Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Spontaneously dual built-in electric fields in S-scheme heterojunction for enhanced photocatalytic H_2O_2 production

Junxian Huang[a#], Haiyang Shi[a#], Xuefei Wang[a*], Ping Wang[a], Feng Chen[a], Huogen Yu[b*]

[a] School of Materials Science and Engineering, and School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, PR China

[b] Laboratory of Solar Fuel, Faculty of Materials Science and Chemistry, China University of Geosciences, 388 Lumo Road, Wuhan, 430074, P. R. China

[*] Corresponding authors: xuefei@whut.edu.cn and yuhuogen@cug.edu.cn

SI-1 Characterization

The crystal structure was researched by an X-ray diffractometer (XRD, Rigaku Ultima III, Japan). The morphology of photocatalyst was observed by a field emission scanning electron microscope (FESEM, JSM-7500F, Japan) and a high-resolution transmission electron microscope (HRTEM, Thermo Fisher, USA). The chemical state of element was researched by an X-ray photoelectron spectroscopy (XPS, KRATOA XSAM800, UK). The Ultraviolet visible diffuse reflectance spectra were attained by a UV-2450 Shimadzu spectrophotometer. The time-resolved photoluminescence (TR-PL) spectra was tested by a fluorescence spectrophotometer (F-7000). The electrochemical transient photocurrent response (*i-t* curves) and electrochemical impedance spectroscopy (EIS) were performed by a CHI660E electrochemical workstation. Furthermore, the Mott-Schottky plots were performed to evaluate the flat band potentials of the photocatalytic materials, which is based on the data of electrochemical measurements operated at a constant frequency of 1 kHz in darkness. Electron paramagnetic resonance (EPR) spectra were obtained on an EPR spectrometer (MEX-nano, Bruker, UK) with a modulation frequency of 100 kHz and a microwave power of 25 mW.

SI-2 The procedures of photo-electrochemical test

The transient photocurrent response was studied via employing a three-electrode CHI660E electrochemical apparatus in a Na_2SO_3 electrolyte (0.5 M) with FTO glass (loading with photocatalysts), saturated calomel electrode and Pt plate as working electrode, reference electrode and counter electrode, respectively. The reaction system

can be measured with the LED irradiator (420 nm, 3 W) as light source. To compare the photocurrent density in same condition, The photocurrent responses (*i–t* curves) can be obtained at a +0.5 V bias potential during the repeated ON/OFF with a set time period of 60 s. A frequency from 0.001 to 10^6 Hz and amplitude of 0.01 V was used to conduct electrochemical impedance spectra.

SI-3 The procedures of cycling H_2O_2-production test

In general, the repeating test of photocatalytic materials includes the centrifugation, washing, drying and re-dispersion of photocatalysts after finishing one cycle of test. However, in this work, to exclude the possible loss of photocatalysts, the resulting suspension solution was centrifugated, washed and directly re-dispersed for the following successive cycling test. In detail, 50 mg MnOOH/$BiVO_4$/Cu_2O sample was added into 50 mL solution of 0.1 M PBS. After bubbled with O_2 for 30 min, the above solution was irradiated by visible light under continuous stirring. The produced amount of H_2O_2 was tested every 30 min by colorimetric method. After finishing 1st run, the above suspension solution was directly filtrated, washed and re-dispersed for H_2O_2-production test. In this case, the 2nd, 3rd, 4th and 5th runs were coherently tested under the same process.

