Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

Supporting information

Elucidation of opto-electronic and photoelectrochemical properties of FeVO₄

photoanodes for solar water oxidation

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Figure S1. X-ray diffractograms of (**a**) as-deposited and (**b**) annealed (650 $^{\circ}$ C in air for 2 mins) FeVO₄ films with various thicknesses.



Figure S2. XRD patterns for FeVO₄ films deposited on quartz substrates. Both the unannealed and annealed films show pure phase of triclinic FeVO₄. The broad hump at 2 theta value of around 20° is the signature of the underlying quartz substrate.



Figure S3. SEM image of the as-deposited FeVO₄ film.



Figure S4. Cross-section SEM images of annealed samples sprayed with (a) 50 mL and (b)

100 mL precursor.



Figure S5. Absorption spectra of annealed FeVO₄ with various thicknesses.



Figure S6. UV-Vis absorption spectra of FeVO₄ films deposited on quartz and FTO substrates.



Figure S7. Photograph of annealed FeVO₄ films with various thicknesses.



Figure S8. Enlarged partial J-V curve of the 400 nm-thick annealed $FeVO_4$ showing the onset potential at ~0.68 V vs. RHE.



Figure S9. Mott-Schottky plot of undoped and 2% Mo doped FeVO₄ films (200 nm-thick) measured at 1200 Hz in 0.1 M KPi.



Figure S10. Ultraviolet photoelectron spectroscopy (UPS) spectra of undoped FeVO₄ using He I source. The work function (ϕ) of FeVO₄ is calculated by $\phi = hv - W$, where *W* is the width of emitted electrons subtracted from the spectrum (16.1 eV) and *hv* is the energy of He I source (21.2 eV).



Figure S11. X-ray diffractograms of undoped and Mo doped FeVO₄ films.



Figure S12. XRD peak positions as a function of Mo dopant indicating the peak shift after Mo doping. The selected three peaks, (0 1 2), (-2 0 1), and (-2 1 1), are characteristic peaks in the FeVO₄ XRD pattern.



Figure S13. SEM image of 2% Mo doped FeVO₄ film.



Figure S14. Absorption spectra of undoped and Mo doped FeVO₄ films. All samples are 200 nm thick.



Figure S15. XPS survey spectra of undoped and 2% Mo doped films. The adventitious carbon on the surface is estimated to be ~18% from the C1s peak.



Figure S16. Charge injection and separation efficiency of undoped and 2% Mo doped 200 nm sample.



Figure S17. TRMC signals recorded for 2% and 4% Mo doped samples under different photon intensities. The curves are overlapped to better show that there is no dependence on the decay profile.

No.	System	Fabrication method	Photocurrent at 1.23 V vs. RHE (mA cm ⁻²)	Electrolyte	Reference
1	FeVO ₄	Drop casting	<0.08	0.5 M NaOH, pH unknown	[1]
2	FeVO ₄	Layer-by- layer	0.05	0.1 M KPi, pH=7	[2]
	W:FeVO ₄	coating	0.1		
3	FeVO ₄	Drop casting	~0.025	0.1 M SO ₄ ²⁻ , pH=7	[3]
4	FeVO ₄	Drop	<=0.1	0.2 M Na ₂ SO ₄ + 0.1 M Pi buffer,	[4]
	Fe ³⁺ :FeVO ₄	casting	0.25	pH=7	
5	FeVO ₄	Spray	0.04	0.1 MKB; pH=7	This work
	Mo:FeVO ₄	pyrolysis	0.05	0.1 WI KFI, pH-7	THIS WOLK

Table S1. Comparison of photocurrent on $FeVO_4$ -based photoanodes.

Table S2. Comparison of carrier properties of other metal oxides.

