

Supporting information

Electrode preparation

A piece of carbon paper (1.8 cm × 1.0 cm) was ultrasonically cleaned with acetone, ethanol and redistilled water in sequence three times for 5 min per time, and then washed with redistilled water three times. The washed paper was dried on the evaporating dish at 30°C and reserved.

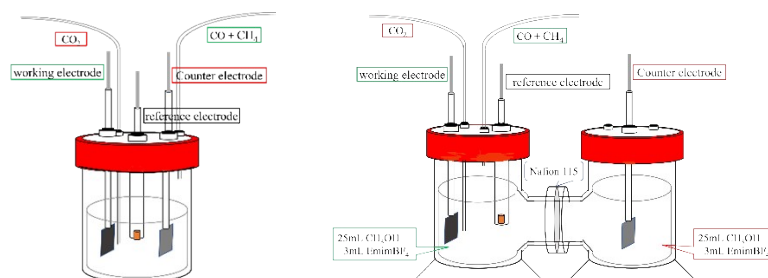
3.5 mg CuCo@NC, 20 μL dehydrated ethanol, 15 μL PTFE emulsion, and 15 μL Nation solution (perfluoro sulfonic acid resin) were mixed and ultrasonically dispersed at 25°C for 20 min. The obtained ink-shaped mixture was uniformly coated on pretreated carbon paper (1.8 cm × 1.0 cm), dried, and used as a cathode.

Cyclic voltammetry and CO₂ reduction test

Cyclic voltammetry was measured with a CHI760E electrochemical workstation. the prepared electrode (electrode area 1.0 cm²) and platinum sheet ultrasonically cleaned with acetone and redistilled water in sequence were used as working and counter electrodes, respectively, and saturated calomel as reference one. Before measurement, the electrolytic cell was purged by CO₂ for 20 min, and then the cyclic voltammetry was determined at a scanning rate of 50 mV/s in EmimBF₄ (3.5 mL)-methanol (25 mL) solution with a potential range of -2.0-2.0 V.

Electrochemical reduction of CO₂ to CO + CH₄ was conducted in an undivided five-neck bottle cell. The cell was equipped with a three-electrode system. In a typical procedure, 25 mL (0.618 mol) methanol and 3.5 mL EmimBF₄ ionic liquid were charged into the cell. The electrolyte solution was saturated with ca. 4 mL/min CO₂ controlled by a mass flowmeter (PLR-WFGD, Perfect Light Co.) and the outlet was injected into methanol to absorb gaseous organic products. The electrochemical reaction was performed at an initial potential of -2.0 V for 24 h by chronoamperometry

(Amperometric i-t Curve). After the electrolysis, the reaction mixture was distilled to separate the methanol and products from the IL. The distillate was directly analyzed by GC (Agilent 7820) with an FID detector and HP-5 column. The gaseous products were qualitatively determined by GC (9790 Plus) with FID detector, Porapak Q column, and TCD, TDX-01 column. The product distribution was identified by GC-MS (Agilent 7890A-5975C). The conversion was calculated based on methanol. An H-type cell with a cation exchange membrane (Nafion 115, Dupont) was used as a reactor in order to recognize anodic and cathodic products. Each compartment contained 25 mL (0.618 mol) methanol and 3.5 mL EmimBF₄ IL. The single and H-type cells are shown in Scheme 1. The FE_{C1} for CO + CH₄ and FE_{DMM} for DMM (calculated on the basis of HCHO due to the equal mole quantity to the produced DMM) is calculated by the following equations:



Scheme 1 Single (left) and H-type (right) cells

$$FE_{C1} = V_i \cdot r \cdot nFp^0/RTI$$

V_i : the volume concentration of CO or CH₄; r : flow rate of gas

n : the number of transferred electrons for certain product; F : 96485 C mol⁻¹;

P^0 : 1.01×10⁵ Pa; R : 8.314; T : temperature (K);

I : the steady-state current measured during constant-potential electrolysis.

$$FE_{DMM} = V_0 \cdot c \cdot nF/Q$$

V_0 : the volume of methanol in the working cell; c : the concentration of liquid product;

n : number of transferred electrons for certain product; F : 96485 C mol⁻¹;

Q : total charge consumed in the electrolysis.

