# High Throughput Discovery of Effective Metal Doping in FeVO<sub>4</sub> for Photoelectrochemical Water Splitting

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FeVO<sub>4</sub> is a potential photoanode candidate with favorable bandgap energy for absorbing visible light in the solar spectrum. However, the achieved photocurrents are still much lower than the theoretical photocurrent due to poor bulk carrier separation efficiency. In this study, we aim to improve FeVO<sub>4</sub> charge transport properties by searching for suitable metal doping using combinatorial methods. Thin film FeVO<sub>4</sub> libraries with different doping ratios of Zn, Ni, Cr, Mo and W were fabricated on FTO substrates using combinatorial inkjet printing and their photoelectrochemical properties screened using photo-scanning droplet cell. Mo and W doping show higher current density compared with undoped FeVO<sub>4</sub>; while the photocurrent decreases for Ni and Zn doped samples. The best photocurrent was achieved with 7% doping ratio of Cr. This study discovered Cr as a promising dopant for the first time, which is more

effective than reported Mo or W for FeVO<sub>4</sub> photoanode. The replacement of  $Cr^{3+}$  to Fe<sup>3+</sup> in FeVO<sub>4</sub> crystal lattice helps to mainly improve the catalytic activity for charge transfer, which results in enhancement of photoresponse of the FeVO<sub>4</sub> photoanode.

#### **1. Introduction**

The demand for utilization of clean and renewable energy has motivated researchers to investigate various strategies for harvesting solar energy. Among them, direct solar water splitting, which generates hydrogen from water using sunlight in photoelectrochemical (PEC) system is a promising approach towards clean fuel generation. Semiconductor photoelectrodes are the main component in the PEC water splitting system.<sup>[1-4]</sup> The key requirements for a semiconductor to perform efficient water splitting include: a sufficiently narrow band gap for absorbing the visible spectrum, appropriate band edge positions and high chemical and electrochemical stability.<sup>[5-7]</sup> In general, binary metal oxides (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, ZnO etc.) with high stability for photoelectrochemical water oxidation are often used as photoanodes.<sup>[8-19]</sup> However, the application of these materials into commercial devices is still limited by either their band gaps that are often too large or their poor charge carrier dynamics.

Recently, by combining high throughput calculations and experiments, a list of promising VO<sub>4</sub>-based ternary metal vanadate photoanodes was reported.<sup>[20]</sup> Among them, FeVO<sub>4</sub>, which contains earth abundant elements (Fe and V) and has a favorable bandgap energy for visible light absorption, is identified as a potential candidate for photoanode. Several groups have reported the fabrication of FeVO<sub>4</sub> thin films using magnetron co-sputtering, spray pyrolysis, drop-casting and sol-gel methods with reported band gap energy of 2.0 - 2.1 eV.<sup>[21-31]</sup> However, the achieved photocurrents are still very low as compared to the theoretical photocurrent based on the band gap energy. We have previously identified that the main problem causing the low performance of FeVO<sub>4</sub> films is the poor bulk carrier separation.<sup>[22]</sup> This limitation can be overcome by introducing metal dopant into the films; indeed, Mo- and

W-doped FeVO<sub>4</sub> films have been demonstrated to show higher performance than the undoped films.<sup>[22,25]</sup> Other dopants, which may very well improve the photocurrent further, have however not been explored.

In the present study, we fabricated FeVO<sub>4</sub> thin films by inkjet printing. With the advantage of drop-on-demand feature, inkjet printing is a versatile method which enables deposition of materials with a certain composition at specific area. This allows relatively simple fabrication of a combinatorial material library consisting of multiple compositions on a single substrate. We investigated the alloving of FeVO<sub>4</sub> with various metals, i.e., Zn, Ni, Cr, Mo and W to reduce the band gap of the film or to increase the charge carrier density.<sup>[21,22]</sup> Reduced band gap would allow extended light absorption, which implies potentially better solar energy harvesting, while an increased charge carrier density would improve the conductivity and the charge transport, thereby reducing electron-hole pair recombination. A quick screening of the photoelectrochemical behavior of the fabricated films was then performed using a photoilluminated scanning droplet cell. Upon identification of the optimized composition, more detailed characterizations were performed to elucidate the effects of metal doping to properties of FeVO<sub>4</sub> films. Mo and W doping showed higher photocurrent density as compared to the undoped FeVO<sub>4</sub>, while the photocurrent decreased for the Ni and Zn doped samples, due to their low injection and separation efficiencies. Based on the results, photocurrent improvement of more than 2-fold as compared to pristine FeVO<sub>4</sub> film was achieved for Cr doped sample with the best photoresponse achieved with 7% Cr/(Fe + V) doping ratio. For the first time, Cr was discovered as a promising dopant, which is more effective than reported Mo- or W- FeVO<sub>4</sub> photoanodes.<sup>[22, 25]</sup> The replacement of Cr<sup>3+</sup> to Fe<sup>3+</sup> in FeVO<sub>4</sub> crystal helps to improve the photoelectrochemical performance of the photoanode. This study provides a direction to further improve the photoanode efficiency of PEC system toward practical applications.

