Supplementary Information for

Facile Growth of Porous $Fe_2V_4O_{13}$ Films for Photoelectrochemical Water Oxidation

Ding Tang,[ab] Alexander J. E. Rettie,[a] Oluwaniyi Mabayoje,[a] Bryan R. Wygant,[a] Yanqing Lai,*[b]

Yexiang Liu,[b] and C. Buddie Mullins*[a]

[a]*McKetta Department of Chemical Engineering and Department of Chemistry, University of Texas at Austin, 1 University Station C0400, Austin, Texas 78712-0231, USA. E-mail: mullins@che.utexas.edu; Fax: +1-512-471-7060; Tel: +1-512-471-5817*

[b]*School of Metallurgy and Environment, Central South University, Changsha 410083, China. E-mail: laiyanqingcsu@163.com; Fax: +86 731 88710171; Tel: +86 731 88830649*

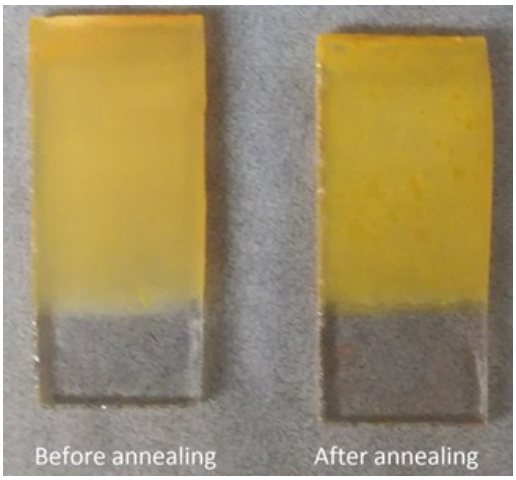

Fig S1 Digital images of $Fe_2V_4O_{13}$ films on FTO before and after annealing at 500 °C for 1 h.

