Supplementary Information

Acetylenic carbon-rich frameworks on copper foam as conjugated polymer photocathodes for efficient and stable water reduction †

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Experimental Section

Chemicals and materials. A 1 mm thick copper foam supplied by Suzhou Taili New Energy Materials Co., Ltd. (China), was cut into pieces of 50 × 10 mm^2. Pyridine (99.5 %), methanol (99.9 %) and dichloromethane (AR) were purchased from Macklin Chemical and used as received. Piperidine (99.5 %) and TEB were bought from SCR Chemical. A Fresnel lens with diameter of 12 inch was purchased from Edmund Optics.

Synthesis of PTEB on Cu foam. TEB (5 mg, 0.033 mmol) and piperidine (10 μL, 0.1 mmol) were added to a glass vial of 10 mL pyridine as a solvent, and they were mixed well. Copper foam ultrasonic cleaned with deionized water for two minutes was immersed in the reaction mixture. Subsequently, the vial was sealed and heated in an oven to 60 ° C for 24 hours. After reaction, the samples were immediately washed sequentially with pyridine, dichloromethane and methanol for 2 minutes. At last, the samples were blow-dried by dry nitrogen jet and the surface of the sample was covered with a golden yellow film.

Materials Characterization. The samples were heated in Blast Drying Oven (DHG-9030A). The morphologies of samples were characterized by scanning electron microscopy (SEM, S4800, Hitachi), and transmission electron microscopy (TEM, JEOL JEM 2100). The structure of the samples was analyzed by Fourier transform infrared spectroscopy and DXR Raman Microscope (ThermoFisher Scientific) with excitation of 532 nm laser. The X-ray photoelectron spectroscopy (XPS) was carried out to reveal hybridization of elements, collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<10^{-8} torr) and using a monochromatic Al Kα X-ray source, with binding energies referenced to the C 1s binding energy of 285.0 eV. The diffuse reflectance UV-vis adsorption spectra were recorded on a spectrophotometer (Shimadzu, UV 3600), with the reference of $BaSO_4$ powder. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu Kα radiation (1.540598 Å)), showing it's amorphous.

Photoelectrochemical (PEC) measurements. All the PEC measurements were employed with CHI 660E electrochemical working station (Chenhua Instrument Co., Ltd., Shanghai), in a three-electrode system: the reference electrode is Ag/AgCl with saturated KCl solution, the counter electrode is a platinum foil, and the working electrode is the PTEB / Cu foam photocathode that we synthetized. The supporting electrolyte was a 1 M Na_2SO_4 solution with pH equaling to 4.9, which uses 0.1 M KH_2PO_4 to adjust it. The potential relation between Ag/AgCl with saturated KCl solution and reversible hydrogen electrode (RHE) is as follows:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{\circ}_{Ag/AgCl}$$

while $E^{\circ}_{Ag/AgCl} = 0.1976$ V at 25 °C

Linear scanning voltammetry (LSV) has a scanning rate of 5 mV s^{-1}. The intensity of the light source was regulated with a Si diode (Model 818, Newport) to simulate AM 1.5 illumination (100mW cm^{-2}). The photocurrent was measured under an irradiation from a 300 W Xe lamp (PLS-SXE300, PE300BF). In addition, the range of the potential is from 0.1 V to -0.6 V vs. Ag/AgCl when performing LSV. The stability of the compound was detected under 0V vs. RHE. The electrochemical impedance spectra (EIS) were measured by a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with an excitation signal of 10 mV amplitude. Afterward, Mott-Schottky measurement was performed at fixed frequency of 5 kHz.

