Electronic Supplemental Information:

1. Experimental Section

1.1 Synthesis of YVO₄ films

The YVO₄ films were fabricated by a long-term hydrothermal method. First, 0.03 M NH₄VO₃ was dissolved in distilled water, heated at 40 °C and stirred for 10 min to form solution A. 0.03 M Y(NO₃)₃•6H₂O was dissolved in distilled water and stirred for 5 min to form solution B. Next, solution B was slowly poured into solution A to obtain a yellow precursor solution. The pH value of the precursor solution was adjusted to be 1 by adding 1 M diluted HCI. The FTO glass was placed in the Teflon lined stainless steel autoclave with the conductive surface of the FTO glass facing downwards. The precursor solution was transferred to the Teflon lined stainless steel autoclave at 180 °C for 48 h and cooled down naturally and the FTO was slowly washed with deionized water and dried in air. Finally, the YVO₄ films were prepared.

1.2 Characterizations

The morphologies and microstructures of samples were studied by JEOL JSM-7800F scanning electron microscope (SEM) and JEOL JEM-2100 transmission electron microscope (TEM) operated at the accelerating voltage of 10 kV. The energy dispersive X-ray spectroscopy (EDS, AZtec from Oxford) was applied to test the elements of samples. The X-ray diffraction (XRD) (Rigaku-D/max-2500 with Cu Ka radiation) at 40 kV and 200 mA was adopted to measure the crystalline structures of samples. The surface chemical composition and oxidation states of samples were detected by X-ray photoelectron spectroscopy (XPS), it was based on the C-C standard peak at 284.6 eV which recorded on a Thermo ESCALAB 250XI system with an Al-K α X-ray source (hv=1486.6 eV). The DU-8B UV-vis double-beam spectrophotometer was used to examine the optical absorption property of samples. Photoluminescence (PL) spectra of samples were investigated by fluorescence spectrometer (FLS-920) at 293 K with a Xe lamp as light source. The VB edge position of samples was determined by ultraviolet photoelectron spectroscopy (UPS).

Band gap (E_g) of YVO₄ was estimated by the following equation:

$$(\alpha h v)^n = A(h v - E_g) \tag{1}$$

Where α , hv and A is absorbance coefficient, incident light intensity and constant, respectively. The value of n is 2 because YVO₄ is a direct band gap semiconductor.

PEC performance was tested via an electrochemical workstation, adopting a standard three-electrode system which include working electrode (prepared samples),

counter electrode (platinum foil) and reference electrode (Ag/AgCl electrode), 0.5 M Na_2SO_4 solution as the electrolyte (pH=7), and irradiated with a xenon lamp (CHF-XM500, 100 mW·cm⁻²). The Ag/AgCl potential was transformed into reversible hydrogen electrode (RHE) potential through the following formula:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059pH + 0.1976 V$$
⁽²⁾

The electrochemical impedance spectra (EIS) was measured by a three-electrode system, with amplitude of 600 mV and frequency range between 100 kHz to 0.1 Hz.

Mott-Schottky of YVO₄ was characterized by an electrochemical workstation at a fixed frequency. Mott-Schottky plot was obtained according to the following formula:

$$1/C^{2} = (2/e_{0}\varepsilon\varepsilon_{0}N_{d})[(V_{a}-V_{fd})-kT/e_{0}]$$
(3)

Were *C* is specific capacitance, e_0 is fundamental electric charge, ε is dielectric constant, ε_0 is permittivity of vacuum, N_d is concentration of charge carriers, V_a is applied potential, $V_{\rm fd}$ is flat band potential, *k* is Boltzmann constant and *T* is temperature.

Charge separation efficiency of YVO₄ films in bulk (η_{bulk}) and surface (η_{surface}) according to the following equations:

$$J_{\rm H2O} = J_{\rm abs} \times \eta_{\rm bulk} \times \eta_{\rm surface} \tag{4}$$

$$J_{\rm Na2SO3} = J_{\rm abs} \times \eta_{\rm bulk} \tag{5}$$

$$\eta_{\text{bulk}} = J_{\text{Na2SO3}} / J_{\text{abs}} \times 100\% \tag{6}$$

$$\eta_{\text{surface}} = J_{\text{H2O}} / J_{\text{Na2SO3}} \times 100\% \tag{7}$$

Where J_{H2O} is measured photocurrent density at 1.23 V vs. RHE. J_{abs} is light absorption expressed as a current density. Owing to the slow kinetics of water oxidation reaction, the PEC oxidation reaction is performed by adding 0.1 M Na₂SO₃ as a hole scavenger into a 0.5 M Na₂SO₄ electrolyte. With the existence of Na₂SO₃, the oxidation kinetics of the samples becomes rapid. The surface recombination of charge is limited effectively, yet it has no effect on internal charge separation. Therefore, the η_{surface} is estimated as 100%. From equations (4)-(7), the η_{bulk} and η_{surface} can be obtained.

