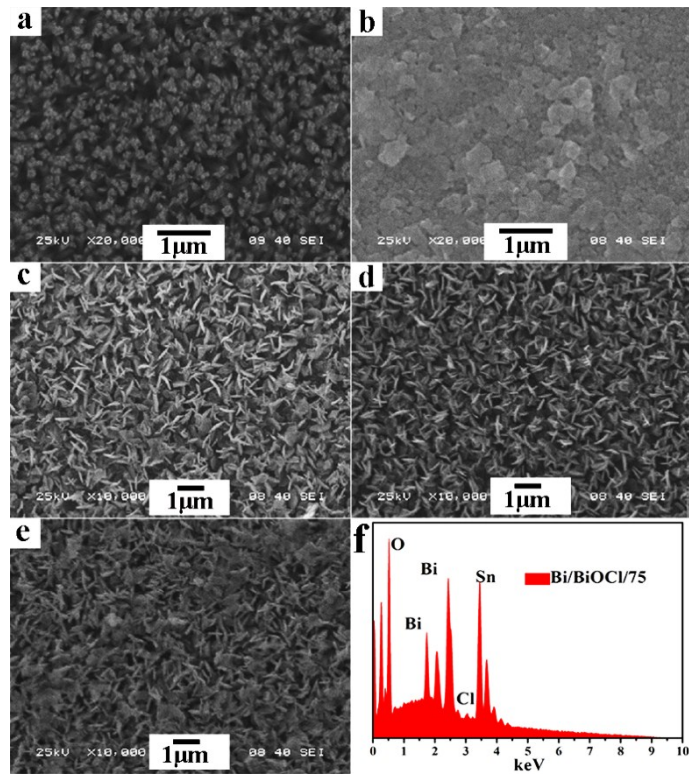


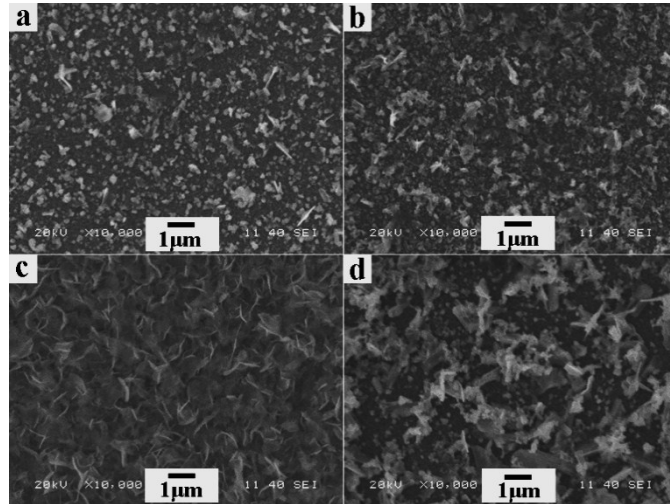
## **Supporting Information**

### **An In-situ Photoelectroreduced Approach to Fabricate Bi/BiOCl Heterostructure Photocathode: Understanding the Role of Bi Metal for Solar Water Splitting**

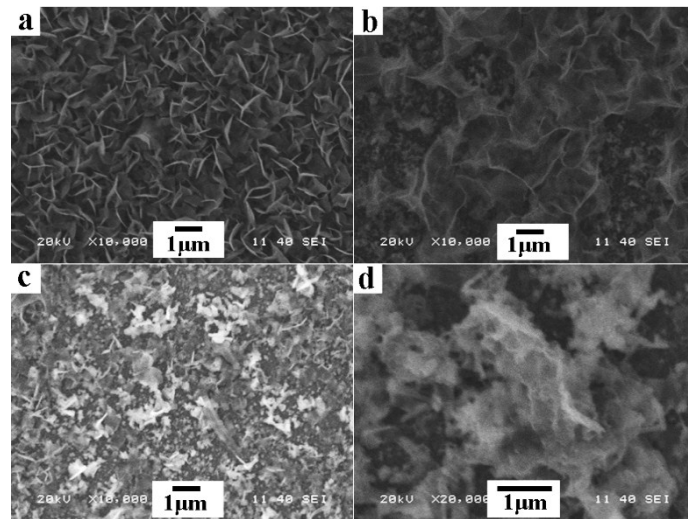
Weiqliang Fan, Chunfa Li, Hongye Bai, Yanyan Zhao, Bifu Luo, Yongjun Li, Yilin Ge,  
Weidong Shi,\* Hongping Li\*



