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Supporting Information

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Unbiased Photoelectrochemical Water Splitting in Z-Scheme Device Using W/Mo-Doped BiVO_4 and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$

Hyun S. Park, Heung Chan Lee, Kevin C. Leonard, Guanjie Liu, and Allen J. Bard^{*[a]}

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Figure S1. Home-built glass cell for gas chromatography-mass spectroscopy

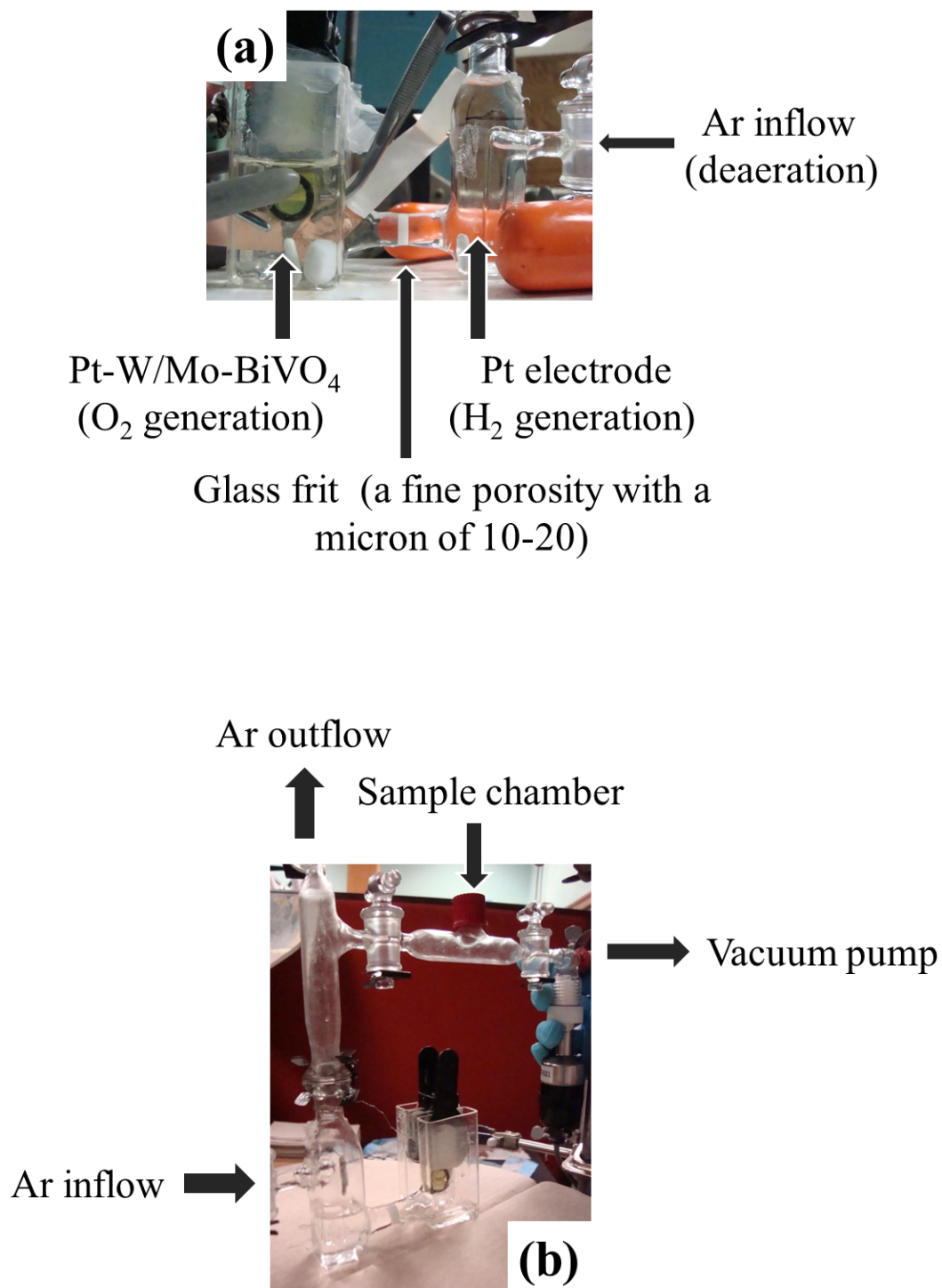


Figure S2. Photographic images of upper front (a) and side views (b) of the Z-scheme device.