#### 2. Results and Discussion

For combinatorial synthesis, FeVO<sub>4</sub> thin film libraries were fabricated using a Dimatix model DMP-2800 piezoelectric inkjet printer. A 5- row by 8-column printing template as shown in Figure 1a was created with 0.6 cm  $\times$  0.6 cm individual squares spaced by 0.6 cm. In each square a predetermined amount of the metal salt precursors was printed, the photographs of printed samples are shown in Figure S1. Figure 1b shows the photocurrent density color map of material libraries with different metal doping (Zn, Ni, Cr, Mo and W), corresponding to the fabricated samples using the printing template (Figure 1a). The addition of Cr and Mo results in a significant increase of the photocurrent whereas the introduction of Zn, Ni and W does not affect the photocurrent much (< 20% improvement). The maximum photocurrent density was observed at 7% of Cr doped FeVO<sub>4</sub> ( $\times$  3) and 2% of Mo doped FeVO<sub>4</sub> ( $\sim$   $\times$  2). The optimum Mo dopant concentration is in a good agreement with our previous study.<sup>[22]</sup> Although the improvement factor is not as large as Cr and Mo doping, we also observed the optimal concentrations for Zn, Ni and W, being 5%, 2% and 2%, respectively. For further detailed characterizations, five larger-area  $(3 \text{ cm}^2)$  thin films with these optimal doping ratios of metals and pristine FeVO<sub>4</sub> were prepared using the same inkjet printing setup on both quartz and FTO substrates.

The composition of metal doping ratios in the larger-area samples was confirmed using EDX (**Table S1**). All the doped samples have doping ratios slightly lower than the initial added amount; this might be related to the loss during annealing process. XRD diffraction measurements were performed on the films deposited on quartz substrates (**Figure 2a**). All of the films show the main peaks at 20 of 25.09° and 27.75° assignable to the reflection of standard reported pattern of triclinic FeVO<sub>4</sub>.<sup>[21,22]</sup> No significant peaks corresponding to secondary phases were observed, which means no substantial impurity phases in fabricated samples. The ionic radii of Fe<sup>3+</sup> and V<sup>5+</sup> are 65 pm and 54 pm, respectively; while the ionic

radii of Ni<sup>2+</sup>, Mo<sup>6+</sup> and W<sup>6+</sup> are larger (Ni<sup>2+</sup>: 72 pm, Mo<sup>6+</sup>: 73 pm and W<sup>6+</sup>:75 pm). However, there is no clear shift of FeVO<sub>4</sub> main peaks in Ni, Mo and W doped samples possibly because of the low doping concentration of 2%. For higher doping ratio of Cr (7%) and Zn (5%), the main peaks slightly shift more than the other dopants as shown in **Figure 2b**. The Cr peak shifts to higher 2 $\theta$  angle as Cr<sup>3+</sup> (62 pm) is smaller than Fe<sup>3+</sup> while Zn doped sample shifts to lower 2 $\theta$  angles as Zn<sup>2+</sup> (74 pm) is larger than Fe<sup>3+</sup>. The observed shifts of the main peaks are indications of the partial replacements of Fe with Cr and Zn to form mixed FeVO<sub>4</sub> crystal instead of the formation of various separate phases.<sup>[23,32]</sup> Raman spectra (**Figure S2**) of undoped and Cr doped samples also confirm the crystalline form of FeVO<sub>4</sub> with no observation of secondary phases.<sup>[33,34]</sup>

The top-view and cross-section SEM images of the samples are shown in **Figure 2c-j**. From the top-view SEM, all the films were composed of interconnected grains, which is in agreement with the high crystallinity from XRD patterns. In the undoped film, appreciable voids were observed with an average grain size of 169 nm, whereas the voids seem to be relatively smaller and the grain size is larger for all the doped samples (~200 nm, **Figure S3**), except for the Zn-doped sample. The cross-sectional SEM images show that compact and homogeneous films with thickness of about 400 nm were successfully fabricated on FTO substrates (**Figure 2d and h**).