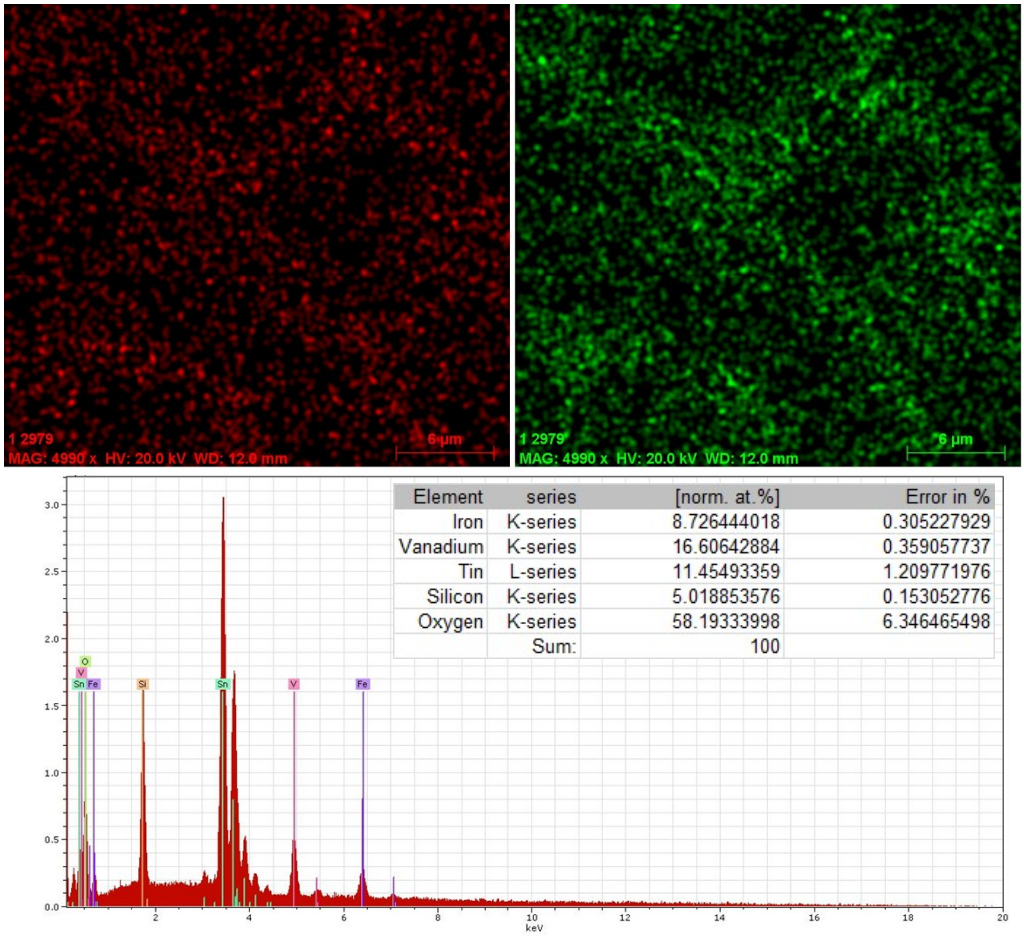

Fig S2 Elemental mapping with Fe and V color coded and EDS spectrum of as-prepared $Fe_2V_4O_{13}$ film. The Sn and Si peaks in the EDS spectrum are from the FTO substrate. Insert table shows the EDS elemental results. The atomic ratio of Fe and V approximately equals to 1:2.

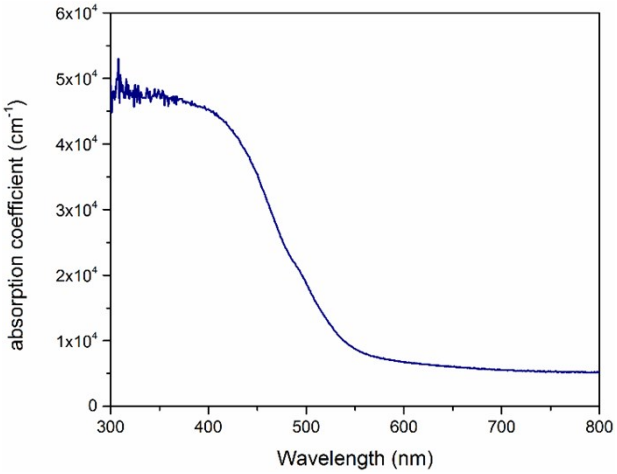

Fig. S3 Absorption coefficient spectra of $Fe_2V_4O_{13}$ film.

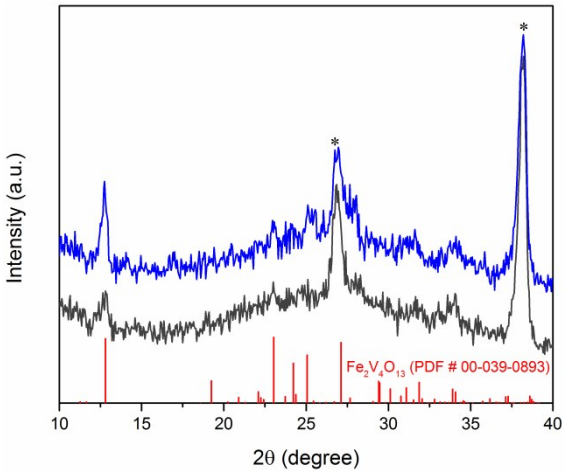

Fig. S4 XRD patterns of $Fe_2V_4O_{13}$ films annealed at 400 °C for 12 h and 500 °C for 6 h, respectively. Peaks marked (*) arise from FTO.