Two Pt-W/Mo-BiVO₄ electrodes are placed between two glass cells and two Pt electrodes are in 25 mM/25 mM I⁻/IO₃⁻ and 0.1 M Na₂SO₄ solution (pH 7, 0.2 M sodium phosphate buffered).

Electrodes are wired as described in Figure 3.

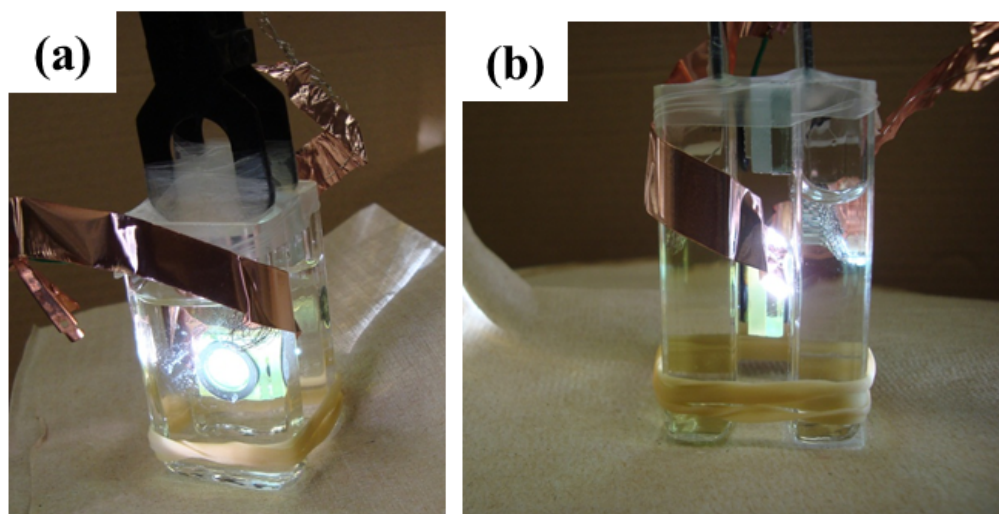
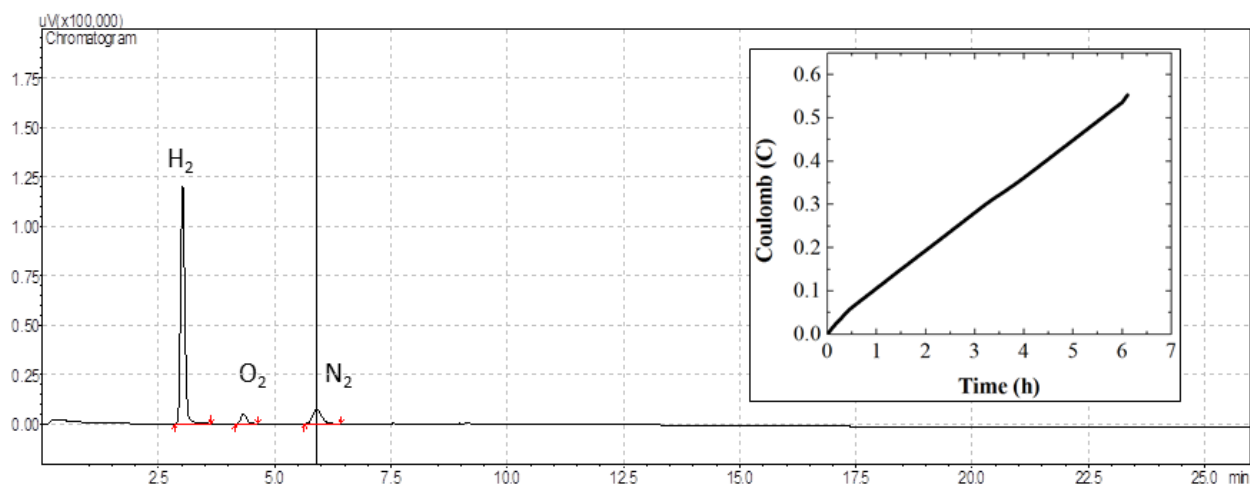