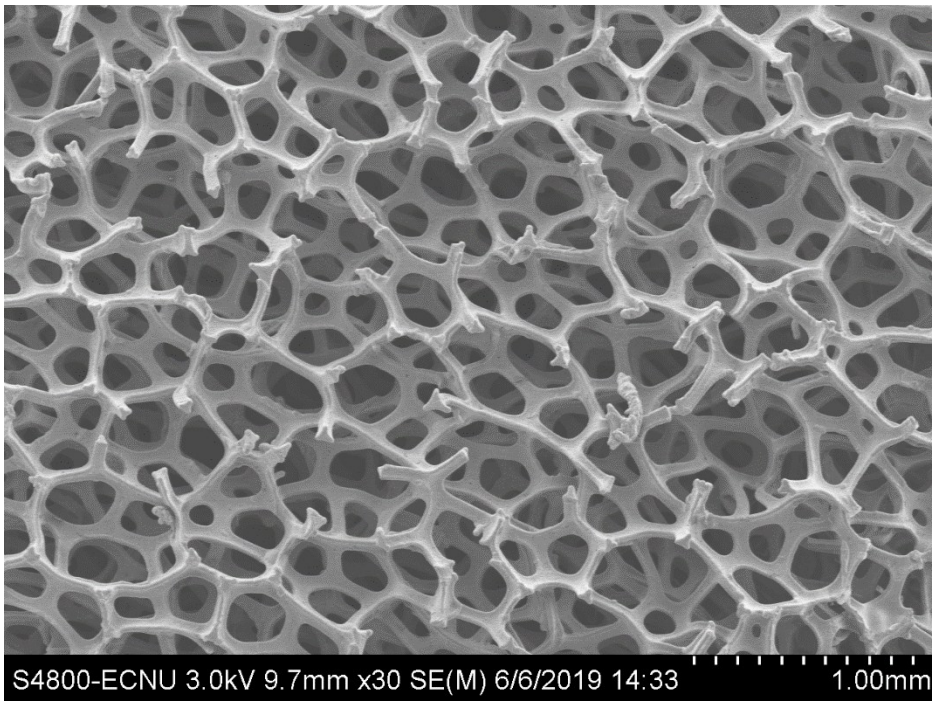

Fig. S1 SEM image of PTEB/CF in large view.

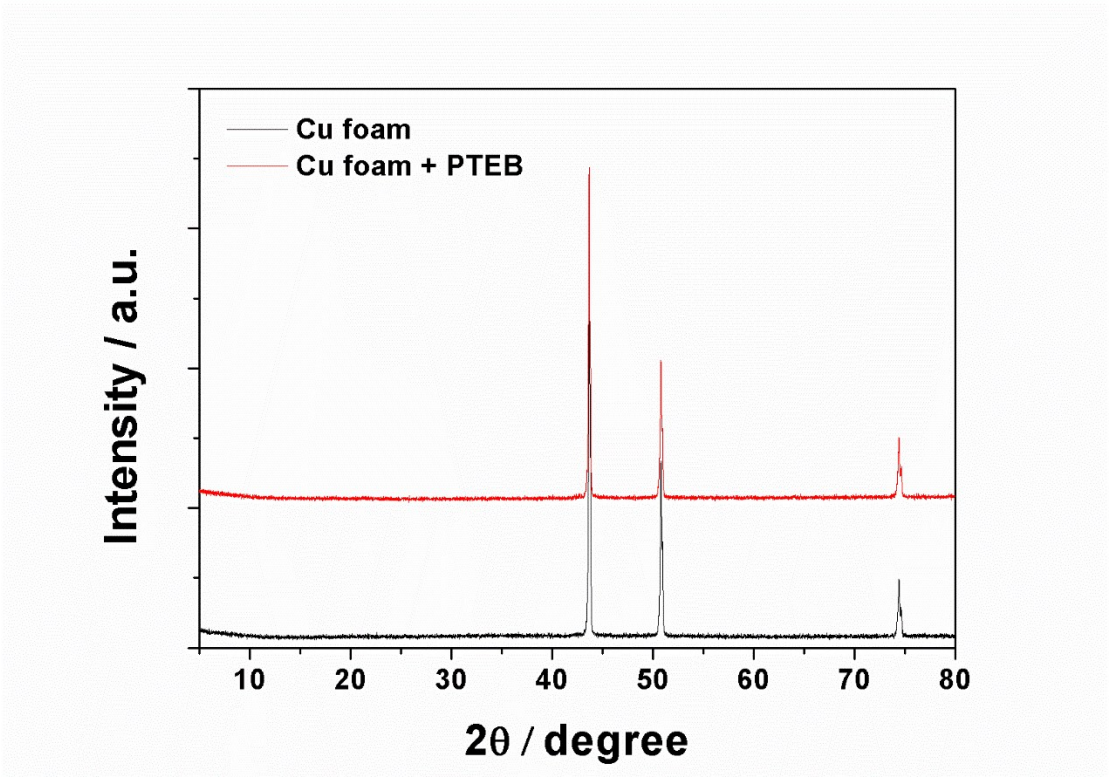

Fig. S2 XRD patterns of CF and PTEB/CF.

