

## Supporting Information

### Revisit the photocharging effect on BiVO<sub>4</sub> (010) surface by identifying the charge reaction kinetics

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## **1. Experimental Sections**

### **1.1 Materials and chemicals**

Analytical grade reagents including bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), vanadium acetylacetonate ( $\text{VO}(\text{acac})_2$ ), and ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) were purchased from Sinopharm Chemical Reagent (Shanghai) or Alfa Aesar Chemical (Shanghai). Other chemical reagents such as boric acid ( $\text{H}_3\text{BO}_3$ ), sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), potassium hydroxide (KOH), hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ , 30%), dimethyl sulfoxide (DMSO), ammonia and other common reagents were obtained from Titan-Tansoole Lab shop (Shanghai Titan Technology Co., Ltd.) and used as received. The F-doped tin oxide (FTO,  $7 \Omega/\text{square}$ ) substrate was purchased from South China Xiangcheng Technology Co., and were ultrasonically cleaned with  $\text{NH}_3\text{-H}_2\text{O}_2\text{-H}_2\text{O}$  (v/v 1:1:1) solution prior to use.

### **1.2 $\text{Bi}_2\text{O}_3$ film preparation**

To prepare bismuth nitrate solution, the appropriate amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was weighed and dissolved into ethylene glycol as a precursor to achieve a concentration of 0.7 M. The solution was subjected to an ultrasonic treatment until it became clear. A pipette tip cast 30  $\mu\text{L}$  of precursor solution on the FTO substrate. After that, on a KW-4a spin-coater, the excess precursor solution was spin-coated on FTO at 2000 rpm for 30 seconds and followed by drying in air. The precursor film was annealed in a muffle furnace at  $600^\circ\text{C}$  for 3 h, with a heating rate of  $5^\circ\text{C}/\text{min}$ , to obtain the bismuth oxide thin film.

### **1.3 Preparation of $\text{BiVO}_4$ films with (010) orientation:**

The conversion of  $\text{Bi}_2\text{O}_3$  to  $\text{BiVO}_4$  followed a process similar to the previous transformation from  $\text{BiOI}$  to  $\text{BiVO}_4$ .<sup>1</sup> Briefly, 20  $\mu\text{L}$  of 0.1 M  $\text{VO}(\text{acac})_2$  in DMSO solution was pipetted onto the bismuth oxide film, which was dried naturally in an oven at 60 °C before being placed in a muffle furnace. The sample underwent annealing at 500 °C for 2 hours, with the temperature increasing at a rate of 2 °C per minute. Following the annealing process, the film was immersed in a 1 M NaOH solution for 40 minutes to remove excess  $\text{V}_2\text{O}_5$ , forming a bismuth vanadate film.

To achieved (010) orientation of  $\text{BiVO}_4$  films, further hydrothermal etching was conducted in a 2%  $\text{HNO}_3$  solution ( $\sim 0.2$  M) at 180 °C for 12-24 hours. The growth mechanism mimicked hydrothermal precipitation under quasi-equilibrium condition.<sup>2</sup>

#### **1.4 Preparation of $\text{BiVO}_4$ particles with (010) orientation**

2 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was weighed and dissolved into 50 mL of 2 M nitric acid solution, stirred on a magnetic stirrer until completely dissolved. Subsequently, 2 mmol of  $\text{NH}_4\text{VO}_3$  was weighed and added to the solution, followed by stirring. The pH of the solution was adjusted to 2 using ammonia. The resulting yellow opaque solution was stirred at room temperature for 2 hours. Next, the mixture was transferred to an autoclave liner and subjected to hydrothermal treatment at 180 °C for 12-24 hours. The precipitation was then washed three times with pure water and ethanol, followed by centrifugation at the speed of 1000 rpm for 5 min. Finally, the resulting powder was vacuum-dried at 60 °C for 12 hours.

