

Supporting Information

Achieving Efficient CO₂ Electrochemical Reduction on Tunable In(OH)₃ Coupled Cu₂O Derived Hybrid Catalyst

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1. Experimental section

1.1. Electrocatalyst synthesis

Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99+%, ACROS Organics), sodium hydroxide (NaOH, 97%, Fisher Chemical), L-Ascorbic Acid (AA, 99%, Fisher Chemical) and Indium(III) nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.99%, Alfa Aesar) were used without further purification. Potassium bicarbonate (KHCO_3 , 99.7%, Fisher Chemical) was used for the electrolyte.

In a typical procedure, 90 mL of deionized water was introduced into a 200-mL beaker. Subsequently, 1 mL of 0.1 M CuSO_4 solution was added to the beaker. The beaker was kept in a water bath at 35 °C throughout the synthesis. Next, 4.75 mL of 1.0 M NaOH solution was introduced into the beaker with vigorous stirring. Then, it was observed that the solution turned light blue immediately, indicating the formation of $\text{Cu}(\text{OH})_2$ precipitate. With the addition of 5 mL of 0.2 M AA solution, the above solution turned to orange-yellow from light green gradually. The solution was stirred for 10 min for Cu_2O crystal growth in the water bath. Then the different volumes (0, 3, 6 and 7 mL) of 0.01 M $\text{In}(\text{NO}_3)_3$ solution were added to the above solution. After another 10 min, pure Cu_2O and $\text{In}(\text{OH})_3$ coupled Cu_2O hybrid materials of ICC-HM-3, -6, and -7 were respectively collected by suction filtration and washed with deionized water and ethanol thoroughly to remove residual ions and dried in a vacuum oven at 60°C for 12 hours for further characterization.

1.2. Structural characterizations

The crystalline structure of the samples was characterized by X-ray diffraction

(XRD) analysis with a Rigaku XRD Ultima IV diffractometer using Cu K α radiation generated at 40 kV and 44 mA. The XRD pattern was recorded within a 2 θ range from 20 to 80 at 2° min⁻¹. The morphology of the materials was imaged using a Zeiss Sigma Field Emission SEM (FESEM). The composition was analyzed with an Orbis PC Micro-XRF Analyzer. Transmission electron microscopy (TEM) characterization was performed using an H-9500 environmental transmission electron microscope with an accelerating voltage of 300 kV. Scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS) was carried out at a JOEL 2200 FS Field Emission Transmission Electron Microscopy (FETEM) with Schottky field emission gun at 200 kV.

1.3. Electrochemical measurements

To prepare the working electrode, a suspension with a proportion of 15 mg of powders (10 mg of electrocatalysts and 5 mg of carbon black), 0.76 mL of ethanol, 1.14 mL of DI water, and 100 μ L of 5 wt.% Nafion solution was sonicated to achieve a homogeneous dispersion. The resulting suspension was then painted onto one side of a Toray carbon paper (1 cm \times 2 cm, Toray TGP-H-060, Toray Industries Inc.) to achieve an electrocatalyst loading of 1 mg cm⁻². All the potentials were recorded against the reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale by the equation, $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.0591 \times \text{pH}$. The pH values of CO₂-saturated 0.1, 0.3, 0.5, and 0.7 M KHCO₃ were 6.8, 7.2, 7.5, and 7.6, respectively. The current densities in this work were all normalized to the geometric surface area.

All the experiments were carried out on a potentiostat/galvanostat (Autolab

PGSTAT302N) in a two-compartment gastight H-cell separated by a Nafion membrane (Nafion[®] 117, Alfa Aesar) with a saturated calomel electrode (SCE) reference electrode and a piece of platinum gauze (3 cm × 3 cm) counter electrode. Each compartment contains 39 mL of electrolyte and leaves a headspace of about 31 mL. The KHCO₃ aqueous solution was used as electrolyte directly without any purification. Prior to the CO₂ reduction, the cathodic electrolyte was saturated with CO₂ (99.99%, Praxair Canada Inc.) at a flow rate of 20.0 mL min⁻¹ controlled by a mass flow controller (Brooks Instrument). In order to enhance the mass transport of CO₂, the catholyte was magnetically stirred during the electrolysis. The gas products of CO₂ electroreduction from the cathode compartment were analyzed using the on-line gas chromatography (GC, Agilent 6890N) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID with methanizer was used to quantify CO, CH₄, C₂H₄, and C₂H₆, and the TCD was used to quantify H₂. A standard gas mixture composed of CH₄, C₂H₄, C₂H₆, CO, H₂, and CO₂ (Praxair Canada Inc.) was applied to obtain the calibration curve for each component. Argon was employed as the carrier gas. Every GC run lasts for 8.4 min. For every potential, the first GC run was initiated at the 10th min, and thereafter reinitiated every 8.4 min for twice. The average of the results from these three measurements was used in the data analysis. The liquid phase products were measured by ¹H NMR.