Current density – voltage (J-V) plot FeVO<sub>4</sub> films measured in 0.1M KPi (pH = 7) under chopped AM1.5 illumination is shown in **Figure 3a**. All films exhibit anodic photocurrents, indicating n-type behavior. Compared to the undoped film, the photocurrent increases for Cr, Mo and W doped samples and decreases for Ni and Zn doped samples. At 1.6 V vs. RHE, the photocurrent density of Cr, Mo and W doped FeVO<sub>4</sub> photoanode reaches 62  $\mu$ A cm<sup>-2</sup>, 55  $\mu$ A cm<sup>-2</sup> and 43  $\mu$ A cm<sup>-2</sup>, respectively, showing a significant improvement compared to the 29  $\mu$ A cm<sup>-2</sup> of undoped FeVO<sub>4</sub> (**Figure 3b**). Overall, the achieved photocurrent is comparable with other reports on FeVO<sub>4</sub> photoanodes in the literature, as summarized in **Table S2**. The

decreasing dark currents are observed due to the oxidation peak, which most probably arises from the intrinsic defects. For Cr doped sample, the dark current also increases at higher potentials, which we speculate to be related to the (dark) catalytic ability of Cr for water oxidation. To exclude the surface limitation, the photocurrent was also measured in KPi with added Na<sub>2</sub>SO<sub>3</sub> as a hole scavenger. The hole scavenger photocurrent trend is similar to that in KPi, with the Cr doped sample showing the highest photocurrent compared to the undoped and other doped samples (Figure S4). Since the surface loss mechanisms are assumed to be negligible in the presence of the hole scavenger, the enhanced photocurrent indicates a more efficient hole transport to the surface of Cr doped sample. The achieved photocurrents are still low compared to the predicted photocurrent or our previous reported photocurrent value, but this result shows that Cr doping is superior than other dopants.<sup>[22]</sup> It should be noted that all other samples show almost the same photocurrent onset potential at 0.95 V vs. RHE while a cathodic shift (~100 mV) to lower potential was observed for the Cr doped sample, suggesting that a change of the flat band potential is induced by Cr incorporation (Figure 3c). Stability of the photoanodes was tested in KPi under simulated sunlight and applied potential of 1.6 V vs. RHE. The photocurrent density of Cr doped sample remains stable up to 1000 s (Figure S5). In contrast, the photocurrent of undoped sample is degraded by roughly 40% within the same timeframe. Incident photon-to-current conversion efficiencies (IPCE) measurements of the undoped and Cr doped samples were carried out as shown in Figure S6. The Cr doped sample shows a strongly enhanced efficiency in the range of 340 - 480 nm, consistent with the AM1.5 photocurrent result. The IPCE of Cr doped sample reaches a value of 8.7 % at wavelength of 350 nm, while that of undoped sample is only 5.2 %. At longer wavelengths, the IPCE is also improved, but remains lower than 1 %.

The optical absorption spectrum of the undoped  $FeVO_4$  film was obtained from UV-vis-NIR spectrophotometer as shown in **Figure S7**. The absorption edge of the undoped  $FeVO_4$  film was observed at about 600 nm. Based on the absorption spectrum and the measured film

thickness of 400 nm from cross-sectional SEM image, the absorption coefficient ( $\alpha$ ) can be calculated by using the following equation:

$$\alpha = \frac{-\ln(1-A)}{d}$$

where A is the absorption at specific wavelengths and d is the film thickness. **Figure 5b** shows the absorption coefficient as a function of the photon energy. At around the absorption edge (~600 nm), the absorption coefficient is in the order of  $10^3$  cm<sup>-1</sup> and it increases to  $10^4$  cm<sup>-1</sup> at wavelengths less than 540 nm. This obtained absorption coefficient spectrum is consistent with other reports.<sup>[12]</sup>

Tauc plots were calculated to determine the band gap values as shown in **Figure S8**. The undoped FeVO<sub>4</sub> sample shows the x-axis intercept of the slope at 2.08 eV and 2.56 eV corresponding to the indirect and direct band gaps, respectively, which is in agreement with our previous study.<sup>[22]</sup> The Mo and W doped samples also have similar direct band gap with undoped sample, implying the low content of Mo and W does not affect to the indirect band gap energy of FeVO<sub>4</sub> film. However, the indirect band gap slightly increases to 2.13 eV and 2.16 eV for the Ni and Zn doped samples, respectively. For the Cr-doped sample, the indirect band gap is slightly reduced to 2.03 eV, consistent with better light absorption and higher photocurrent.

