Supporting information

Cooperative catalytic behavior of CoS and Bi2S3 nanoparticles on Zr:BiVO4 photoanodes for enhanced photoelectrochemical sulfite oxidation coupled with pharmaceutical pollution degradation

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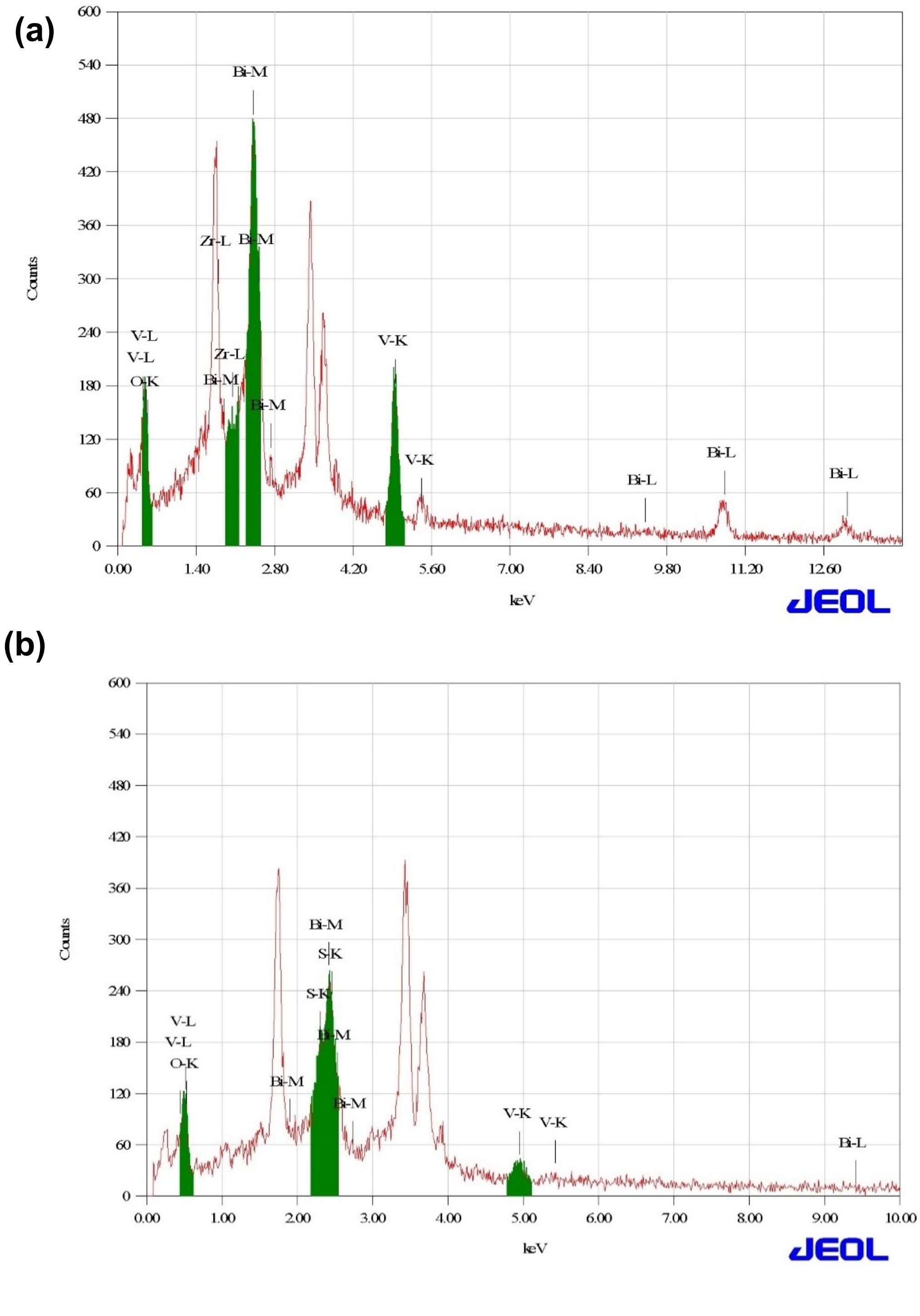
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(b)
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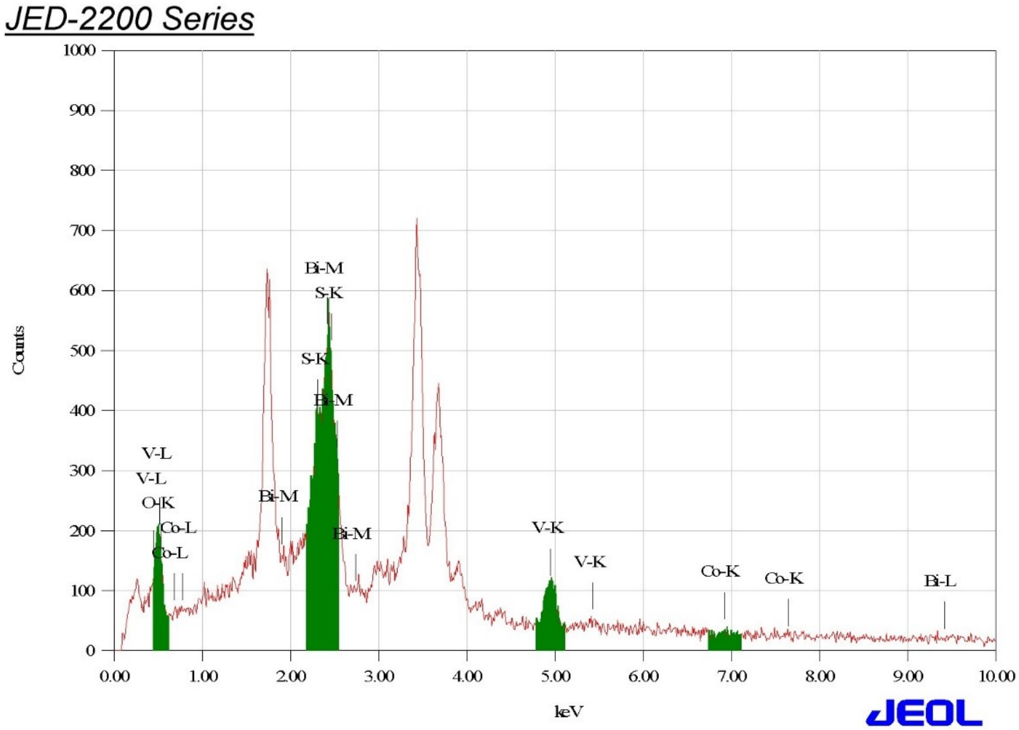