2. Supplementary Figures (Figure S1-S10)

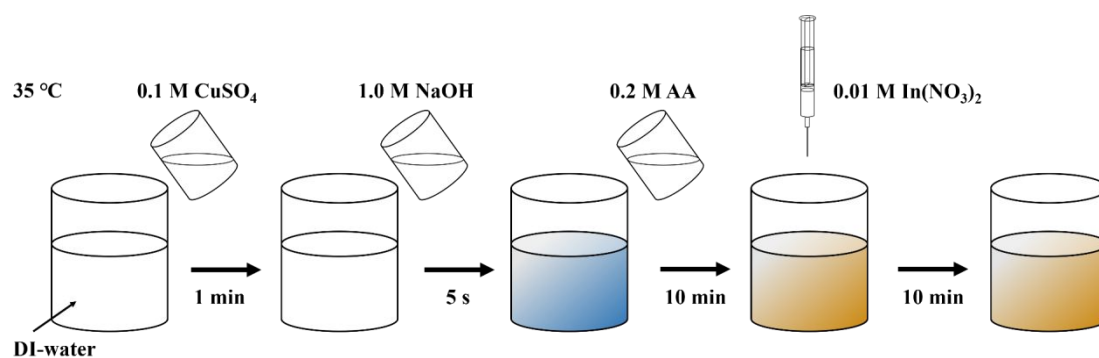


Figure S1. Schematic illustration of the fabrication procedures of $\text{In}(\text{OH})_3$ coupled Cu_2O hybrid material.

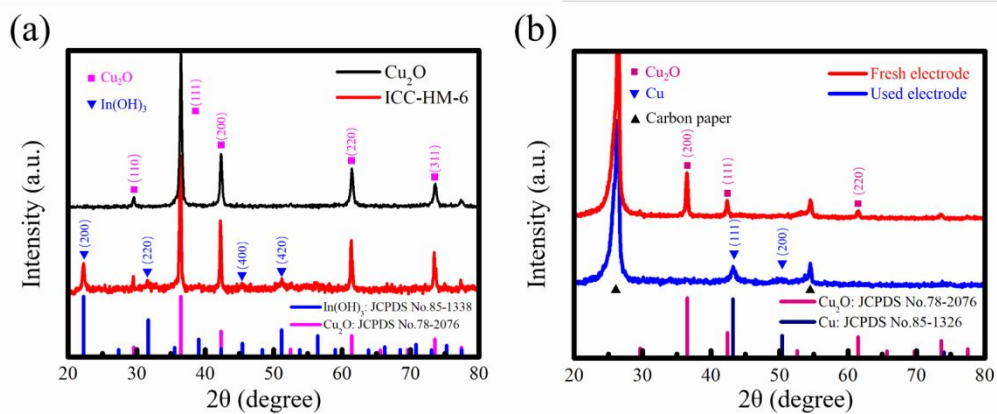


Figure S2. (a) X-ray diffraction (XRD) patterns of as-prepared Cu_2O and ICC-HM-6.

(b) XRD patterns of freshly prepared and electrochemical reduced electrodes of ICC-HM-6.

