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## **Supporting Information**

## Ultrathin Insulating Under-Layer of Hematite Thin Film for Enahnced Photoelectrochemical (PEC) Water Splitting Activity

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**Figure S1.** Spectral Match data of 1 sun light source (HAL-320, Asahi spectra, Japan) compared with standard solar light (JIS certified).  $(300 \sim 1100 \text{ nm}, \text{ with AM (air mass)} 1.5 \text{ filtered}).^{s1}$ 



**Figure S2**. (a) Schematic drawings for fabrication Ti doped hematite film and ultrathin  $SiO_2$  under-layered Ti doped hematite film. (b) optical images of pure hematite film, Ti doped hematite film and  $SiO_2$  under-layered Ti doped hematite film.



**FigureS3.** TEM images of 3 times deposited  $SiO_2$  under-layer (a, a-1, a-2) and 1 time deposited  $SiO_2$  under-layered Ti doped hematite film (b, b-1, b-2). (The scale bar is 0.5 µm, 100 nm and 20 nm, respectively)



**Figure S4**. XPS data of SiO<sub>2</sub> under-layered Ti doped hematite film. (a) survey scan, (b) Ti 2p, (c) Fe 2p and (d) Si 2p. Depth profiling of (e) Ti 2p, (f) Fe 2p in SiO<sub>2</sub> under-layered Ti doped hematite film.



**Figure S5**. TEM EDXS point analysis of  $SiO_2$  under-layered Ti doped hematite film. (a) STEM image for position of points, (b) acquired spectrum, (c) Table of atomic percentage for Si, Ti, Fe and Sn. (point 1 for hematite film, point 2 for interface between hematite and FTO substrate and point 3 for inside of FTO substrate).



**Figure S6**. Photocurrent density curves of  $SiO_2$  under-layered Ti doped hematite film with (a) different Si precursor concentration for  $SiO_2$  under-layer (1 time deposited) and (b) different DA cycle number of  $SiO_2$  under-layer with 0.45 M of Si precursor.



**Figure S7**. (a) Incident photon to current conversion efficiency (IPCE) curve and (b) UV-Vis spectrum for pure hematite, Ti doped hematite and SiO<sub>2</sub> under-layered Ti doped hematite film.



**Figure S8**. Tauc plot for pure hematite, Ti doped hematite and SiO<sub>2</sub> under-layered Ti doped hematite film.



**Figure S9**. Reverse current magnified transient J-V curve for Ti doped hematite and  $SiO_2$  under-layered Ti doped hematite film (1.23 V vs. RHE potential applied).



**Figrue S10.** AFM images and 3-D topography of pure hematite film (a-1, a-2), Ti doped hematite film (b-1,b-2) and SiO<sub>2</sub> under-layered Ti doped hematite film (c-1, c-2), respectively (all scales are 5  $\mu$ m by 5  $\mu$ m).



**Figure S11.** Refined EXAFS spectrum of pure hematite with furrier transformed in R space and fitted with ifeffit algorithm-based calculation.



**Figure S12.** (a) X-ray absorption fine structure (XAFS) spectra and (b) X-ray absorption near edge spectra (XANES) for pure hematite, Ti doped hematite,  $SiO_2$  under-layered hematite and  $SiO_2$  under-layered Ti doped hematite film.

## **Reference for Supporting Information**

[S1] The Asahi-spectra USA online, <u>http://www.asahi-spectra.com/opticalinstrument/hal320.html</u>, (accessed June 2015).