Electronic supplementary information (ESI) for

Low-Voltage Altering Current Powered Polydopamine-Protected Copper Phosphide Nanowire for Electroporation-Disinfection in Water †

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1. Experimental section

1.1. Electrode fabrication.

The copper-phosphide-nanowire-modified copper foam (PDA-Cu_3PNW-Cu) electrode was prepared according to our earlier study with minor modifications.[1] Typically, the Cu foam (Zhuoer, China, pore size 200 μm) was cut into Φ = 10 mm × 2 mm as cylinder electrode and washed with 1 M HCl (Sigma) and subsequently with deionized water for 3 times to remove surface impurities. The cleaned Cu foam was then anodized in an alkali solution (1.5 M NaOH, Sigma) for 15 min with a fixed current density (12.5 mA cm^{-2}) using a digital source meter (Keithley, 2400). Then the copper-hydroxide nanowires ($Cu(OH)_2$NWs) grew on the copper foam surface. To prepare copper-phosphide nanowires (Cu_3PNWs), excess sodium hypophosphite (Sigma) was placed at the center of the tube furnace and the $Cu(OH)_2$NWs-modified copper foam ($Cu(OH)_2$NW-Cu) electrode was placed at the downstream side of the furnace. After flushed with the argon for 20 min, the center of the furnace was generally elevated to 300 °C with a heating rate of 2.5 °C min^{-1}, and the $Cu(OH)_2$NW-Cu electrode was kept at ~100 °C. After 2 h, the furnace cooled down naturally to room temperature under the argon atmosphere, and the Cu_3PNW-modified copper foam (Cu_3PNW-Cu) electrode was obtained.

The polydopamine (PDA) coating process was performed based on the previous study with minor modification.[2] The prepared Cu_3PNW-Cu electrode was immersed in a dopamine (Sigma) solution (2.5 g L^{-1}) buffered with Tris (Sigma, 0.01M, pH 8.5) at 40 °C for 4 h in the open air for one coating-cycle. The coating layer thickness was controlled by different coating cycles (2, 3, 4,

and 6) corresponding to coating time for 8, 12, 16, and 24 h. The Cu_3PNW-Cu that underwent 8, 12, 16, and 24 h of PDA coating were referred to as PDA-Cu_3PNW-Cu_8, PDA-Cu_3PNW-Cu_12, PDA-Cu_3PNW-Cu_16, and PDA-Cu_3PNW-Cu_24, respectively.

1.2. Material characterization.

The morphology of the electrode was characterized by a scanning electron microscope (SEM, Hitachi, SU8220) and a transmission electron microscope (TEM, JEOL, JEM 2010F), respectively. The corresponding element distribution was analyzed by energy dispersive X-ray (EDX) spectroscopy on the TEM (JEOL, JEM 2010F). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD, PANalytical, Alpha 1 MPD). The chemical compositions were analyzed by an X-ray photoelectron spectroscopy (XPS) with an Axis Ultra instrument (Kratos Analytical, K-alpha) under ultrahigh vacuum ($<10^{-8}$ Torr) and by using a monochromatic Al Kα X-ray source. Raman spectra were measured using Raman spectroscopy (Renishaw, inVia Reflex) at wavelengths ranging from 600 to 1800 cm^{-1}.

1.3. The device construction and disinfection performance analysis.

Two of the Cu_3PNW-Cu or PDA-Cu_3PNW-Cu (PDA-Cu_3PNW-Cu_12, PDA-Cu_3PNW-Cu_16, or PDA-Cu_3PNW-Cu_24) electrodes were fitted into a plexiglass coaxial electrode holder to prepare an electroporation-disinfection cell (EDC). The distance between the two electrodes was fixed at 2 mm. Altering current (AC) with a peak voltage of 1 V and different frequencies form 10 to 10^8 Hz was applied across the two electrodes using a waveform generator (RIGOL, DG5000).