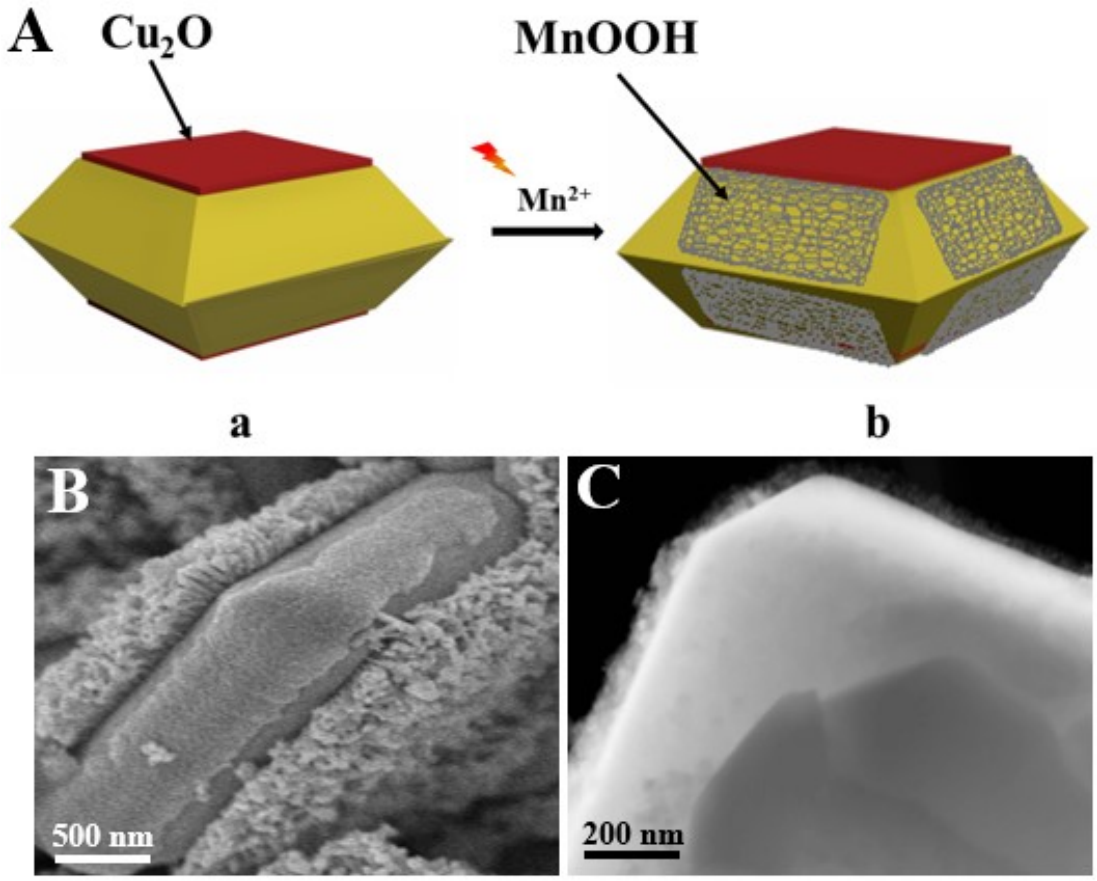

Fig. S1 (A) Schematic diagram illustrating the controllable preparation of the $MnOOH/BiVO_4/Cu_2O$ photocatalysts: (a) $BiVO_4/Cu_2O$ and (b) $MnOOH/BiVO_4/Cu_2O$; (B) SEM image and (C) TEM image of dark field of $MnOOH/BiVO_4/Cu_2O$ photocatalyst.

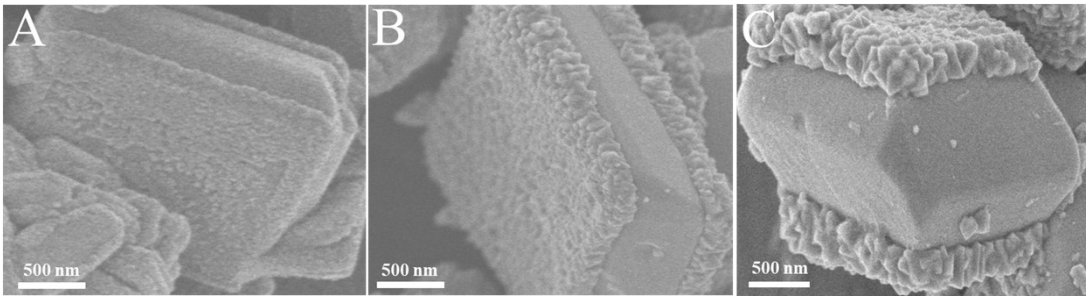

Fig. S2 SEM images of (A) $BiVO_4/Cu_2O$ (2:1), (B) $BiVO_4/Cu_2O$ (1:2) and (C) $BiVO_4/Cu_2O$ (1:5).

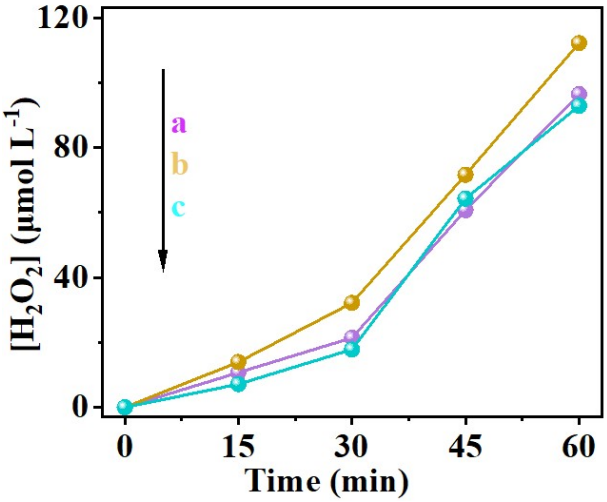

Fig. S3 Photocatalytic H_2O_2 production of (a) MnOOH/$BiVO_4$/Cu_2O (2:1), (b) MnOOH/$BiVO_4$/Cu_2O (1:2) and (a) MnOOH/$BiVO_4$/Cu_2O (1:5).