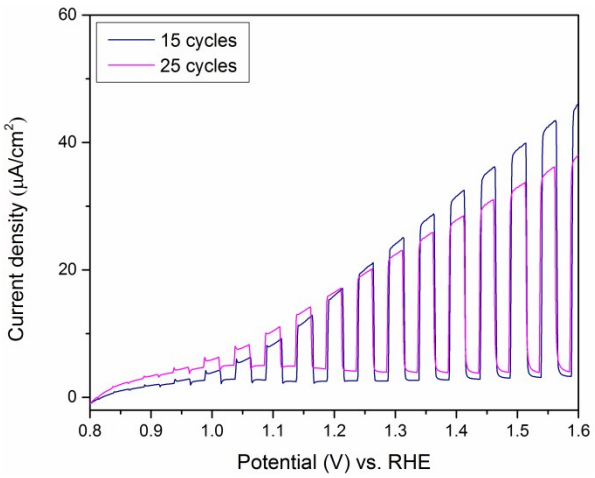

Fig. S5 Chopped LSVs of $Fe_2V_4O_{13}$ films with different thicknesses (controlled by number of cycles) annealed at 500 °C for 1 h in 0.1 M sodium borate buffer solution (pH 9.2).

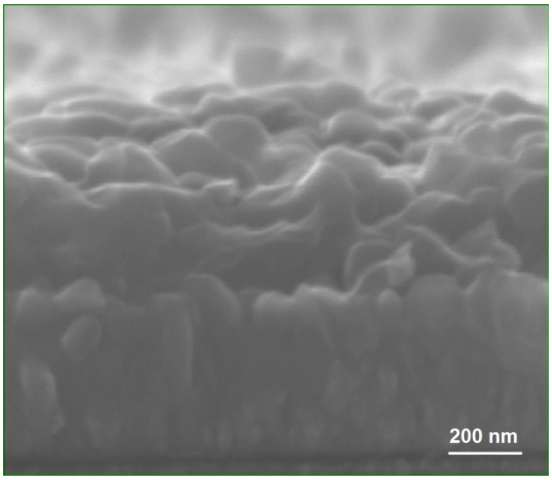

Fig. S6 Cross-sectional SEM image of $Fe_2V_4O_{13}$ film obtained by repeating 20 cycles.

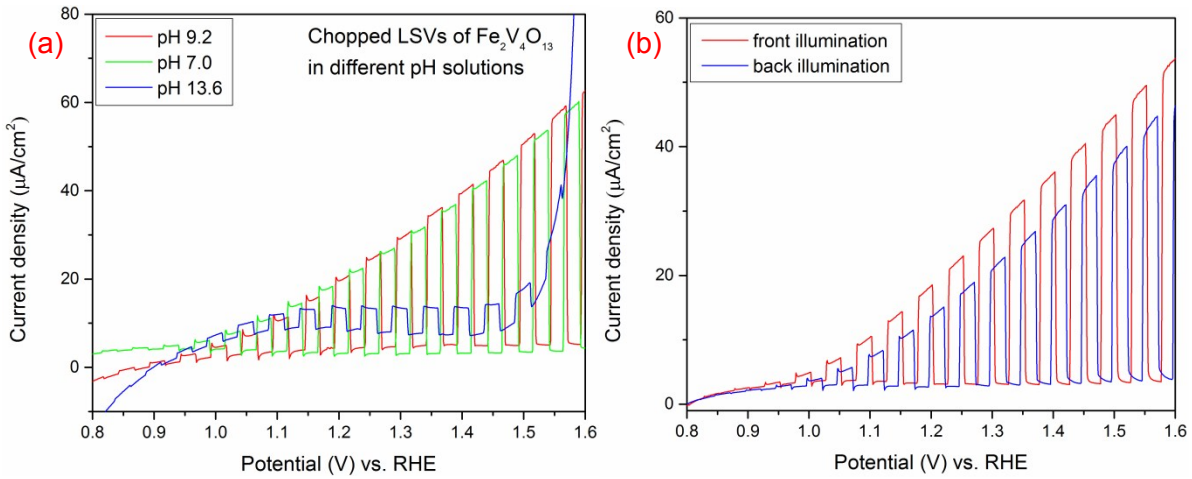

Fig. S7 (a) Chopped LSVs of $Fe_2V_4O_{13}$ films in different buffer solution (0.1 M sodium borate buffer solution, pH 9.2; 0.1 M potassium phosphate buffer soltion, pH 7.0; 1 M KOH solution, pH 13.6); (b) Chopped LSVs of $Fe_2V_4O_{13}$ films in 0.1 M sodium borate buffer solution (pH 9.2) with different illumination direction.