EDC disinfection performance was evaluated using five model microorganisms, including four model bacteria *Escherichia coli* (*E. coli*, ATCC 15597), *Enterobacter hormaechei* (*E.*

hormaechei, ATCC 700323), *Enterococcus durans* (*E. durans*, ATCC 6056), and *Bacillus subtilis* (*B. subtilis*, ATCC 6051) and one model virus MS2 (ATCC 15597-B1). Bacteria samples were cultured in a Tryptic Soy Broth (TSB, Sigma) to log phase (12 h) and harvested by centrifugation at 1500 g (HITACHI, RX2 series) and suspended in deionized water.[3-6] After washed with deionized water for 3 times, bacterial cells were suspended in deionized water to achieve the desired concentration of ~10^7 colony forming units per milliliter (CFU mL^{-1}). The MS2 was grown with the *E. coli* host on a shaker table set to 150 rpm at 37 °C for 24 h. MS2 was isolated and concentrated using the polyethylene glycol (PEG) precipitation method.[7] A solution of ~10^6 plaque forming units per milliliter (PFU mL^{-1}) was prepared using deionized water. The *E. coli* were also dispersed into the lake water (after 0.2 μm membrane filtration) and the tap water to ~10^7 CFU mL^{-1} (Table S1). Secondary effluents were collected from two wastewater treatment plants (WWTPs) with a bacterial concentration of ~10^4 CFU mL^{-1} (Table S2).

Each water sample flowed through the EDC device at a designated flow rate. Given that the cross-section area of the electrode (φ 10 mm) was 0.785 cm^2, flow rates were kept in the range of 1.3-20.9 mL min^{-1}, corresponding to the flux of 1.0 to 16.0 m^3 h^{-1} m^{-2}. After treated for 10 min, the microorganism samples were collected. The bacteria and the virus concentrations in the influent (C_{in}) and effluent (C_{eff}) samples were measured using a standard spread plating technique and a double agar layer plating technique, respectively.[7, 8] Each sample was serially diluted and each dilution was plated in triplicate. All the results for each sample were averaged, and the standard deviation was calculated. Disinfection efficiency was calculated [$E = -\log (C_{eff}/C_{in})$] to evaluate the disinfection performance.

1.4. Bacterial storage after operation.

A normal saline solution (9.0 g L^{-1} sodium chloride) was sterilized at 121 °C for 20 min. Powered by AC (peak voltage of 1 V and frequency of 10^6 Hz) and applied with a fixed flux (4 m^3 h^{-1} m^{-2}), *E. coli* samples after EDC operation were harvested by centrifugation at 1500 g for 15 min at 15 °C (HITACHI, RX2 series), and supernatants were removed. Then *E. coli* samples were then resuspended in the sterilized normal saline solution to maintain the osmotic pressure between the cytoplasm and the solution. After that, treated samples were stored at 25 °C, which represents a typical temperature of a natural aquatic environment. Then *E. coli* concentrations of samples were measured using standard spread plating techniques.

1.5. Bacterial sample preparation for SEM.

The morphology of bacteria before and after EDC operation was investigated by SEM (Hitachi, SU8220). The bacterial sample for SEM was prepared according to the previous study with minor modifications.[9] Powered by AC (peak voltage of 1 V and frequency of 10^6 Hz) and applied with a fixed flux (4 m^3 h^{-1} m^{-2}), bacterial samples (*E. coli*) before and after EDC operation were harvested by centrifugation at 1500 g for 15 min at 15 °C (HITACHI, RX2 series), and supernatants were removed. Then the bacteria were fixed overnight in the fixative containing 0.1 M phosphate-buffered solution (pH 7.3; Sigma), 2% glutaraldehyde (Sigma), and 4% paraformaldehyde (Sigma) at 4 °C. Samples were then dehydrated with increasing concentrations of an ethanol solution (50, 70, 90, and 100%; Sigma) and dried in 100% *tert*-Butyl alcohol (Sigma) by a critical point drying process (Quorum, K850). All the bacterial samples were dispersed on a metal grid in preparation for SEM characterization.

1.6. Long-term disinfection performance analysis.

The Cu_3PNW-Cu, PDA-Cu_3PNW-Cu_16, and PDA-Cu_3PNW-Cu_24 electrodes were used to test the long-term disinfection performance. The long-term disinfection performance was tested by treating the prepared bacterial samples (*E. coli*, ~10^7 CFU mL^{-1}) for 15 days a continuously and monitoring the disinfection efficiency over time. The bacterial solution was changed every 12 h to keep the concentration of live bacteria stable (~10^7 CFU mL^{-1}). The flux was fixed at 4.0 m^3 h^{-1} m^{-2}. The applied voltage was AC with a peak voltage of 1 V and frequency of 10^6 Hz generated by a waveform generator (RIGOL, DG5000).