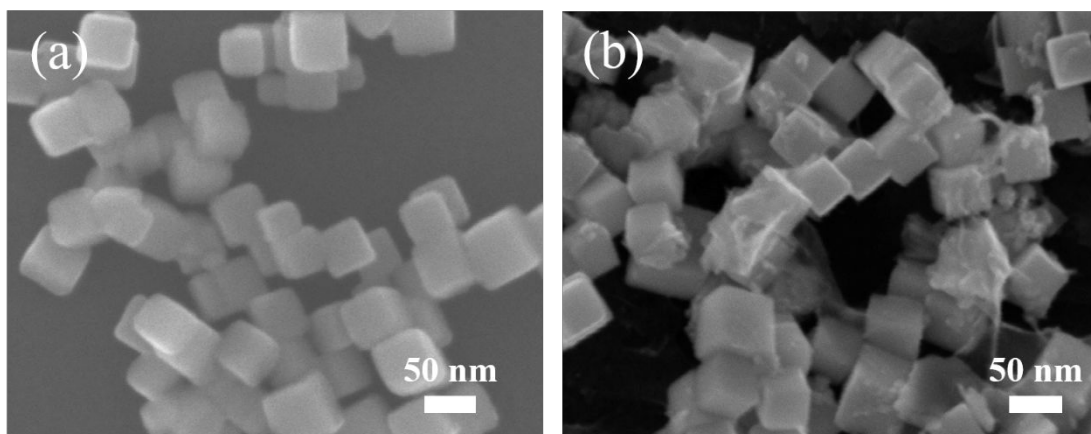


Figure S3. SEM images of (a) Cu₂O and (b) ICC-HM-6.

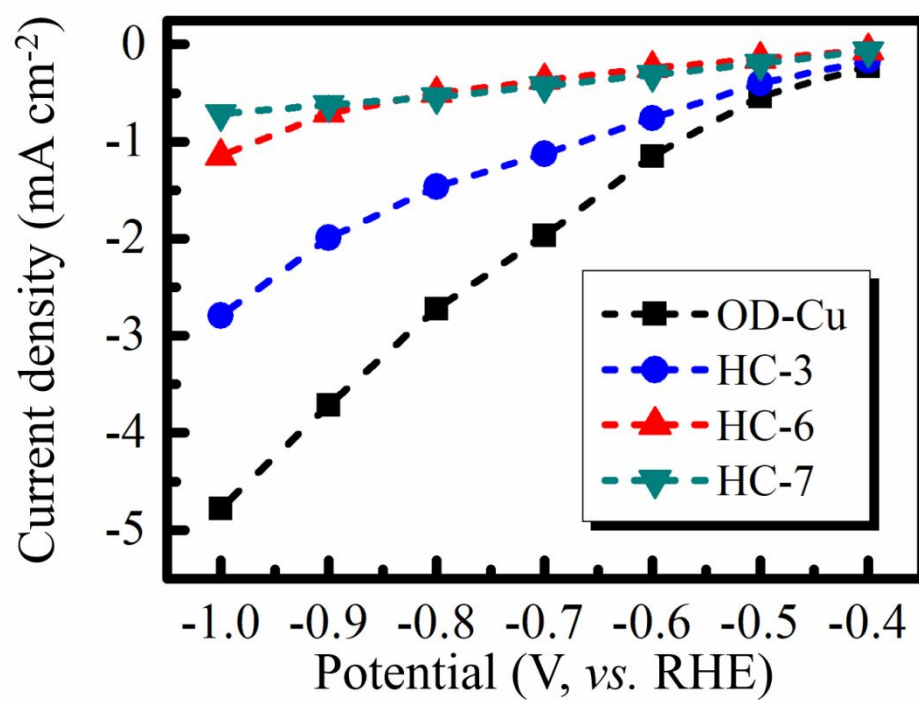


Figure S4. H₂ partial current density at each potential of the different catalysts.