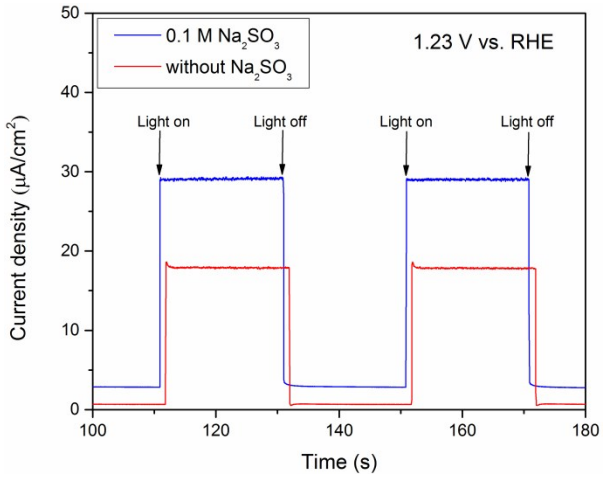

Fig. S8 Amperometric *i-t* curves of $Fe_2V_4O_{13}$ film under illumination in 0.1 M sodium borate buffer solution with/without 0.1 M Na_2SO_3 solution (pH 9.2) at 1.23 V *vs.* RHE.

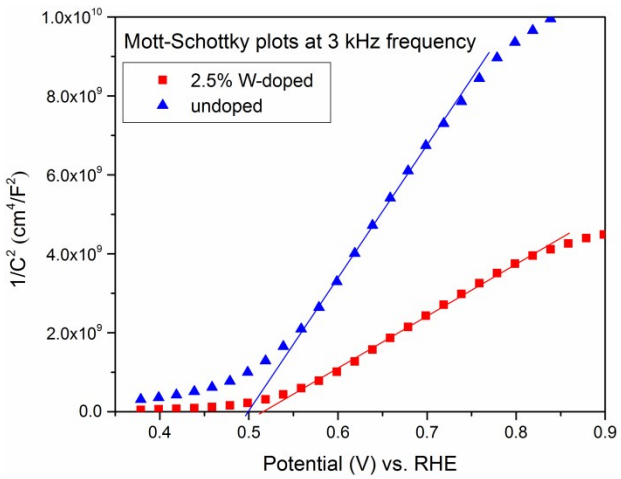

Fig. S9 Mott-Schottky plots at 3 kHz frequency of undoped and 2.5% W-doped $Fe_2V_4O_{13}$ films obtained in 0.1 M sodium borate buffer solution (pH 9.2). As shown in the figure, 2.5% W-doped $Fe_2V_4O_{13}$ film shows a smaller slope compared to undoped films, which indicates the higher carrier density based on the following equation:

$$N_d = (2/e\varepsilon\varepsilon_0)[d(1/C^2)/dV]^{-1}$$

where N_d is the concentration of charge carriers, e is the elemental charge, ε is the dielectric constant of the material, ε_0 is the permittivity of vacuum, C is the space charge layer capacitance and V is the applied potential [1].

