Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information:

Construction of Unique Heterojunction Photoanodes through *in-situ* Quasi-Epitaxial Growth of $FeVO_4$ on Fe_2O_3 Nanorod Arrays for Enhanced Photoelectrochemical Performance

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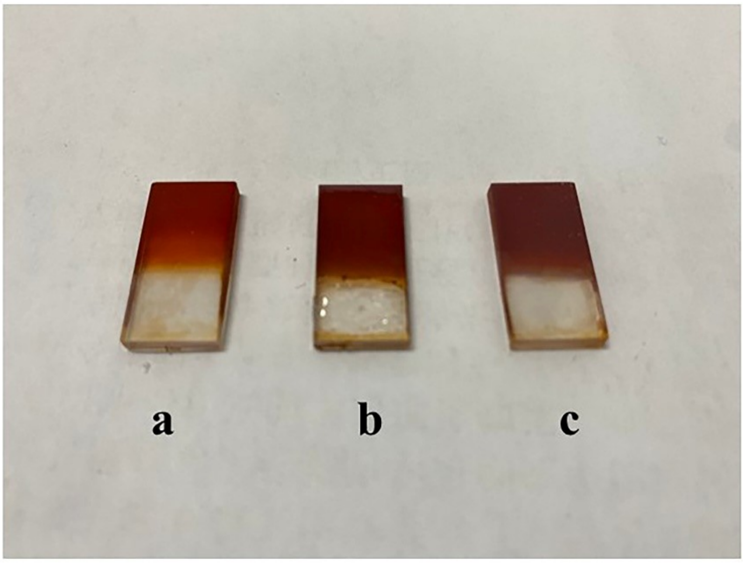

Figure S1. Color diagram of the photoanodes.

Figure S1 is the color schematic diagram of the prisitine Fe_2O_3 photoanode (a), $FeVO_4$-Fe_2O_3 photoanode with 7 mM vanadyl acetylacetonate (b) and $FeVO_4$-Fe_2O_3 photoanode with 20 mM vanadyl acetylacetonate (c) . It can be seen that as the concentration of vanadyl acetylacetonate increases, the color of the photoelectrode also changes. Compared with the prisitine Fe_2O_3 photoanode, the $FeVO_4$-Fe_2O_3 photoanode with 20 mM vanadyl acetylacetonate has shown obvious color deepening.

