

Supporting Information for

## Electrostatic Field Enhanced Photocatalytic CO<sub>2</sub> Conversion on BiVO<sub>4</sub> Nanowires

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### S1 Experimental Calculations

#### S1.1 Calculation of the Incident Photon-to-Current Efficiency (IPCE)

Incident photon-to-current efficiency (IPCE) utilized light from a 300 W Xe lamp passed through a monochromator, and recorded LSV using electrochemical workstation. The incident light interval was 10 nm from 400 nm to 600 nm, and it was calibrated by a standard Newport Si PV module [S1]. The equation used to obtain the IPCE values was:

$$\text{IPCE} = \frac{\text{electrons}}{\text{photons}} = \frac{J_{\text{ph}} \times 1239.8}{P_{\text{mono}} \times \lambda}$$

Among them,  $J_{\text{ph}}$  was the photocurrent density minus the dark current density, and  $P_{\text{mono}}$  was determined by calibrated Newport Si PV module.  $\lambda$  was the Incident light wavelength [S2]. For example, the IPCE at 400 nm under 0 V could be calculated as follows:

$$\text{IPCE} = \frac{J_{\text{ph}} \times 1239.8}{P_{\text{mono}} \times \lambda} = \frac{(0.0190334981) \times 1239.8}{\frac{0.0124}{0.227 \times 0.25} \times 400} \times 100\% = 26.99\%$$

#### S1.2 Calculation of the Apparent Quantum Yields (AQE)

The apparent quantum yields (AQE) were calculated from the incident light intensity and generation rate of CH<sub>4</sub> and CO according the equation:  $\text{AQE} = (8 \times \text{number of evolved CH}_4 \text{ molecules} + 2 \times \text{number of evolved CO molecules}) / \text{number of incident photons} = (8 \times R_1 + 2 \times R_2) N_A h c / A P \lambda$  [S3], in which  $R_1$  and  $R_2$  were the generation rate of CH<sub>4</sub> and CO;  $N_A$  was Avogadro constant;  $h$  and  $c$  were the Planck constant and light speed;  $P$  and  $\lambda$  were the intensity and the wavelength of incident light, respectively. The used light source was a 500 W Xenon lamp equipped with a bandpass filter, and BVO-NWs/PDMS/PZT was used as photocatalyst. The area of incident light ( $A$ ) was  $9\pi \text{ cm}^2$ , which was determined by the size of filter. The light

intensity was determined by means of standard silicon solar cell. The detailed information about intensity of incident light and corresponding generation amount of CH<sub>4</sub> and CO were shown in Table S1. Hence, its AQE value at 400 nm could be calculated as follows:

$$AQE_{(400nm)} = \frac{(8 \times R_1 + 2 \times R_2) \times N_A \times h \times c}{AP\lambda}$$

$$AQE_{(400nm)} = \frac{[(8 \times 15.94 + 2 \times 9.02) \times 10^{-6} / (8 \times 3600)] \times 6.02 \times 6.626 \times 3 \times 10^{-3}}{9\pi \times 10^{-4} \times (9.02 \times 10^{-3} / 10^{-4}) \times 400 \times 10^{-9}} \times 100\% = 0.59\%$$

### S1.3 Calculation of the Charge Carrier Diffusion Lengths (L)

The charge carrier diffusion lengths (L) of BVO-NWs/PDMS/PZT were estimated with Gartner model [S4] and the equations were as follows:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_d} \left( V - V_{fb} - \frac{k_B T}{e} \right) \dots\dots\dots (S1)$$