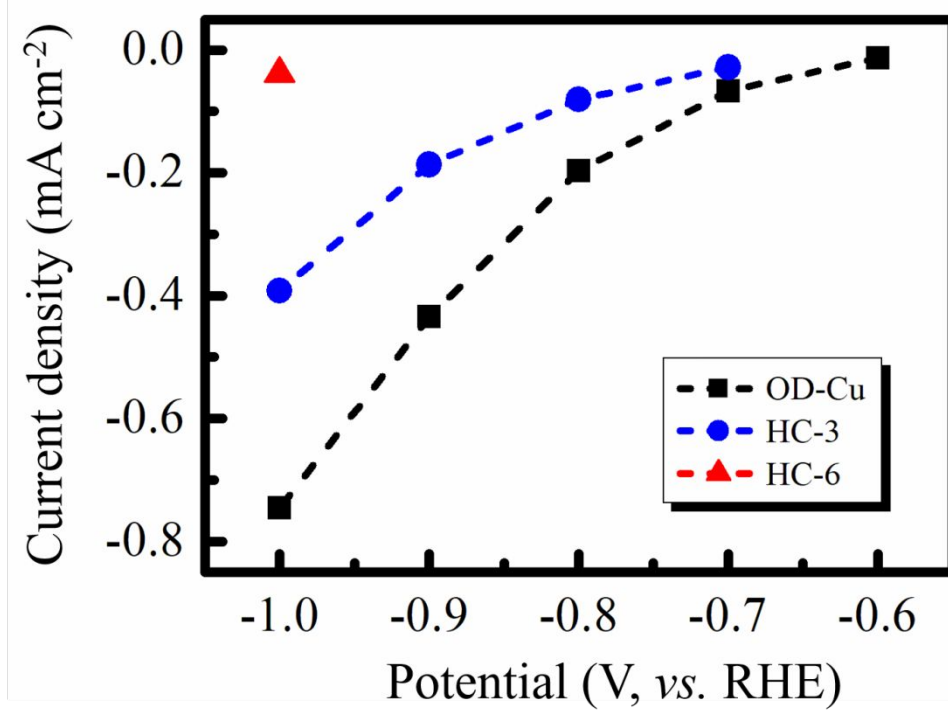


Figure S5. C_2H_4 partial current density at each potential of the different catalysts.

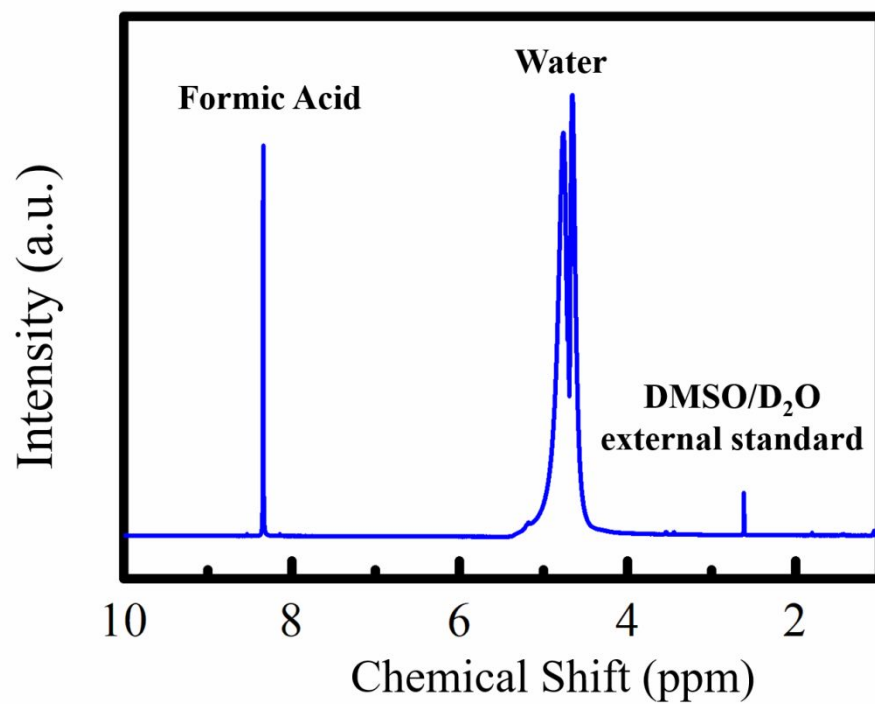


Figure S6. ^1H NMR spectrum on the electrolyte after the 12 hours of electrolysis.