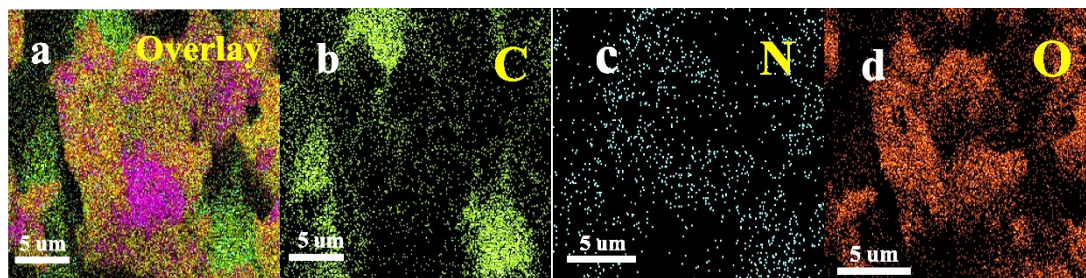


Fig. S1 Element mapping of CuCoCN-400

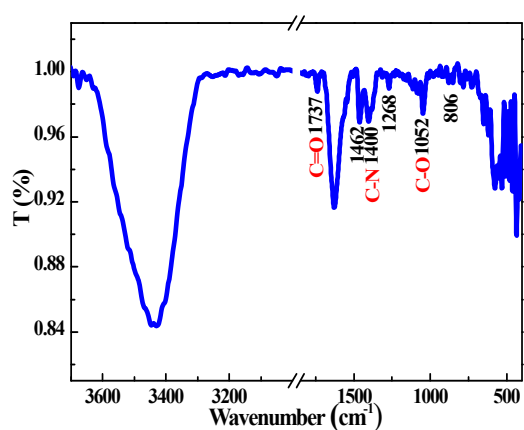


Fig. S2 IR spectrum of CoCu@NC-400 sample

Table S1 Magnetic properties versus account of Ma

n(Cu):n(Co):n(Ma)	Ms(emu/g)	Mr(emu/g)	Hc(Oe)
1:1:0	0.1	0	0
1:1:0.5	0.2	0	0
1:1:1	8.6	0	0
1:1:1.5	45.3	1.9	42.7
1:1:2	59.7	12.3	284.0

Table S2 Magnetic properties versus account of Cu

n(Cu):n(Co):n(Ma)	Ms(emu/g)	Mr(emu/g)	Hc(Oe)
0:1:1	124.3	15.5	169.8
0.5:1:1	57.2	1.8	41.3
1:1:1	8.6	0	0
1.5:1:1	0.2	0	0
2:1:1	0.2	0	0