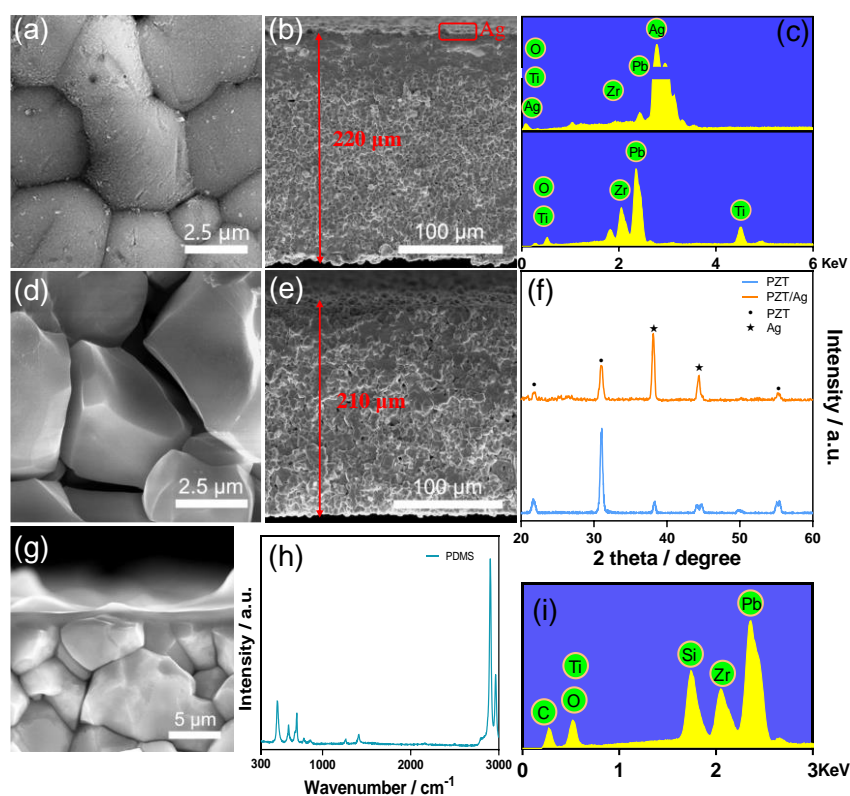
$$W = \sqrt{\frac{2\epsilon_0\epsilon(V - V_f)}{qN_d}} \dots\dots\dots (S2)$$

Where C was the space charge layer capacitance,  $\epsilon$  was the relative permittivity of BiVO<sub>4</sub> [S5],  $\epsilon_0$  was the vacuum permittivity, A was the electrode exposed area, e was electronic charge, N<sub>d</sub> was the charge carrier density, V was the applied potential, V<sub>fb</sub> was the flat band potential, k<sub>B</sub> was the Boltzmann constant, T was the temperature. According to the Mott-Schottky plots (Fig. 5b) and Eq. (S1), the charge carrier density can be calculated. W was the depletion width and it can be calculated by Eq. (S2).

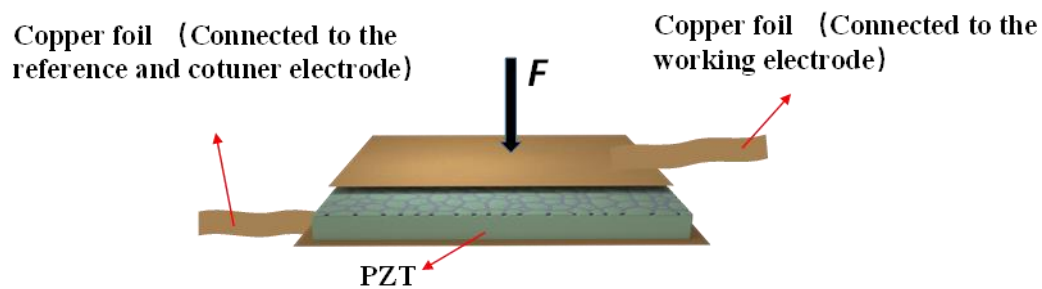
$$L = \frac{\frac{e^{-\alpha W}}{1 - \eta_{sep}} - 1}{\alpha} \dots\dots\dots (S3)$$

Where L was the charge carrier diffusion lengths,  $\eta_{sep}$  was the quantum efficiency which was determined by APCE in 0.5 M Na<sub>2</sub>SO<sub>3</sub>.  $\alpha$  was the absorption coefficient at 400 nm. The calculation results were shown in **Tab. S4**.