Figure S1 a) EDS spectrum of the a) Zr:$BiVO_4$, b) Zr:$BiVO_4$@Bi_2S_3, and c) Zr:$BiVO_4$@Bi_2S_3-CoS electrode.

Table S1. Elemental composition obtained from EDAX spectra of prepared materials

Samples	Bi %	V %	Zr %	S %	Co%	O%
Zr:$BiVO_4$	52.91	22.81	0.22	-	--	24.06
Zr:$BiVO_4$/Bi2S3	73.31	6.92	-	2.307	-	12.58
Zr:$BiVO_4$/Bi2S3@CoS	70.97	13.11	-	8.37	1.87	5.69

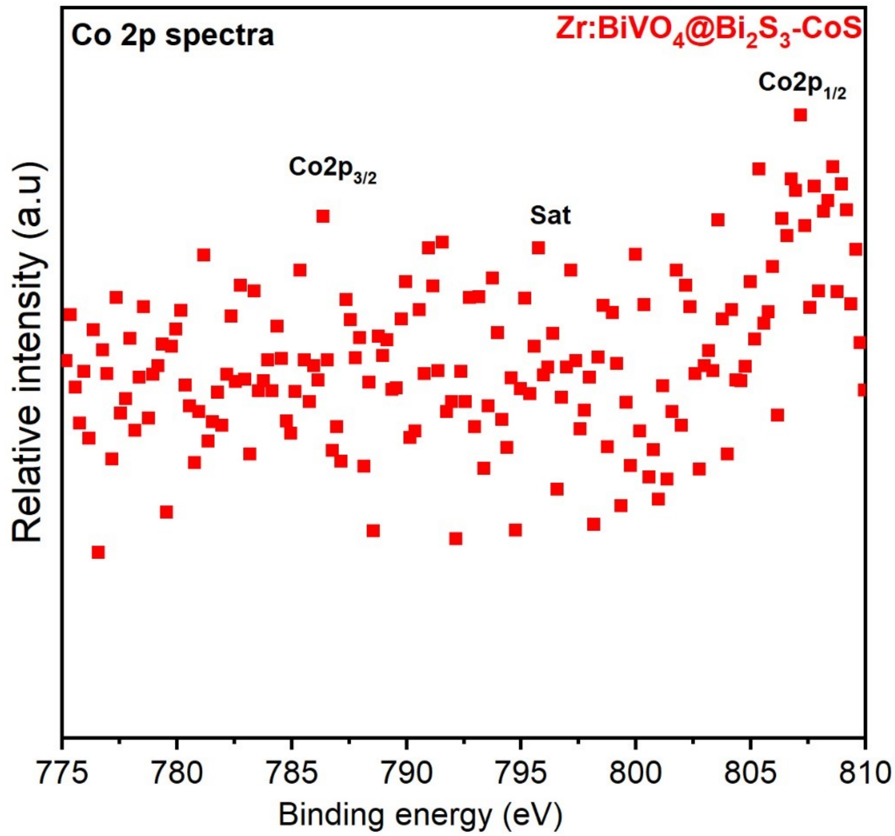

Figure S2. Core level Co 2p XPS spectra of Zr:$BiVO_4$@Bi_2S_3-CoS films

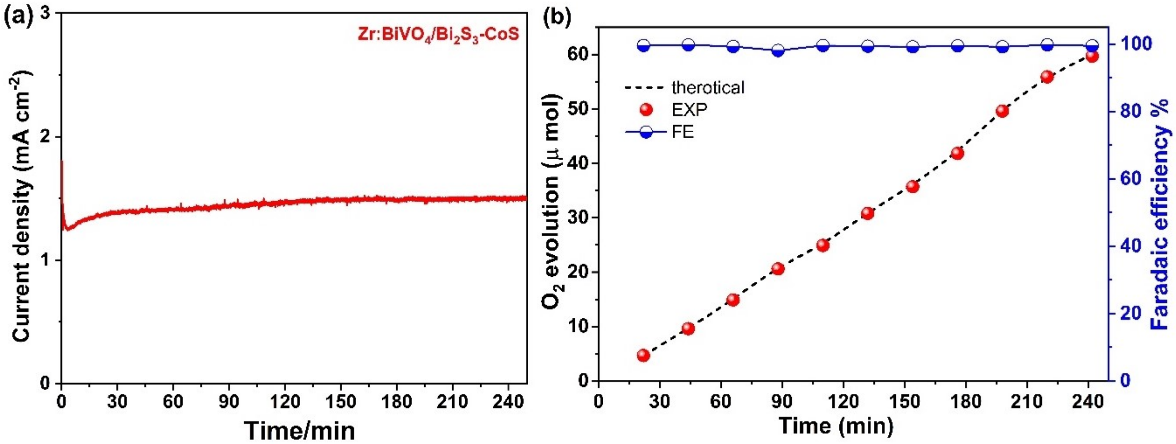

Figure S3. (a) Chronoamperometry measurements of fabricated electrodes of Zr:$BiVO_4$@Bi_2S_3-CoS at 0.1 $V_{Ag/AgCl}$ in 0.5 M Na_2SO_4. (b) Faradaic efficiency of Zr:$BiVO_4$@Bi_2S_3-CoS electrodes for the theoretically calculated and experimentally measured O_2 at a potential of 0.1 $V_{Ag/AgCl}$.

The Faradic efficiency of oxygen production for Zr:$BiVO_4$@Bi_2S_3-CoS photoanode was determined through galvanostatic catalysis at 0.1 $V_{Ag/AgCl}$ (Figure S3a). Oxygen generation was measured every 22 minutes by a gas chromatography (Agilent GC-8890) using a constant current over a period of 4 h. At this point, the theoretically calculated oxygen generation and the actual oxygen generation were compared. The theoretically calculated amount of oxygen was determined using the following equation from Faraday's law [1](Mo sa et al., 2016) as follows:

$$\eta_{H2} \text{ (theoretical)} = Q/nF = I \times t/nF \qquad (1)$$

where η_{O2} is the theoretically calculated amount of O_2, Q is the amount of applied charge, n is the number of electrons participating to produce one O_2 molecule (4 electrons), F is the Faraday constant (96485.3 s A mol^{-1}), i is the applied current, and t is the reaction time.