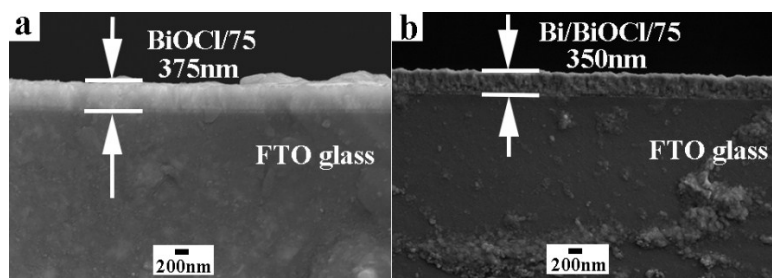
**Fig. S1.** SEM images of TiO<sub>2</sub> nanorods (a), and BiOCl with different cycle times prepared by the CBD method on FTO substrate for BiOCl/25(b), BiOCl/50(c), BiOCl/75 (d) and BiOCl/100 (e). The EDS profile recorded from Bi/BiOCl/75 nanosheets (f).



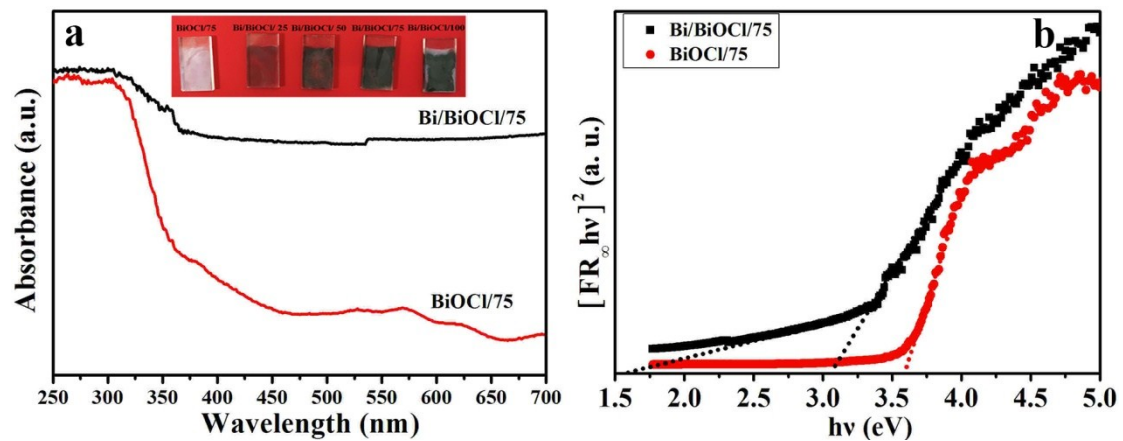
**Fig. S2.** SEM images of Bi/BiOCl/25(a), Bi/BiOCl/50(b), Bi/BiOCl/75(c) and Bi/BiOCl/100 (d).



**Fig. S3.** SEM images of Bi/BiOCl/75/0.5h (a), Bi/BiOCl/75/1h (b), Bi/BiOCl/75/2h(c) and Bi/BiOCl/75/8h.



**Fig. S4.** The cross-sectional SEM images of BiOCl/75 nanosheets (a) and Bi/BiOCl/75 photocathode (b).



**Fig. S5.** UV-vis diffuse reflectance spectra (DRS) (a) and Kubelka-Munk function plot (b) of synthesized BiOCl/75 and Bi/BiOCl/75. The color change of the samples on the surface can be clearly seen in the inset.