1.7. Electrode degradation mechanism analysis.

The electrode degradation process was investigated for a continuous 15-day EDC operation. The flux was fixed at 4.0 m^3 h^{-1} m^{-2}, and the applied voltage was either direct current (DC) with a voltage of 1 V generated by a digital source meter (Keithley, 2400) or AC with a peak voltage of 1 V and frequency of 10^6 Hz. The released Cu concentration in the EDC effluent was measured according to the previous study:[1] (1) a 1-mL aliquot of effluent was collected and dosed in 1-mL HNO_3 (2 M; Sigma) ensuring the final HNO_3 concentration to 1 M and analyzed by the inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific, XSERIES 2) to determine the total Cu concentration (C_T); (2) another 1-mL aliquot was centrifuged (HITACHI, RX2 series) at 14500 rpm, corresponding to 17600 g, for 15 min under 15 °C, and the Cu concentration in the supernatant was measured by ICP-MS to determine the dissolved Cu^{2+} concentration (C_{dis}); (3) the suspended Cu particles caused by detaching (C_{det}) was then calculated [$C_{det} = C_T - C_{dis}$]. The detection limit was 0.1 μg L^{-1}. The electrodes after operation were taken out from the EDC carefully

and dried in a desiccator (VWR) overnight. After drying, the electrodes were characterized using SEM (Hitachi, SU8220), XRD (PANalytical, Alpha 1 MPD), and XPS (Kratos Analytical, K-alpha) to determine the electrode morphology, structure, and chemical composition, respectively.

1.8. Electrode stability analysis.

The Cu_3PNW-Cu and PDA-Cu_3PNW-Cu_24 electrodes were used to investigate the electrode stability. The EDC was operated with different fluxes (4.0, 6.0, 8.0, and 16.0 $m^3\ h^{-1}\ m^{-2}$). The applied voltage was AC (fixed peak voltage of 1 V and frequency of 10^6 Hz). The Cu concentration, including electrode detachment and dissolution, was measured after a 30-min EDC operation. The release rate was then calculated (release rate = Cu concentration × flow rate).

2. Figures

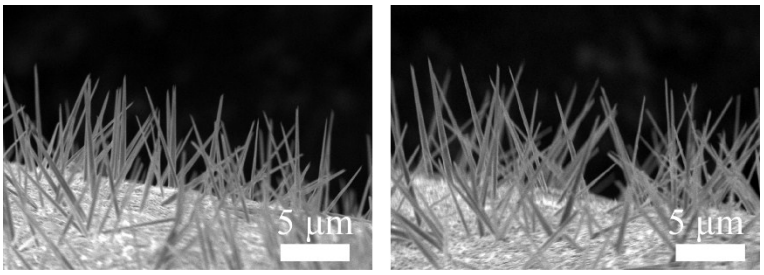

Fig. S1 Scanning electron microscope (SEM) images of copper-phosphide-nanowire-modified copper foam (Cu_3PNW-Cu) electrode.

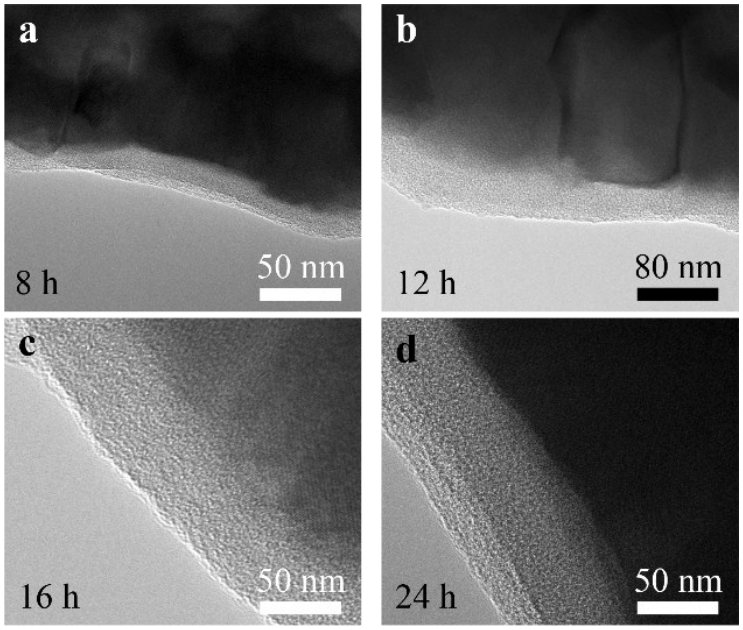

Fig. S2 Transmission electron microscope (TEM) images of Cu_3PNWs after polydopamine (PDA) coating for 8 h (a), 12 h (b), 16 h (c), and 24 h (d).