S2 Supplementary Figures and Tables



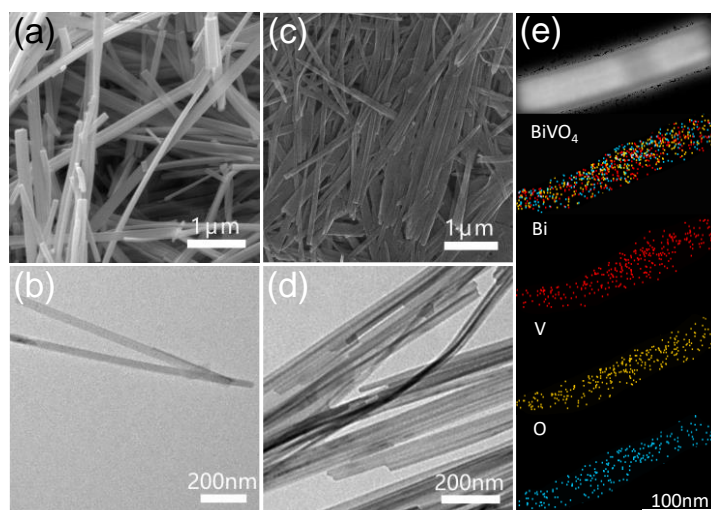
**Fig. S1** SEM images of PZT with silver coating on the surface (a, b) and silver coating removed (d, e). The corresponding EDX spectra (c) and XRD pattern (f). SEM image (g), Raman spectra (h) and EDX spectra (i) of PDMS layer



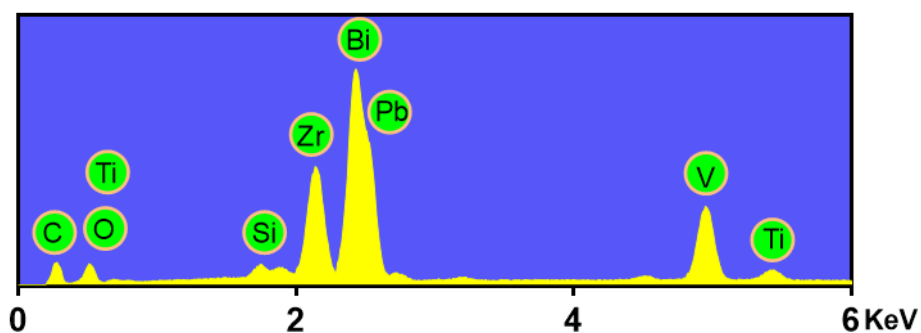
**Fig. S2** Two-electrode structure for piezoelectric measurement



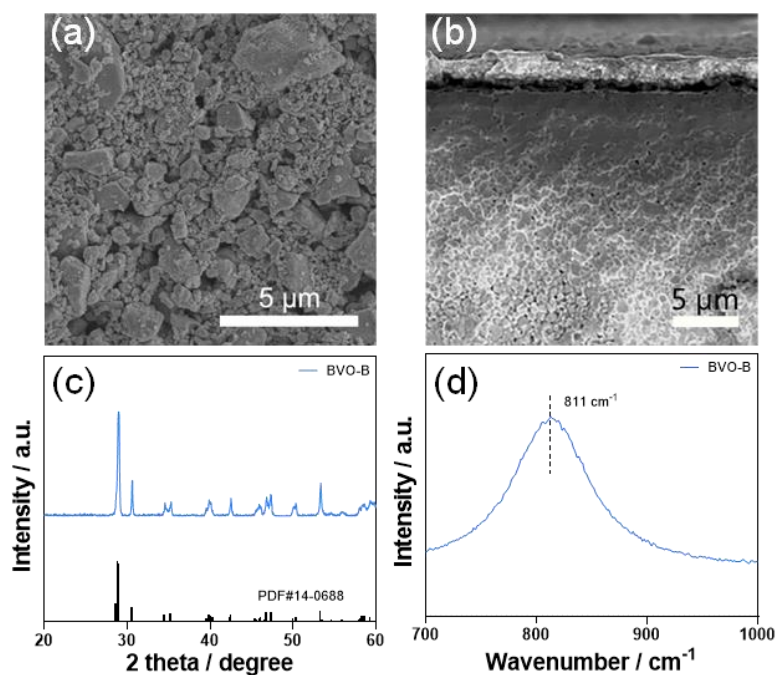
**Fig. S3** The diagram of covered quartz glass



