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Iodide-mediated electroreduction of carbon dioxide for efficient and selective electrosynthesis of multicarbon products over copper iodide microcrystals

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Interface Science

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3	microcrystals
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Abstract

18 Electrochemical CO₂ reduction (e-CO₂RR) to multicarbon (C₂₊) products serves as a sustainable route for renewable energy storage, chemical synthesis, and mitigating CO₂ 19 20 emission. In this study, we report on the CuI microcrystals modified gas-diffusion electrode 21 (microCuI), prepared with the successive ion layer adsorption and reaction method, with high-22 performance towards the generation of C_{2+} products from *e*-CO₂RR. The *micro*CuI electrode 23 exhibited remarkably high current efficiency towards the generation of C₂₊ products (*i.e.*, 24 ethylene, ethanol, and 1-propanol), but suffered instability due to the formation of inactive copper (II) carbonate hydroxide within 2-h electrolysis. As compared to other halide ions, the 25 inclusion of a suitable amount of I⁻ ions during the electrolysis minimized the corrosion and 26 effectively regulated the oxidation state of surface copper species (OS_{Cu}) and transformed 27 microCuI into aggregates of Cu⁰/Cu₂O nanoparticles, with Cu⁰ embedded in a Cu₂O matrix. 28 The suitable OS_{Cu} (~ 0.7) combined with synergistic catalytic effects from Cu^0 and Cu_2O 29 enabled high stability and realized high current efficiency (73.6 \pm 2.2%) and high energy 30 31 efficiency (48.8 \pm 1.8%) for the generation of C₂₊ products in the prolonged electrolysis at -100 mA cm⁻². Finally, the I⁻ ion-mediated e-CO₂RR scheme was also demonstrated to 32 effectively boost the current efficiency and energy efficiency of the *micro*CuI electrode towards 33 the generation of C₂₊ products from the electrocatalytic reduction of low-concentration CO₂ in 34 35 the simulated biogas atmosphere.

36

Keywords: Cu oxidation state; Electrochemical upcycling of CO₂; multicarbon product;
 SILAR deposition; Synergistic catalysis.

40 **1. Introduction**

Electrochemical CO₂ reduction (e-CO₂RR), powered by renewable energy, to chemical 41 feedstocks and fuels, has been considered as a cornerstone for carbon neutrality, sustainable 42 43 chemical production, and the resolution of the energy and environmental crisis [1-4]. Nonetheless, as CO₂ is an inert gas and its conversion involves a complicated multiple proton-44 coupled electron transfer process, e-CO₂RR often suffers sluggish kinetics and diverse 45 competing reactions, leading to low product selectivity. To make e-CO₂RR an economically 46 viable technology, developing robust and efficient electrocatalysts with high selectivity for the 47 production of targeted products is indispensable. 48

49 The production of multi-carbon products (C₂₊ products), such as ethylene, ethanol, and propanol, via e-CO₂RR is of great interest and importance due to their high energy density and 50 51 economic value. To date, copper (Cu) has been recognized as a highly effective element for the 52 selective production of C₂₊ products via e-CO₂RR. Among the developed copper-based 53 electrocatalysts, e-CO₂RR using halide-derived copper (HD-Cu) and oxide-derived copper (OD-Cu) have been intensively studied as these Cu-based electrocatalysts showed satisfactory 54 55 current efficiency (CE_{C2+}) towards the production of C_{2+} products [5-13]. The enhanced CE_{C2+} 56 of these HD-Cu and OD-Cu electrocatalysts is mainly attributed to the synergistic catalysis of Cu⁺-Cu⁰ pairs, in which Cu⁰ species activates CO₂ and facilitates the subsequent electron 57 transfer, while Cu⁺ species strengthens the adsorption of *CO intermediate, facilitating C-C 58 coupling and subsequent generation of C₂₊ products [14-23]. Nevertheless, during *e*-CO₂RR, 59 the oxidation state of surface copper species (OS_{Cu}) dynamically changes, resulting in 60

61 significant restructuring of the catalyst [24] and degradation of the active site. For example, 62 Cu^+ species can be reduced to Cu^0 or disproportionated to Cu^0 and Cu^{2+} species. This 63 continuous transformation impacts the product selectivity and stability of these Cu-based 64 electrocatalysts, highlighting the importance of controlling and stabilizing OS_{Cu} during *e*-65 CO_2RR to enhance the *e*-CO₂RR performance of the Cu-based electrocatalysts.