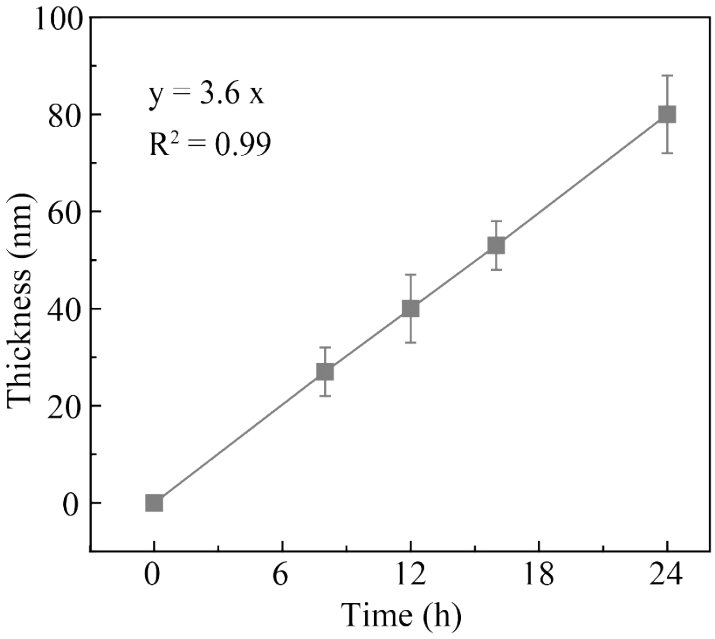

Fig. S3 Linear relationship between the coating time and the average thickness of the PDA film.