In order to understand the effect of metal doping on PEC performance, charge injection efficiencies ( $\eta_{inj}$ ) and charge separation efficiencies ( $\eta_{sep}$ ) can be obtained by deconvoluting J-V curves in electrolytes with and without hole scavenger (Na<sub>2</sub>SO<sub>3</sub>); the efficiency values at 1.0 V vs. RHE are shown in **Figure 4**. The Zn, Ni, Mo and W doped samples showed lower surface charge injection efficiency, indicating higher recombination at the surface of photoanodes. However, the Cr-doped sample has  $\eta_{inj}$  higher than that of the undoped sample; this is due to the enhancement of catalytic activity of Cr-rich surface for OER (explained further in the following part). Compared to the undoped FeVO<sub>4</sub>, the charge separation

efficiencies were increased for the Cr, Mo and W doped samples, suggesting that the bulk property of FeVO<sub>4</sub> was improved. This can be attributed to better morphology of less voids and larger grain size in the doped samples (Figure S3). However,  $\eta_{sep}$  remains low of less than 0.5 % at 1.0 V vs. RHE. Therefore, further study to improve bulk carrier separation is necessary. For the Ni and Zn doped samples, the  $\eta_{inj}$  as well as  $\eta_{sep}$  are lower, indicating poor surface and bulk properties for these samples. This is not surprising, since substitution of Ni<sup>2+</sup> and Zn<sup>2+</sup> on Fe<sup>3+</sup> lattice site would be accompanied by either a decrease of donor density or the formation of oxygen vacancy defects.

To clarify the mechanism of the enhancement in Cr, Mo and W doped samples compared to undoped FeVO<sub>4</sub> photoanode, electrochemical impedance spectroscopy (EIS) measurements were further employed to provide details of the electrochemical properties. Figure 5a shows the Nyquist plot of the undoped and Cr, Mo, W doped samples under AM1.5 illumination at 1.23 V vs. RHE in 0.1 M KPi. Compared to undoped FeVO<sub>4</sub>, it is easy to observe that the radius of the semicircle was significantly decreased for the doped samples, implying that the electron transport was improved, which explains for the higher photocurrent response in Figure 3. For more detailed analysis, an equivalent circuit composed of two resistance and capacitance elements in series was used to fit the EIS data (inset in Figure 5b). The fitting parameters of R<sub>ct</sub> related to charge transfer at the electrode and electrolyte interface and R<sub>bulk</sub> for the electron transport inside the semiconductor bulk were shown in Figure 5b. From the fitted resistance values,  $R_{ct}$  of 0.88 k $\Omega$  for the Cr doped sample is largely reduced in comparison with the undoped sample (3.28 k $\Omega$ ), which is consistent with the higher surface injection efficiency at low potential in Figure 4a. For Mo and W doped samples, the R<sub>ct</sub> values are comparable with the undoped sample, indicating similar charge transfer properties at the electrode and electrolyte interface of these samples. Otherwise, the R<sub>bulk</sub> values of all doping samples are significantly decreased compared to undoped sample, which implies the improvement of electron transport inside the semiconductor bulk of doping samples. This is

consistent with the higher separation efficiency of doping samples (Figure 4b). Hence, the decreasing resistance of both at the bulk and interface of Cr doped sample indicated the improved charge transfer in the PEC water splitting circuit, which is beneficial for higher charge separation efficiency and faster charge transport rate. This result explains the superior performance of this sample as compared to the other samples (Figure 3).

**Figure 5c** shows the Mott – Schottky plots of undoped and Cr, Mo, W doped samples. Flat band potentials and donor densities could be calculated from the slope of these plots using the following equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 q N_D A^2} \left( E - E_{FB} - \frac{k_B T}{q} \right)$$

where C is the capacitance of space charge layers,  $\varepsilon$  is the dielectric constant of the semiconductor,  $\varepsilon_0$  is the permittivity of a vacuum, q is the electron charge,  $N_D$  is the carrier density in cm<sup>-3</sup>, A is the actual area of the electrode exposed to the electrolyte, E is the applied potential,  $E_{FB}$  is the flat band potential,  $k_B$  is the Boltzmann constant, and T is the temperature in K. From the calculated result (Table S4), it was found that the undoped and Cr doped samples have comparable carrier density while Mo and W doped samples have much higher ones. The negligible difference of carrier density between the Cr doped sample and the undoped one might be caused by sample-to-sample variation or fitting error. This is reasonable, since the incorporation of  $Cr^{3+}$  to FeVO<sub>4</sub> replacing Fe<sup>3+</sup> does not change the number of carriers, while substitution of Mo<sup>6+</sup> and W<sup>6+</sup> to V<sup>5+</sup> in FeVO<sub>4</sub> will help to increase electron concentration. These donor density values are comparable with the reported value in the literature.<sup>[24]</sup> The Mott-Schottky plots also revealed the flat band potential of the samples. All undoped and Mo, W doped samples have close flat band potential with each other of approximately 0.8 V vs. RHE except the significant cathodic shift of 119 mV Cr doped sample compared the undoped sample. This result is consistent with the cathodic shift (~ 100 mV) of the photocurrent onset potential observed in Figure 3c. Qualitatively, the shift is in

agreement with the larger change in open circuit potential under dark and illumination ( $\Delta OCP$ ) for the Cr-doped sample (87 ± 18 mV) than that for the undoped sample (11 ± 4 mV). We tentatively attribute this shift to a change of the surface dipole in the Cr doped sample, which is related to the presence of Cr-rich phase at the surface of the sample (vide infra).