Material	Mobility (cm ² V ⁻¹ s ⁻¹)	Carrier lifetime	Diffusion length (nm)	Reference	
Fe₂O₃ ~0.01 3 ps		2-4	[5]		
BiVO4	~0.04	40 ns	70-100	[6, 7]	
FeVO ₄	~4.6×10 ⁻⁵	~29 ns	~2	This work	
2%Mo:FeVO4	~1.5×10 ⁻⁴	~136 ns	~7	This work	

Supplementary note 1: Calculation of charge separation/injection efficiency

The charge separation efficiency (η_{sep}) and charge injection efficiency (η_{inj}) can be calculated with the following equations as reported before.[8, 9]

$$\eta_{sep} = J_{Na_2SO_3}/J_{abs} \qquad (S1)$$
$$\eta_{inj} = J_{H_2O}/J_{Na_2SO_3} \qquad (S2)$$

 J_{abs} is the photocurrent converted from photon absorption rate (**Table S3**), J_{H_2O} is the photocurrent for water oxidation and $J_{Na_2SO_3}$ is the photocurrent measured in electrolyte with hole scavenger Na₂SO₃. Upon the addition of Na₂SO₃, η_{inj} is assumed to be unity (without surface efficiency loss).

Table S3. Calculated absorbed photocurrent density (J_{abs}) for samples with different thicknesses.The calculation was done by integrating the product of the absorption curves (Figure S5),AM1.5 spectrum and elementary charge.

Film thickness (nm)	25	50	100	200	400	600	800
J_{abs} (mA cm ⁻²)	2.29	3.87	5.17	5.78	7.72	8.71	9.27
(ma cm)							

Supplementary note 2: Mott-schottky measurements

Donor density can be determined by Mott-schottky measurements. For Mott-Schottky analysis to be valid, the assumption is that changes in applied potential only result in changes of the capacitance of the space charge layer. Therefore, the following two criteria should be satisfied at the measurement frequency; in the Bode plot the real part of impedance is independent of frequency, and the imaginary part has a slope of -1 (or close to -1) in a log-log scale as a function of frequency. The undoped and doped samples as shown in **Figure S18** generally fulfill the two requirements. The donor density can be calculated from the linear part of the Mott-Schottky plot (**Figure S9**) using the following equation,

$$\frac{1}{C^2} = \frac{2}{eN_{\rm D}\varepsilon_0\varepsilon_{\rm F}A_{\rm s}^2} \left(V_{\rm app} - V_{\rm FB} - \frac{kT}{e} \right)$$
(S3)

where *e* is the charge of electron, N_D is the donor density, ε_0 is the permittivity in vacuum, ε_r is the relative permittivity of FeVO₄ (take $\varepsilon_r = 10$ at 300 K[10]), A_s is the measured surface area, V_{app} is the applied potential, V_{FB} is the flat-band potential, *k* is the Boltzmann constant and *T* is the temperature.



Figure S18. Bode plots of (**a**) undoped and (**b**) 2% Mo doped samples measured at 1 V vs. Ag/AgCl (1.6 V vs. RHE). The frequency range marked with red dash lines satisfies the criteria for a reliable Mott-Schottky measurement.

Supplementary note 3: Fabrication of Fe_{1-x}Bi_xVO₄ films

All samples are fabricated using a modified recipe of FeVO₄ by spray pyrolysis under same conditions, except the Bi/Fe composition in the precursor. The precursor solution was prepared by dissolving c mM Fe(C₅H₇O₂)₃ (99.9%, Sigma Aldrich) and 4-c mM Bi(NO₃)₃ 5H₂O (98%, Alfa Aesar) in acetic acid (98%, Sigma Aldrich) and absolute ethanol (Sigma Aldrich) (volumetric ratio1:9). The value of c in this study ranges from 0 to 4. The hot plate temperature was set at 450 °C and other spray conditions were kept same as that of FeVO₄. Finally, all the samples were annealed in a muffle furnace at 450 °C in air for 2 h.



Figure S19. X-ray diffractograms of films with different ratio of Fe/Bi.



Figure S20. UV-vis spectra of Fe_{1-x}Bi_xVO₄ films (a) $0.8 \le x \le 1$, (b) $0.5 \le x \le 0.8$, (c) $0 \le x \le 1$

0.5.

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