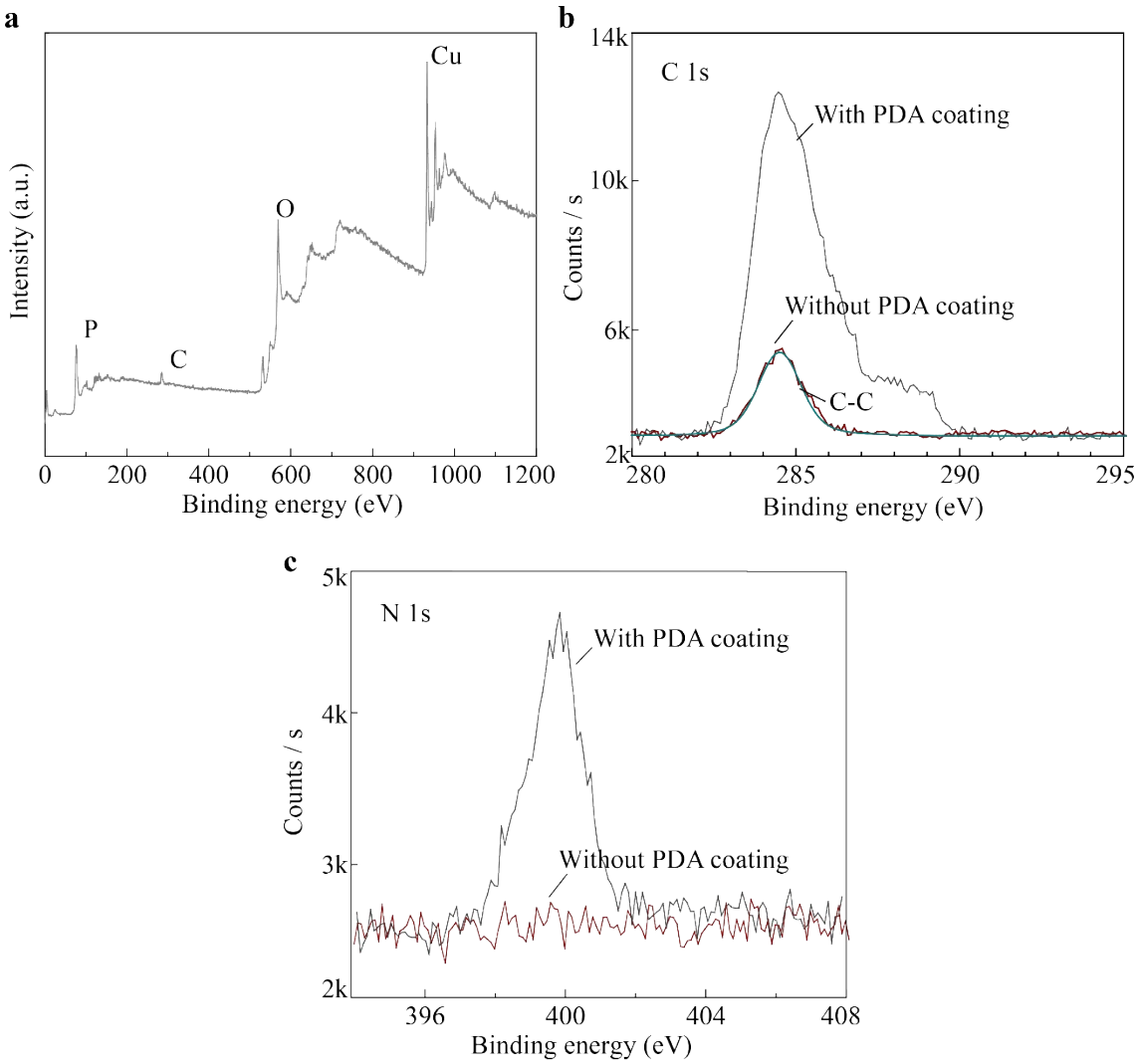

Fig. S4 X-ray photoelectron spectroscopy (XPS) survey spectrum (a), C 1s spectrum (b), and N 1 s spectrum (c) of Cu_3PNW-Cu.

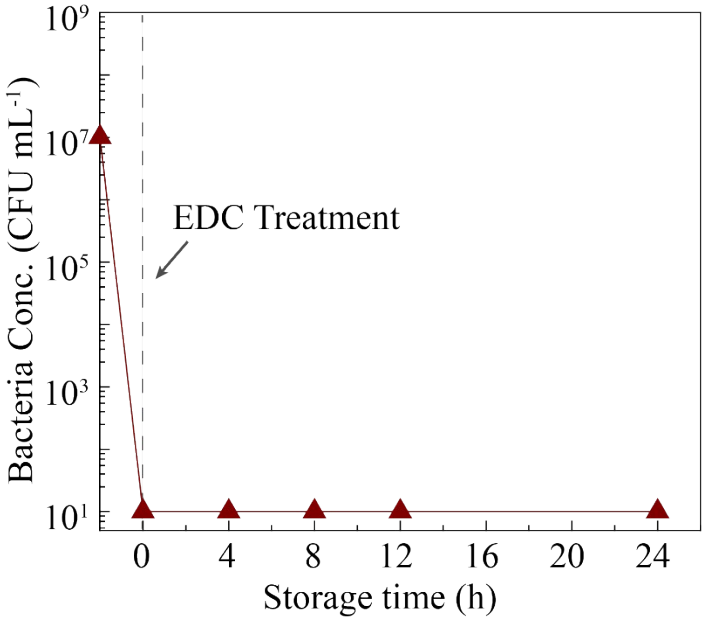

Fig. S5 Bacterial storage after operation. *E. coli* samples after EDC operation were harvested and resuspended in the sterilized normal saline solution. Treated samples were stored at 25 °C, and after 24 h storage process, no bacteria regrowth occurred.