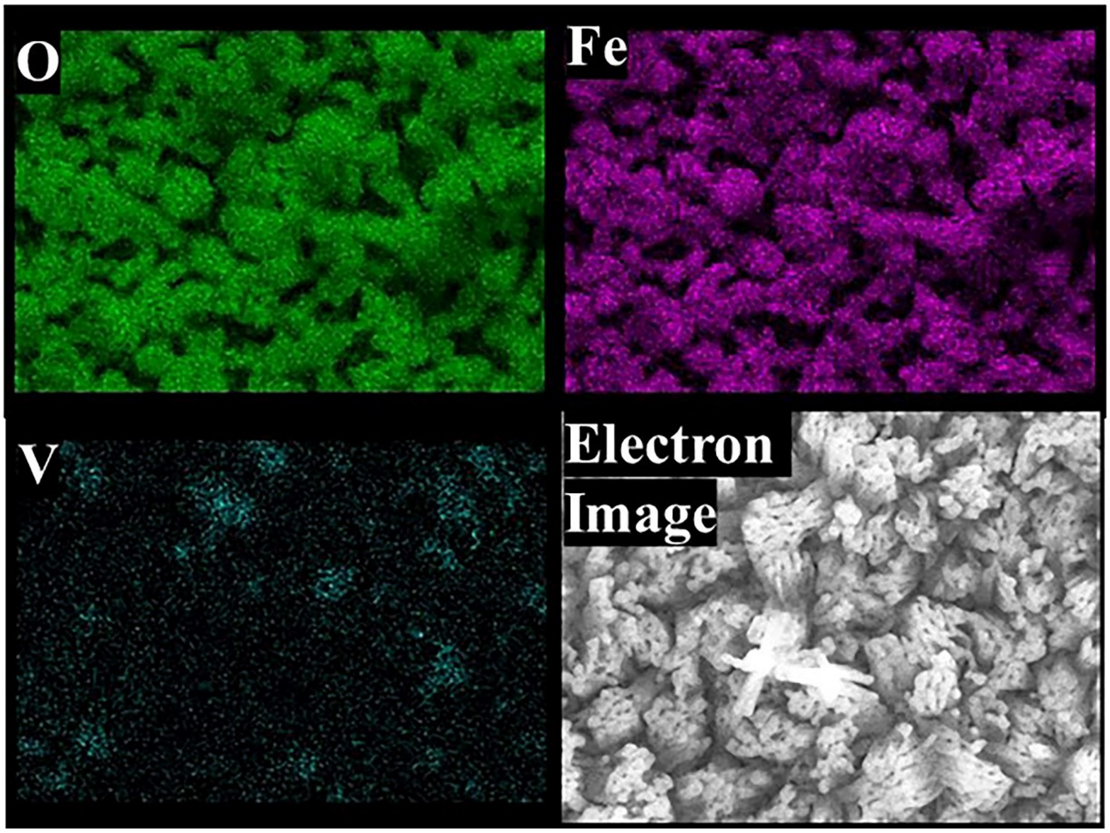

Figure S2. EDS elemental mapping of the $FeVO_4$-Fe_2O_3 photoanode.

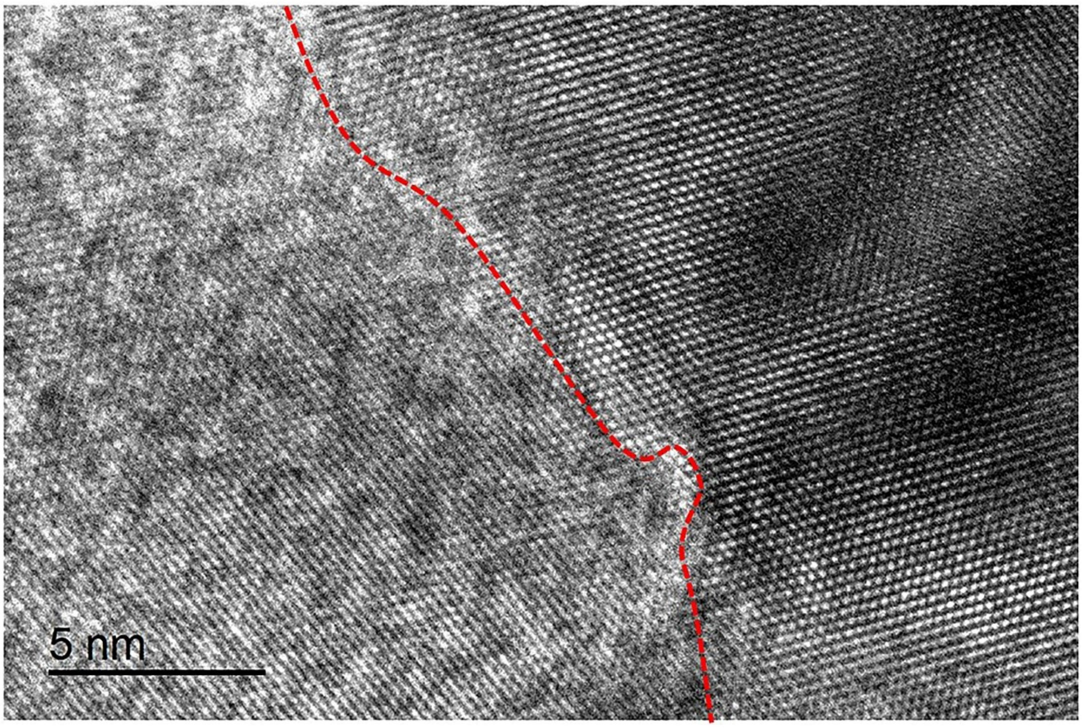

Figure S3. TEM image of the $FeVO_4$-Fe_2O_3 photoanode.