Figure S3. Gas chromatography-mass spectroscopy data



Peak#	Ret.Time	Area	Height	Conc.	Units	Compound
1	3.016	747472.7	120073.4	2953.72093	ppm	H ₂
2	4.325	44153.3	5034.9	1601.86132	ppm	O ₂
3	5.904	99367.6	7260.6	4214.20354	ppm	N ₂

Calculations on GC-MS H₂ generation

- Volume of head space (gas) : 19 mL
- Volume of water : 18 mL
- Henry's constant for H₂ in water : $k = 1282$ [atm L /mol]

$$p = kC$$

where p is partial pressure and C the concentration.

- Electric charge flow: 0.55 C
- Number of moles of H₂ for 0.55 C : $0.55 \text{ [C]} / 96485 \text{ [C/mol]} / 2 = 2.85 \times 10^{-6} \text{ [mol]}$

$$\text{Volume} : 2.85 \times 10^{-6} \text{ [mol]} * 22.4 \text{ [L/mol]} * 1000 \text{ [mL/L]} = 0.0638 \text{ mL}$$

- Assume no gas bubbles in solution and simple Henry's law

- Define p as concentration in gas (also partial pressure or mole fraction) and c as concentration in solution

$$p = kc$$

$$2.85 * 10^{-6} [\text{mol}] = (p/1282) [\text{mol/L}] * 0.018 [\text{L}] + p * 0.019 [\text{L}] / 22.4 [\text{L/mol}]$$

$$p = 3.30 * 10^{-3} = 3300 \text{ ppm}$$

- Experimental value : 2953 ppm

$$2953 / 3300 * 100 = 89.48 [\%]$$

- 89 % of generated electric charge is detected as a hydrogen gas by gas chromatography.

Figure S4. H₂ detection using membrane electrode assembly (MEA)

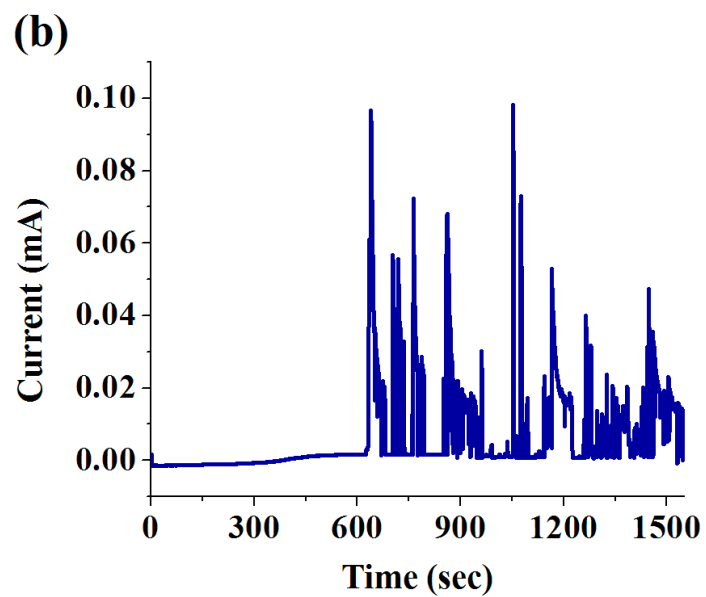
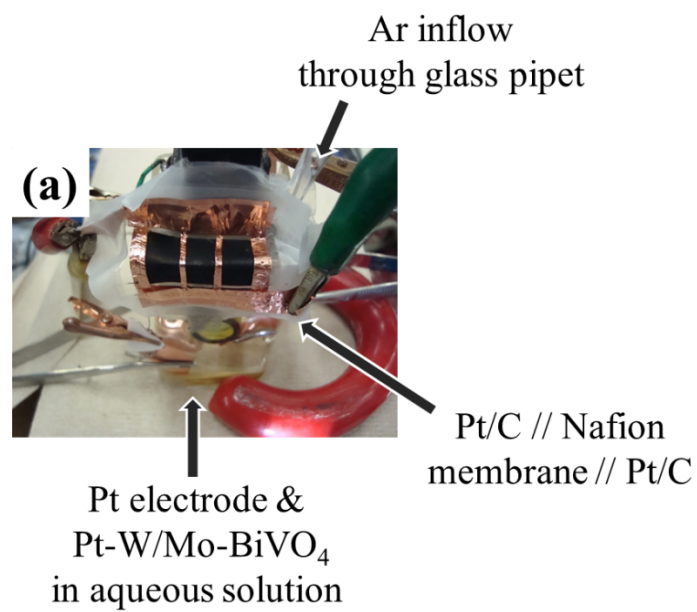


