Electronic supplementary information

Modulation of Cu/Cu_2O nanoparticles to promote photocurrent response for light-enhanced pseudocapacitive charge storage

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1. Experimental section

All the solvents and chemicals were used without any purification. Before electrodeposition, the commercial carbon cloth (CC) substrates (WOS1009, Cetech Co, Ltd) were cut into 3×3 cm^2 and cleaned ultrasonically with deionized (DI) water and ethanol for 30 min. Then the cleaned CC substrates were treated with concentrated nitric acid (HNO_3) by gradient heating method to make CC surface hydrophilic.

1.1 Synthesis of CC@Cu/Cu_2O: The CC@Cu/Cu_2O samples were prepared by a facile electrodeposition/calcination method. In a typical process, a mixed solution of 50 mL DI water and 50 mL ethanol containing 1.208 g of $Cu(NO_3)_2 \cdot 3H_2O$ was used as the electrolyte. The electrodeposition was performed in a standard three-electrode system at room temperature (RT). Then the CC (1×1.5 cm^2), platinum foil and saturated calomel electrodes (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. The electrodeposition process was carried out by cyclic voltammetry (CV) within a voltage window from -1.2-0.2 V at a scan rate of 5 mV s^{-1} for 6 cycles, using an electrochemical workstation (IVIUM, V38120). The obtained samples were cleaned with DI water and ethanol several times, and then dried at 60 °C in an air-flow oven for 10 h. The as-obtained CC@Cu/Cu_2O sample is named as CC@Cu_xO. To obtained the typical CC@Cu_yO sample, the dried CC@Cu_xO sample powder was then annealed in a muffle furnace at 300 ^{o}C for 2 h with a heating rate of 5 ^{o}C min^{-1}.

1.2 Material characterizations: The crystalline phases of the CC@Cu/Cu_2O samples were examined by X-ray diffraction (XRD, Rigaku D/max 2500, Cu Kα radiation, λ = 0.154 nm). The elemental compositions and states were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha ESCALAB 250XI) with Al Kα X-ray source (1486 eV). The structures and morphologies were identified by a field-emission scanning electron microscope (FE-SEM, Quanta FEG 250) equipped with an energy-dispersive spectrometer (EDS), and a transmission electron microscope (TEM, Titan G2 60-300) equipped with a mapping system. The contact angles of the CC before and after acid treatment were measured by a contact angle meter (SDC-500).

1.3 Electrochemical measurements: The electrochemical performances of the as-prepared CC@Cu/Cu_2O samples were evaluated using an electrochemical workstation (IVIUM, V38120). The as-prepared CC@Cu/Cu_2O samples (1×1.5 cm^2) were directly used as working electrodes in a 2 M KOH aqueous solution. A saturated calomel electrode (SCE) and a platinum foil (1×1 cm) were used as the reference electrode and counter electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCCD) were performed at different scan rates and current densities. The specific capacitances were calculated from the discharge curve according to the following equation:

$$C = \frac{I \times \Delta t}{A \times \Delta V}$$

Where C (F cm^{-2}) is the specific areal capacitance, I (A) is the discharge current, Δt (s) is the discharge time, A (cm^2) is the area of the electrode, and ΔV is the discharge voltage window.

The electrochemical measurements under light irradiation were carried out in a sealed quartz glass cell. The three-electrode electrochemical setup and the electrolyte remained unchanged. A 300 W xenon arc lamp (Perfect Light PLS-SXE300) was used as the light source (light power = 50 W; spotlight radius = 30 mm). At the same time, a cooling fan was used to keep the temperature of the test cell at 18 °C to exclude the photothermal effects. The photocurrent measurements were carried out under the conditions of open-circuit potentials. All the potentials mentioned in the text and figure captions throughout the manuscript are versus SCE if there is no specific instruction.

2. Supplementary figures (Fig. S1-S5)

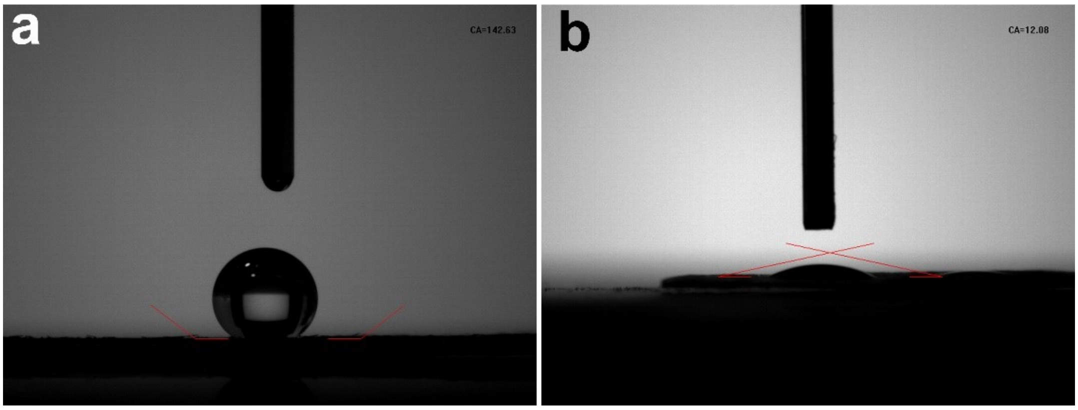

Fig. S1 A comparison of contact angles of the carbon cloth before (a) and after (b) acid treatment.