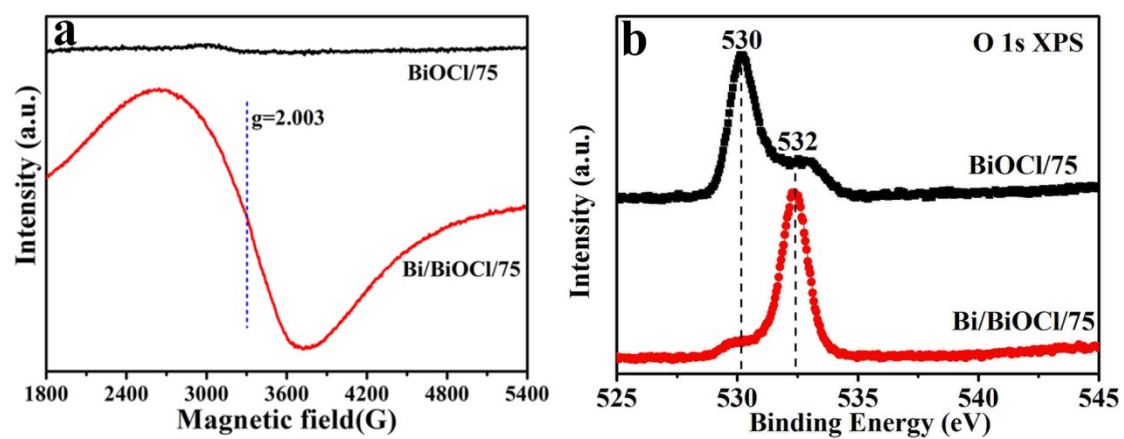
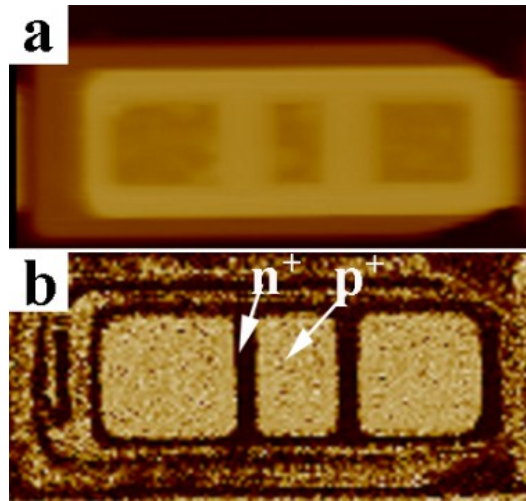
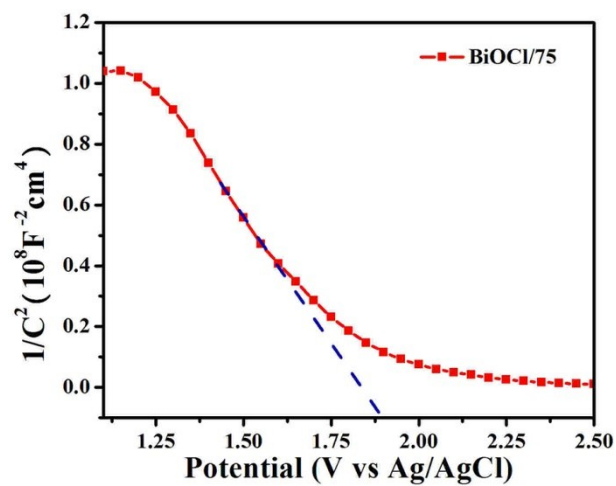


Fig. S6. The EPR spectra (a) and XPS spectra (b)



**Fig. S7.** Topography (a) and SCM-Data (b) of SRAM sample. The SRAM sample was obtained from Bruker Company (CA, USA).





**Fig. S8.** Mott-Schottky plots of bare BiOCl.

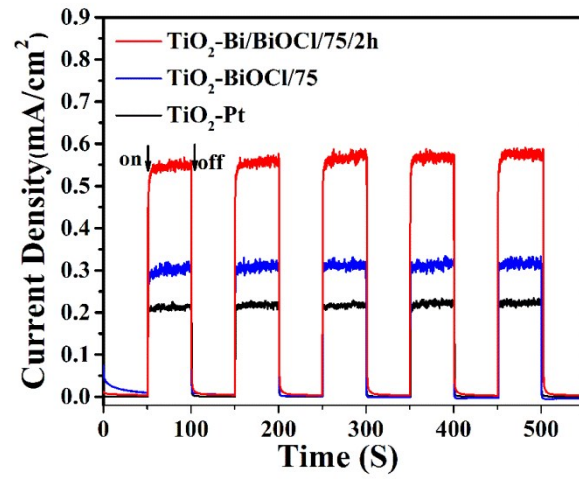
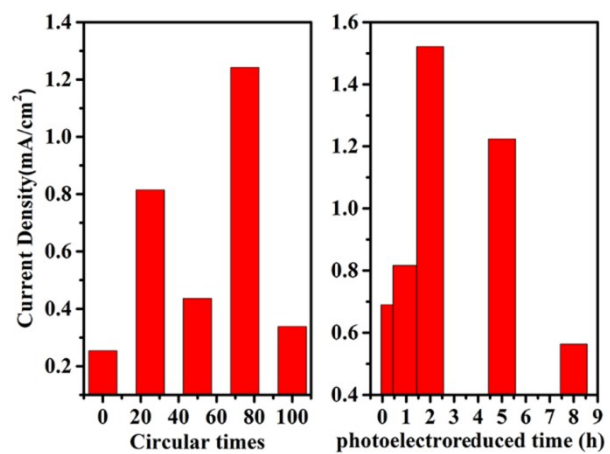
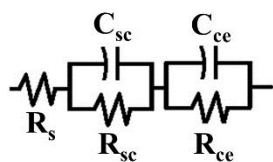


