Robust electrochemical metal oxide deposition using an electrode with superhydrophobic surface

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Experimental Section

Chemical.

Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, ≥98.0%), DL-Lactic acid ($C_3H_6O_3$, 90%), Zinc chloride ($ZnCl_2$, ≥98%) were purchased from Sigma (USA). Sodium hydroxide (NaOH, ≥96.0%), potassium chloride (KCl, ≥99.8%), Sodium Sulfate (Na_2SO_4, ≥99.0%), Potassium ferricyanide ($K_3[Fe(CN)_6]$, AR), Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$, AR), Phenolphthalein ($C_{20}H_{14}O_4$, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cerium (III) Chloride Anhydrous ($CeCl_3$, ≥93%) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). All chemicals were directly used without further purification. All solutions were prepared with Milli-Q water.

The conducting carbon fiber substrate subjected to a polyfluortetraethylene treatment; and then one side of the substrate is exposed to a short-term oxygen plasma (100 mW, 2 min) treatment. The carbon fibers based triphase electrode substrates and the fluorine doped tin oxide films (FTO) based hydrophilic diphase electrode substrates were cleaned sequentially, before deposition, by acetone and ethanol (for 15 min each) in an ultrasonic bath and then thoroughly rinsed with water.

Materials Characterization.

The morphologies and microstructures of samples were investigated using a field-emission scanning electron microscope (FE-SEM, HITACHI-S4800, Japan). X-ray diffraction (XRD) analysis was taken on X-ray powder diffractometer (X'Pert PRO, PANalytical, Almelo, Netherlands). The transmission electron microscopy (TEM) images were taken using Tecnai F20 (FEI, Hillsboro, OR, USA) microscope at an accelerating voltage of 200 kV.

Electrochemical deposition of Cu_2O: A solution composed of $CuSO_4$ (0.3 mol/L) and lactic acid (3 mol/L) was used as the electrolyte. The pH value of the bath was adjusted by the addition of 5 M sodium hydroxide. For the electrochemical deposition, FTO substrate and carbon fiber substrate (with the superhydrophobic side exposed to the gas phase) were used as the working electrode, a clean platinum wire used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The ECD process was carried out on the CHI 660E electrochemical analysis system (CHI Instruments Inc., Austin, USA) in a galvanostatic mode with the current density -0.3 mA/cm^2.

Electrochemical deposition of ZnO: ZnO samples were prepared by cathodic electrodeposition from an aqueous solution composed of 5 mmol/L $ZnCl_2$ and 1.0 mol/L KCl kept at 70 °C for 1 h. Electrodeposition was carried out on a CHI 660E electrochemical analysis system with a platinum wire as the counter electrode and a SCE as a reference electrode.

Electrochemical deposition of CeO_2: ECD of CeO_2 was carried out in an aqueous solution of 0.01 mol/L $CeCl_3$ adjusted to pH 5.6 at room temperature. Electrodeposition was carried out in a galvanostatic mode with the current density -1.5 mA/cm^2 for 1 h.