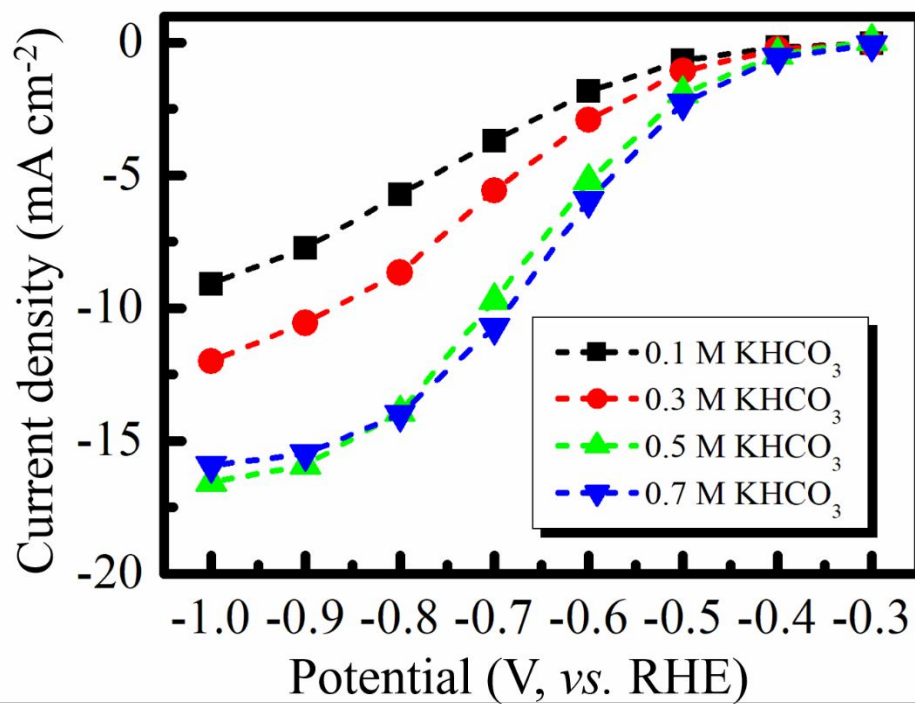


Figure S7. CO partial current density of HC-6 at each potential in different concentrations of KHCO₃.

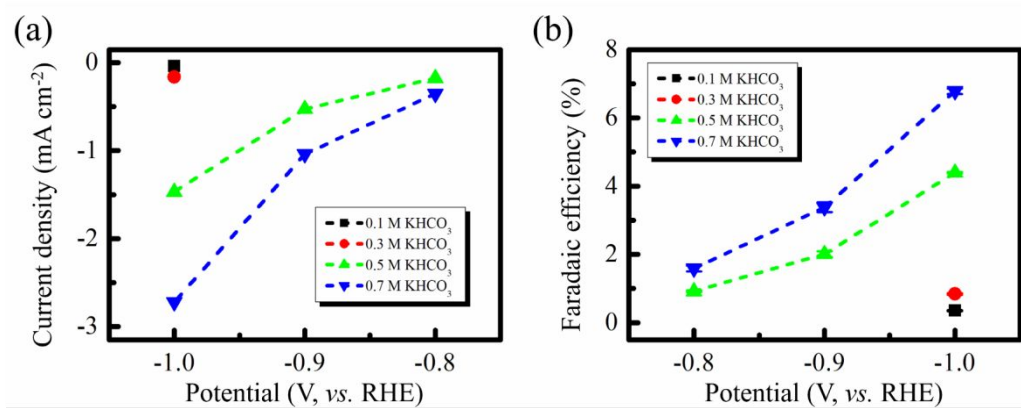


Figure S8. (a) C_2H_4 partial current density and (b) FEs of C_2H_4 for HC-6 at each potential in different concentrations of $KHCO_3$.

