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Compositional Dependent Activity of Cu-Pt Nanocrystals for Electrochemical Reduction of CO_2

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Experimental details

Preparation of the Electrocatalysts

The Pt-Cu NCs were prepared according to a modified procedures described by Fang et al. Briefly, the synthesis was carried out by simultaneous reduction of different molar ratio(1:2, 1:1, 2:1, 3:1, 5:1) of copper(II) acetylacetonate ([$Cu(acac)_2$]) and platinum(II) acetylacetonate ([$Pt(acac)_2$]) by 1,2-hexadecanediol (HDD) in 1-octadecene (ODE) as solvent, which also contained tetraoctylammonium bromide (TOAB), oleylamine (OLA), and a trace amount of 1-dodecanethiol (DDT). The morphology of the catalysts was characterized by transmission electron microscope (TEM, JEOL JEM-2100F). The obtained products were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Cu Kα radiation, 40KV, 40 mA). Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was carried on Profile Spec to determine the content of copper element.

Eletrochemical Measurements

The electrochemical measurements were performed in a home-made H-type electrochemical cell separated by a cation exchange membrane (Nafion®, 117). Linear sweep voltammetry(LSV) and cyclic voltammetry (CV) were performed using a standard three-electrode configuration. The working electrode was a glassy carbon electrode (GCE, 3.0 mm diameter CH Instruments). A Pt wire and a saturated calomel electrode (SCE, Analytical Sensor, Inc.) were used as the counter electrode and the reference electrode, respectively. Before the experiment of LSV, the electrolyte in the cathodic compartment was saturated with CO_2 by bubbling CO_2 gas for at least 30 min. During the CO_2 reduction experiments, the electrolyte in the cathodic compartment was stirred at 900 rpm. Finally, potentiostatic electrolysis for CO_2 reduction was carried out under sealed conditions to detect gas production and to estimate the faradaic efficiency. The gaseous products were analyzed by gas chromatography. H_2 was determined using a TCD detector, and CH_4 were determined using a FID detector attached to a Shimadzu GC-2014 gas chromatograph.

The faradaic efficiency (FE) for formation of (CH_4 or H_2) was calculated as below:

$$FE = \frac{2FvGp}{RTi} \times 100\%$$

v (vol%) is the volume concentration of CH_4 or H_2 in the exhaust gas from the electrochemical cell (GC data). G (mL min^{-1} at room temperature and ambient pressure) is the gas flow rate. i (mA) is the steady-state cell current. P =1.01 x 10^5 Pa, T = 273.15 K, F = 96485 C mol^{-1}, R = 8.314 J mol^{-1} K^{-1}.

Tables and Figures

Table S1. Onset potentials for all the Cu-Pt NCs samples in N_2- or CO_2-saturated environment. The current density of CO_2 reduction outcompeting HER (E= -1.3 V *vs.* SCE) obtained with different samples.

Samples	Onset potential N_2 (*vs.* SCE)	Onset potential CO_2 (*vs.* SCE)	Current density (mA cm^{-2}) E= -1.3 V CO_2 (*vs.* SCE)
Cu-Pt-1#	-1.076	-1.252	-0.167
Cu-Pt-2#	-1.076	-1.172	0.071
Cu-Pt-3#	-1.268	-1.119	0.106
Cu-Pt-4#	-1.357	-0.972	0.598
Cu-Pt-5#	-1.297	-1.166	0.068

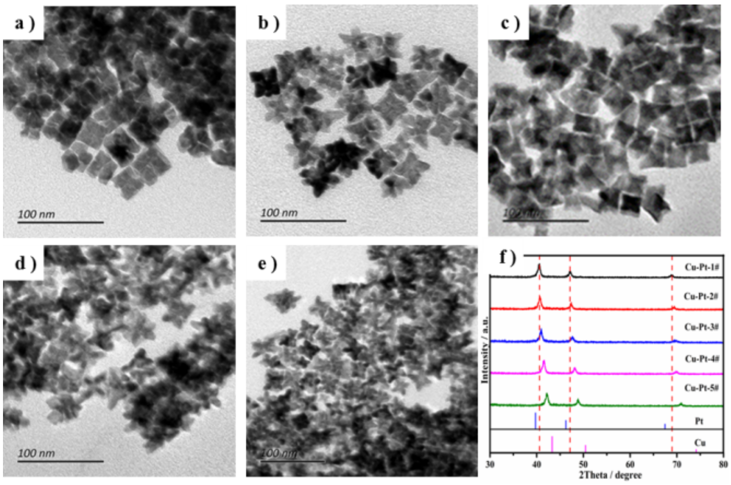

Fig. S1 (a-e) TEM images of Cu-Pt NCs, (a) Cu-Pt-1#, (b) Cu-Pt-2#, (c) Cu-Pt-3#, (d) Cu-Pt-4#, (e) Cu-Pt-5#. (f) The corresponding XRD patterns of the as-prepared samples, with the references for face-centered cubic (fcc) Pt (JCPDS #04-0802) and fcc Cu (JCPDS #04-0836) also shown for comparison.

