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Enhancement of Photoelectrocatalytic Performance of Copper Cobaltate Nanoflowers Modified with 5,10,15,20-Tetrakis (4-carboxylphenyl) Porphyrin for Methanol Oxidation under Light

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Characterization

Scanning electron microscopy (SEM, JEOL, Japan) and transmission electron microscopy (TEM, JEOL, Japan) were used to determine the microstructure and morphology of the nanocomposites. The physical phases of the electrocatalysts were characterized by powder X-ray diffraction (XRD) (D/Max2500PC, Rigaku). The valence states of the elements in the catalyst were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250Xi, America). Fourier transform infrared (FT-IR, NICOLET 380, USA) was used to determine the composition of the catalyst. The Brunauer-Emmett-Teller surface areas of nanoparticles were performed at 77 K on a fully automatic specific surface area and porosity analyzer (MIKE Micromeritics ASAP2460).

Electrochemical tests

The electrochemical tests were implemented by a typical three-electrode system. A platinum foil (3 cm × 3 cm), a saturated calomel electrode (SCE) and a modified glass carbon electrode (GCE) (3 mm in diameter) were used as the counter electrode, the reference electrode and the working electrode, respectively.

The catalyst inks were gained as follows: 50 μL of nafion solution (5 wt%) and 4 mg of the synthesized catalyst were added into 950 μL of ethanol to form a homogeneous suspension by ultrasonication. Then, the ink (3 μL) was dropped on the surface of the working electrode and dried naturally at ambient temperature. The loading capacity of the catalysts (0.17 mg cm^{-2}) was kept constant for all the samples in order to comparatively investigate. The current densities of MOR were calculated according to

the geometric area of the GCE.

Cyclic voltammograms (CVs) the linear scanning voltammetry (LSV) curves were performed in N_2-saturated KOH solution with and without CH_3OH at the scan rate of 50 mV s^{-1}, and the electrochemical active surface areas (ECSAs) of catalyst samples were obtained from the double-layer capacitance (C_{dl}) in the CVs. Moreover, impedance spectroscopy (EIS) was carried out using SCE (frequency 0.1 Hz-100 kHz) at the potential 0.5 V. I-t tests and the CVs for 500 cycles were conducted for evaluating the electrochemical durability of the materials.

The working electrode was irradiated through a xenon lamp (300W) for photo-electrochemical measurements.

Reagents and chemicals

Cobalt (II) chloride hexahydrate ($CoCl_2•6H_2O$), Copper (II) chloride dihydrate ($CuCl_2•2H_2O$) were commercially available from Aladdin Biochemical Technology Co., Ltd. Potassium hydroxide (KOH) was procured from Macklin (Shanghai, China). Urea (CH_4N_2O), ammonium fluoride (NH_4F), ethanol (C_2H_5OH), ethanediol ($C_2H_6O_2$), isopropanol (C_3H_8O), glycerol ($C_3H_8O_3$) and methanol (CH_3OH) were purchased from China Beijing chemical Reagent Co., Ltd. Nafion solution (5 wt% aqueous solution) was purchased from Suzhou Sinero Technology Co., Ltd. H_2TCPP was synthesized according to the publication.[1,2]

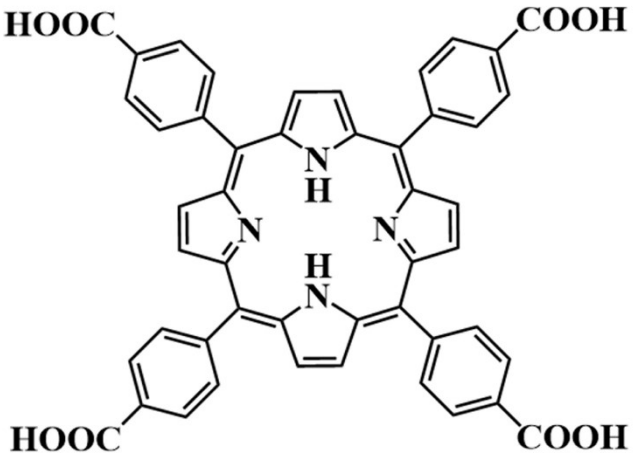

Fig. S1. The molecular structure of 5, 10, 15, 20-tetrakis (4-carboxylphenyl) porphyrin (H_2TCPP).