Applied bias photon-to-current efficiency (ABPE) of sample was calculated according to the following equation:

$$\eta = J(1.23 - V_{\rm app})/P_{\rm light} \times 100\%$$
 (8)

Where η is ABPE, *J* is externally measured photocurrent density, V_{app} is measured applied voltage, P_{light} is power density of the illumination of 100 mW·cm⁻² (AM 1.5 G).

2. Theoretical calculation about the band edges of $\ensuremath{\mathrm{YVO}_4}$

The band edges of YVO₄ can be calculated using concepts of Mulliken

electronegativity:

$$E_{\rm CB} = \chi - E_{\rm e} - 0.5 E_{\rm g} \tag{9}$$

$$E_{\rm VB} = E_{\rm CB} + E_{\rm g} \tag{10}$$

Where E_g is band gap energy. E_e is energy of the free electrons on the hydrogen scale (4.50 eV). χ is Mulliken electronegativity, which is the geometric mean of the electronegativities of the constituent atoms. For YVO₄, χ (Y), χ (V) and χ (O) is 3.19 eV, 3.60 eV and 7.54 eV, respectively. The Mulliken electronegativity values of different atoms are shown in Tab.S3. The value of χ (YVO₄) is calculated as follows:

1

$$\chi(YVO_4) = [(3.19)^1 \times (3.60)^1 \times (7.54)^4]^{[1/(1+1+4)]} = 5.77 \ eV \tag{11}$$

Fig.S1 Unit cell structure of YVO₄

Fig.S2 XRD pattern (a), TEM image (b) and HRTEM image (c) of YVO₄ films

Fig.S3 XPS spectra (a), high-resolution spectra of O 1s (b), V 2p (c) and Y 3d (d) of YVO₄ films

Fig.S4 Band structure schematic diagram (a) and UPS spectrum (b) of YVO₄

Fig.S5 Mott-Schottky plots of YVO₄ films

Fig.S6 Bulk charge separation efficiency η_{bulk} (a), surface charge separation efficiency η_{surface} (b), applied bias photon-to-current efficiency (c) and photocurrent density-time curves measured in 0.5 M Na₂SO₄ electrolyte at 1.23 V vs. RHE under simulated sunlight illumination for 2 h (d) of YVO₄ films

Fig.S7 XRD patterns and SEM images of the same YVO₄ films before and after 2 h PEC stability test

Fig.S8 Top-view SEM image and cross-section SEM image of YVO₄ films with pH=1 (a) and YVO₄ films with pH=3 (b)

Fig.S9 UV-vis spectra (a), photocurrent density-voltage (J-V) curves (b), electrochemical impedance spectra (EIS) (c) and photoluminescence (PL) spectra (d) of YVO₄ films with different pH value

Tab.S1 Correlation table of YVO₄ catalyst reported recently

Tab.S2 Summary of XPS data about Y 3d, C 1s, O 1s and V 2p of prepared YVO₄ films

Tab.S3 First ionization energy (I^a), Electron affinity (A^b) and absolute electronegativity (χ) of atoms constituting YVO₄



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Serial Number	Fields	References		
[23]	Photodegradation of Rhodamine B and methylene blue.	Mater. Res. Bull. 2015, 68, 276-282.		
[24]	Photocatalytic decomposition of methyl orange.	J. Phys. Chem. C. 2015, 119, 13502-13508.		
[25]	Degradation of methyl orange.	Appl. Catal., B. 2018, 224, 586-593.		
[26]	Photocatalytic discoloration of Rhodamine B.	J. Environ. Chem. Eng. 2018, 6, 2846-2854.		
[27]	Degradation of methylene blue dye.	Micro Nano Lett. 2019, 14, 711-716.		

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films

Name	Atomic %	Start BE	End BE	Peak BE	Height CPS	Area (P) CPS.eV	Peak Type
¥ 3d	9.414	163.5	154.5	157.518	34037.232	75770.403	Standard
C 1s	40.016	296.5	281.5	284.823	23187.385	51784.7023	Standard
O 1s	40.161	540.5	526.5	529.908	76230.715	158244.3983	Standard
V 2p	10.409	527.27	511.97	517.08	28798.643	60037.6639	Standard

Atom	I ^a	A ^b	χ
Ο	13.62	1.46	7.54
V	6.70	0.50	3.60
Y	6.38	0.00	3.19

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