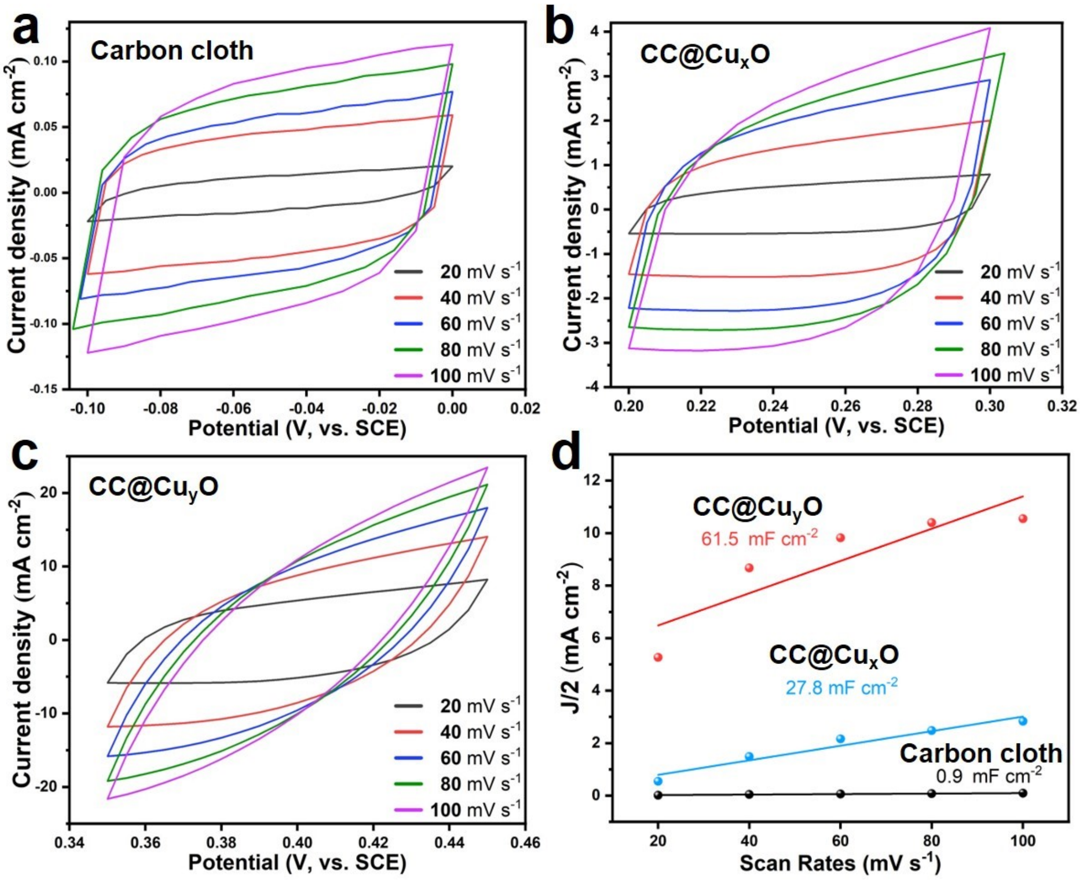

Fig. S2 CV curves (a-c) obtained from the non-Faradaic regions, and the capacitances (d) calculated from the respective CV curves of the carbon cloth, CC@Cu$_x$O, and CC@Cu$_y$O samples.