Table S1. The Fe^{2+}elemental content of the photoanodes

	Area of Fe^{2+} $2p_{3/2}$	Area of Fe^{2+} $2p_{1/2}$	Sum
$FeVO_4$-Fe_2O_3 photoanode	12106.05	5186.25	17292.3
Fe_2O_3 photoanode	14262.23	3864.48	18126.71

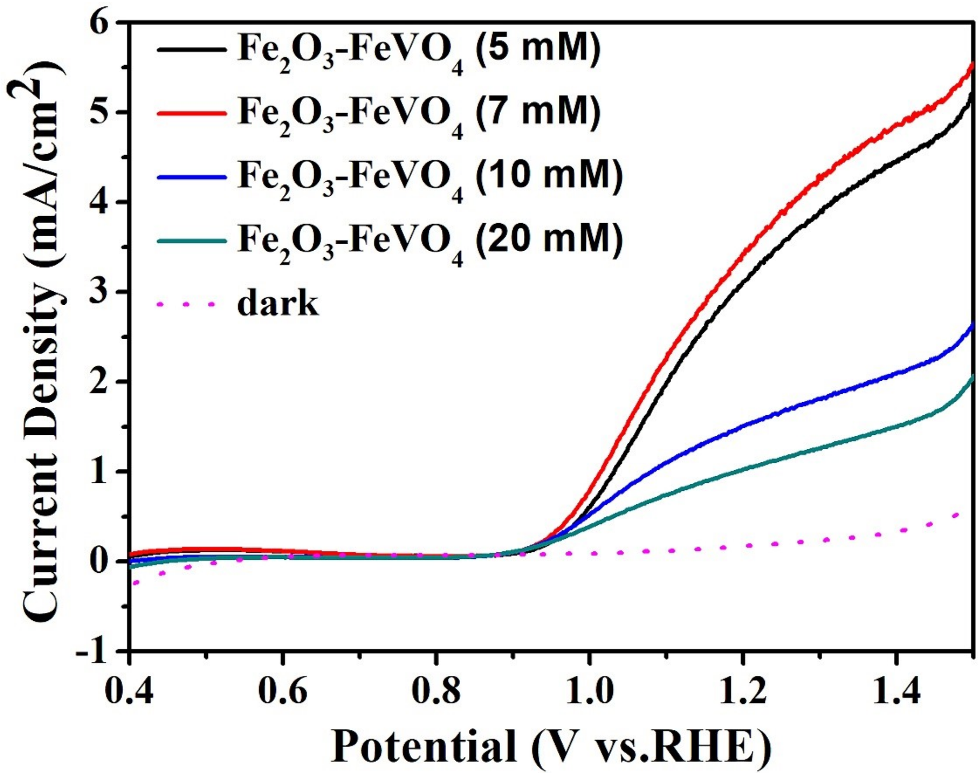

Figure S4. LSV curves of $FeVO_4$-Fe_2O_3 photoanode of various concentrations of vanadyl acetylacetonate.

Table S2. The IPCE of the photoanodes

wavelength	400 nm	435 nm	450 nm	475 nm	500 nm	550 nm	600 nm	650 nm
IPCE of the $FeVO_4$-Fe_2O_3 photoanode (%)	22.67	15.51	11.03	6.76	4.93	2.43	0.95	0.67
IPCE of the pristine Fe_2O_3 photoanode (%)	9.26	6.39	4.54	2.78	2.07	0.92	0.54	0.46

