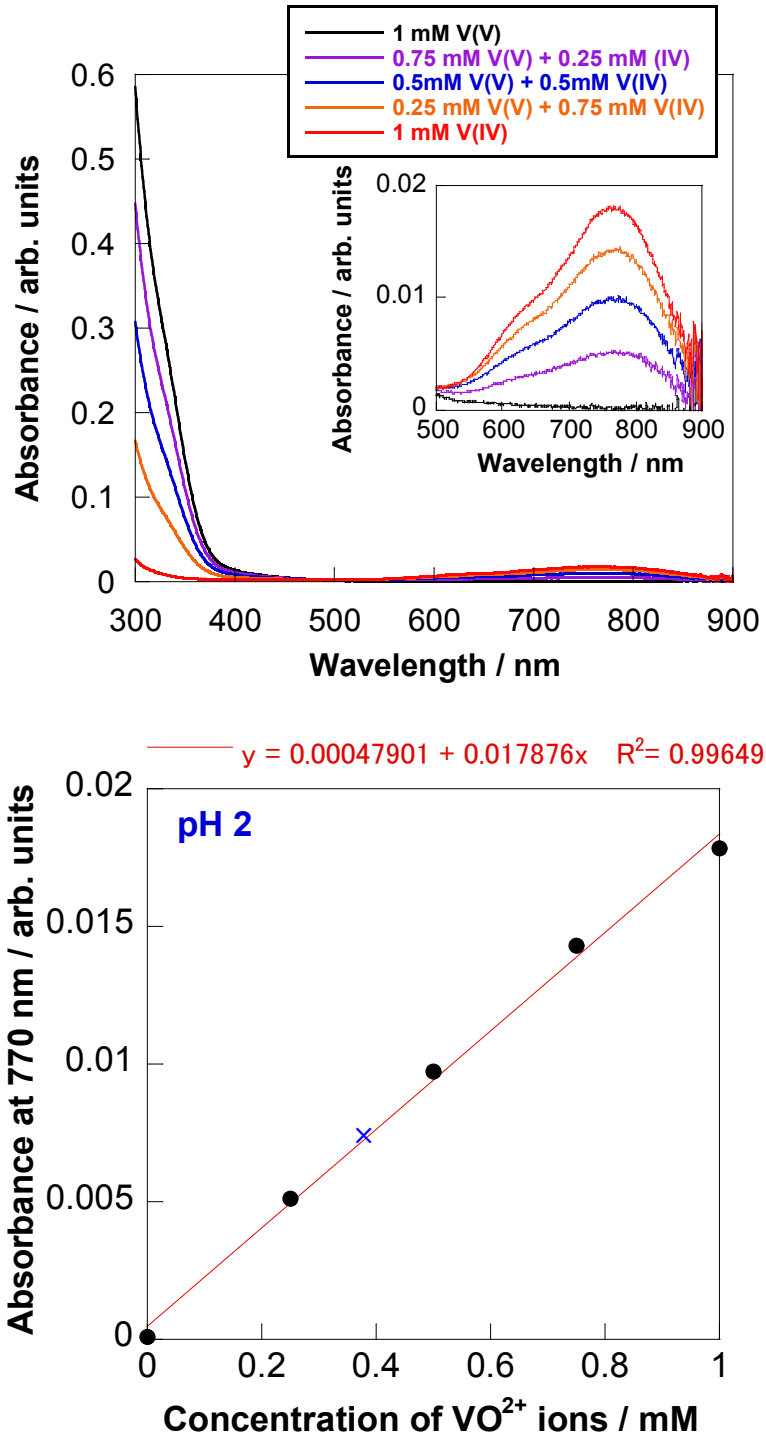

Figure S7 (A) Absorption bands of the mixing solution of VO^{2+} (V(VI)) and VO_2^{+} (V(V)). (B) Calibration curve of VO^{2+}. Cross mark is shown the absorbance at 770 nm of the reactant solution after photocatalytic reaction of Figure 4