Supporting information for

Degradation of organics with simultaneous recovery of silver in a simple visible-light responsive dual photoelectrode photocatalytic fuel cell

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1. The characterizations of BiVO$_4$-CuO/Cu$_2$O PFC system

![Graphs showing the open-circuit voltages and photovoltage-time curves](image)

**Fig. S1** The open-circuit voltages of (a) Cu$_2$O/CuO photocathode and (b) BiVO$_4$ photoanode. (c) and (d) correspond to the photovoltage-time curve and photocurrent-time curve of PFC system.

**Text. S1** As shown in Fig. S1a and 1b, photovoltage of Cu$_2$O/CuO photocathode and BiVO$_4$ photoanode were measured respectively in the dark and under a Xe lamp with a UV-cut filter ($\lambda > 420$ nm) irradiation with 0.1 M Na$_2$SO$_4$ as the electrolyte. Both Cu$_2$O/CuO photocathode and BiVO$_4$ photoanode show quick photoresponse of which the photovoltage values shift from 0.17 V to 0.36 V and 0.03 V to 0.30 V instantly when the light source was turned on. Fig. S1c and S1d were photovoltage-time and photocurrent-time curves of PFC system. Fig. S1c indicates that an interior bias about 0.55 V was provided by Cu$_2$O/CuO photocathode and BiVO$_4$ photoanode. Fig. S1d shows the short circuit currents ($J_{SC}$) for the BiVO$_4$-Pt and Pt-Cu$_2$O/CuO
systems under chopped light. The corresponding values were 0.10 and 0.15 mA·cm⁻², respectively. By contrast, the $J_{sc}$ of BiVO₄-Cu₂O/CuO system was measured to be 0.30 mA·cm⁻², which was higher than the sum of photocurrents of the individual photoanode and photocathode, suggesting the existence of a synergistic effect between the photoanode and the photocathode. This synergistic effect might have been caused by the mismatch of $E_F$'s of the two electrodes[33].
Fig. S2 SEM images of the BiVO₄ photoanode at 0 min and 5 min.

Condition: [Na₂SO₄]₀ = 0.1 M, [Phenol]₀ = mg/L, [Ag⁺]₀ = 40 mg/L, pH = 7.0, λ ≥ 420 nm.
Fig. S3 XPS diffraction of Photoanode for Various Reaction Times with initial concentration of Ag$^+$

Condition: $[\text{Na}_2\text{SO}_4] = 0.1$ M, $[\text{Phenol}]_0 = \text{mg/L}$, $[\text{Ag}^+]_0 = 40 \text{ mg/L}$, pH = 7.0, $\lambda \geq 420$ nm
Fig. S4 SEM images of the Cu$_2$O/CuO photocathode in different reaction time at 0 and 5 min. Condition: Electrolyte: 0.1 M Na$_2$SO$_4$, [Phoh]$_0$ = 5 mg/L, [Ag$^+$]$_0$ = 30 mg/L, pH = 7.0, $\lambda \geq$ 420 nm.

Fig S5. EIS spectra of the photoelectrodes.