To evaluate the effect of Cr incorporation to FeVO<sub>4</sub> film, the oxidation states of the elements in Cr doped FeVO<sub>4</sub> was analyzed using X-ray photoelectron spectroscopy (XPS). Fe 2p 3/2 spectra are shown in Figure S9a, the peaks located at 710 to 715 eV corresponding to the attribution of Fe3+ multiplets, which confirm the presence of Fe3+ in the sample.<sup>[22,35]</sup> The high resolution V 2p 3/2 spectra in Figure S9b exhibit the main peak at 517 eV, indicating 5+ valence state of vanadium in the sample.<sup>[36]</sup> An additional peak is also observed at 517.9 eV, which has also been attributed to vanadium in 5+ in the literature.<sup>[34]</sup> The O 1s spectra (Figure S9c) can be contributed from Cr-O bond with the binding energy is 530 eV close to the expected surface lattice oxygen peak at 529.9 eV.<sup>[15]</sup> The successful doping of Cr to FeVO<sub>4</sub> film can be confirmed from the intensity of Cr 2p peak at Figure S9d. The binding energies of Cr 2p 3/2 at 576.48 eV and 577.68 eV correspond to the present of Cr in 3+ oxidation state.<sup>[38,39]</sup> The shift of the main XRD peaks of the Cr doped sample to higher 20 angles and the relatively unchanged carrier density for Cr doped sample confirm that  $Cr^{3+}$  are incorporated into the Fe<sup>3+</sup> sites. The additional small peak at 579.35 assigned to the oxidation of Cr<sup>6+</sup>, indicating the presence of other Cr phases in the sample.<sup>[39]</sup> It is rather unlikely that Cr<sup>6+</sup> substitutes V<sup>5+</sup> based on Pauling's first rule on the crystal structure of ionic compounds, since the ionic radius of  $Cr^{6+}$  (44 pm) is quite significantly smaller than that of  $V^{5+}$  (54 pm). Theoretical study reported by Z. Zhao et al. predicted that Cr<sup>6+</sup> doping to BiVO<sub>4</sub> forms isolated impurity energy band in forbidden band, and therefore shows a negative effect on the performance of doped BiVO<sub>4</sub> sample.<sup>[40]</sup> However, in this study, its existence may be in the form of some amorphous impurity phase. The relative amount is also very small amount and

it does not seem to have harmful effects for PEC of  $FeVO_4$  since the majority of Cr in the sample is in the 3+ oxidation state.

We briefly note that the photocurrents of our Cr-doped FeVO<sub>4</sub> films may be attributed to the oxidation of  $Cr^{3+}$  to  $Cr^{6+}$  instead of water oxidation. To evaluate this possibility, we integrated the photocurrent measured over a 10-hour long-term measurement and obtained a total charge density of ~2.2 C cm<sup>-2</sup>, which is equivalent to  $1.38 \times 10^{19}$  electrons cm<sup>-2</sup>. This amount is more than two orders of magnitude larger than the amount required to fully oxidize all the Cr<sup>3+</sup> to Cr<sup>6+</sup> in our 400-nm thick film (1.06 × 10<sup>17</sup> electrons cm<sup>-2</sup>). This therefore suggests that the Faradaic efficiency in our measurements is > 99%.

To evaluate oxygen evolution reaction (OER) activities of Cr to FeVO<sub>4</sub>, photoelectrochemical measurements of undoped and Cr doped FeVO<sub>4</sub> films were performed in 0.1M KPi (pH = 7) under the dark condition. As displayed in Figure S10, the onset potential of Cr-doped sample occurs at 1.85 V vs. RHE and the over potential to obtain 20 µA cm<sup>-2</sup> current density is 700 mV (1.93 V - 1.23 V = 0.7 V) while the onset potential of undoped sample is 1.9 V vs. RHE with the over potential at 20  $\mu$ A cm<sup>-2</sup> current density is 750 mV (1.98 V - 1.23 V = 0.75 V). This indicates the higher OER activity of Cr doped sample compared to undoped sample. In addition, the OER kinetics were evaluated by Tafel plots derived from polarization curves. As shown in Figure 5d, Cr doped sample exhibit smaller Tafel slope of 124 mV dec<sup>-1</sup> which is better than that of undoped sample (181 mV dec<sup>-1</sup>), suggesting that Cr doped sample has faster OER kinetics. While the exact role of  $Cr^{3+}$  still needs to be further investigated, the Cr doping helps to improve the OER activity and may be the main reason for the improvement of PEC performance as reported in literature.<sup>[41-45]</sup> Hence, this result is in good agreement with EIS results of lower charge-transfer resistance and it confirms the enhanced catalytic activity for charge transfer at the electrode/electrolyte interface of Cr doped compared to undoped FeVO<sub>4</sub> sample.