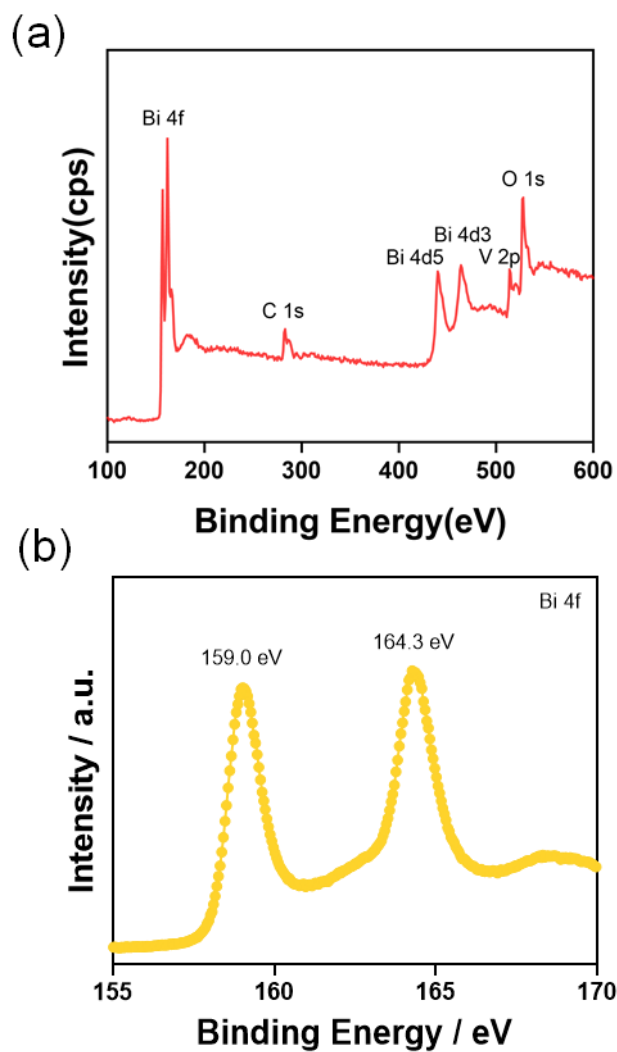
**Fig. S4** SEM and TEM images of BiVO<sub>4</sub> nanowires (a, b) and Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·3H<sub>2</sub>O nanowires (c, d). The elemental maps of BiVO<sub>4</sub> nanowires (e)



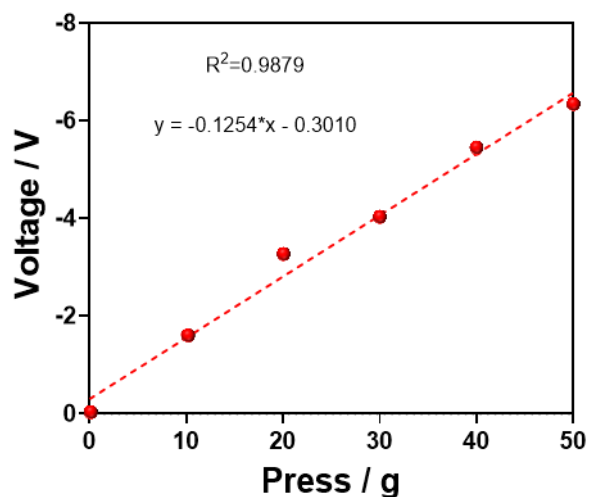
**Fig. S5** EDX spectra of BVO-NWs/PDMS/PZT



**Fig. S6** SEM images (a-b), XRD pattern (c) and Raman spectrum (d) of the bulk BiVO<sub>4</sub>. The bulk BiVO<sub>4</sub> particles were prepared by a hydrothermal method and were denoted as BVO-B [S6].