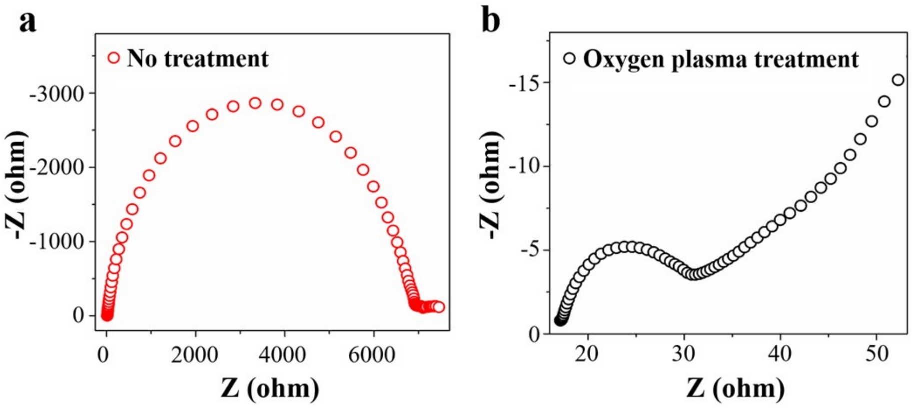

Fig. S1. Electrochemical impedance spectroscopy (EIS) recorded in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ +0.01 M KCl on superhydrophobic triphase electrode with or without oxygen plasma treatment. (a) EIS diagrams and (b) magnification of EIS diagrams. EIS parameters: frequency range of $5\times10^{-3}\sim1\times10^{5}$ Hz, and 5 mV amplitude of sine voltage signal. The electron transfer resistance between the electrode and electrolyte was decreased by about three orders of magnitude after a short time oxygen plasma treatment.

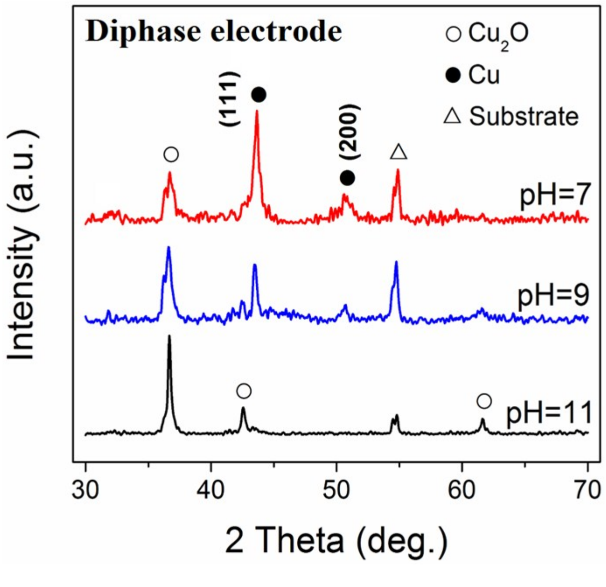

Fig. S2. Powder XRD patterns of cuprous oxide samples deposited in electrolytes with pH values of 7 (red curves), 9 (blue cures), and 11 (black curves) using a conducting carbon fiber substrate wihout superhydrophobic treatment.

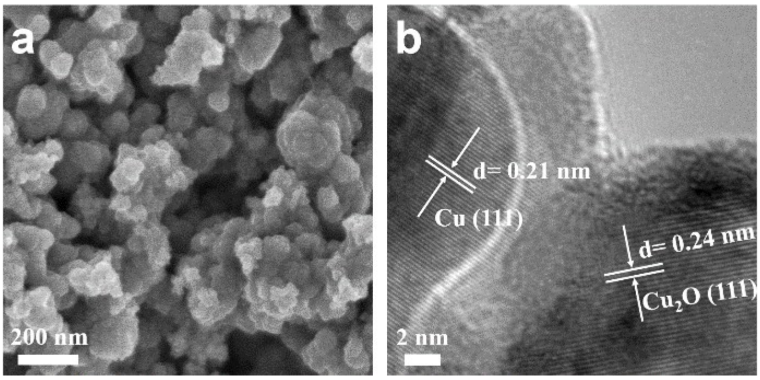

Fig. S3. (a) and (b) are, respectively, FE-SEM and HR-TEM images of the Cu_2O/Cu composite deposited using the diphase electrode in a pH 9 electrolyte.

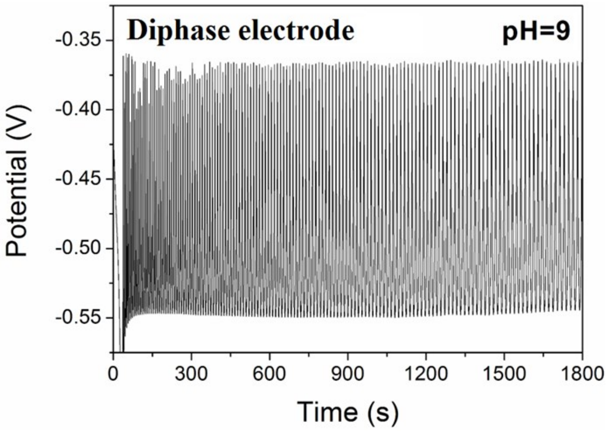

Fig. S4. Potential-time curve recorded during Cu_2O/Cu ECD using a traditional diphase electrode (FTO substrate).