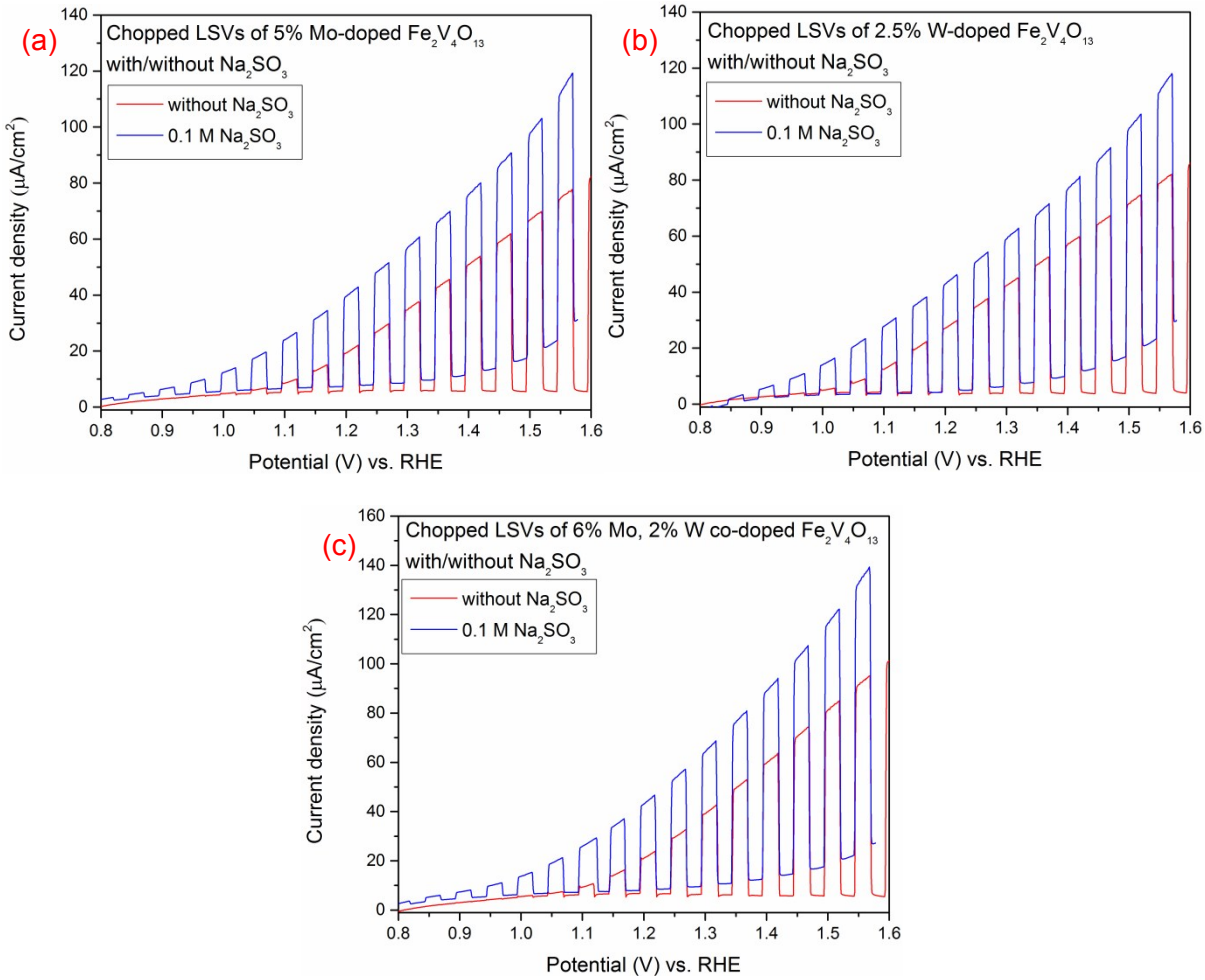

Fig. S10 Chopped LSVs of doped $Fe_2V_4O_{13}$ films in 0.1 M sodium borate buffer solution with/without 0.1 M Na_2SO_3 (pH 9.2): (a) 5% Mo-doped; (b) 2.5% W-doped; (c) 6% Mo, 2% W co-doped.