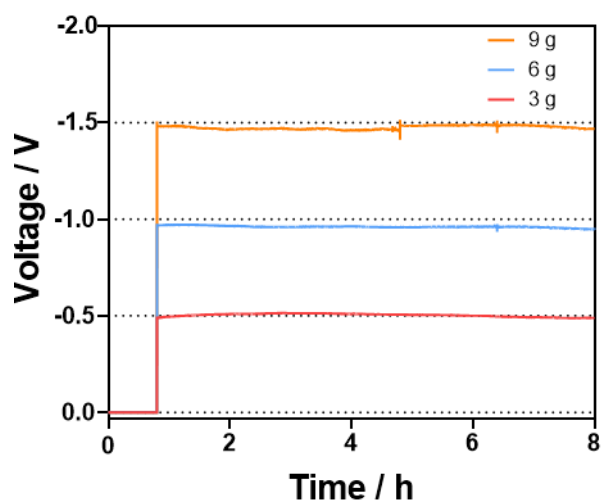


**Fig. S7** XPS survey spectrum (a) and high resolution XPS spectra (b) of BiVO<sub>4</sub> nanowires

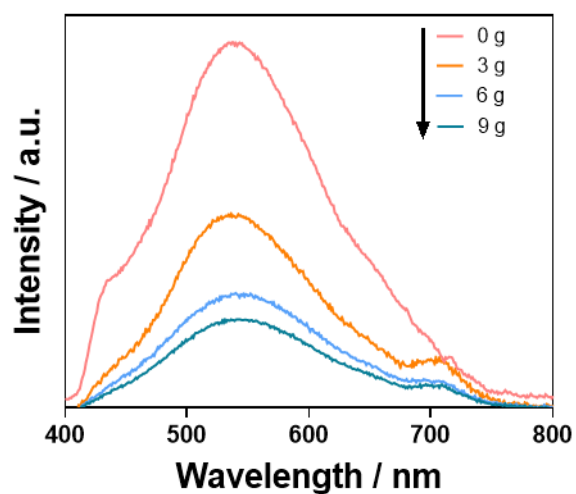


**Fig. S8** The relationship between stress and piezoelectric potential

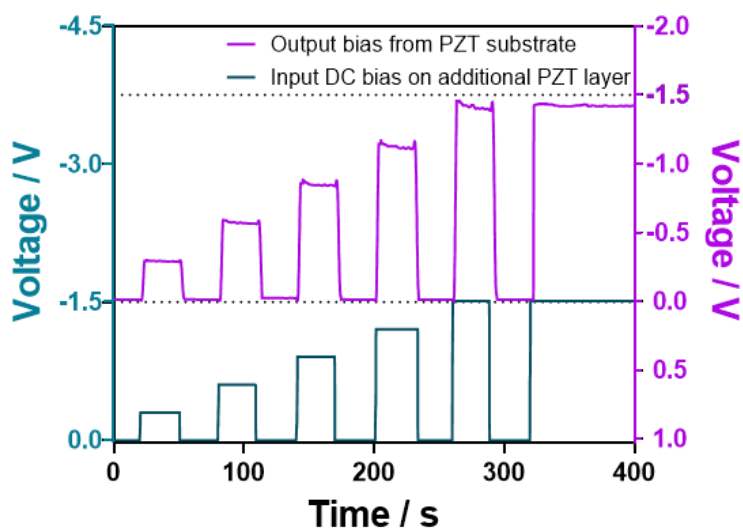
### Nano-Micro Letters



**Fig. S9** Long time piezoelectric performances of PZT substrate under different stresses



**Fig. S10** The