## Supporting information

# Photoelectrocatalytic Reduction of Cr(VI) in Wastewater with a $CuBi_2O_4$ Thin Film Photocathode

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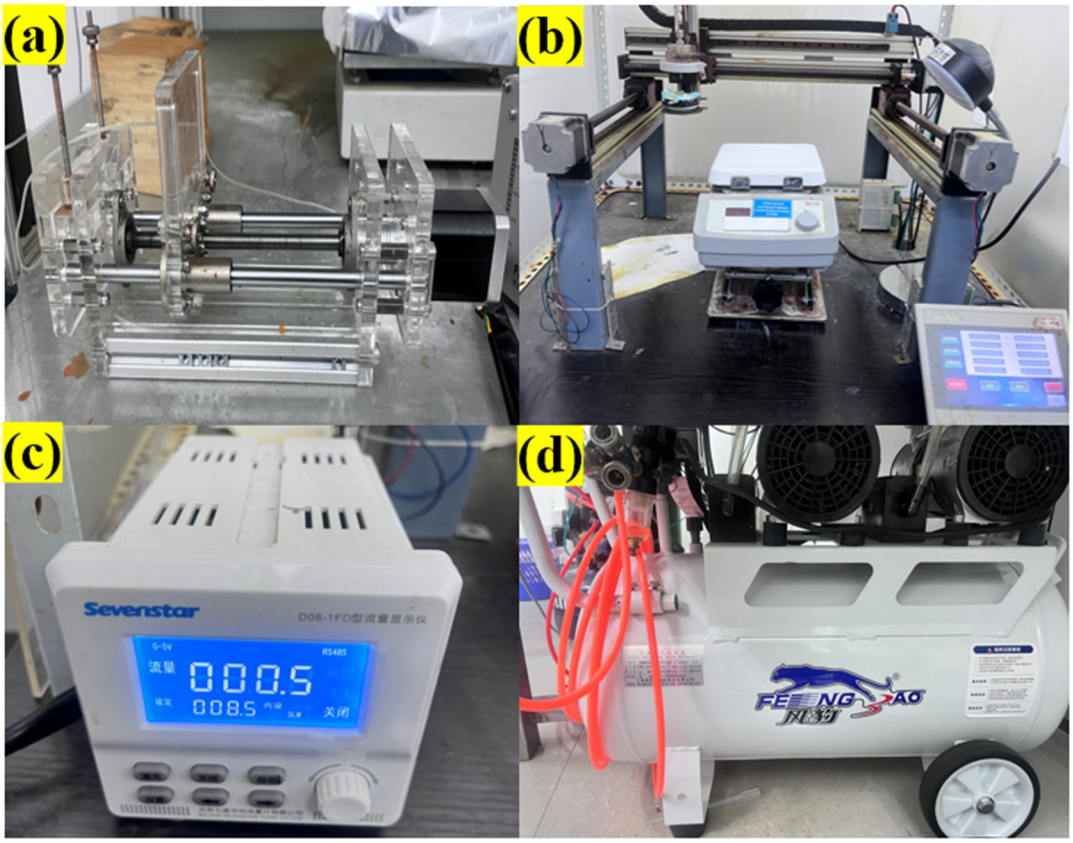


**Figure S1.** Digital photographs of the spray pyrolysis equipment: (a) liquid injection syringe; (b) ultrasonic atomizing nozzle, x-y-z triaxial motion system, and the heating platform; (c) proton flowmeter; (d) air compressor