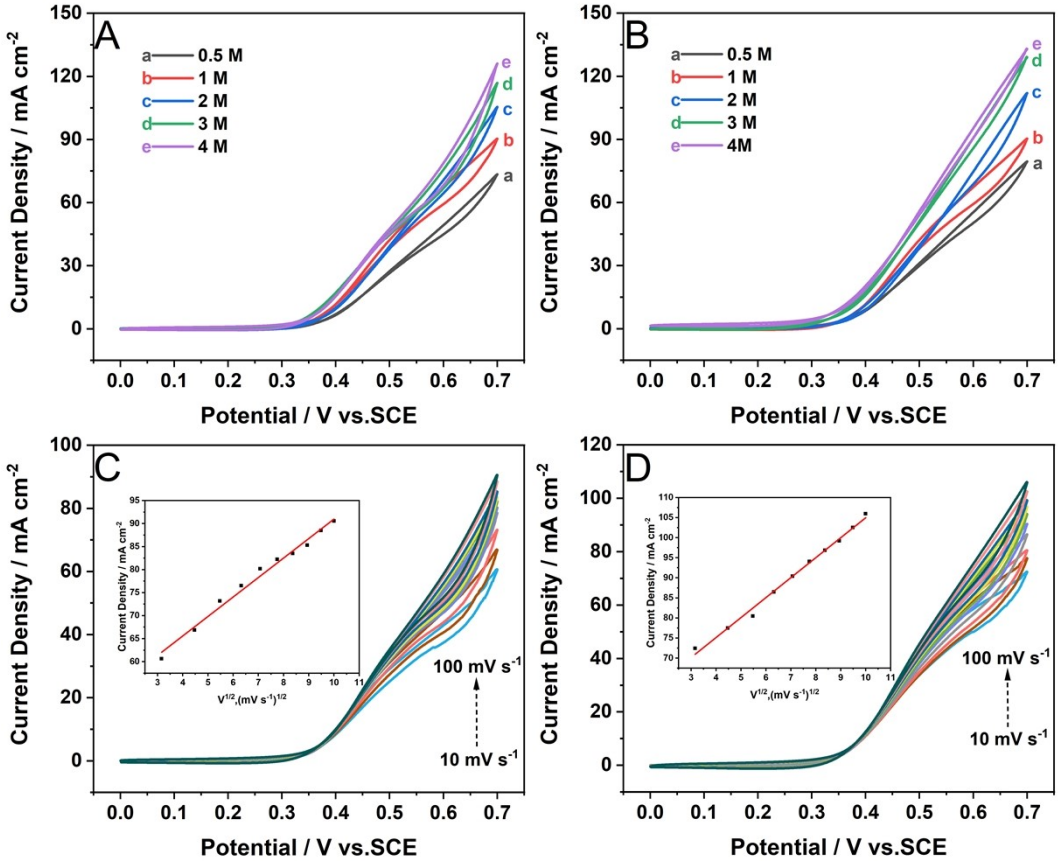

Fig. S2. CV curves of $H_2TCPP/CuCo_2O_4$ for MOR with different KOH concentrations (0.5−4 M) in 1 M CH_3OH solution at 50 mV s^{-1} (A). CV curves of $H_2TCPP/CuCo_2O_4$for MOR with different CH_3OH concentrations (0.5−4 M) in 1 M KOH solution at 50 mV s^{-1} (B).CV curves of $H_2TCPP/CuCo_2O_4$ under dark (C) and light (D) conditions for scan rates of 10-100 mV s^{-1} in 1 M KOH and 1 M CH_3OH solution, and the inset is a plot of the square root of the scan rate versus the

anodic peak current density.

