Electronic Supplementary Information

A cost-effective Indium/carbon catalyst for highly efficient

electrocatalytic reduction of CO₂ to HCOOH

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2. Experimental section

2.1. Materials

Carbon black (Vulcan XC-72R) was purchased from Cabot (USA). In(NO₃)₃, C_2H_5OH (99.9%), KHCO₃, Hexadecyl trimethyl ammonium bromide (CTAB) and polyvinyl pyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co. Ltd (China). D₂O, DMSO, HCOOH, disodium citrate (CA) are purchased from Aladdin Company (China), and all the used chemicals are of analytical grade. The water used in the experiment is deionized water with the high purity of 18.25 M Ω cm, and high purity N₂ was used to remove oxygen before using.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained from an X' pert Pro diffractometer (PANalytical, Netherlands). X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB 250 electron spectrometer (Thermo Scientic, USA) to analyze the surface components of the as-synthesized catalysts. The spectra were excited using with an Al-Kα radiation source (1486.6 eV) and binding energy was referenced to C 1s peak at 284.8 eV. The software "XPSPEAK (Version 4)" was used to treat curve fitting based on a non-linear least-square regression method, and Linear type background corrections. The morphology was observed on high-resolution transmission electron microscope (HRTEM, TECNAI G2, FEI) and scanning electron microscopy (SEM, HITACHI, Hitachi Corp, Japan), respectively.

2.3. Electrochemical measurements

All electrochemical experiments were carried out on a CHI 650E electrochemical

analyzer (CH Instruments, China). The electrochemical CO₂ reduction reaction (CO₂RR) were measured using a three-electrode cell with two compartments in which a platinum column and silver chloride electrode were served as a counter and reference electrode, respectively, and the electrolyte was 0.5 M KHCO₃ solution saturated with CO_2 . The working electrode was prepared as follows: 5 mg of the catalyst was ultrasonically dispersed into the mixture solution of 900 µl ethanol and 100 µl 5% Nafion solution. After ultrasonic treatment for 1 h, 60 µl uniformly dispersed catalyst was dropped onto the carbon paper (1cm \times 1cm). In electrolyzing process, the working electrode and the reference electrode were placed in the cathode chamber, and the counter electrode in the anode chamber. The anode and cathode chambers were separated by Nafion 117 ion exchange membrane. Before electrolysis, high purity of CO_2 was introduced into the cathode chamber at a flow rate of 30 ml min⁻¹ for 1 h. Linear sweep voltammetry (LSV) test were conducted at a scan rate of 10 mV s⁻¹ in the CO2 and N2-saturated KHCO3 solution, respectively. The timing current curve (Chronoamperometry test) is measured in the CO₂-saturated KHCO₃ solution at a fixed potential, with a constant speed magnetic stirring. In this paper, a reversible hydrogen electrode (RHE) is represented, and its conversion formula is:

E (vs RHE) = E (vs. Ag/AgCl) + 0.210 + 0.0591 × pH [1, 2].

2.4. Product analysis

The gaseous products were directly transferred into the gas sampling loop of a gas chromatograph (GC, FL9790II, Fuli Analytical Instruments Co., Ltd, China), equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Argon was used as carrier gas, the column temperature was 100 °C, the FID temperature was 150 °C, the TCD temperature was 120 °C, and the auxiliary furnace temperature was 350 °C. The TCD and 5A molecular sieve filled column were used to detect the retention time of H₂, and the FID was used to detect the CO. The FE of CO and H₂ can be calculated as followed [3]: $FE_{CO} = z n_{CO} F / Q \times 100\%$, $FE_{H2} = z n_{H2} F / Q \times 100\%$, where z is the number of electrons exchanged (for example, z = 2 for reduction of CO₂ to CO), F is the Faraday constant (96485 C • mol⁻¹), n _{CO} and n _{H2} is the number of moles for CO and H₂ respectively, and Q is the total electricity capacity.

The liquid product was analyzed qualitatively and quantitatively by nuclear magnetic resonance spectroscopy (NMR, Buker 400MHz, Brook Company, Switzerland). The specific operation is as follows: 0.5 mL cathode electrolyte was mixed with 0.1 mL D₂O and 5 *H*L dimethyl sulfoxide (DMSO) solution, in which DMSO was used as internal standard for qualitative analysis and quantitative calculation. The formula for calculating the FE of formic acid is as follows [4, 5]: $FE_{HCOOH} = 2 n_{total} F / Q$, where 2 is the number of electrons transferred when formic acid is produced, n total is the amount of total formic acid deriving from the quantitative analysis results of NMR, F is the Faraday constant (96485 C • mol⁻¹) and Q is the total charge transferred in the reaction system. All potentials were converted into a RHE potential using the formula: $E_{RHE} = E_{SCE} + 0.059 \times pH + E^{0}_{SCE} (E^{0}_{SCE} = 0.241 vs. normal hydrogen electrode (NHE) at 25 °C) [6, 7].$



Fig. S1. SEM images: (A) In/C (CT), (B) In/C (PV), (C) In/C (ET), (D) In/C

(CA)**.**



Fig. S2. TEM images: (A) In/C (CT), (B) In/C (PV), (C) In/C (ET), (D) In/C

(CA)**.**

Catalysts	In (0)	In (III)
In/C (CT)	73.1%	26.9%
In/C (PV)	75.0%	25.0%
In/C (ET)	63.9%	36.1%
In/C (CA)	60.6%	39.4%

Table S1. The content of In (0) and In (III) in different catalysts.



Fig. S3. GC chromatogram analysis of CO_2 electrolysis for In/C (CT), at

-0.61V vs. RHE with Ar as carrier gas to determine H_2 .



Fig. S4. GC chromatogram analysis of CO_2 electrolysis for In/C (CT) at

-0.61V vs. RHE with Ar as carrier gas to determine CO.



Fig. S5. NMR spectrum:(A) 1H-NMR spectrum, (B) WATERSUP spectrum of the electrolyte after electrolysis for 3 h in CO₂-saturated 0.5 M KHCO₃ aqueous

solution on In/C (CT) at -0.61V vs. RHE.

Catalusta	Flastuskita	Main	E/V vs.	J _{Product} /	Highest	Defuences
	Electrolyte	Products	RHE)	mA	FE/%	Kentences
In/C (CT)	0.5 M KHCO ₃	НСООН	-1.01	-8.4	89	This Work
hp-In	0.1 M KHCO ₃	НСООН	-1.2	-	90	[8]
In–Sn alloy	0.1 M KHCO ₃	НСООН	-1.2	-9.6	78.6	[9]
Nanocubic In(OH) ₃	0.5M K ₂ SO ₄	НСООН	-1.1	~ 4	77	[10]
InxCuy NPs	0.1 M KHCO ₃	НСООН	-1.2	-3.59	90	[11]
SnInOx films	0.1 M KHCO ₃	НСООН	-1.0	-	80	[12]
Cu-In ₂ O ₃ /C	0.5 M KHCO ₃	СО	-1.08	~ -14	86.7	[13]
Ag _{85.4} In _{14.6}	0.5M KHCO ₃	СО	-1.5V vs.SCE	~ -4.5	75.5	[14]

Table S2. Electrochemical performance of the reported indium-based

catalysts	for	$CO_2RR.$	
catalysts	tor	$CO_2 RR.$	

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