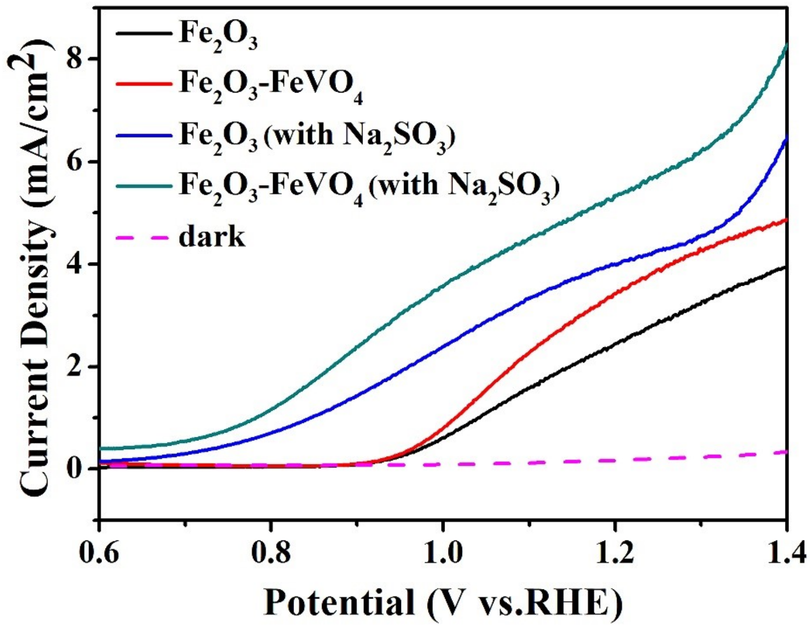

Figure S5. LSV curves of pristine Fe_2O_3 photoanode and $FeVO_4$-Fe_2O_3 photoanode with and without hole scavenger.

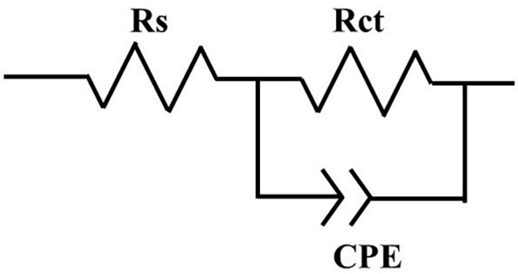

Figure S6. EIS equivalent circuit diagram.

photoanode	Rs (Ω)	Rct (Ω)
Fe_2O_3	11.01	329.9
$FeVO_4$-Fe_2O_3	10.82	239.1

Figure S7. EIS parameters of pristine Fe_2O_3 photoanode and $FeVO_4$-Fe_2O_3 photoanode.

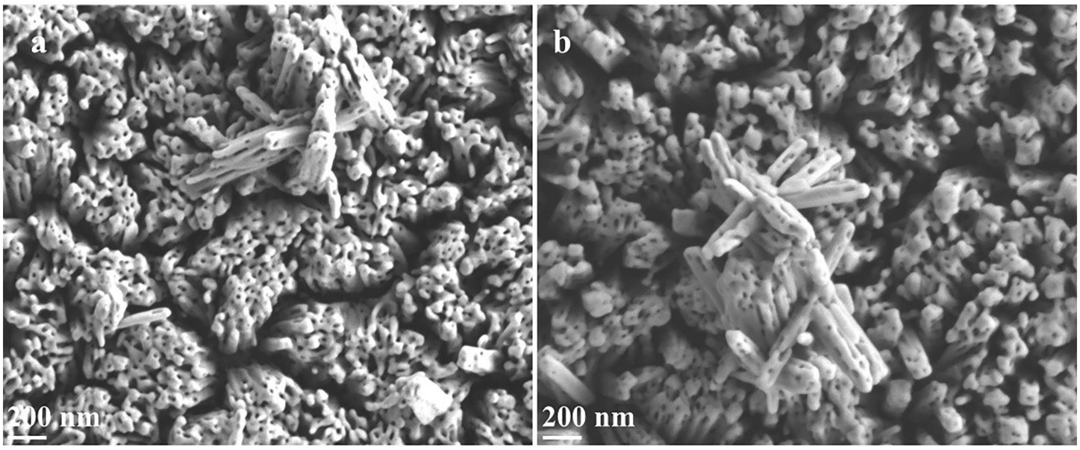

Figure S8. SEM images of the $FeVO_4$-Fe_2O_3 photoanode (a) before and (b) after the stability test.