Several strategies have been explored to adjust OS_{Cu} during the e-CO₂RR process, 66 67 including the application of pulse current/potential during e-CO₂RR [25-27] and the addition 68 of halide ions in the electrolyte solution for e-CO₂RR [27-31]. Xu et al., applied a positive potential pulse to *in-situ* regenerate Cu⁺ species thus create Cu⁺-Cu⁰ pairs periodically during 69 e-CO₂RR, resulting in a satisfactory partial current density (~18.4 mA cm⁻²) with a high current 70 efficiency (81.2%) for C_{2+} products at the expense of a highly cathodic potential (-1.2 V vs. 71 RHE) [27]. The enhancement of CE_{C2+} of copper-based electrocatalysts in the presence of 72 73 concentrated halide ions (≥ 0.1 M), on the other hand, was attributed either to the facilitated 74 CO₂ activation by partial charge donation from the halide ions to CO₂ [28], or to the 75 stabilization of the intermediates by the Cu⁺ species [27, 29, 30]. Recently, Jiang et al., reported that the addition of I₂ facilitated the re-oxidization of Cu⁰ to form CuI and thus regulated 76 77 Cu^0/Cu^+ interface, resulting in significant enhancement in the CE_{C2+} of the Cu nanoparticles 78 under the acidic conditions [31]. Nevertheless, most of these studies on the effects of halide ions on the e-CO₂RR performance of the Cu-based electrocatalysts for producing C₂₊ products 79 were limited to short electrolysis period (≤ 1 h) and low current regimes (< -100 mA cm⁻²) at 80 the expense of high overpotential [27-30], and the effects of halide ions on long-term stability, 81

82	<i>i.e.</i> , maintenance of OS_{Cu} in the prolonged electrolysis, and CE_{C2+} of the copper-based
83	electrode at the industrially relevant current density (> -100 mA cm ⁻²) in alkaline pH have not
84	been investigated yet. Recently, the adsorbed iodine species, generated from the reconstruction
85	of Cu-CuI composite, was suggested to play a beneficial role in improving CO adsorption, and
86	thus promoting C–C coupling and the formation of C_{2+} products [13]. Nonetheless, the loss of
87	adsorbed iodine species occurred and decreased CE_{C2+} in the prolonged electrolysis [10], which
88	suggests that the supplement of iodine species during e-CO ₂ RR would be necessary to maintain
89	the high CE_{C2+} .

90 In the present contribution, we report the facile preparation of the CuI microcrystals 91 modified gas-diffusion electrode (microCuI), using the successive ion layer adsorption and 92 reaction (SILAR) method, and the application of the prepared microCuI electrode for the 93 generation of C₂₊ products from *e*-CO₂RR. The effects of electrolysis conditions (e.g., 94 electrolyte composition, electrolyte pH, applied current density, and CO₂ atmosphere) on the 95 e-CO₂RR performance of the *micro*CuI electrode were thoroughly investigated and optimized. 96 OS_{Cu} was found to be a key factor in determining the current efficiency of the microCuI 97 electrode towards the generation of C₂₊ products, and the inclusion of a suitable amount of I⁻ 98 ions effectively regulated OS_{Cu} and realized high current efficiency (73.6 ± 2.2%) and high 99 energy efficiency (48.8 \pm 1.8%) for the generation of C₂₊ products in the prolonged electrolysis 100 at -100 mA cm⁻². Finally, the I⁻ ion-mediated e-CO₂RR scheme was proposed and 101 demonstrated for the first time to effectively boost the current efficiency and energy efficiency of the *micro*CuI electrode towards the generation of C₂₊ products from the electrocatalytic
reduction of low-concentration CO₂ in the simulated biogas atmosphere.