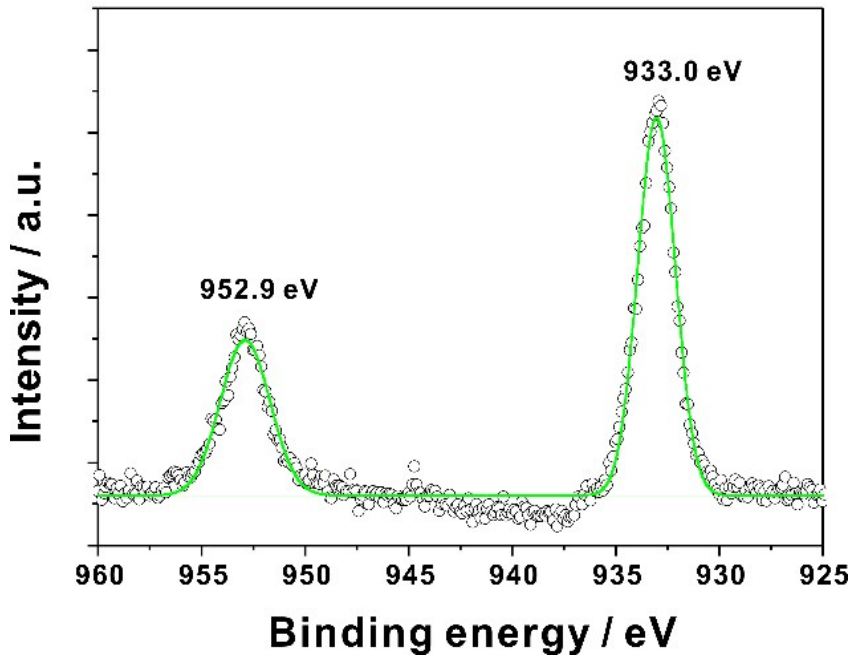

Fig. S3 Core-level XPS of Cu 2p.

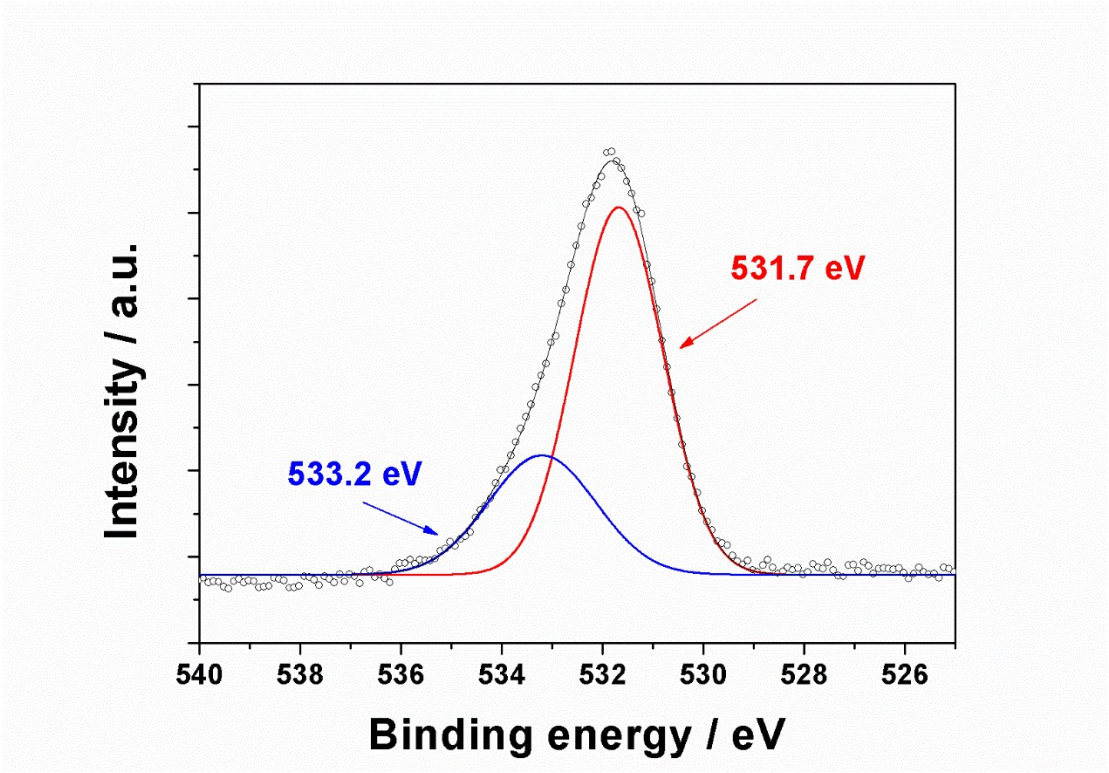

Fig. S4 Core-level XPS of O 1s.

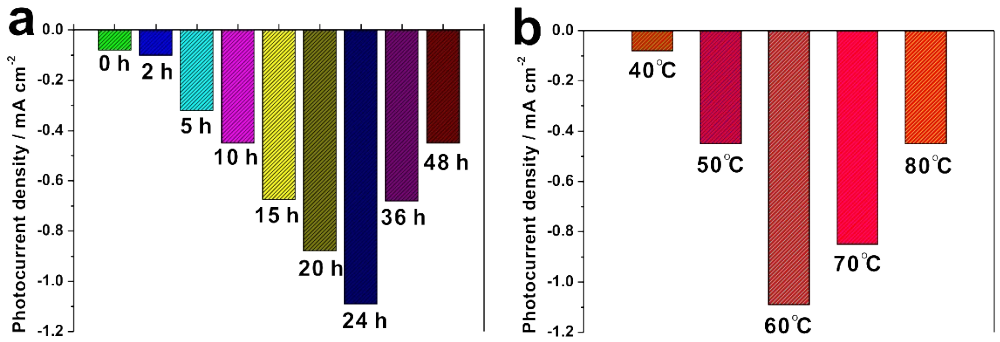

Fig. S5 Optimization of parameters of duration and temperatures for PTEB synthesis.