#### **1.5 Structure and morphology characterizations**

The surface morphology and sizes of the bismuth vanadate thin films and powders were

investigated using scanning electron microscopy (SEM, JEOL JSM IT800, 10 kV). The crystal structure was performed using X-ray diffractometry (XRD, Bruker D8 Advance,  $\lambda=1.5418\text{\AA}$ , 40 kV, 40 mA). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were conducted on a Thermo Fisher Scientific FEI TALOS F200s at an accelerating voltage of 200 kV with a resolution 0.12 nm). Surface hydrophilicity of the films was measured by a contact angle analyzer (DSA25E, KRUSS Scientific) using DI water as the detecting liquid. The UV-Vis absorption spectra were obtained using a spectrometer (Shimazu UV2900) over wavelengths ranging from 280 nm and 700 nm. The surface electronic configurations of the films were comprehensively investigated through X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha, Al K $\alpha$  source at 1486.6 eV). The binding energy of the C 1s peak, calibrated to 284.9 eV, served as a reference for accurate interpretation of the spectra.

## 1.6 Photoelectrochemical measurements

Thin BiVO<sub>4</sub> films were utilized as working electrode, with all unused parts insulated using cross-linked rubber. An electrochemical workstation (CH Instrument 760E) employing a three-electrode configuration was typically used. The electrolyte consisted of a potassium borate solution (1 M borate acid, adjusted by 1 M KOH to pH = 10, 1 mol/L), with Ag/AgCl (saturated KCl, 0.197 V vs. NHE) serving as reference electrode, and a platinum wire as counter electrode. The applied potential were referenced to the reversible hydrogen electrode (RHE) using the Nernst equation ( $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ V} \times \text{pH}$ ). The current-potential polarization ( $J$ - $V$ ) curves were collected both

in the dark and under simulated sunlight conditions (Perfectlight, AM 1.5G, 100 mW/cm<sup>2</sup>).

The photocharging treatment, similar to the previous report<sup>3</sup>, involved illuminating the BiVO<sub>4</sub> photoanode under a white LED light source (Zahnar, LS1925, 100 mW/cm<sup>2</sup>) for varying duration, denoted as photocharged (PC) BiVO<sub>4</sub>. Conversely, the BiVO<sub>4</sub> electrode without photocharging treatment was labeled as UT BiVO<sub>4</sub>.

The Mott-Schottky plots were measured under dark conditions at frequencies of 2000 Hz, with a relative dielectric constant of 68. Intensity-modulated photocurrent spectroscopy (IMPS) was measured at 0.6 V vs. RHE, using an incident photon flux of 500 W/m<sup>2</sup> and an AC amplitude of 200 mV. The frequency ( $f$ ) corresponding to the maximum photon is the sum of the charge transfer rate constant ( $k_{\text{trans}}$ ) and the recombination constant ( $k_{\text{rec}}$ ). The surface charge transfer efficiency, which ranges from 0 to 1, is determined by the intercept of the x-axis at lower frequencies.

### **1.7 Rate-law study**

To obtain rate-order kinetics for the photoelectrochemical water oxidation, the chronoamperometric (I-t) measurements were carried out using three electrode configurations. A potentiostat (CH Instrument 760E) was used for photocurrent measurement, and the chopped white LED light (Zahner LS1925, 10-70 mW/cm<sup>2</sup>, on Zahner Zennium Pro) with varying light intensities was applied. The surface charge density ( $Q$ ) was calculated using the electrochemical capacitance ( $C$ ) on the electrode and the photovoltage ( $V_{\text{ph}}$ ). The capacitance was acquired from the electrochemical equivalent circuit (R(C(R(RC)))) and electrochemical impedance spectroscopy (EIS)

under same LED light (Zahner LS1925) at 1 mol/L potassium borate and at an applied voltage of 1.23 V vs RHE. For each rate-law measurement (of charges and reaction rate), the photocharging time for 1 h was applied. The photovoltage was calculated by polarization curve ( $J$ - $V$ ) of the same photoanodes measured under dark condition and light condition at a specific current density ( $V_{\text{ph}}=V_{\text{light}}-V_{\text{dark}}$ ), respectively. The surface charge density was calculated by multiplying of surface capacitance and the photogenerated voltage ( $Q=C \cdot V_{\text{oc}}$ ).

The charge transfer rates at various illumination intensities were obtained from the steady photocurrent in  $I$ - $t$  curves. To minimize the influence of measurement and photocharging history, each photoanode was equilibrated in the electrolyte under dark condition for 20 min and photocharging treatment was applied before each test.