104 2. Experimental Setup

105 **2.1 Chemical and materials**

All the chemicals used for the preparation of electrodes and electrolyte solutions, including 106 copper (II) sulfate (≥98.5%, J.T. Baker), potassium iodide (≥99.5%, Honeywell FlukaTM), 107 potassium hydroxide (≥85%, Honeywell FlukaTM), potassium bicarbonate (99%, Alfa Aesar), 108 potassium chloride (≥99.0%, Sigma-Aldrich), potassium bromide (99%, VetecTM), potassium 109 nitrate (≥99.0%, Honeywell FlukaTM), sodium hydroxide (≥98%, Honeywell FlukaTM), 110 hydrochloric acid (≥37%, Honeywell FlukaTM), and hydrogen peroxide solution (30%, 111 Honeywell FlukaTM), were used as received from commercial suppliers without further 112 purification. Nickel foam (> 99%) with a thickness of 1.0 mm was purchased from Central 113 Research Company, Taiwan. GDL-340 carbon paper (thickness of 340 µm) with microporous 114 115 layer, used as the gas diffusion electrode substrate, was purchased from CeTech Co., Ltd., Taiwan. Deionized water (18.2 MQ·cm; DIW) was used for the electrode rinsing and 116 117 electrolyte preparation throughout the work.

118 **2.2 Electrode preparation**

The *micro*CuI electrode was prepared using the SILAR method at ambient temperature. Prior to the electrode preparation, GDL-340 carbon paper was successively cleaned with nitric acid for 5 min, ethanol for 5 min, and DIW for 10 min under sonication. Thereafter, the *micro*CuI 122 electrode was prepared by subjecting the cleaned GDL-340 carbon paper to the SILAR process for 20 cycles. Each cycle of SILAR process consists of three steps, including (i) surface-123 modification of GDL-340 carbon paper with Cu²⁺ ionic layer via the incubation of the cleaned 124 125 GDL-340 carbon paper in aqueous CuSO₄ solution (2 M) for 20 s, (ii) formation of CuI nuclei via chemical reaction between I⁻ ions and the adsorbed Cu²⁺ ions by incubating the electrode 126 obtained in step (i) in KI aqueous solution (0.1 M) for 20 s, and (iii) removal of poorly-adsorbed 127 128 CuI and excessive I⁻ ions by thoroughly rinsing the electrode obtained in step (ii) with DIW. For performance comparison, a Cu microcrystals modified gas-diffusion electrode (*micro*Cu) 129 130 was prepared by subjecting the cleaned GDL-340 carbon paper to the electrochemical deposition process in the plating solution containing H_2SO_4 (1.0 M) and KI (5 mM) at -0.5 V 131 vs. RHE for 300 s. The obtained microCu electrode was rinsed with DIW before use. 132

133 **2.3 Physical characterization**

134 OS_{Cu} of the copper species in the *micro*CuI electrode was analyzed by X-ray photoelectron spectroscopy (XPS) and Auger Spectroscopy (AES) with a PHI 5000 VersaProbe system 135 (ULVAC-PHI, Chigasaki, Japan). The binding energy (BE) scale of the obtained XPS spectra 136 137 was calibrated with adventitious carbon species at 284.6 eV. Surface morphology and chemical composition of the prepared modified electrodes were characterized using a scanning electron 138 139 microscope (SEM, Hitachi SU-8010) equipped with energy-dispersive X-ray spectroscopy (EDS). Detailed structural and elemental analyses of *micro*CuI were performed by transmission 140 electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) 141

with a JEM-2100F microscope (JEOL Ltd., Japan). The TEM sample for the as-prepared *micro*CuI electrode was prepared by detaching *micro*CuI from electrode under ultrasonication, whereas that for the *micro*CuI electrode obtained after 8-h electrolysis was prepared with the help of the focused ion beam-SEM (FIB-SEM). Prior to the FIB-SEM, the sample was covered with a platinum protective layer using electron and ion beams. The amount of Cu species on the *micro*CuI electrodes before and after electrolysis were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES; Horiba Jobin Yvon JY2000-2).