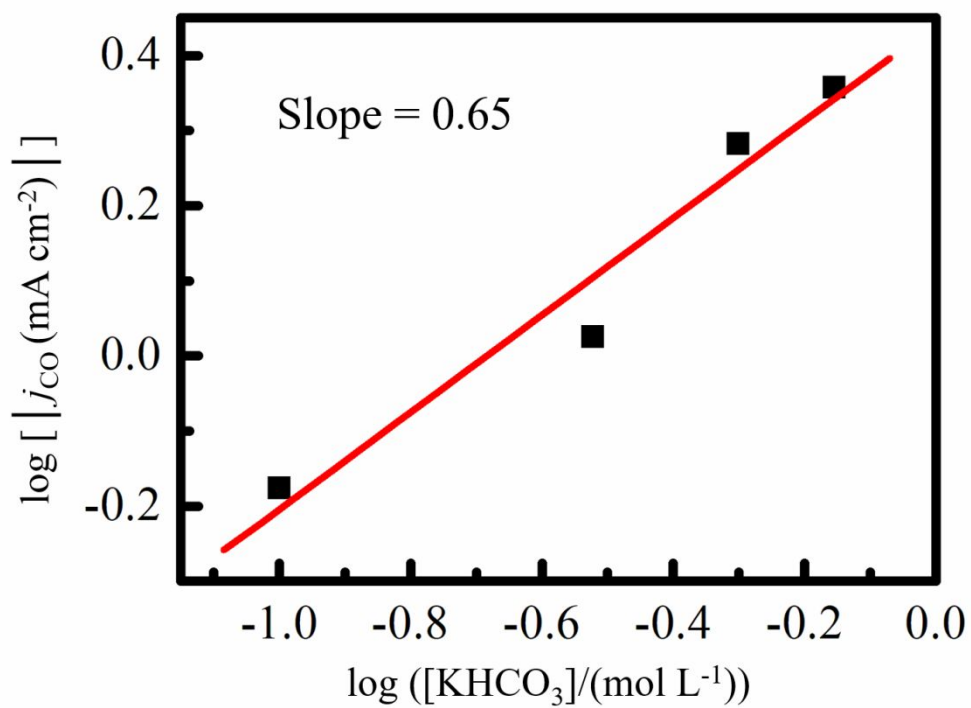


Figure S9. Partial CO current density of HC-6 vs. potassium bicarbonate concentration at a constant potential of -0.5 V vs. RHE.

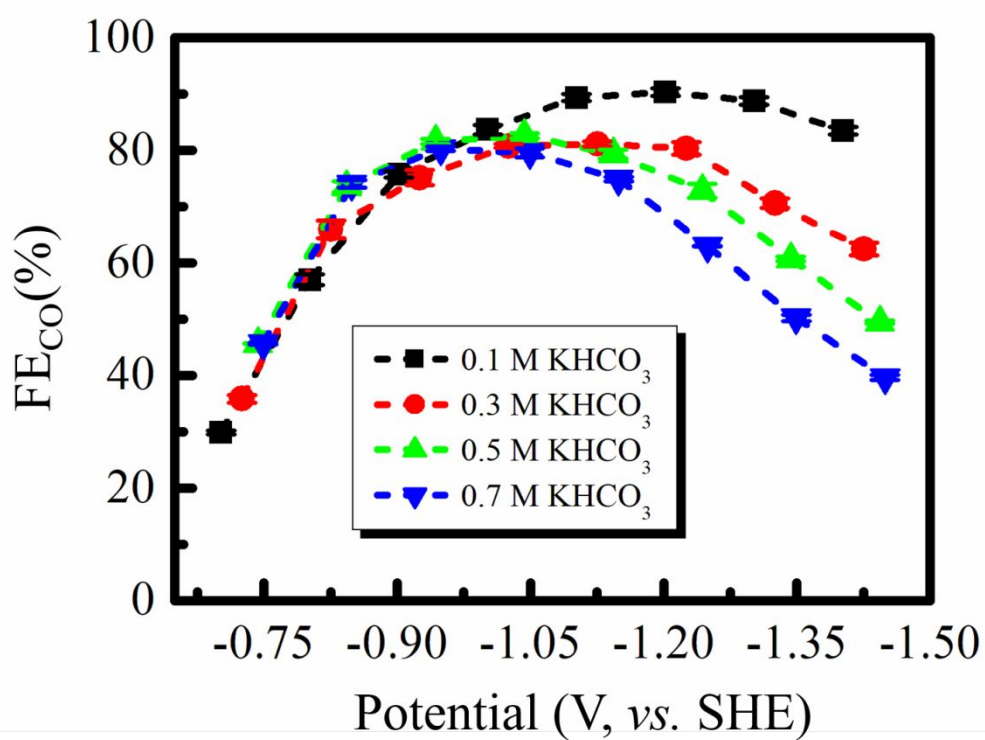


Figure S10. Faradaic efficiencies of CO (FE_{CO}) for HC-6 in CO_2 -saturated $KHCO_3$ solution with different concentrations as a function of potential on the SHE scale.

3. Supplementary Table (Table S1)

Table S1. In content of the as-prepared catalysts expressed as the atomic ratio of In to (Cu+In).

	HC-3	HC-6	HC-7
In/(Cu+In)%	1.43	2.46	4.21