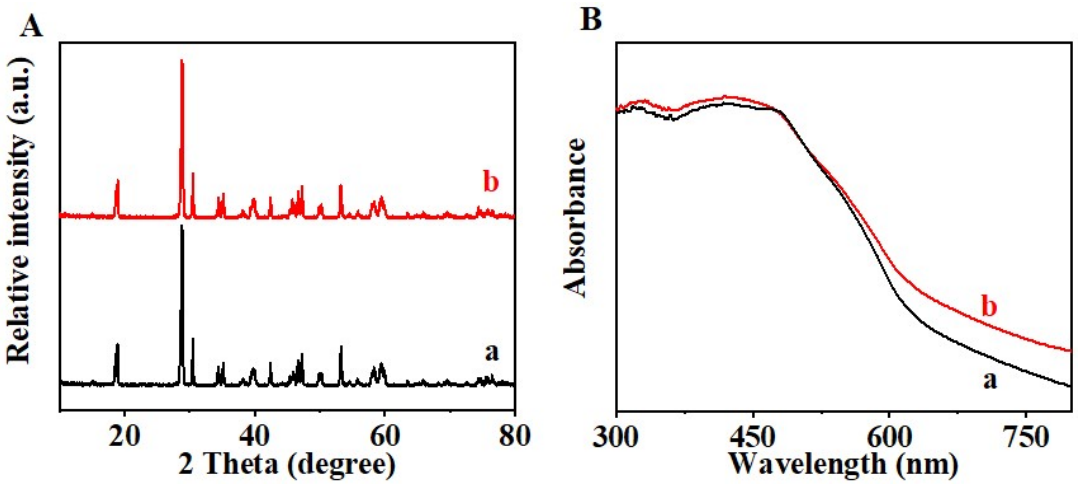

Fig. S4. (A) XRD pattern and (B) UV–vis spectra of the MnOOH/$BiVO_4$/Cu_2O sample (a) before and (b) after 4 cyclic tests.

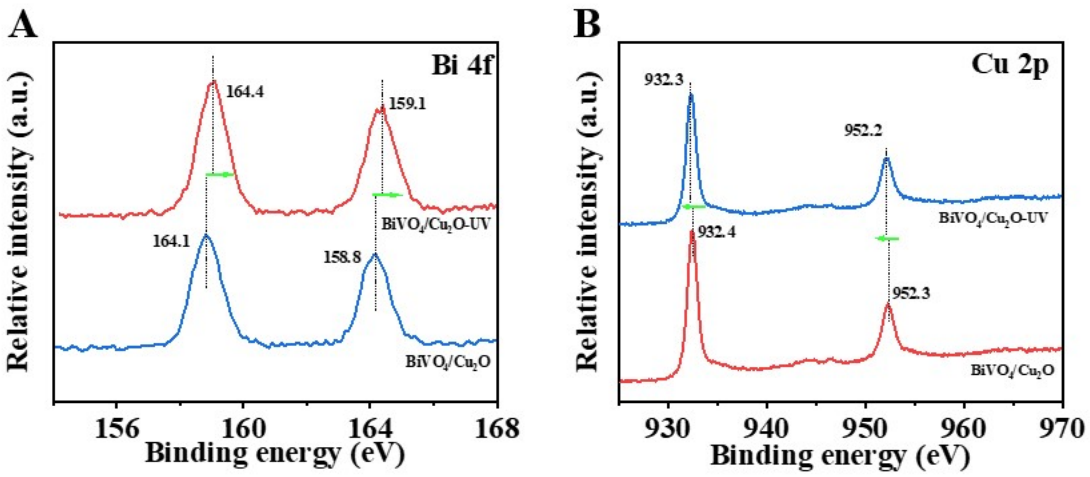

Fig. S5 High-resolution XPS spectra of (A) Bi 4f and (B) Cu 2p under darkness and light irradiation.