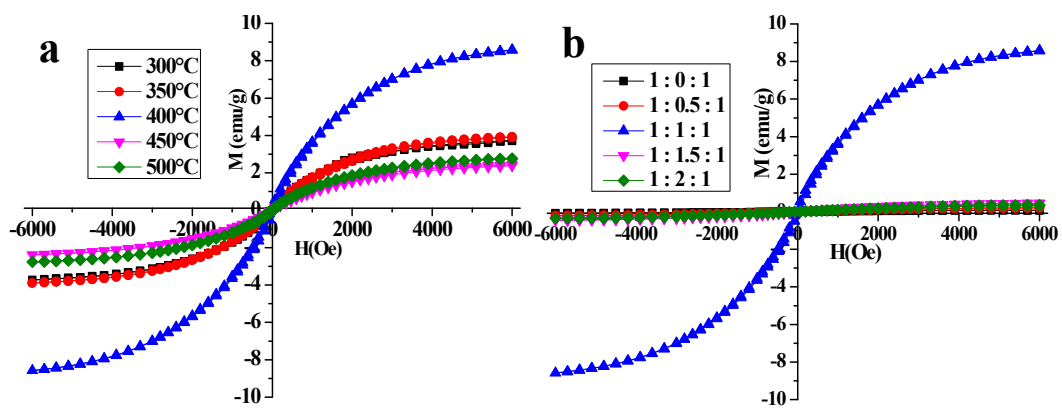


Fig. S3 The magnetic properties of CuCo@NC

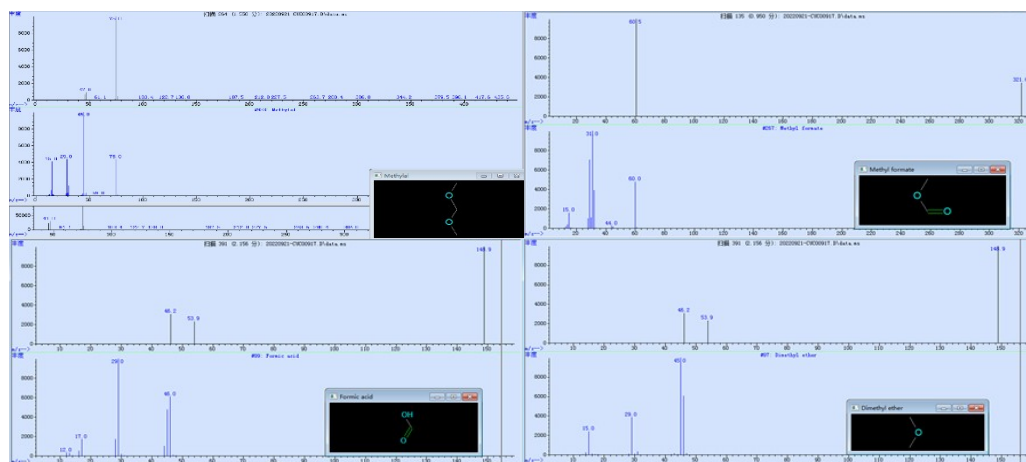


Fig. S4 The liquid product distribution

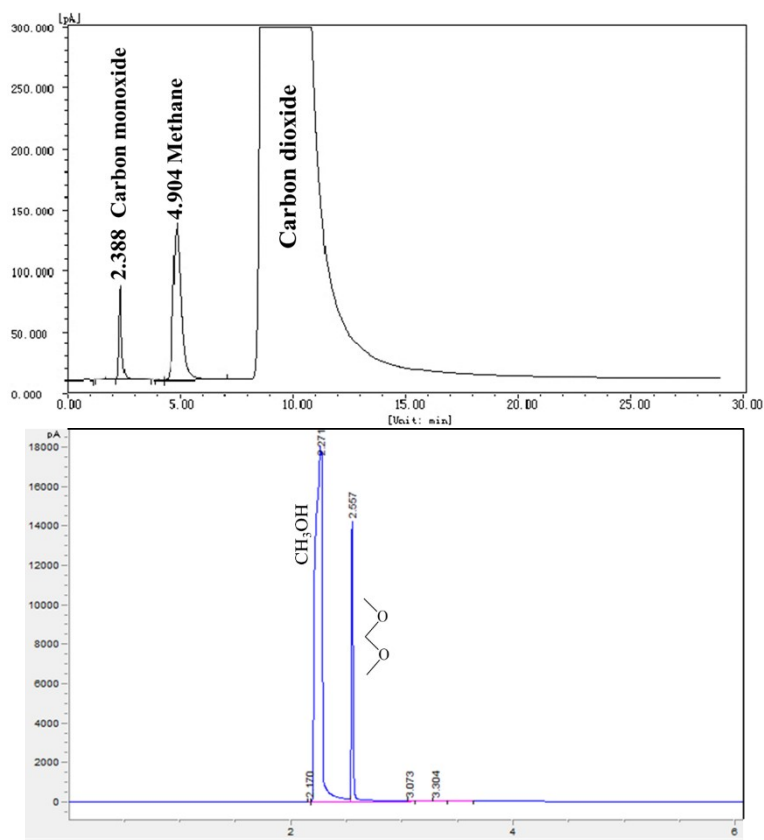


Fig. S5 The GC chart of the products

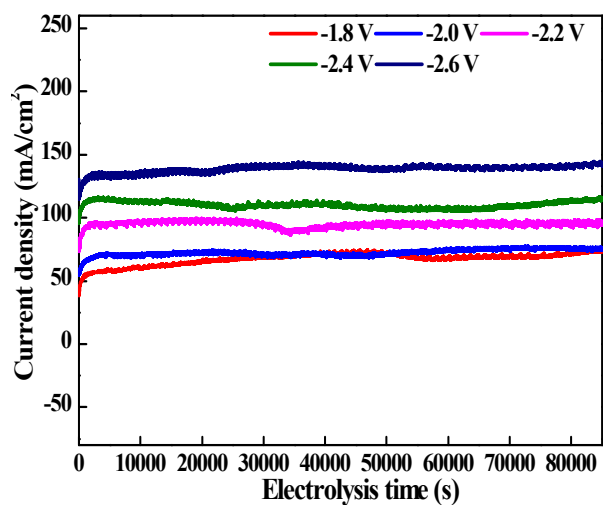


Fig. S6 The current versus reaction time

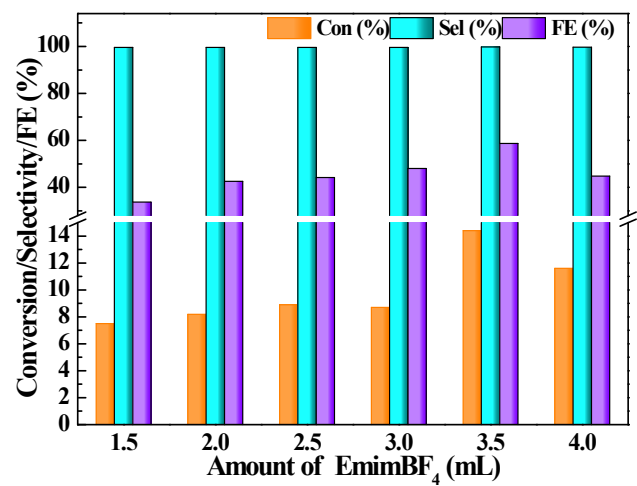


Fig. S7 The catalytic activity versus the amount of IL