Faraday efficiency is calculated using the following equation.

$$\text{Faradaic efficiency} = \eta_{O2} \text{ (measured)}/\eta_{O2} \text{ (theoretical)} \qquad (2)$$

Furthermore, the photoelectrode produced 14.6 μmol of oxygen in an hour (**Figure S3b**), with a Faraday efficiency close to 100%.

Table S2. Various kinds of $BiVO_4$-based electrode materials are loaded with different co-catalysts and their PEC properties for water-splitting reactions.

S.No	Electrode	Electrolyte (pH)	Co-catalyst (Method)	Current density (mA/cm^2)	Ref.
1	$BiVO_4/FeVO_4$	0.2 M Na_2SO_4 pH = 7	Electrospray technique	0.4 @ 1.23 V_{RHE}	[2]
2	$BiVO_4$/CoFe-NiOOH	0.5 M Na_2SO_4 pH = 7	Lifting method/chemical process	1.54 @ 1.23 V_{RHE}	[3]
3	$BiVO_4$/rGO/NiFe	0.5 M Na_2SO_4 pH = ~6.9	Potentiostatic electrodeposition	1.30 @ 1.23 V_{RHE}	[4]
4	CoPi/$BiVO_4$	0.5 M Na_2SO_4	Photodeposition	1.1 @ 1.23 V_{RHE}	[5]
5	CoFe-PB/$BiVO_4$	0.1 M KPi	Wet processing method	1.0 @ 1.23 V_{RHE}	[6]
6	Ag/Ni-Zr:$BiVO_4$	0.1 M PBS pH 7.5	Electrochemical deposition process	3.14 @1.23 V_{RHE}	[7]
7	NiFePB/Zr:$BiVO_4$	0.1 M PBS pH 7.5	Electrodeposition process	3.23 @1.23 V_{RHE}	[8]
8	$BiVO_4/Bi_2S_3$	0.5 M Na_2SO_4	Photoassisted electrodeposition process	1.43 @1.23 V_{RHE}	[9]
9	$BiVO_4/Bi_2S_3$	0.35 M Na_2SO_3/0.25 M Na_2S	PEC transformation	3.3 @1.23 V_{RHE}	[10]
10	$Bi_2O_3/BiVO_4$	0.1 M Na_2SO_4	pulsed laser deposition	2.1 @1.23 V_{RHE}	[11]
11	Bi/Bi_2O_3	0.2 M Na_2SO_3	Magnetron sputtering	0.5 @ 0.6 $V_{Ag/AgCl}$	[12]
12	$Bi_2O_3/BiFeO_3$	0.1 M KOH	pulsed laser deposition	0.084 @ -0.68 $V_{Ag/AgCl}$	[13]
13	$BiFeO_3/Bi_2O_3$	-	Flame annealing process	-0.21 @ 0.38 V_{RHE}	[14]
14	$BiVO_4/Bi_2S_3$/FeOOH	0.1 M Na_2SO_4	Hydrothermal process	0.8 @0.4 V_{SCE}	[15]
15	Mo:$BiVO_4$	0.1 M Na_2SO_4	Pulsed laser deposition	2.1@1.23 V_{RHE}	[16]
16	$BiVO_4$/V-	1 M KBi	Hydrothermal method	5.43 @ 1.23 V_{RHE}	[17]

	NiOOH/FeOOH				
17	$BiVO_4/Bi_2S_3/BiPS_4$	0.1 M PBS/Na2S pH 10	Ion-exchange reactions	3.85 @1.23 VRHE	[18]
18.	$Zr:BiVO_4@Bi_2S_3$-CoS	0.1 M Na2S/Na2SO4	Ion-exchange reactions	3.09 @1.23 VRHE	This work

Table S3. Electrochemical Impedance parameter obtained from the best fitted to the equivalent circuit for the EIS spectra observed under continuous irradiation conditions at 0.8 V vs RHE.

Samples	R_s (ohm)	Q1 (µMho)	R_{ct} (Ω)	L
$Zr:BiVO_4$	29.8	322	8883	1.10 kH
$Zr:BiVO_4@Bi_2S_3$	41.6	164	1011	72.5 H
$Zr:BiVO_4@Bi_2S_3$-CoS	40.5	180	998	40.3 H

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