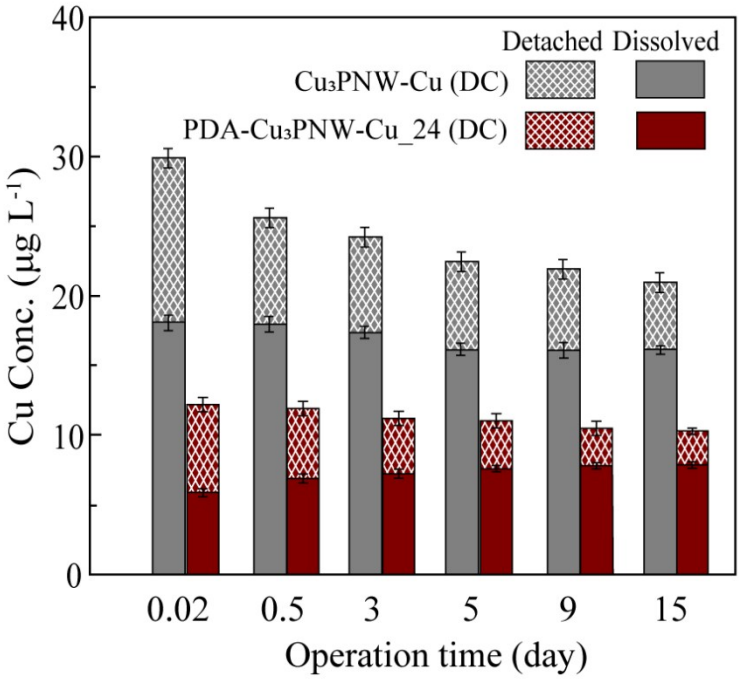

Fig. S6 Cu release of the Cu_3PNW-Cu and PDA-Cu_3PNW-Cu electrodes during the long-term electroporation-disinfection cell (EDC) operation (15 days). The EDC was powered by direct correct (DC; voltage of 1 V) with a fixed flux (4 m^3 h^{-1} m^{-2}).

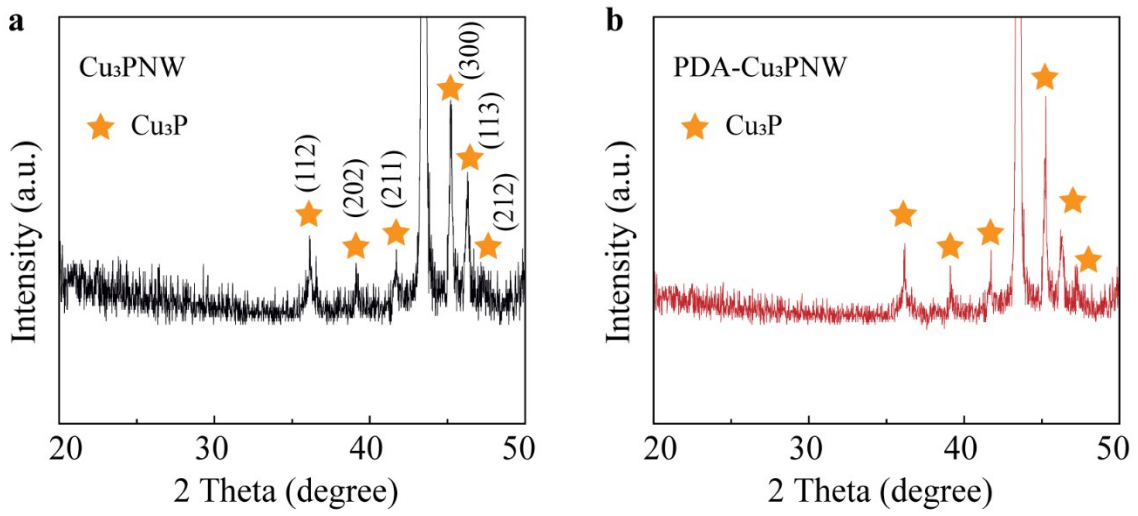

Fig. S7 X-ray diffraction (XRD) patterns of the pristine Cu_3PNW-Cu (a) and PDA-Cu_3PNW-Cu (b) electrodes before EDC operation. The diffraction pattern of the Cu_3PNW–Cu and PDA-Cu_3PNW-Cu both exhibits six broad peaks at 36.0°, 39.1°, 41.6°, 45.1°, 46.2°, and 47.3°, corresponding to (112), (202), (211), (300), (113), and (212) of the Cu_3P phase (JCPDS 71-2261), respectively. [10]