For the photovoltage measurement, the potential difference at the same current level ( $0.04 \text{ mA/cm}^2$ ) was determined from the polarization ( $J$ - $V$ ) curves measured under both dark and light conditions (with illumination matching the rate-law conditions). This approach provides kinetic data before and after light charging of the electrode surface.

## 2. Scheme and results

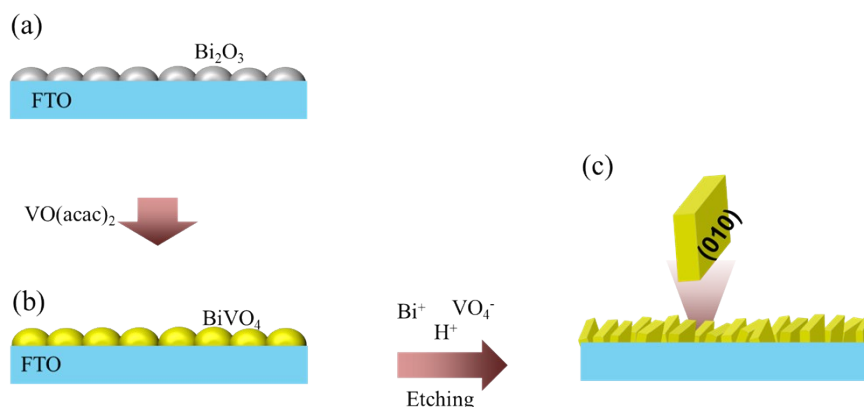


Fig. S1. Scheme of (010) oriented BiVO<sub>4</sub> films: (a) the formation of Bi<sub>2</sub>O<sub>3</sub>, (b) the conversion of Bi<sub>2</sub>O<sub>3</sub> to BiVO<sub>4</sub> in presence of VO(acac)<sub>2</sub>, (c) the hydrothermal acid etching of the BiVO<sub>4</sub> films.

In presence of HNO<sub>3</sub>, the Bi and V moieties could be dissolved into solution forming Bi<sup>+</sup> (or Bi<sup>3+</sup>) cations, VO<sub>4</sub><sup>-</sup> (or VO<sub>4</sub><sup>3-</sup>) anions at the high energy region, which could be redeposited on a certain region (e.g., (010)). This plate-like structure is analogous to those hydrothermal precipitation.

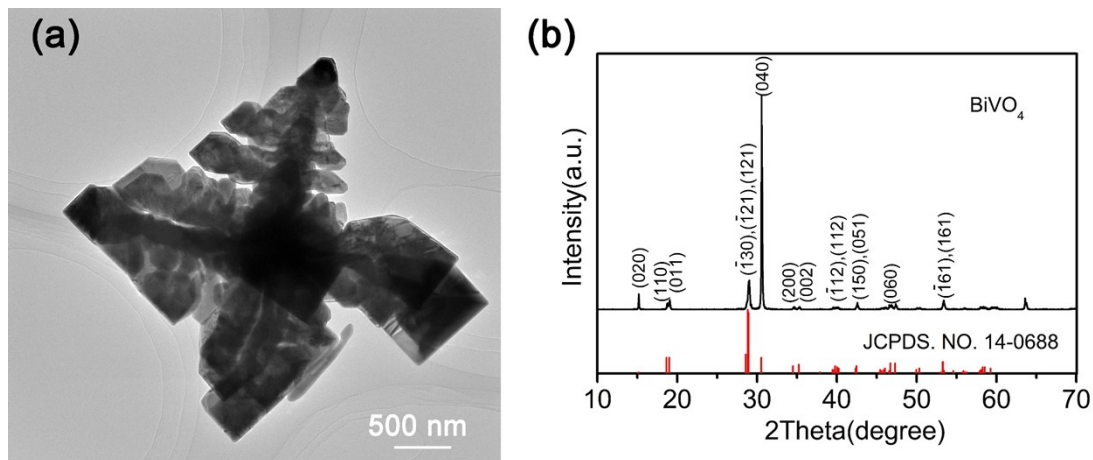


Fig. S2: (a) TEM image and (b) XRD pattern of plate-like BiVO<sub>4</sub> dendrite, prepared in presence of HNO<sub>3</sub> (pH=2) at 180 °C.