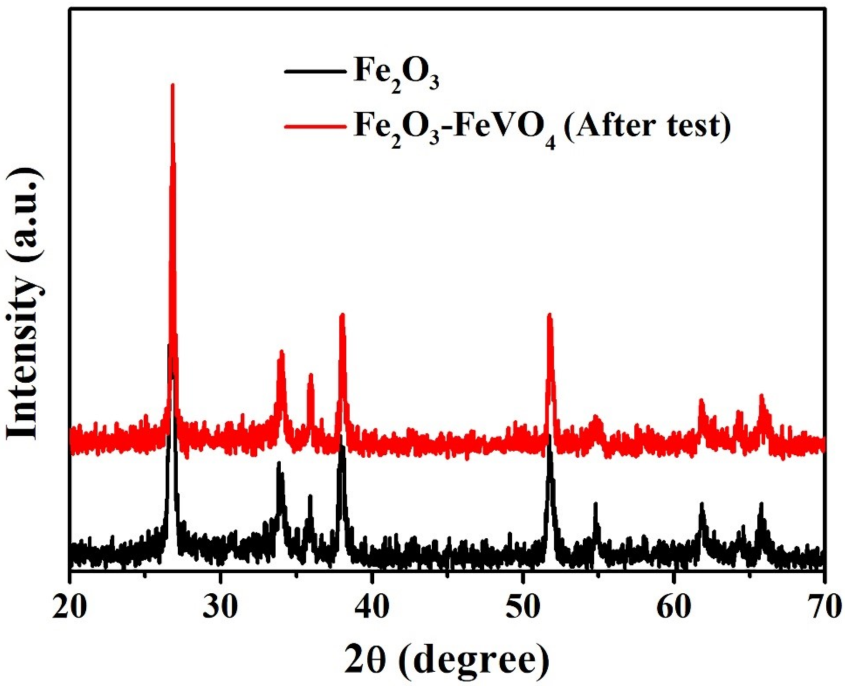

Figure S9. XRD image of the $FeVO_4$-Fe_2O_3 photoanode before and after the stability test.

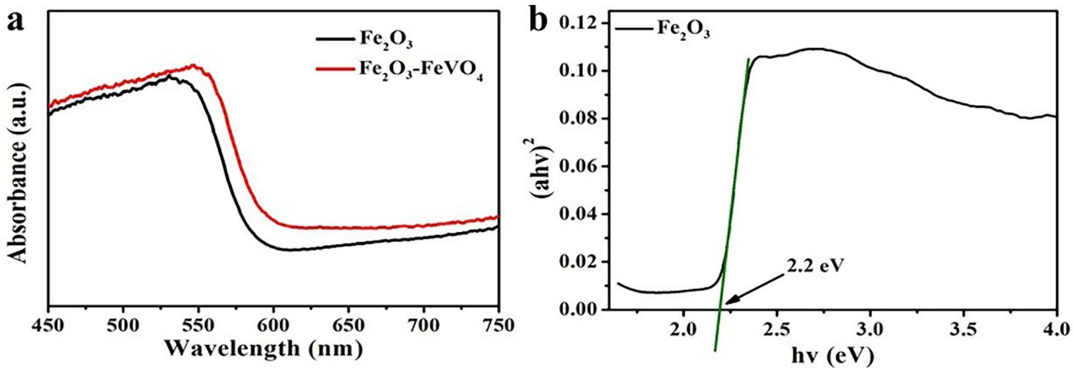

Figure S10. (a) UV-vis diffuse reflectance spectra of pristine Fe_2O_3 and $FeVO_4$-Fe_2O_3 photoanodes, (b) the Tauc plot of pristine Fe_2O_3 photoanode.

