## **Supplementary Materials**

Achieving photocatalytic water reduction and oxidation over narrow bandgap FeVO<sub>4</sub>

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Supplementary Figure 1. X-Ray diffraction (XRD) pattern of FeVO<sub>4</sub>.



**Supplementary Figure 2.** Scanning electron microscope (SEM) images of (A) FeVO<sub>4</sub>·1.1H<sub>2</sub>O and (B) FeVO<sub>4</sub>.



Supplementary Figure 3. Mott-Schottky plots of FeVO<sub>4</sub>.



Supplementary Figure 4. Tauc plot of FeVO<sub>4</sub> (obtained from Figure 1A).

Sample	The molar ratio of Cr/(Cr+Fe) (%)			
	Theoretical value	Measured value		
FeVO <sub>4</sub> :Cr(2.5%)	2.5	1.4		
FeVO <sub>4</sub> :Cr(3.0%)	3.0	1.8		

Supplementary Table 1. The molar ratio of Cr/(Cr+Fe) measured by ICP-OES



**Supplementary Figure 5.** SEM images of (A) FeVO<sub>4</sub>:Cr·1.1H<sub>2</sub>O and (B) FeVO<sub>4</sub>:Cr samples. (C) Energy dispersive X-ray spectroscopy (EDS) mapping images of FeVO<sub>4</sub>:Cr sample.



**Supplementary Figure 6.** Transmission electron microscopy (TEM) images of (A) FeVO<sub>4</sub> and (B) FeVO<sub>4</sub>:Cr samples. (C) High-resolution TEM (HRTEM) images of (C) FeVO<sub>4</sub> and (D) FeVO<sub>4</sub>:Cr samples.



**Supplementary Figure 7.** (A) XRD patterns and (B) enlarged XRD patterns of FeVO<sub>4</sub>:Cr samples with different doping proportions. Herein, 1: FeVO<sub>4</sub>:Cr(1.5%), 2: FeVO<sub>4</sub>:Cr(2.0%), 3: FeVO<sub>4</sub>:Cr(2.5%), 4: FeVO<sub>4</sub>:Cr(3.0%), 5: FeVO<sub>4</sub>:Cr(3.5%).



**Supplementary Figure 8.** Rietveld refined XRD patterns of (A) FeVO<sub>4</sub> and (B) FeVO<sub>4</sub>:Cr samples.

Samples .	Lattice parameters							
	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)		
FeVO <sub>4</sub>	6.7824	8.0682	9.3358	96.678	106.226	101.842		
FeVO <sub>4</sub> :Cr	6.7728	8.0601	9.3191	96.696	106.176	101.854		

Supplementary Table 2. Lattice parameters of FeVO<sub>4</sub> and FeVO<sub>4</sub>:Cr samples obtained by XRD Rietveld refinement



**Supplementary Figure 9.** (A) Raman spectra and (B) enlarged Raman spectra of FeVO<sub>4</sub> and FeVO<sub>4</sub>:Cr samples.



**Supplementary Figure 10.** (A) The ultraviolet-visible diffuse reflectance spectra obtained using Kubelka-Munk function and (B) Tauc plots of FeVO<sub>4</sub> and FeVO<sub>4</sub>:Cr samples.



**Supplementary Figure 11.** X-ray photoelectron spectroscopy (XPS) (A) Cr 2p, (B) Fe 2p, (C) V 2p and (D) O 1s of FeVO<sub>4</sub> and FeVO<sub>4</sub>:Cr samples.



Supplementary Figure 12. Effect of (A) the calcination temperature and (B) the loaded proportion of  $CoO_x$  on the initial  $O_2$  evolution rate over  $CoO_x/FeVO_4$ :Cr sample (the molar ratio of Cr/(Cr+Fe) is 2.5%). Reaction conditions: 0.1 g of photocatalyst; 100 mL of AgNO<sub>3</sub> aqueous solution (50 mM); 0.1 g of La<sub>2</sub>O<sub>3</sub>; 300 W Xe lamp with a cutoff filter ( $\lambda \ge 420$  nm).



Supplementary Figure 13. Effect of the loaded proportion of Pt on the initial H<sub>2</sub> evolution rate over Pt/FeVO<sub>4</sub>:Cr sample (the molar ratio of Cr/(Cr+Fe) is 3%). Reaction conditions: 0.1 g of photocatalyst; 100 mL of ascorbic acid aqueous solution (10 mM); 300 W Xe lamp with a cutoff filter ( $\lambda \ge 420$  nm).



Supplementary Figure 14. (A) The recycling test of H<sub>2</sub> generation over FeVO<sub>4</sub>:Cr photocatalyst loaded with Pt cocatalyst. Reaction conditions: 0.1 g of photocatalyst (1.0 wt% Pt is loaded); 100 mL of ascorbic acid aqueous solution (10 mM); 300 W Xe lamp with a cutoff filter ( $\lambda \ge 420$  nm). (B) XRD patterns of FeVO<sub>4</sub>:Cr samples before and after the HER (hydrogen evolution reaction). The molar ratio of Cr/(Cr+Fe) in FeVO<sub>4</sub>:Cr is 3%.

The recycling test with three cycles was conducted to evaluate the stability of the FeVO<sub>4</sub>:Cr photocatalyst, and no obvious decrease was observed in the long-term test (Supplementary Figure 14A). XRD results also show that there is no obvious difference between the photocatalysts before and after the reaction (Supplementary Figure 14B).



Supplementary Figure 15. XPS Co 2*p* of CoO<sub>x</sub>/FeVO<sub>4</sub> and CoO<sub>x</sub>/FeVO<sub>4</sub>:Cr samples.



**Supplementary Figure 16.** SEM images of (A) FeVO<sub>4</sub>, (B) CoO<sub>x</sub>/FeVO<sub>4</sub> and (C) CoO<sub>x</sub>/FeVO<sub>4</sub>:Cr samples. EDS mapping images of (D) CoO<sub>x</sub>/FeVO<sub>4</sub> and (E) CoO<sub>x</sub>/FeVO<sub>4</sub>:Cr samples.

As shown in Supplementary Figures 16A-C, compared with FeVO<sub>4</sub>, the surface of  $CoO_x/FeVO_4$  and  $CoO_x/FeVO_4$ :Cr is deposited with numerous  $CoO_x$  nanoparticles in similar particle size. EDS mapping images (Supplementary Figure 16D and E) further confirm that the  $CoO_x$  species evenly distributes on the surface of  $CoO_x/FeVO_4$  and  $CoO_x/FeVO_4$ :Cr samples.