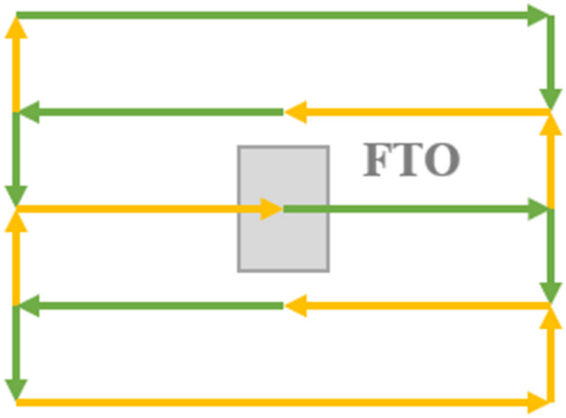


**Figure S2.** The schematic of spray route

The brief schematic of the spray route is shown in Figure S2, FTO substrate is at the very center and an x-y two-axis linkage platform is used to control the

movement of the nozzle. The area through which the nozzle moves is larger than that of the substrate so as to obtain uniform depositions.

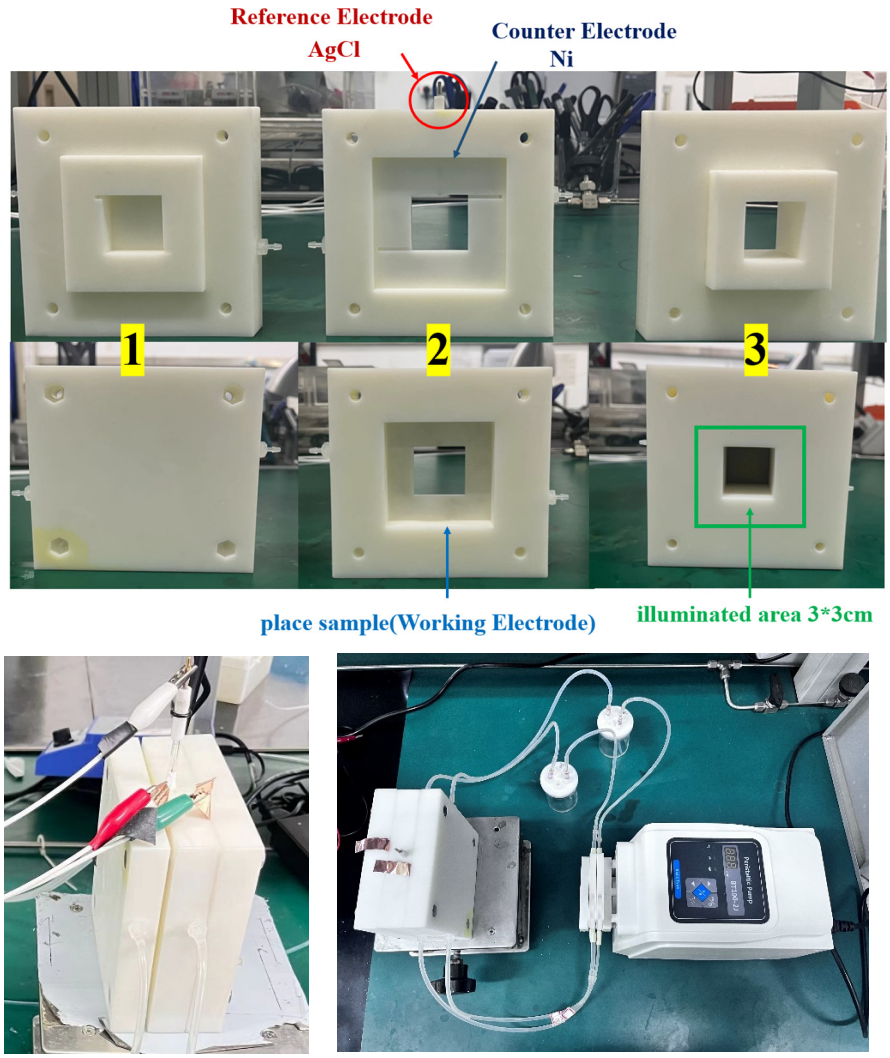


**Figure S3.** Flow cell information, structural design and composition

Our PEC reduction of Cr(VI) was conducted in a flow system, comprising primarily of a flow electrolytic cell and a peristaltic pump. The sample reaction window in the flow cell was designed to be 3×3cm² in area. Throughout all reaction processes, we controlled the liquid flow rate at 10mL/min by adjusting the speed of the peristaltic pump.