Figure S5. (a) Possible electrode configurations for singly-, doubly-, triply-, and quadruply-separated and connected cells in series with a constant area. (b) and (c) show LSVs (solid lines) and power density curves (dotted lines) for the supposed singly- (gray), doubly- (red), triply- (blue), and quadruply- (yellow) connected cells for $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}/\text{CoS}$ (b) and CdSe/CoS (c) thin film electrodes. Black dotted line in (b) and (c) shows the current density and potential relationship for water photolysis using Pt-W/Mo-BiVO₄ and Pt electrodes under UV-visible irradiation. Arrows shown on the right y-axis of (b) and (c) indicate the estimated power density for water splitting under UV-visible irradiation in Z-scheme. Data for the calculations are taken from the measurements shown in Figure 9(a).

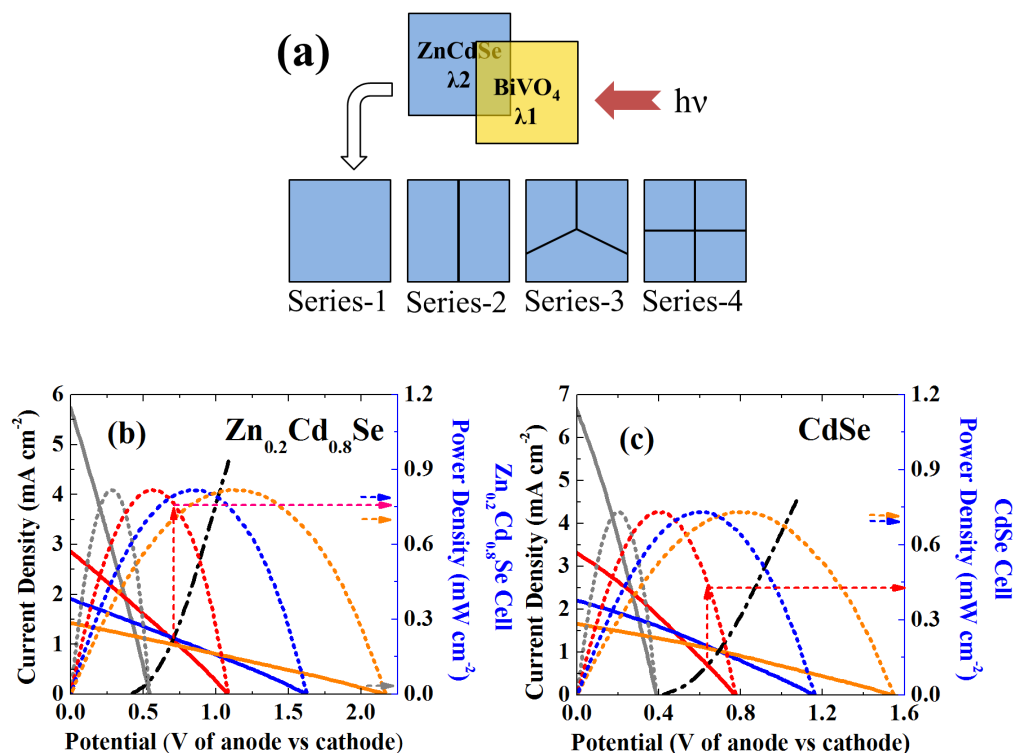


Figure S6. Photographs of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{Se}$ / CoS thin film electrode cells