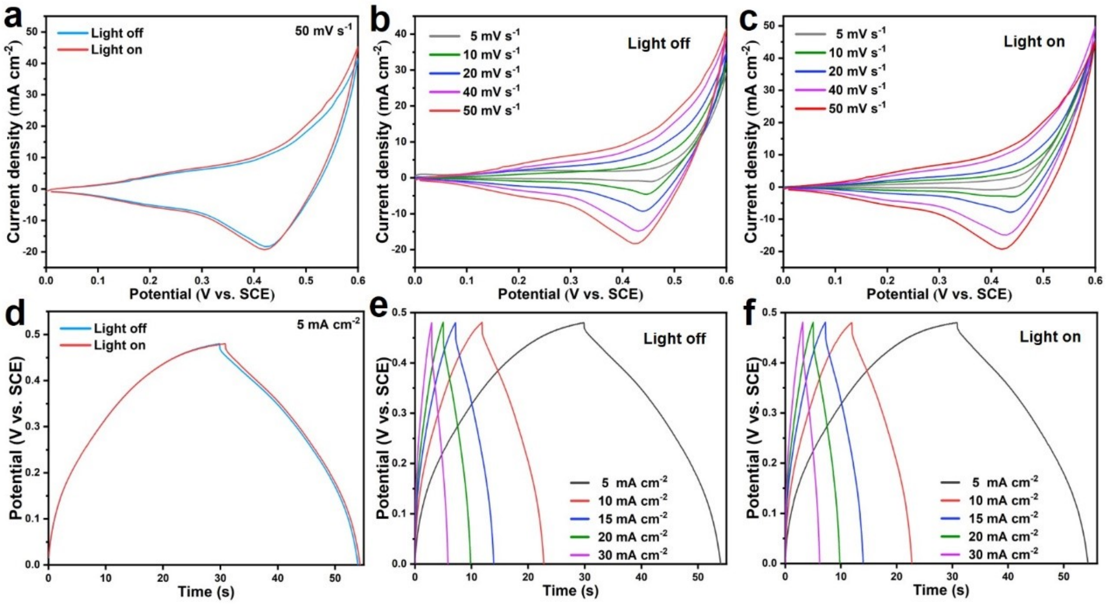

Fig. S3 CV curves (a-c) and GCCD curves (d-f) of the CC@Cu$_x$O sample obtained under light on and off conditions, respectively.

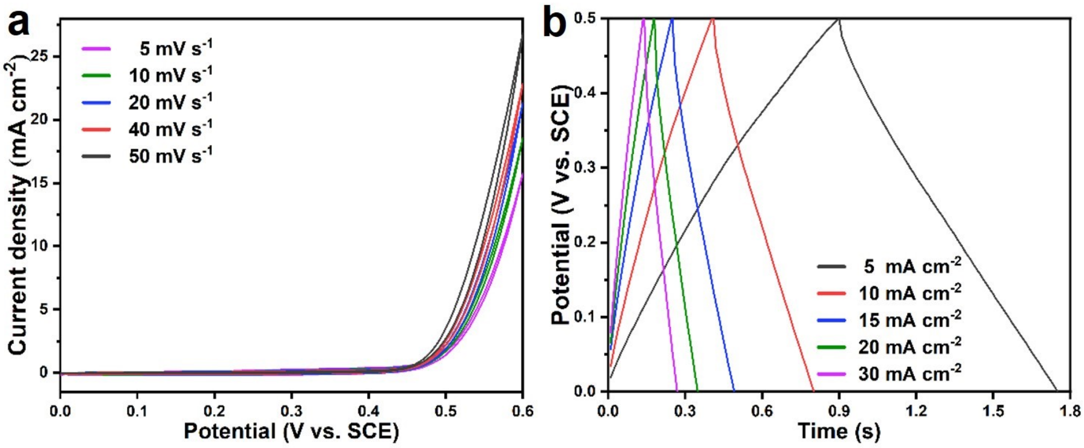

Fig. S4 CV curves at various scan rates (a) and GCCD curves at various current densities (b) of the bare CC sample.

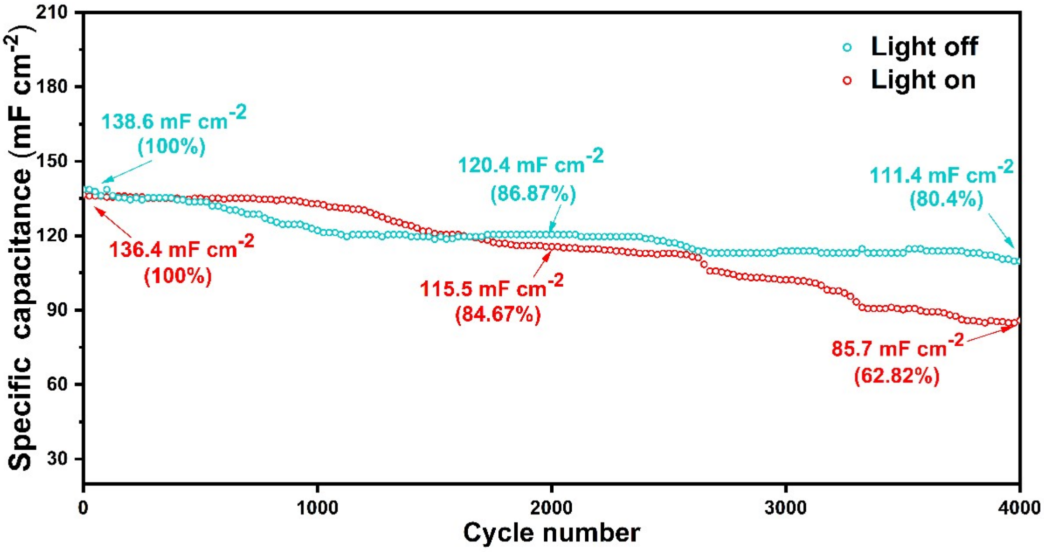

Fig. S5 Cycling performances of the CC@Cu$_x$O sample under light off and on conditions, respectively.