Fig. S9. Transient photocurrent responded with intermittent light



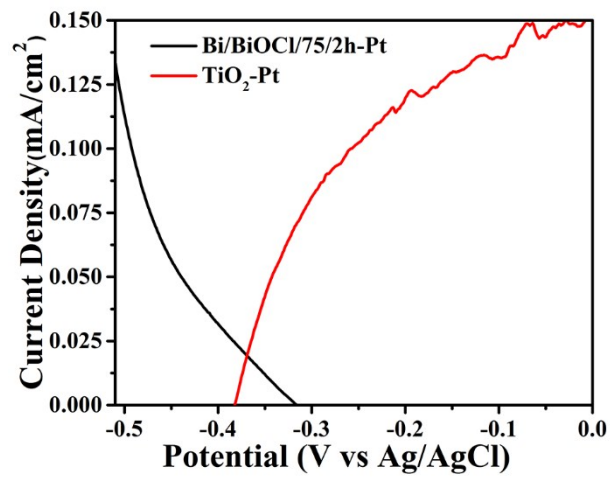
**Fig. S10.** Cross experiment analysis of Bi/BiOCl photocathode based on the conditions of CBD circle times and photoelectroreduced time



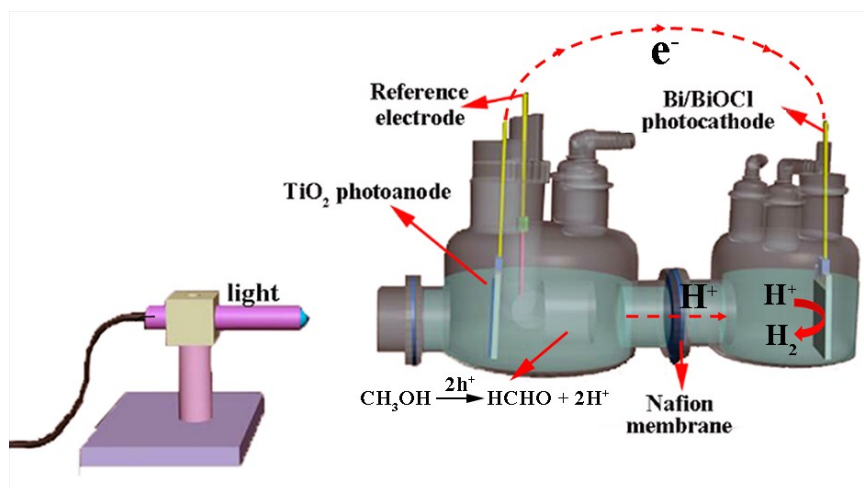
Equivalent circuit

Sample	$R_s$ ( $\Omega$ )	$R_{sc}$ ( $\Omega$ )	$R_{ce}$ ( $\Omega$ )
TiO <sub>2</sub> -Pt	193.7	$276.2 \times 10^3$	$1.318 \times 10^3$
TiO <sub>2</sub> -BiOCl/75	205.7	$187.3 \times 10^3$	$1.219 \times 10^3$
TiO <sub>2</sub> -Bi/BiOCl/75/2h	165.5	$71.7 \times 10^3$	$0.561 \times 10^3$

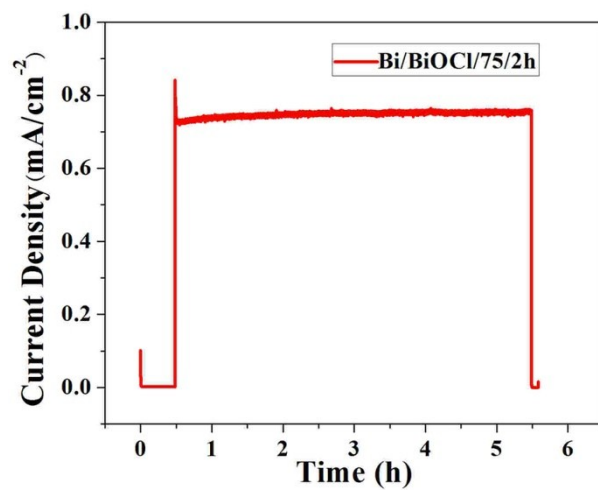
**Table S1.** Equivalent circuit-fitting results



**Fig. S11.** Overlaid current density-potential behaviors for TiO<sub>2</sub> and Bi/BiOCl.



**Fig. S12** Schematic diagram of equipment for PEC hydrogen production.



**Fig. S13** The stability of Bi/BiOCl/75/2h was measured in the TiO<sub>2</sub>—Bi/BiOCl/75/2h water splitting photocell (0 V vs Ag/AgCl).