The hydrothermal deposition and treatment in various pH solution, resulting the morphology change. At the pH of 3~4, dendrite morphology could be obtained. At the pH of 2, plate-like dendrite morphology was found. When the pH of solution decreased to 1, thick plate morphology could be collected. As all the XRD showed the plate-like sample has the strong (040) diffractions, we believed plate surface could be attributed to the (010) orientation. Here, the TEM image (Fig. S2(a)) and XRD pattern (Fig. S2(b)) demonstrate this structure orientation.



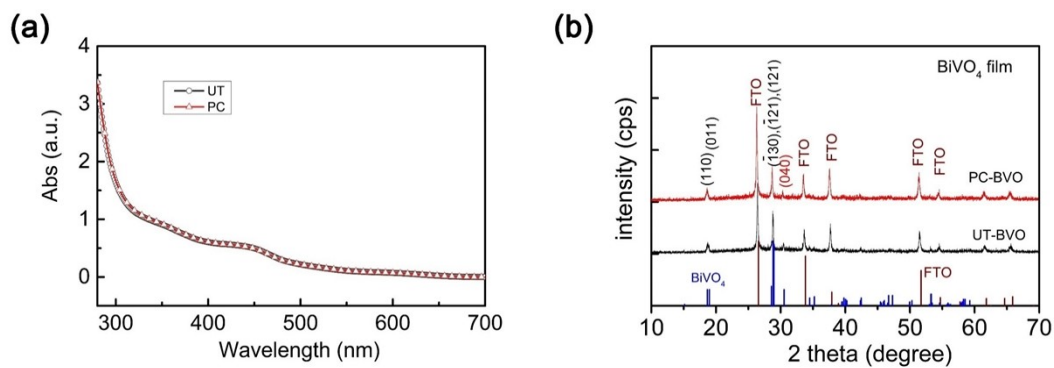


Fig S3. (a) UV-vis absorption spectra and (b) XRD patterns of BiVO<sub>4</sub> films before and after photocharging treatment.

The identical of UV-vis absorption and XRD patterns showed the photo-corrosion of the (010) oriented BiVO<sub>4</sub> films was not serious in alkaline borate solution.

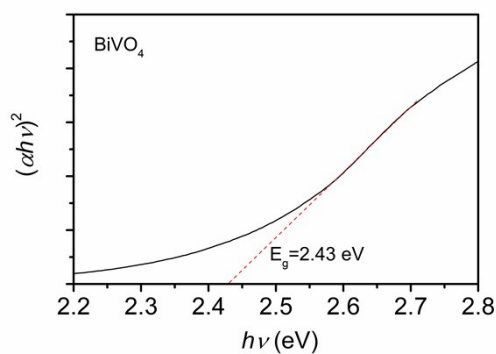


Fig. S4. Tauc plot of BiVO<sub>4</sub>, calculated from UV-vis absorption spectra. The bandgap of the UT and PC films were same as 2.43 eV.