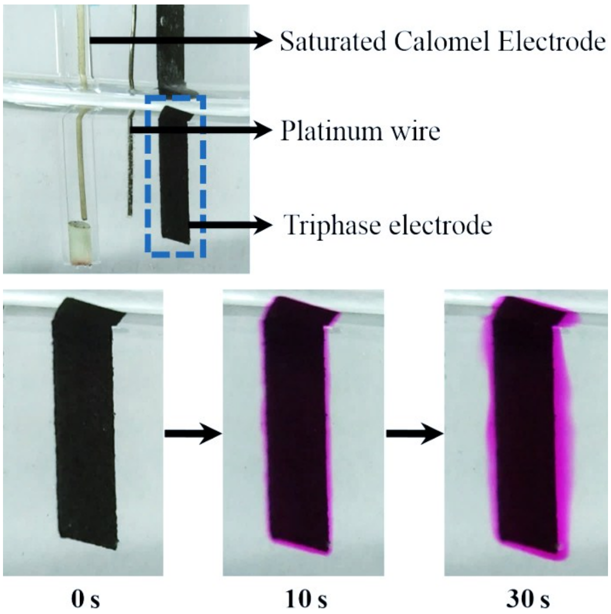

Fig. S5. Photographs for the phenolphthalein indicator test of triphase electrode. The substrate was dipped in solution containing 0.1 M Na_2SO_4 and phenothalin indicator. The test was carried out at a current density of -0.3 mA/cm^2 using a platinum wire counter electrode, and SCE reference electrode. The color of the electrolyte at the electrode surface changes rapidly to red within seconds.

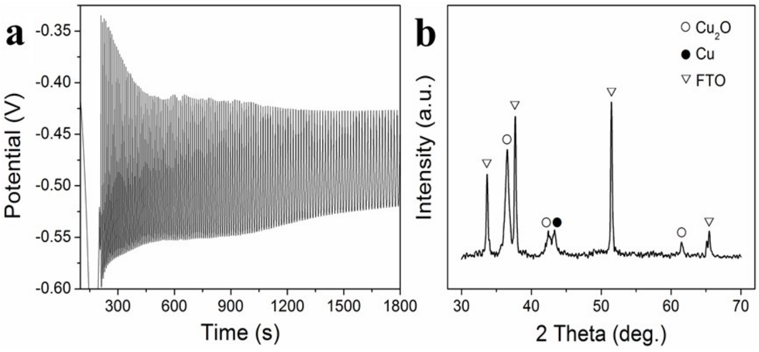

Fig. S6. (a) Potential-time curve recorded during ECD using a diphase electrode in an oxygen-saturated electrolyte with a pH value of 9 after bubbled with oxygen for 30 minutes. (b) Powder XRD patterns of the as-obtained Cu_2O/Cu composite. .

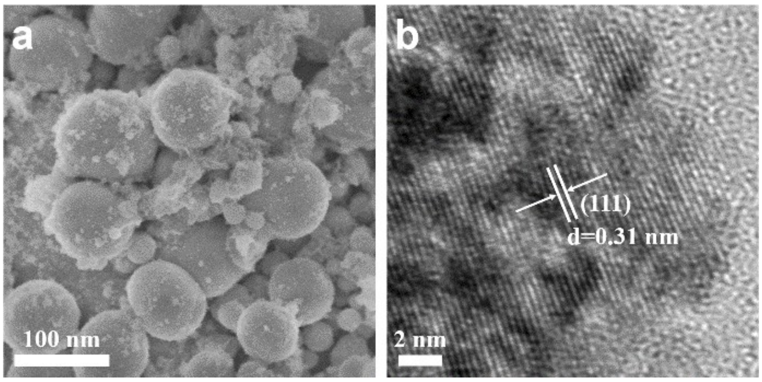

Fig. S7. (a) and (b), respectively, are FE-SEM and HR-TEM image of CeO_2 deposited using the triphase electrode without the use of any special additives at a current density of -1.5 mA/cm^2.