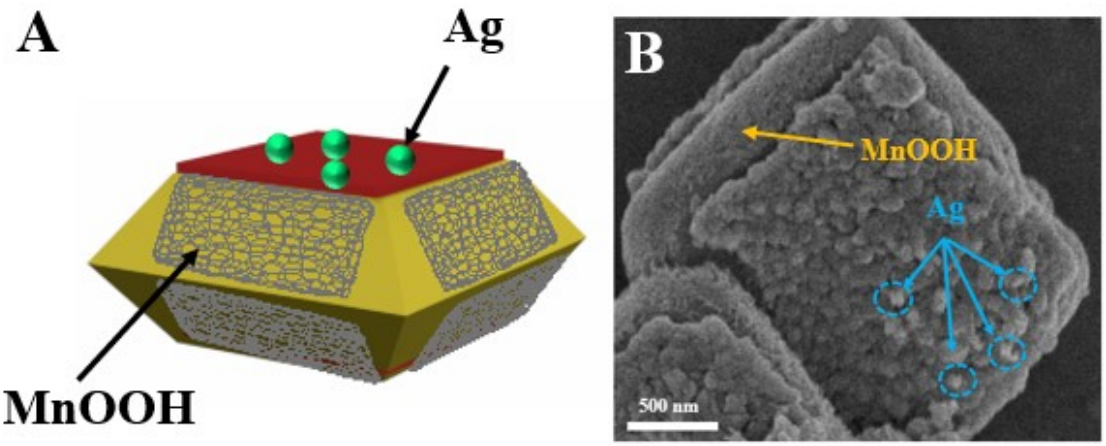

Fig. S6 (A) Schematic diagram and (B) SEM image of MnOOH/$BiVO_4$/Cu_2O/Ag photocatalyst.

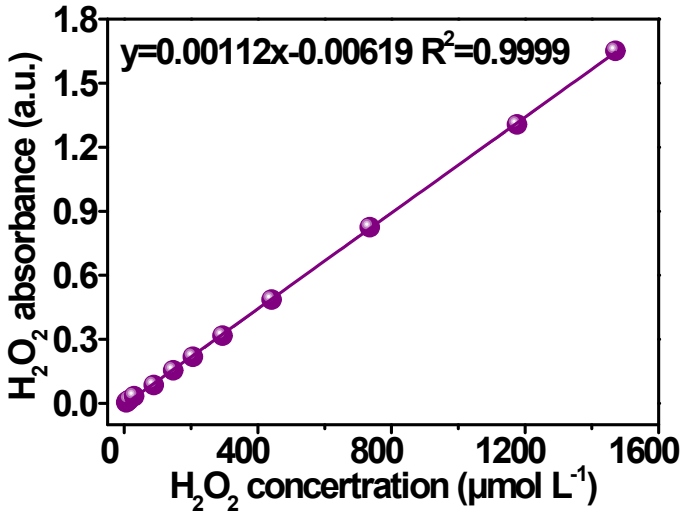

Fig. S7 H_2O_2 concentration-absorbance standard curve.

Table. S1. Comparisons of H_2O_2 production on various photocatalysts.

Photocatalysts	Maximum formed H_2O_2 ($\mu mol \cdot L^{-1}$)	H_2O_2 formation rate ($\mu mol \cdot L^{-1} \cdot h^{-1}$)	k_f ($\mu mol \cdot L^{-1} \cdot min^{-1}$)	k_d (min^{-1})
$BiVO_4$	6.95	6.95	0.18	0.016
Cu_2O	5.49	5.49	0.62	0.015
$BiVO_4/Cu_2O$	24.71	24.71	2.92	0.016
$MnOOH/BiVO_4/Cu_2O$	112.17	112.17	0.14	0.016

Table S2 The fitted parameters obtained from decay curves of (a) $BiVO_4$, (b) $BiVO_4/Cu_2O$ and (c) Cu_2O.

Sample	τ_1	A_1	T_2	A_2	T_3	A_3	Average lifetime
$BiVO_4$	0.45	14168.72	3.04	368.12	42.29	7.54	2.53
$BiVO_4/Cu_2O$	0.62	9834.19	3.05	2374.94	13.11	277.46	4.33
Cu_2O	0.63	11458.81	3.16	1676.03	14.54	165.85	3.77

The above fitted parameters are acquired via the following tri-exponential formulas:

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_{2+} A_3\tau_3)$$

where A_1, A_2 and A_3 represent the tri-exponential factors, and τ_1, $\tau_{2,}$ τ_3 and τ_a correspond to the lifetime in various stages (radiation and non-radiation) and average lifetime, respectively.