#### **3.** Conclusion

In summary, we demonstrated successful fabrication of FeVO<sub>4</sub> thin film libraries with different metal dopants using inkjet printing. The improvement of photoelectrochemical performance was achieved for doped sample as compared to pristine FeVO<sub>4</sub> film with the best photoresponse from Cr-doped FeVO<sub>4</sub> with 7% doping ratio of Cr/(Fe + V). Other samples with Mo, or W doped also showed higher current density compared to undoped FeVO<sub>4</sub>, while the current density was decreased for Ni and Zn doped samples; due to the low injection and separation efficiencies of these samples. In this study, for the first time, Cr was discovered as a promising dopant, which is more effective than reported Mo or W for FeVO<sub>4</sub> photoanode. The replacement of  $Cr^{3+}$  to  $Fe^{3+}$  in FeVO<sub>4</sub> crystal helps to improve the bulk properties and the catalytic activity for charge transfer leading to the improvement of photoelectrochemical performance of the photoanode. The improvement of the bulk properties is intriguing considering the iso-valent nature of the substitution and the similar donor density; the exact reason is not clear, but we speculate that this may be related to the larger grain size and the enlarged band bending in the Cr-doped sample. Nevertheless, separation efficiency remains very low (less than 1.5%) over the potential range. Therefore, further study to improve bulk carrier separation is necessary in the development of FeVO<sub>4</sub> photoanodes.

#### 4. Experimental Section

#### Fabrication of photoanodes:

The FeVO<sub>4</sub> thin film libraries were printed using a Dimatix model DMP-2800 piezoelectric inkjet printer. For ink formulation, iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, 99.9%, Sigma Aldrich) and vanadium (III) chloride (VCl<sub>3</sub>, 97%, Sigma Aldrich) were dissolved in diethylene glycol monoethyl ether (DEGEE) which has suitable surface tension (31.8 dyn/cm) to fit the requirement of the printer. Atomic ratio of Fe and V was kept at 1:1, each with a

concentration of 0.4 M. For metal dopants, zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, 98%, Sigma Aldrich), nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, 99.999% trace metals basis, Sigma Aldrich), chromium (III) nitrate nonahydrate (Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, 99%, Sigma Aldrich), molybdenum (V) chloride (MoCl<sub>5</sub>, 95%, Sigma Aldrich) and tungsten (VI) chloride (WCl<sub>6</sub>, 99.9% trace metals basis, Sigma Aldrich) in DEGEE with concentration of 0.02 M were prepared. All dissolved solutions were then injected into separated empty 1 pL drop volume Fujifilm Dimatix printer cartridges. A  $5 \times 8$  (row × column) printing template as shown in Figure 1a was created with 0.6 cm × 0.6 cm individual squares spaced by 0.6 cm; in each square a predetermined amount of the metal salt precursors was printed. For pristine FeVO<sub>4</sub> films, 5 layers of Fe(NO<sub>3</sub>)<sub>3</sub> and 5 layers of VCl<sub>3</sub> were printed on FTO substrates, followed by heating at 300 °C for 2 min. For doped samples, the dopant concentration was controlled by printing different number of layers of dopant precursor (1 – 10 % metal dopant/(Fe + V) ratio corresponded to 1 – 10 dopant layers). Finally, the printed libraries were annealed at 600 °C for 30 min in air to decompose the precursors into metal oxides.

#### High-throughput characterization and measurements:

High-throughput PEC measurement was performed for all compositions using Scanning Droplet Cell (SDC-006) system from Sensolytics. The SDC setup consists of a three-electrode configuration with a Pt wire as the counter electrode, an Ag/AgCl in 3 M KCl as the reference electrode and the fabricated FeVO<sub>4</sub> film as the working electrode. An optical fiber connected to a 150 W Xe lamp served as the light source. Samples were tested in 0.1 M potassium phosphate (KPi, pH = 7) electrolyte.

All compositions were also fabricated on quartz substrates for X-ray diffraction (XRD) measurements, which were performed using a Shimadzu thin film X-ray diffractometer with Cu K $\alpha$  radiation in a gracing incidence configuration with an incidence angle of 1°. Raman

measurements were performed on a Confocal Raman Spectroscopy (Alpha300 SR) with an excitation wavelength of 488 nm.