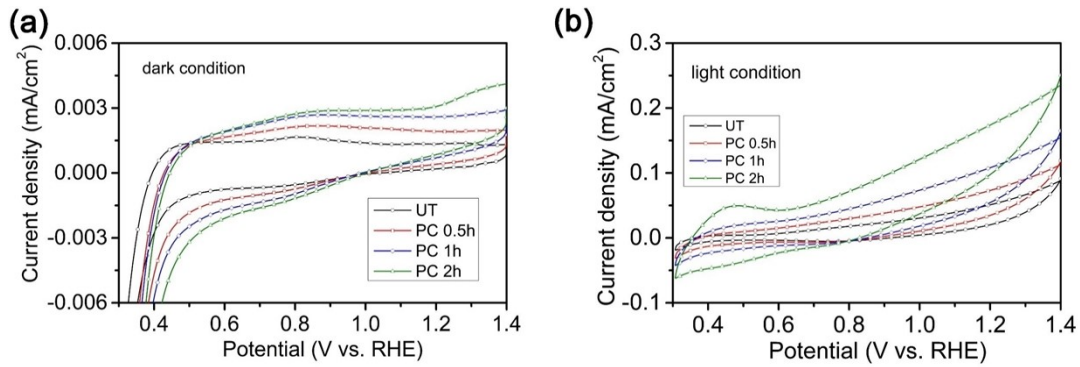


Fig. S5. Cyclic voltammograms of  $\text{BiVO}_4$  films with (010) facet measured in potassium borate (1 M) under: (a) dark condition, (b) under light condition ( $100\text{mw}/\text{cm}^2$ ). Under dark conditions, the current between 0.4 and 1.4 V vs. RHE remained quite low. However, when exposed to light, the photocurrent increased significantly by several orders of magnitude. Notably, the photocharged  $\text{BiVO}_4$  exhibited even more substantial improvements.

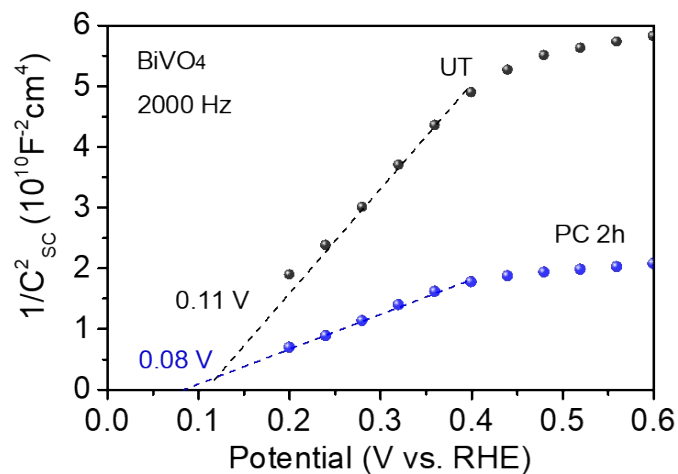


Fig. S6. Mott-Schottky plots of  $\text{BiVO}_4$  photoanode measured under dark condition using an AC signal of 2000 Hz: UT and PC 2 h represent the  $\text{BiVO}_4$  photoanode before and after photocharging treatment.

It is shown that the Flatband of photocharged  $\text{BiVO}_4$  had a slight negative shift from 0.11 V vs. RHE to 0.08 V vs. RHE.

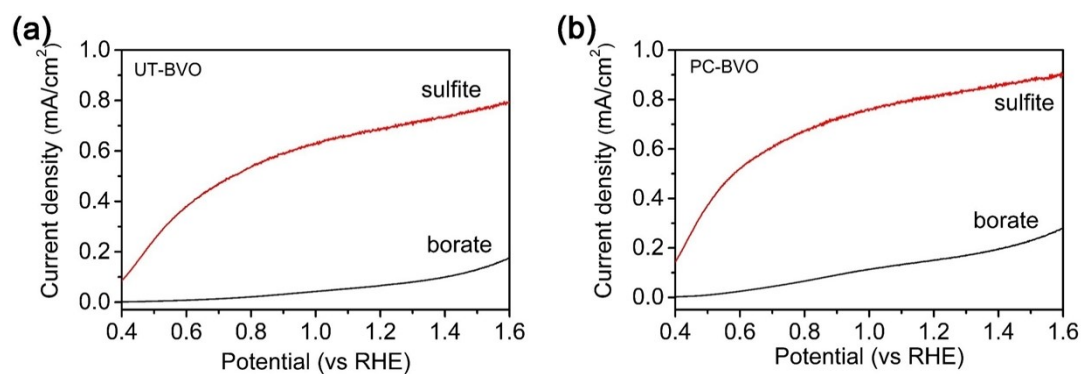


Fig. S7. Potential-photocurrent polarization curves measured in borate (1 M) and sulfite (1 M borate and 0.2 M Na<sub>2</sub>SO<sub>3</sub>): (a) UT-BiVO<sub>4</sub> and (b) PC-BiVO<sub>4</sub>.