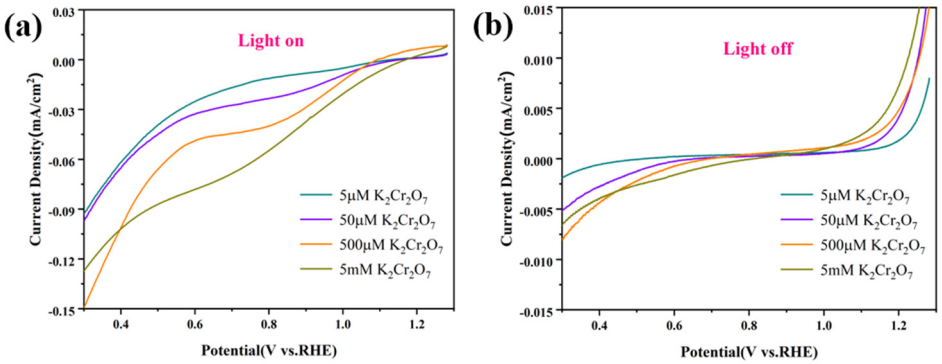


**Figure S4.** (a),(b) LSV testing of nanoporous $CuBi_2O_4$ thin film photoelectrodes in 5μM-5mM $K_2Cr_2O_7$ solution under light and dark conditions

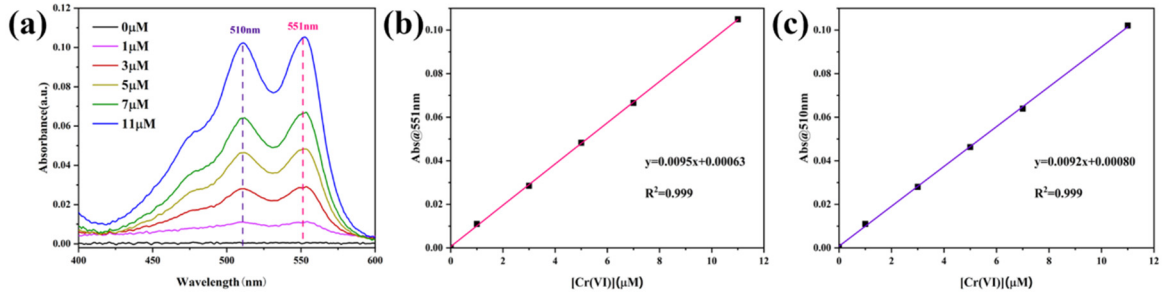


**Figure S5.** (a) Absorption spectra of Cr (VI) solutions with different concentrations after developing color with DPD for 30 minutes; (b),(c) Calibration curve of DPD method for determining Cr (VI) in the 0-10μM range at 510nm and 551nm