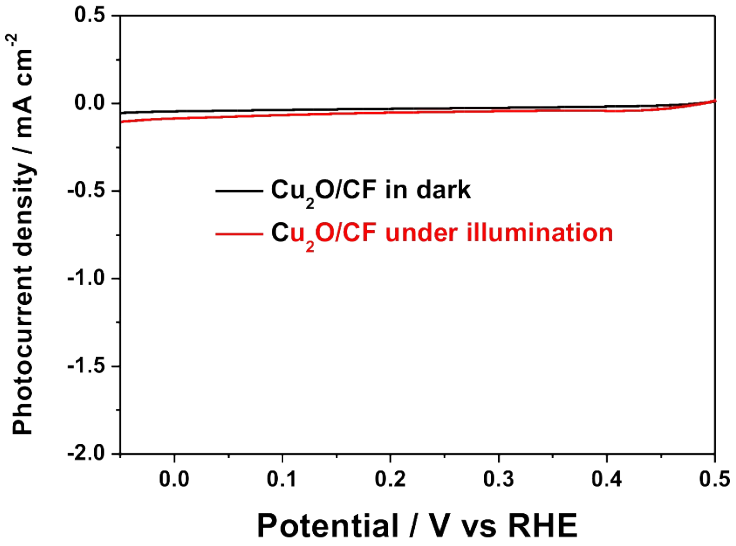

Fig. S6 PEC response of thin Cu_2O layer on copper foam.

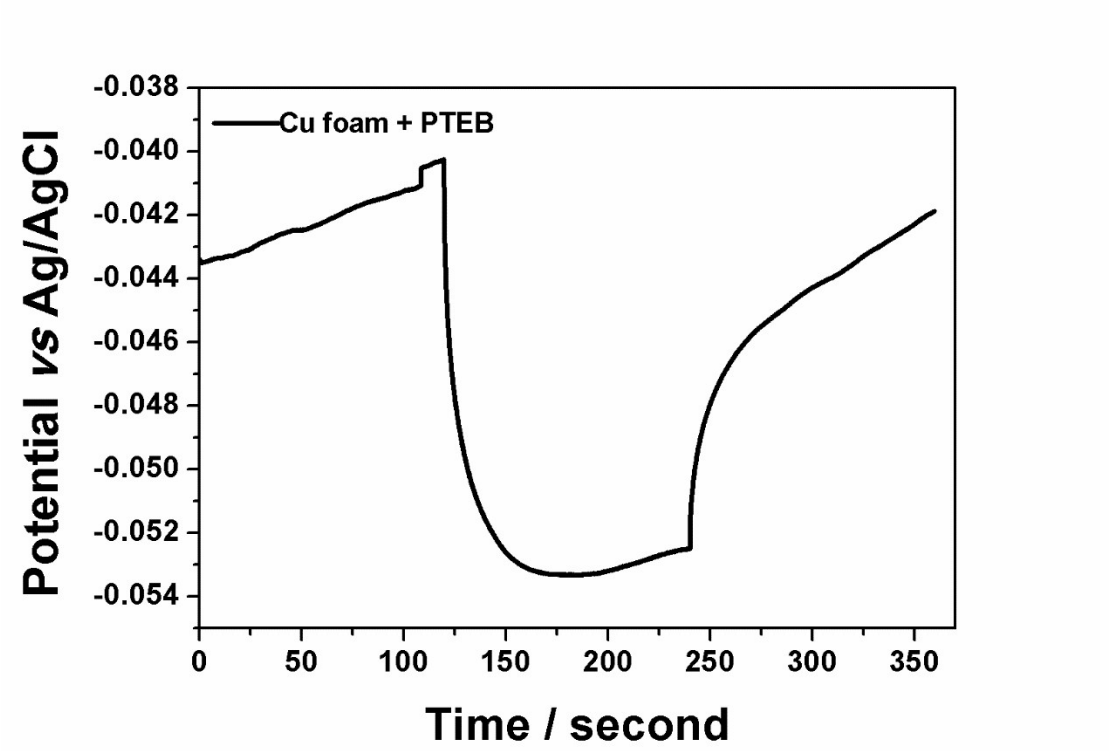

Fig. S7 Open circuit potential plot.