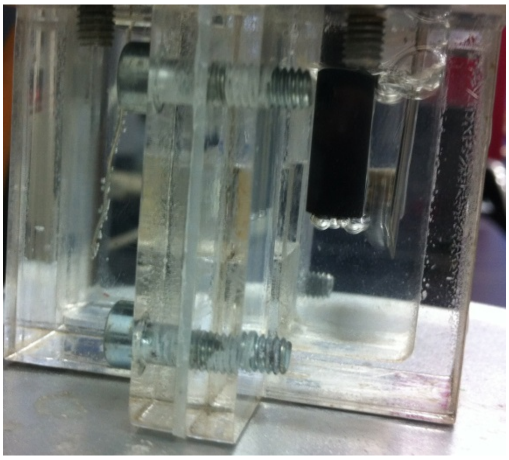

Fig. S2 Photo picture of the home-made three-electrode testing system.

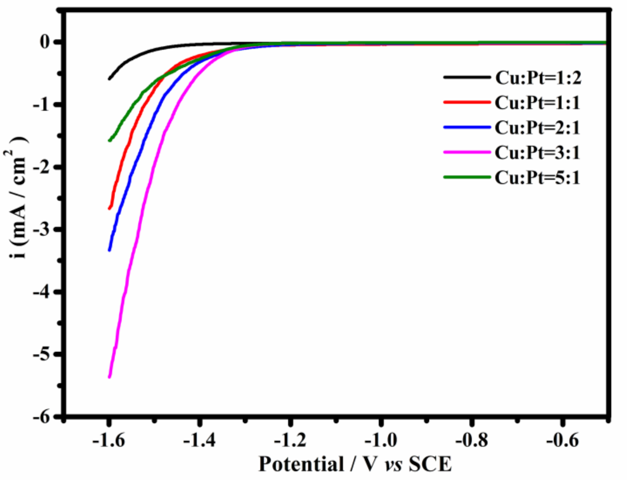

Fig. S3 The LSVs of 5 different Cu-Pt NCs were recorded in CO_2-saturated 0.5 M $KHCO_3$ with a scan rate of 10 mV/s at the potential window from -0.6 to -1.6 V (*vs.* SCE).

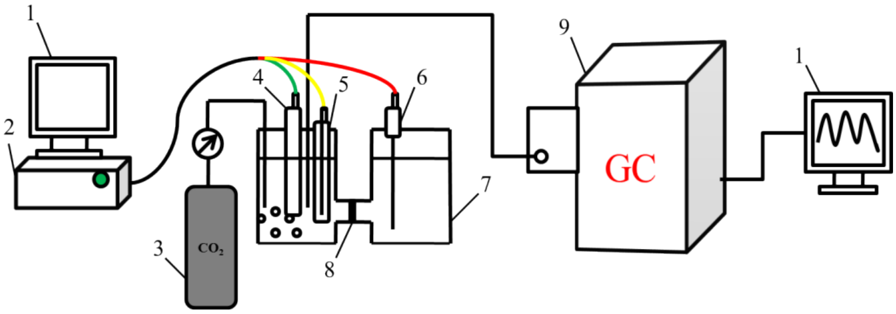

Fig. S4 Schematic drawing of the on-line electrochemical GC setup. 1- PC, 2- CHI 760D electrochemical workstation, 3- CO_2 cylinder, 4- Glass carbon electrode (working electrode), 5- Saturated calomel electrode (SCE, reference electrode), 6- Platinum wire (counter electrode), 7- Home-made H-type electrochemical cell, 8- Cation exchange membrane (Nafion®, 117), 9- Gas chromatography (GC).

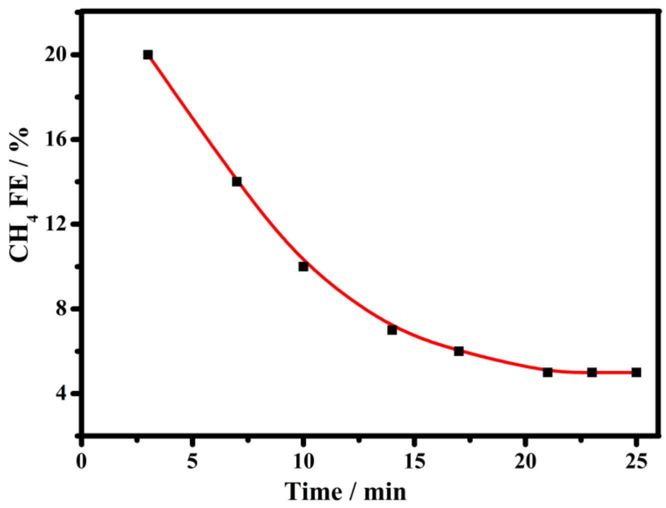

Fig. S5 Faradaic efficiencies toward CH_4 on Cu-Pt-4# for the reduction of CO_2 as a function of time. E =-1.6 V. Electrolyte: 0.5 M $KHCO_3$.