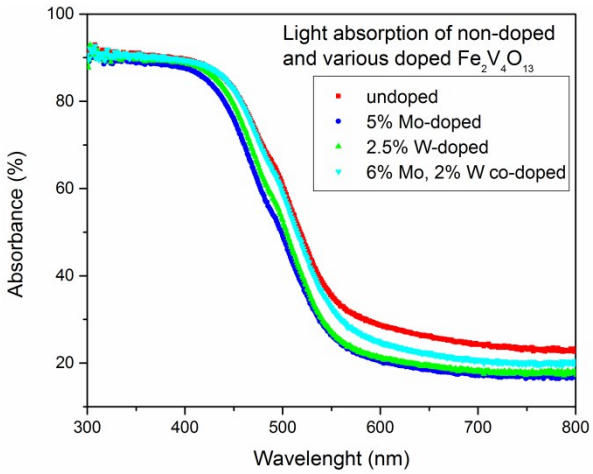

Fig. S11 Absorbance spectrum of undoped, 5% Mo-doped, 2.5% W-doped and 6% Mo, 2% W co-doped $Fe_2V_4O_{13}$ films annealed at 500 °C for 1 h.

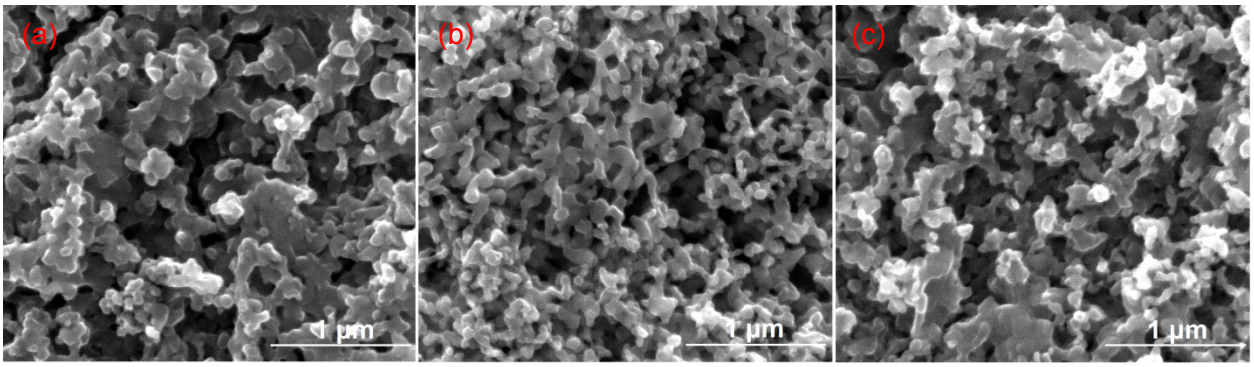

Fig. S12 SEM images of 5% Mo-doped, 2.5% W-doped and 6% Mo, 2% W co-doped $Fe_2V_4O_{13}$ films annealed at 500 °C for 1 h.