photoluminescence spectra of BVO-NWs/PDMS/PZT under different stresses



**Fig. S11** The dependence of output bias from PZT substrate on the applied DC bias on additional PZT layer

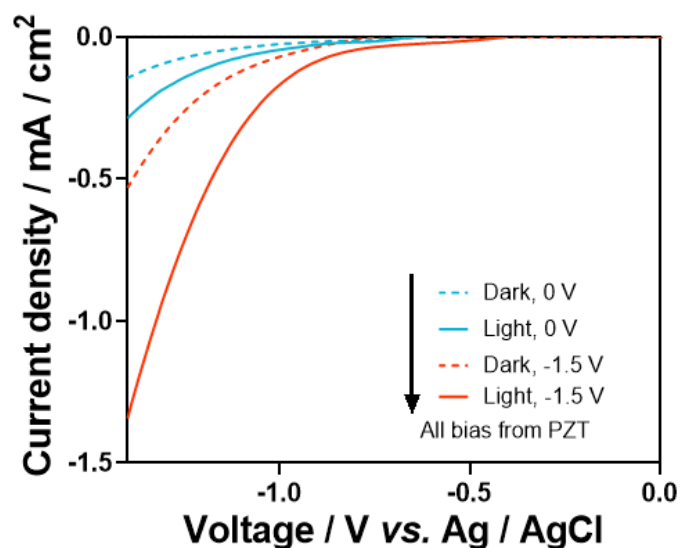


Fig. S12  $I$ - $V$  curves of BVO-NWs in CO<sub>2</sub>-bubbled system

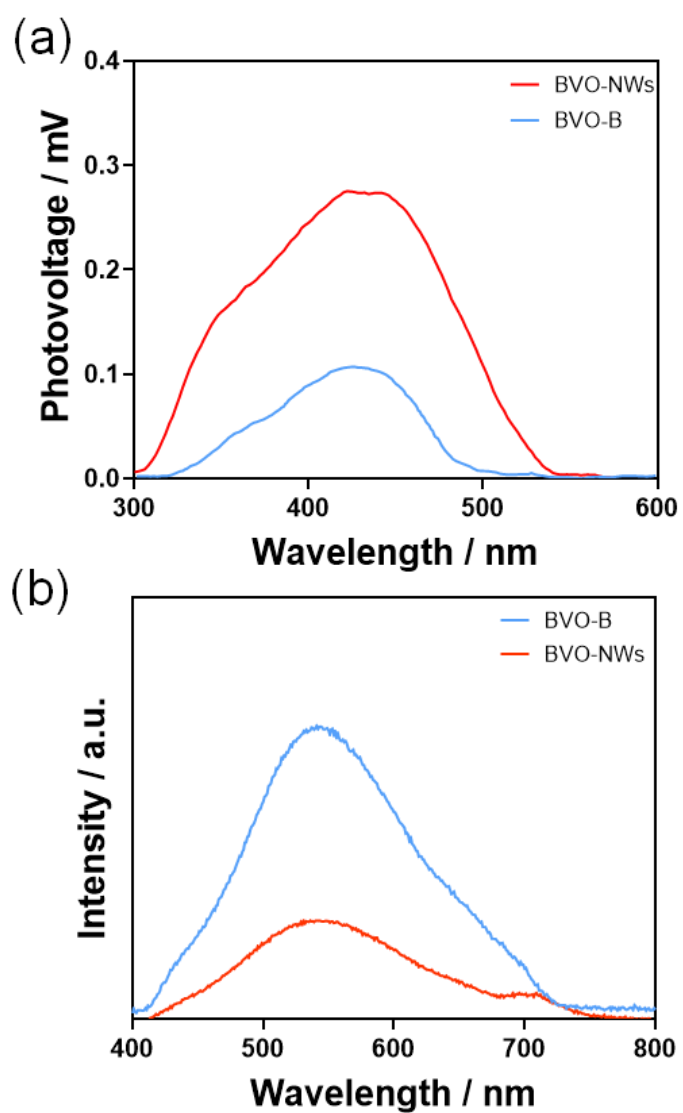


Fig. S13 The surface photovoltage spectra (a) and photoluminescence spectra (b) of samples