Larger area thin films (1.5 cm  $\times$  2 cm) of specific compositions were prepared using the same inkjet printing system for certain characterizations. The morphology of the photoanodes was analyzed using a field emission scanning electron microscopy (FE-SEM). Energy dispersive X-ray spectroscopy (EDX) analysis was performed using an Oxford INCA detector at several positions to obtain the average composition of the films. The UV visible absorption was obtained by using an UV-Vis-NIR spectrophotometer (PerkinElmer, Lambda 750S). Photoelectrochemical (PEC) measurements were performed using 3-electrode cell with our fabricated thin films working as the working electrode, Pt coil (surface area ~ 3.6 cm<sup>2</sup>) as the counter electrode and Ag/AgCl (3M KCl) as the reference electrode in 0.1 M potassium phosphate (KPi, pH = 7) electrolyte. The measurements were carried out using CHI 660D working station (CH Instruments, Inc.) in combination with a 150 W xenon solar simulator (67005, Newport Corp.) equipped with a solar filter (KG 3) to achieve the measured light intensity to AM 1.5G (100 mW cm<sup>-2</sup>). The conversion of voltage vs. Ag/AgCl and reversible hydrogen electrode (RHE) was calculated using the following equation:

E (vs. RHE) = E (vs. Ag/AgCl) +  $E^{\circ}_{Ag/AgCl (reference)} + 0.059 \times pH$ 

where  $E^{\circ} _{Ag/AgCl} (reference) = 0.21$  vs. NHE at 298 K. The illuminated area on the photoanodes was 0.125 cm<sup>2</sup>. Incident photon to current conversion efficiency (IPCE) data were measured from 300 nm to 700 nm wavelength at 1.23 V vs. RHE by using a xenon light source (MAX-302, Asahi Spectra Co. Ltd.) combined with a monochromator (CMS-100, Asahi Spectra Co. Ltd.). Mott-Schottky measurements were performed in 0.1 M potassium phosphate solution (KPi, pH = 7). The surface of the samples was carefully covered by thermal tape, thus exposing only the same measured area to the electrolyte (0.283 cm<sup>2</sup>). The electrochemical active surface area (ECSA) measurements using the same configuration as the PEC measurements in the dark. The potential was swept from 0 V to 0.6 V vs. Ag/AgCl at

different scan rates (20, 50, 100, 150, 200 and 300 mV s<sup>-1</sup>). Based on the similar slope of these capacitive current measurements, the electrochemical active surface area of all films are estimated to be similar (**Figure S11**). The Mott-Schottky assumption is confirmed to be satisfied at the single frequency used (i.e., 100 Hz), as the real impedance is rather independent with frequency and the imaginary impedance has a log-log dependence with frequency having a slope very close to -1 (see **Figure S12**). Electrochemical impedance spectroscopy (EIS) measurements were performed at 1.23 V vs. RHE using an automated potentiostat (Metrohm-Autolab, AUT 83285) in a three-electrode configuration. Elemental valence states were obtained by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K $\alpha$  (1486.6 eV) source and a concentric hemispherical energy analyzer on a VG ESCALAB 220I-XL system.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Figure 1.** (a) Printing template and (b) color map of photocurrent density at 1.4 V vs. RHE of the libraries FeVO<sub>4</sub> films with different ratios of metal doping.



**Figure 2.** (a) XRD patterns of undoped and different metals doped FeVO<sub>4</sub> films and (b) their main peak positions at 2 $\theta$  from 25° to 28°. Top-view and cross-sectional SEM images of (c and d) undoped, (e) Zn, (f) Ni, (g and h) Cr, (i) Mo and (j) W doped FeVO<sub>4</sub> films.

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**Figure 3.** (a) J-V curves measured in 0.1M KPi (pH = 7) under chopped AM1.5 illumination. (b) The photocurrents at 1.6 V vs. RHE of undoped and doped FeVO<sub>4</sub> photoanodes. (c) Comparison of onset potential, defined as the potential at which ~2  $\mu$ A cm<sup>-2</sup> of anodic photocurrent is observed, under chopped AM1.5 illumination.



**Figure 4.** (a) Charge injection efficiencies and (b) separation efficiencies at 1.0 V vs. RHE of the different metals doped FeVO<sub>4</sub> thin films.



Figure 5. (a) Nyquist plots of undoped and Cr, Mo, W doped FeVO<sub>4</sub> samples and (b) resistance values from the equivalent circuit model. The EIS spectra were measured in 0.1 M KPi at 1.23 V vs. RHE under AM 1.5 illumination. (c) Mott-Schottky plots of undoped and Cr, Mo, W doped FeVO<sub>4</sub> samples measure at 100 Hz in 0.1 M KPi. (d) Tafel plots for OER of undoped and Cr doped FeVO<sub>4</sub> samples in the dark.

Using combinatorial methods, Cr was discovered as a promising dopant for the first time, which is more effective than reported Mo or W for FeVO<sub>4</sub> photoanode. It helps to improve not only the bulk properties but also the catalytic activity for charge transfer, which results in enhancement of photoresponse of the FeVO<sub>4</sub> photoanode.