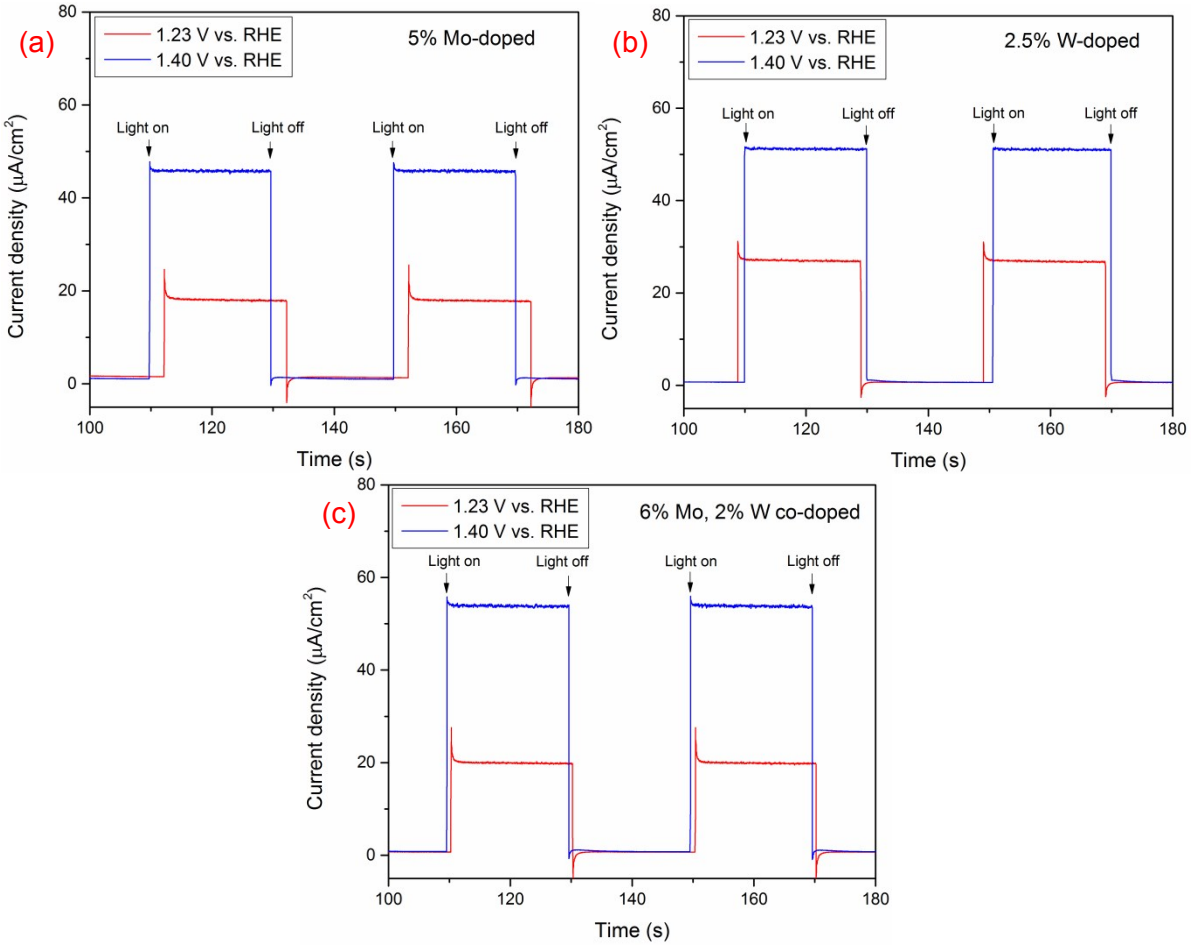

Fig. S13 Amperometric *i-t* curves of 5% Mo-doped, 2.5% W-doped and 6% Mo, 2% W co-doped $Fe_2V_4O_{13}$ films under illumination in 0.1 M sodium borate buffer solution (pH 9.2) at an applied potential of 1.23 and 1.40 V *vs*. RHE.

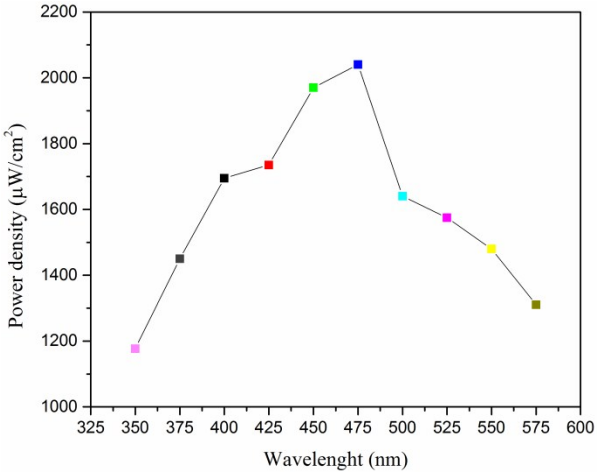

Fig. S14 Incident light power density spectrum (from 340~575 nm) used for the IPCE measurements.

References

1. X. H. Lu, G. M. Wang, S. L. Xie, J. Y. Shi, W. Li, Y. X.Tong and Y. Li, *Chem. Commun.*, 2012, **48**, 7717-7719.