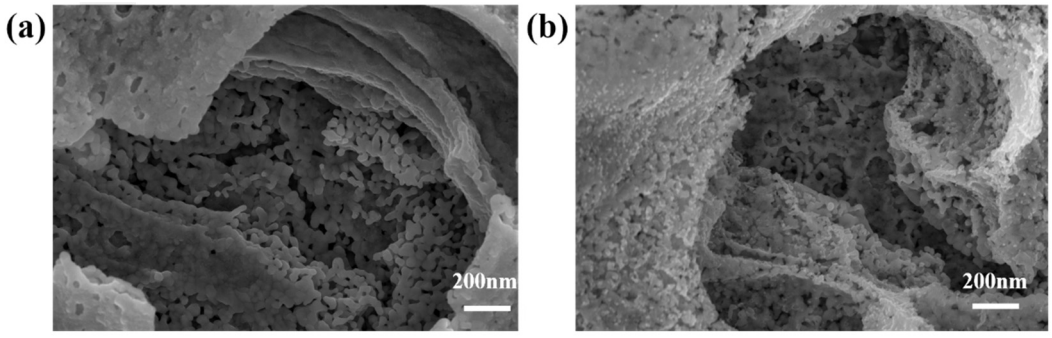


**Figure S6.** The SEM images of $CuBi_2O_4$ before and after participating in the photoelectrocatalytic reaction

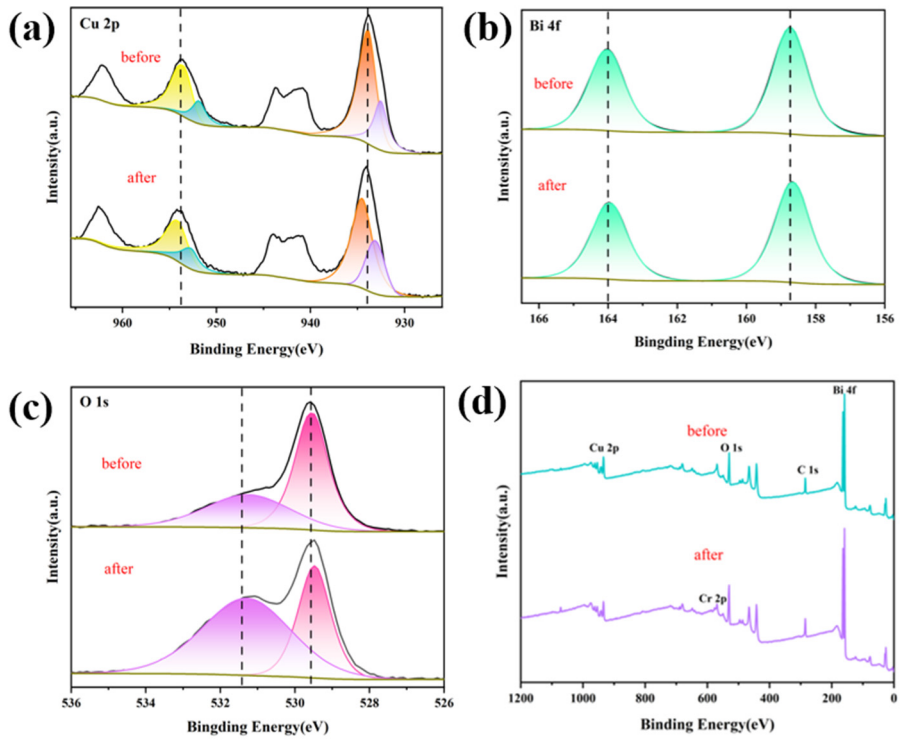


**Figure S7.** XPS spectra of $CuBi_2O_4$ thin film photoelectrodes before and after photoelectrocatalytic reduction of Cr (VI) for 3 hours; (a) Cu 2p; (b) Bi 4f; (c) O1s; (d) XPS full spectrum

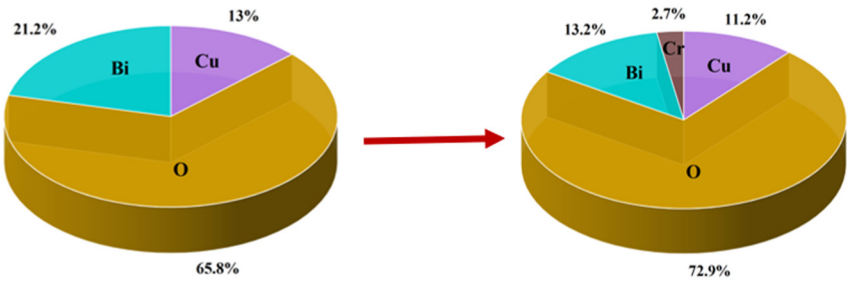


**Figure S8.** Analysis of element content before and after 3 hours of PEC reaction