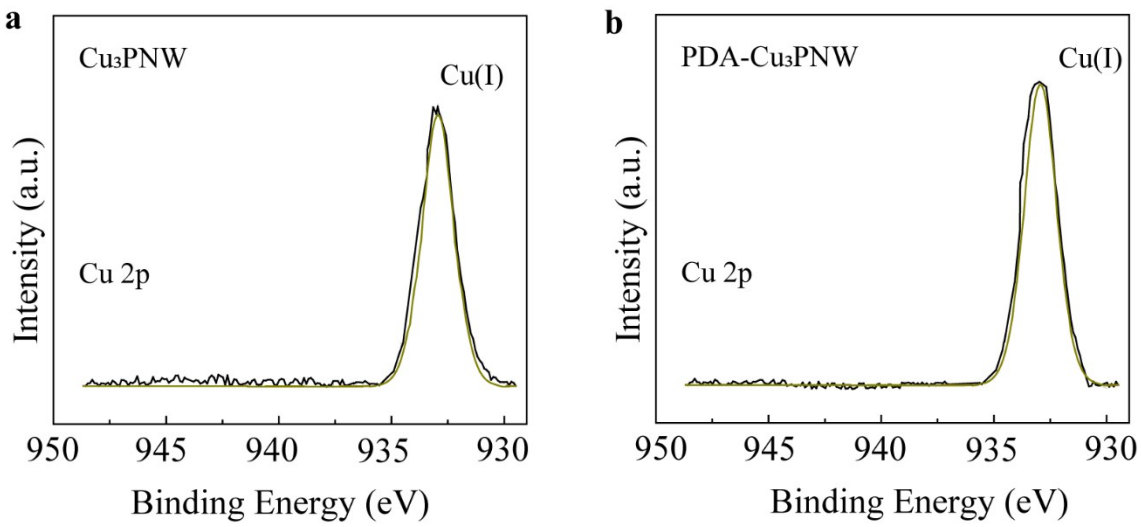

Fig. S8 XPS spectra of the pristine Cu_3PNW-Cu (a) and PDA-Cu_3PNW-Cu (b) electrodes before EDC operation. Both Cu_3PNW-Cu and PDA-Cu_3PNW-Cu shows the Cu 2p spectra with an apparent peak at 932.9 eV, attributed to the binding energy of Cu and P in Cu_3P. [11]

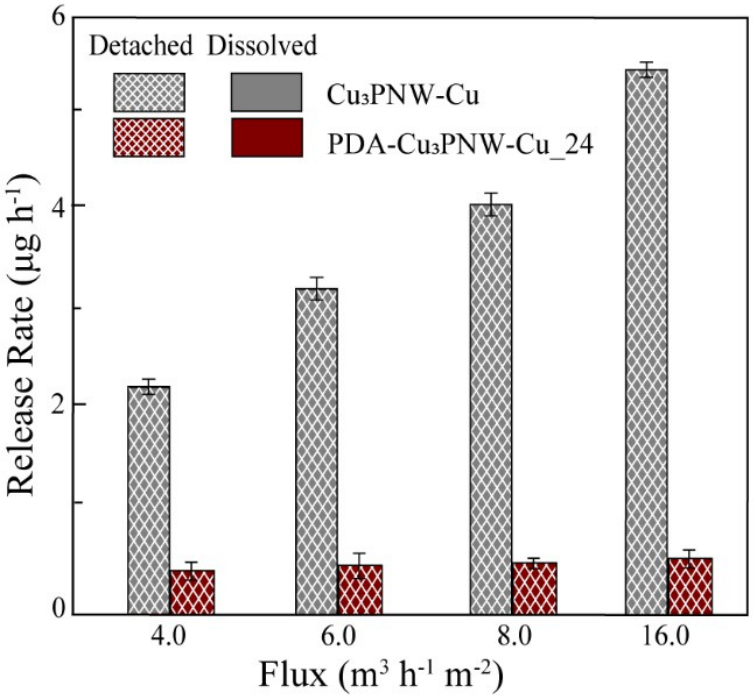

Fig. S9 Electrode stability analysis. Cu release of the Cu_3PNW-Cu and PDA-Cu_3PNW-Cu electrodes during EDC operation with different fluxes (4.0, 6.0, 8.0, and 16.0 m^3 h^{-1} m^{-2}) powered by AC (peak voltage of 1 V, frequency of 10^6 Hz).

3. Tables

Table S1. General information of lake water and tap water.

Name	pH	Total dissolved solids ($mg\ L^{-1}$)
Lake of Olympic Forest Park, Beijing	6.9	202
Tap water	6.5	55

Table S2. General information of secondary effluents from two wastewater treatment plants (WWTPs).

Name	pH	Total dissolved solids ($mg\ L^{-1}$)	Bacteria Conc. ($CFU\ mL^{-1}$)
Xiao Jia He WWTP	6.8	418	32000
Bei Xiao He WWTP	7.2	545	10500

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