Calculation of the electrochemically active surface area

The electrochemically active surface area (ECSA) values is an important parameter for the as-prepared nanocatalysts. We could estimate it by the bilayer capacitance (C_{dl}) using CV curves recorded at different scan rates in the non-Faraday potential range. The non-Faraday region is usually a potential interval with a range of 0.1 V centered on the open circuit voltage. The charging current (I_c) is equal to the product of the C_{dl} and the scan rate v, as shown in Equation (1):

$$I_c = vC_{dl} \quad (1)$$

Therefore, I_c plotted against v can produce a straight line with a slope equal to C_{dl}. The ECSA of the catalyst can be calculated by dividing C_{dl} by the specific capacitance (C_s) of the sample, as shown in Equation (2):

$$ECSA = C_{dl}/C_s \quad (2)$$

According to previous reports in the literature, C_s = 0.04 mF cm^{-2} in 1 M KOH electrolyte solution.[3]

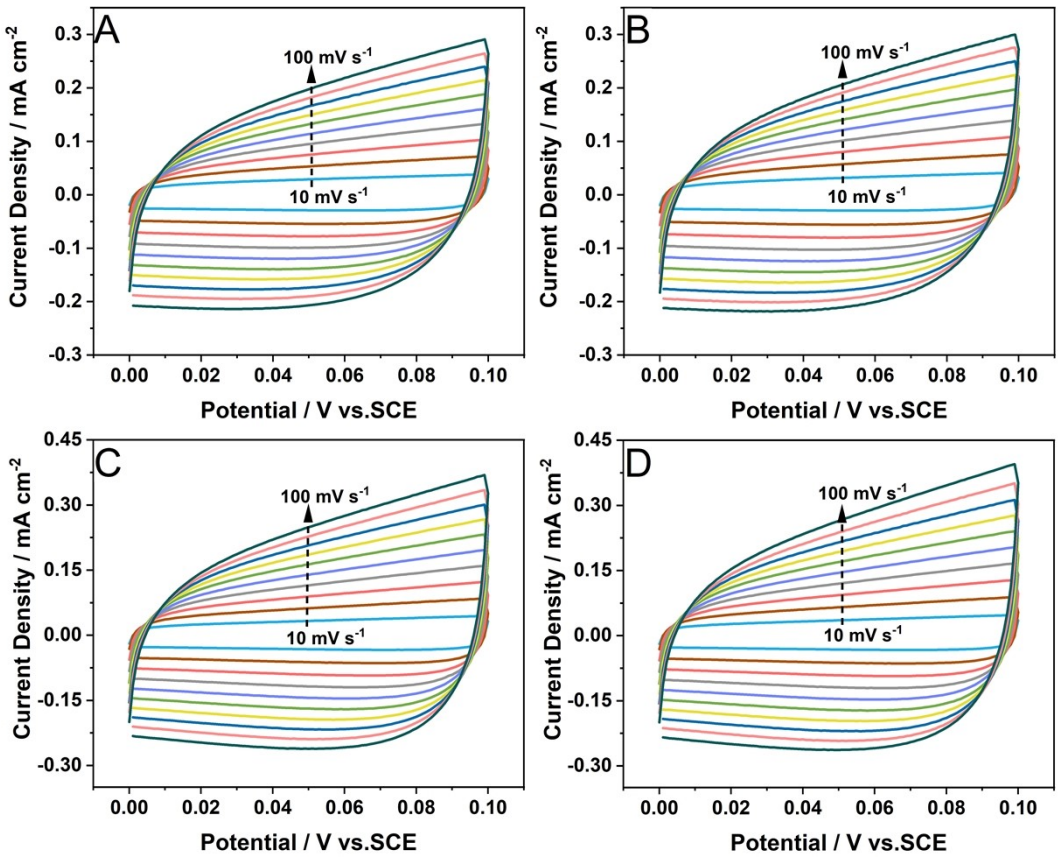

Fig. S3. CV curves at different scan rates in 1 M KOH electrolyte. $CuCo_2O_4$ under dark (A) and light (B) conditions, $H_2TCPP/CuCo_2O_4$ under dark (C) and light (D) conditions.

Reference

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3. McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F., Benchmarking Heterogeneous

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