The UV-vis results show the absorption curve of the $FeVO_4$-Fe_2O_3 photoanode is slightly improved in the whole wavelength range, compared with the curve intensity of the Fe_2O_3 photoanode (Figure 5a). While the absorptive intensity and shift degree do not be improved significantly, but still demonstrate the effect of $FeVO_4$, and the insignificant lifting effect is attributed to the thinness of the $FeVO_4$. Formation of $FeVO_4$-Fe_2O_3 heterojunction could enable the prepared photoanode to utilize visible light efficaciously. The band gap could be calculated according to the following equation:

$$(\alpha hv)^n = A(hv - E_g) \qquad (S1)$$

Where $\alpha, hv, A,$ and E_g are the absorption coefficient, discrete photo energy, a constant and bandgap energy. The n value of Fe_2O_3 and $FeVO_4$ are 2.[1, 2] The calculated result is displayed in Figure 5b, the band gap energies of pristine Fe_2O_3 photoanode is about 2.2 eV, which is consistent with theoretical results.[3]

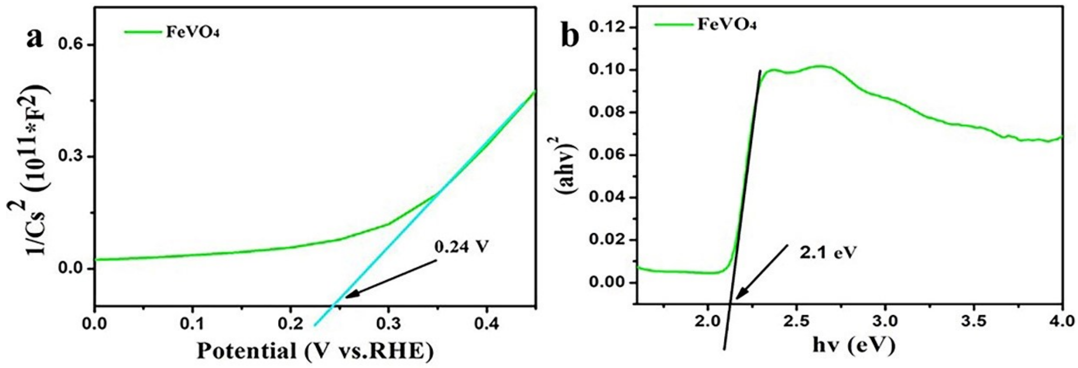

Figure S11. (a)MT result and (b)Tauc plot of pristine $FeVO_4$ photoanode.

The pristine $FeVO_4$ film was prepared on the basis of previously reported methods.[4] The preparation of FeOOH is the same as this work, the original $FeVO_4$ photoanode is prepared by drop casting and annealing process. First, an excess dimethyl sulfoxide (DMSO) solution containing 0.1 M vanadium acetylacetonate (VO (acac)2) is evenly coated on the FEOOH film. After drying on a plate heater at 75°C, it is placed in a muffle furnace, annealed in air at 550°C for 5 hours, and then cooled naturally. The obtained composite membrane was placed in a 0.1 M NaOH solution for 2 h to dissolve the excess vanadium oxide, then washed several times with distilled water, and dried at 60 °C. After that, a $FeVO_4$ photoanode was obtained.

1. J. Ma, Q. Wang, L. Li, X. Zong, H. Sun, R. Tao and X. Fan, *Journal of Colloid and Interface Science*, 2021, **602**, 32-42.
2. A. Chachvalvutikul, J. Jakmunee, S. Thongtem, S. Kittiwachana and S. Kaowphong, *Applied Surface Science*, 2019, **475**, 175-184.
3. G. Yang, S. Li, X. Wang, B. Ding, Y. Li, H. Lin, D. Tang, X. Ren, Q. Wang and S. Luo, *Applied Catalysis B: Environmental*, 2021, **297**, 120268.
4. Q. Zeng, X. Fu, S. Chang, Q. Zhang, Z. Xiong, Y. Liu, G. Peng and M. Li, *Journal of Colloid and Interface Science*, 2021, **604**, 562-567.