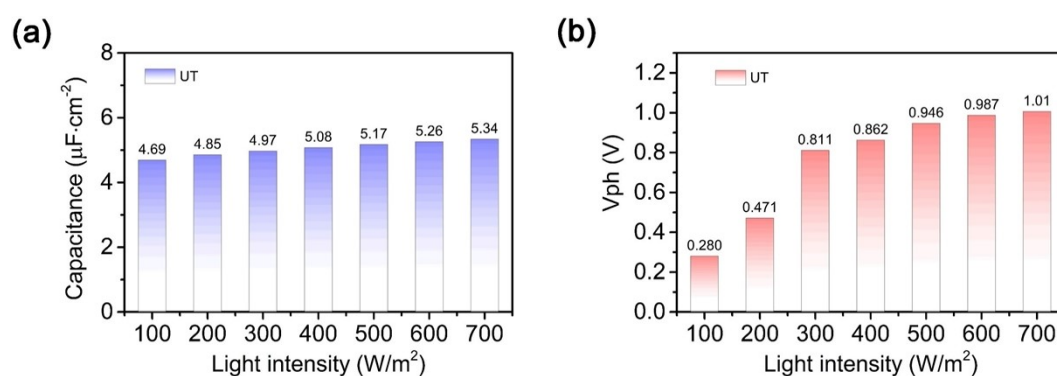


Fig. S8. (a) capacitance and (b) photovoltage of UT BiVO<sub>4</sub> photoanode measured under various light illumination.

The photovoltage increased gradually from 0.28 V to 1.01 V with the light intensity increase. For the capacitance in the space charge region, it slightly increased from 4.69 μF/cm<sup>2</sup> to 5.34 μF/cm<sup>2</sup>.

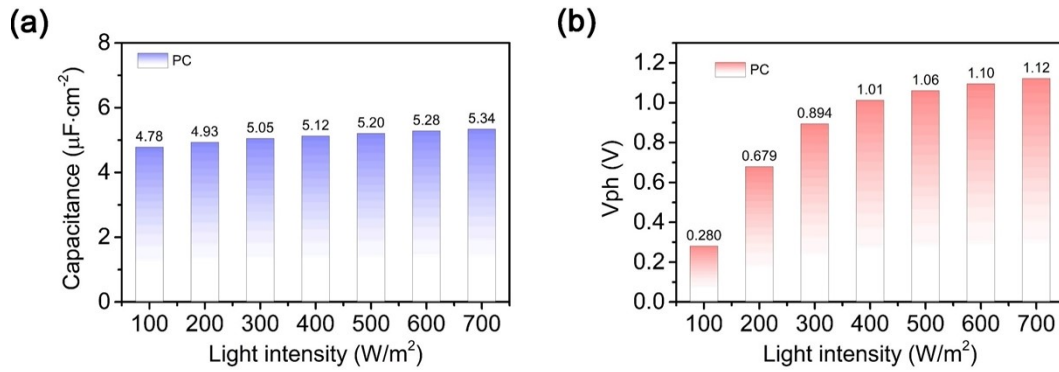


Fig. S9. (a) capacitance and (b) photovoltage of PC BiVO<sub>4</sub> photoanode measured under various light illumination.

The photovoltage increased gradually from 0.28 V to 1.12 V with the light intensity increase. For the capacitance in the space charge region, it slightly increased from 4.78 μF/cm<sup>2</sup> to 5.34 μF/cm<sup>2</sup>.

### 3. Acknowledgements

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### 4. Author Contributions

**Yanjie Liu:** Methodology, deposition, performance study, writing- original draft;

**Meiyong Gong:** data collection, measurement, data analysis; **Jundie Hu:**

Characterization, data analysis, Supervision; **Jiafu Qu:** Characterization and band

structure analysis; **Qingqing Li:** Investigation, data analysis; **Zhichao Zhang:**

Characterization, data collection; **Wei Sun:** Conceptualization, Validation; **Xiaogang**

**Yang:** Conceptualization, Investigation, Funding acquisition, Writing-Review & Editing; **Chang Ming Li:** Conceptualization, Resources, Funding acquisition.

## **5. References:**

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2. C. Hong, Y.-I. Kim, J. H. Seo, J. H. Kim, A. Ma, Y. J. Lim, D. Seo, S. Y. Baek, H. Jung and K. M. Nam, *ACS Applied Materials & Interfaces*, 2020, **12**, 39713-39719.
3. A. Venugopal, R. Kas, K. Hau and W. A. Smith, *Journal of the American Chemical Society*, 2021, **143**, 18581-18591.