149

2.4 Electrochemical characterization

The *e*-CO₂RR performance of the *micro*CuI electrode was characterized in the homemade 150 151 three-electrode two-compartment flow-type electrolyzer (Scheme S1) connecting to an Ivium-152 n-Stat multichannel electrochemical analyzer (Ivium Technologies B.V., Netherlands) under the concentrated CO₂ or simulated biogas environments. The anodic and cathodic 153 compartments of the flow-type electrolyzer were separated with a Neosepta ASE anion 154 155 exchange membrane (ASTOM Corporation, Tokyo, Japan). The microCuI electrode was used as the working electrode (1 cm \times 1 cm or 2 cm \times 2 cm) and placed with Ag/AgCl (sat'd KCl) 156 reference electrode in the cathodic compartment, whereas the nickel foam $(3.5 \text{ cm} \times 3.5 \text{ cm})$ 157 was used as the counter electrode and placed in the anodic compartment. The concentrated CO₂ 158 159 and simulated biogas environments were created by feeding the CO₂/Ar gas mixture (98% CO₂ 160 and 2% Ar; Yun Shan Gas Co., Taiwan) and CO₂/CH₄ gas mixture (40% CO₂ and 60% CH₄; Yun Shan Gas Co., Taiwan), respectively, to the cathodic compartment at a flow rate (ϕ) of 35 161

162	mL min ⁻¹ with a mass flow controller. The relative humidity (RH) of the CO ₂ /Ar gas mixture
163	is 14%, whereas that of the CO_2/CH_4 gas mixture is 33%. To further investigate the effects of
164	humidity, a humidified simulated biogas environment (RH: 81%) was created by firstly passing
165	the CO ₂ /CH ₄ gas mixture (40% CO ₂ and 60% CH ₄ ; Yun Shan Gas Co., Taiwan) through a
166	closed chamber containing saturated KNO ₃ solution [32], followed by feeding to the cathodic
167	compartment of the flow-type electrolyzer. The blank KOH solution (1.0 M) or KI (0.01~0.1
168	M)-containing KOH solution (1.0 M) were used as the catholyte, whereas the NaOH solution
169	(1.0 M) was used as the anolyte. The flow rates of both anolyte and catholyte were set at 35
170	mL min ⁻¹ using peristaltic pumps. Unless otherwise noted, the potential values reported in this
171	work are referenced to the reversible hydrogen electrode (RHE) according to Eq. 1:

172 $E(V vs. RHE) = E(V vs. Ag/AgCl) + 0.197 + 0.059 \times pH$ (1)

173 **2.5 Product analysis**

The main liquid products (i.e., ethanol and 1-propanol) generated from the controlled-174 current electrolysis experiments were analyzed and quantified using a GC-2010 Plus gas 175 chromatography system (Shimadzu; GC) equipped with a Rtx[®]-Volatiles column and a flame 176 ionization detector (FID). The temperature of the GC oven holding the column was initially 177 held at 40 °C for 1 min, and subsequently ramped at 40 °C min⁻¹ to 80 °C for 6 min and at 20 178 °C min⁻¹ to 250°C for another 8.5 min. On the other hand, gaseous products generated from 179 electrolysis experiments were analyzed and quantified using an Agilent 7890B Series gas 180 181 chromatography. Methane, ethylene, and carbon monoxide were analyzed and quantified with a Carboxen®-1006 PLOT column (He carrier gas at a flow rate of approximately 5 mL min⁻¹) and a thermal conductivity detector and a FID detector in series, whereas Hydrogen gas was analyzed and quantified with a HP-PLOT Molesieve 19095P-MS6 column (N₂ carrier gas at a flow rate of approximately 4 mL min⁻¹) and a TCD detector. The temperature of the GC oven holding the Carboxen®-1006 PLOT and HP-PLOT Molesieve 19095P-MS6 columns was kept at 40 °C for the first 8 min, and subsequently ramped at a rate of 40 °C min⁻¹ to 200 °C, and maintained at 200 °C for another 8 min.