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High Throughput Discovery of Effective Metal Doping in FeVO4 for Photoelectrochemical Water Splitting

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#### Supporting Information

# High Throughput Discovery of Effective Metal Doping in FeVO<sub>4</sub> for Photoelectrochemical Water Splitting

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**Figure S1.** Photographs of the printed libraries FeVO<sub>4</sub> films with different ratios of metal doping.



Figure S2. Raman spectra of undoped and Cr doped FeVO<sub>4</sub> samples.

**Table S1.** Compositions of undoped and different metals doped FeVO4 films from EDXresults

Metals	Metal ratio in precursor	Fe	V	0	Metal	Metal/(Fe +V)
Undoped	0	7.13	6.61	86.26	0	0
Zn	5	6.47	3.34	89.78	0.41	4.13
Ni	2	5.68	4.22	89.93	0.17	1.73
Cr	7	3.79	4.14	91.58	0.49	6.14
Mo	2	5.30	6.06	88.49	0.14	1.26
W	2	5.84	6.53	87.43	0.20	1.59

Table S2. Comparison of PEC performance and band gap energy of FeVO<sub>4</sub> photoanodes.

No.	Fabrication	Photocurrent	Indirect	Electrolyte	Reference
	method	at 1.23 V vs.	band gap		
		RHE (µA	(eV)		
		cm <sup>-2</sup> )			
1	Sol-gel	40	2.04	0.1 M KPi, pH	[24]
				= 7	
2	Drop casting	28	~1.90	0.1 M SO4 <sup>2-</sup> ,	[31]
				pH = 7	
3	Layer-by-	50	2.06	0.1 M KPi, pH	[25]
	layer coating			= 7	
4	Spray	40	2.07	0.1 M KPi, pH	[22]
	Pyrolysis			= 7	
5	Inkjet printing	37	2.03	0.1 M KPi, pH	This
				= 7	work



doped FeVO<sub>4</sub> films obtained by measuring major axes of several tens grains in these films.



**Figure S4.** J-V curves measured in 0.1M KPi with hole scavenger (Na<sub>2</sub>SO<sub>3</sub>) under chopped AM1.5 illumination.



Figure S5: Long term stability measurement of undoped and Cr doped FeVO<sub>4</sub> samples for (a) 1000 s and (b) 10 hours under AM 1.5G 100 mW cm<sup>-2</sup> in 0.1M KPi. The higher current densities vs. those in Fig. 3 are due to the contribution of the dark currents.



Figure S6. IPCE of undoped and Cr doped FeVO<sub>4</sub> samples measured at 1.6 V vs. RHE.



Figure S7. Absorption spectrum of undoped and different metals doped FeVO<sub>4</sub> samples.



**Figure S8.** (a) Absorption spectrum, (b) calculated absorption coefficient of undoped  $FeVO_4$  film. (c) Band gap (direct and indirect) values from the Tauc plots of undoped and different metals doped  $FeVO_4$  films.

The values of  $\eta_{inj}$  and  $\eta_{sep}$  can be calculated by the following equations:

$$\eta_{inj} = J_{H_2O}/J_{Na_2SO_3}$$
$$\eta_{sep} = J_{Na_2SO_3}/J_{abs}$$

where  $J_{H_2O}$  is the photocurrent for water oxidation,  $J_{Na_2SO_3}$  is the photocurrent measured in the electrolyte with hole scavenger Na<sub>2</sub>SO<sub>3</sub> with the assumption of no surface efficiency loss, and  $J_{abs}$  is the total absorbed photons expressed in photocurrent, obtained by integrating the product of the absorption curves, the incident photon density in the AM1.5 spectrum, and the electronic charge (**Table S3**).

**Table S3.** Calculated absorbed photocurrent density  $(J_{abs})$  for undoped and metals doped FeVO<sub>4</sub> samples.

Metals doped	Undoped	Zn	Ni	Cr	Mo	W
J <sub>abs</sub>						
$(mA cm^{-2})$	5.66	6.95	7.16	6.03	6.21	7.28

Table S4. Comparison of donor density and flat band potential of the samples

C	Donor density	Flat band potential		
Sample	$(\times 10^{20} \text{ cm}^{-3})$	(mV vs. RHE)		
Undoped	4.11	824		
Cr	4.02	705		
Mo	16.1	796		
W	13.5	792		



3/2 of Cr doped FeVO<sub>4</sub> sample.



**Figure S10.** J-V curves measured in 0.1M KPi (pH = 7) in the dark.



**Figure S11**: Capacitive currents as a function of scan rate for different dopants of FeVO<sub>4</sub> sample.



Figure S12. The real impedance and the imaginary impedance with frequency.