**Table S1** The incident light intensity and amount of generated CH<sub>4</sub> and CO in 8 h of BVO-NWs/PDMS/PZT with different wavelengths

	$\lambda_{\pm 10}$ (nm)					
	400	440	480	520	560	600
Intensity of incident light (mW/cm <sup>2</sup> )	9.02	9.02	11.75	11.75	11.54	10.28
Amount of generated CH <sub>4</sub> ( $\mu$ mol)	15.94	15.73	13.00	10.91	3.15	1.89
Amount of generated CO ( $\mu$ mol)	9.02	9.02	7.55	6.08	1.68	1.05

**Table S2** The comparative study of BiVO<sub>4</sub> NWs sample on photocatalytic CO<sub>2</sub> reduction with other related samples reported

Photocatalyst	Light Source Used	Activity	Sample Quality	Refs.
BiVO <sub>4</sub> microplates	300 W Xe lamp	CO: 0.58 $\mu$ mol/g/h CH <sub>4</sub> : -	10 mg	[S7]
BiVO <sub>4</sub> nanosheets	300 W Xe lamp ( $\lambda > 420$ nm)	CO: 0.29 $\mu$ mol/g/h CH <sub>4</sub> : 0.30 $\mu$ mol/g/h	50 mg	[S8]
BiVO <sub>4</sub> octahedron	300 W Xe lamp ( $\lambda > 420$ nm)	CO: 0.45 $\mu$ mol/g/h CH <sub>4</sub> : 0.59 $\mu$ mol/g/h	100 mg	[S9]
BiVO <sub>4</sub> microspheres	300 W Xe lamp	CO: 1.3 $\mu$ mol/g/h CH <sub>4</sub> : -	10 mg	[S10]
BiVO <sub>4</sub> nanoparticles	300 W Xe lamp ( $\lambda > 420$ nm)	CO: 0.30 $\mu$ mol/g/h CH <sub>4</sub> : -	50 mg	[S11]
<b>BiVO<sub>4</sub> nanowires</b>	<b>300 W Xe lamp</b>	<b>CO: 0.76 <math>\mu</math>mol/cm<sup>2</sup>/h</b> <b>CH<sub>4</sub>: 0.32 <math>\mu</math>mol/cm<sup>2</sup>/h</b>	<b>3.15 cm<sup>2</sup> (~2 mg)</b>	<b>This work</b>

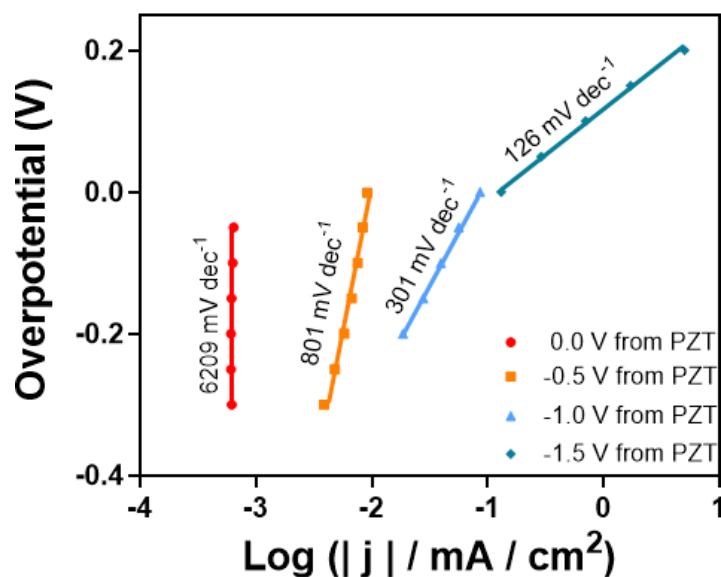


**Table S3** The charge carriers lifetimes of sample under different piezo bias

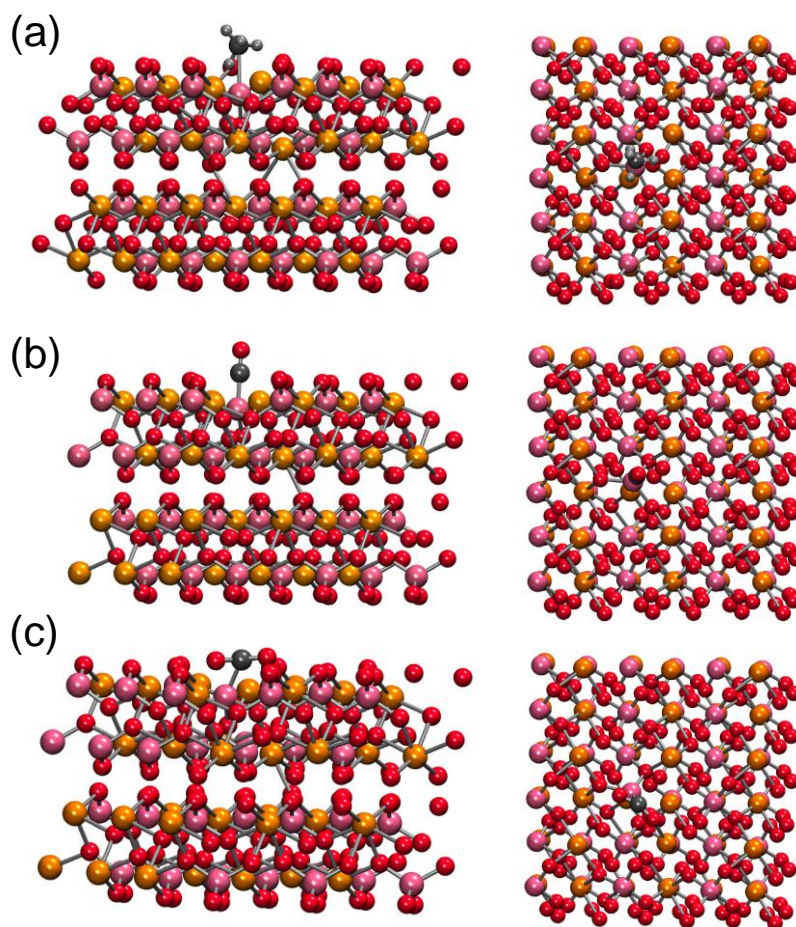
Bias from PZT	$f_{\max}$ (Hz)	lifetime of charge carrier ( $\mu\text{s}$ )
0.0 V	33.11	4.8
-0.5 V	14.13	11.3
-1.0 V	8.32	19.1
-1.5 V	2.51	63.4

**Table S4** The carrier concentrations and hole diffusion lengths of sample under different piezo bias

Bias from PZT	$V_f$ (V vs. SHE)	$N_d$ ( $\text{cm}^{-3}$ )	$W$ (nm)	$\eta_{\text{sep}}$	$L_D$ (nm)
0.0 V	-0.61	$5.13 \times 10^{19}$	15.37	0.2080	39.26
-0.5 V	-0.67	$7.97 \times 10^{19}$	12.56	0.3472	79.51
-1.0 V	-0.75	$1.18 \times 10^{20}$	10.58	0.4541	124.37
-1.5 V	-0.81	$1.52 \times 10^{20}$	9.47	0.5070	153.72



**Fig. S14** Tafel slopes of sample under different bias



**Fig. S15** CH<sub>4</sub> (a), CO (b) and CO<sub>2</sub> (c) gas molecules adsorbed on BiVO<sub>4</sub> layer

### Supplementary References

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