The concentrations of products ($C_{product}$) were obtained by converting the measured TCD and FID signals with routinely updated calibration curves. The generation rate ($R_{product}$) and current efficiency ($CE_{product}$) of products were determined, respectively, by Eq. 3 and Eq. 4:

192
$$\mathbf{R}_{\text{Product}} = \phi \times \mathbf{C}_{\text{product}} \times \frac{P}{RT}$$
(2)

193
$$CE_{product} = \frac{R_{product} \times n_{product} \times F}{J} \times 100\%$$
 (3)

where P is the ambient pressure (*i.e.*, 1 atm), R is the ideal gas constant (*i.e.*, 0.082 L atm K⁻¹ mol⁻¹, T is the working temperature (*i.e.*, 298.15 K), n_{product} is the number of electron transfer for the specific product, F is the Faradaic constant (96,485 C mol⁻¹), and J is the applied current density.

The cathodic energy efficiency (EE_{C2+}) for the generation of C_{2+} products, defined as the ratio of chemical energy stored in the C_{2+} products to applied electrical energy [12], was determined using Eq. 4:

201
$$EE_{C2+} = \frac{(1.23 - E_{C_2H_4}^0) \times CE_{C_2H_4} + (1.23 - E_{EtOH}^0) \times CE_{EtOH} + (1.23 - E_{PrOH}^0) \times CE_{PrOH}}{1.23 - E_{app}} \times 100\%$$
(4)

where $E_{C_2H_4}^0$, E_{EtOH}^0 , E_{PrOH}^0 are the standard reduction potentials for the generation of ethylene (0.06 V vs. RHE), ethanol (0.08 V vs. RHE), and 1-propanol (0.1 V for 1-propanol), respectively, from *e*-CO₂RR.

205 **3. Results and discussion**

206 **3.1 Materials synthesis and characterization**

207 The microCuI electrode was prepared using the SILAR method (See Experimental Section for the details). The XRD analysis (Figure 1a) confirms the successful deposition of cubic CuI 208 209 (JCPDS no. 06-0246) on the GDL-340 carbon paper after the SILAR process. The SEM images, shown in Figures 1b-1c, indicate that the prepared microCuI electrode consists of uniformly-210 211 dispersed CuI microcrystals with size of 1~2 µm. The results of TEM and selected area electron 212 diffraction (SAED) analyses (Figures 1d-1f) reveal that the deposited CuI microcrystal is 213 single-crystal and shows clear lattice fringe with d-spacing of 3.49 and 2.15 Å, corresponding 214 to (100) and (220) plane of cubic CuI (JCPDS no. 06-0246). High-angle annular dark-field (HAADF) image (Figure 1g) and its EDS elemental mapping images (Figures 1h-1i) confirm 215 216 the uniform distribution of Cu and I elements in the CuI microcrystal. Figure 2 illustrates the 217 XPS spectra of the as-prepared *micro*CuI electrode. The XPS features, including (i) the peaks 218 at binding energies of 932.3 eV and 952.1 eV with a separation peak of 19.8 eV in the Cu 2p region and (ii) the peaks at binding energies of 620.0 eV and 631.5 eV with a separation peak 219 220 of 11.5 eV in the I 3d region, confirms the existence of CuI species in the as-prepared microCuI electrode [33-35]. 221

222	Figure 3 shows the electrochemical characterization of the <i>e</i> -CO ₂ RR performance of the
223	microCuI electrode under different operation conditions. As revealed from Figures 3a-3b, the
224	microCuI electrode exhibited remarkably high current efficiency (CE_{C2+}) towards the
225	generation of C ₂₊ products (<i>i.e.</i> , ethylene, ethanol, and 1-propanol), but suffered instability
226	under the constant applied current density of -100 mA cm ^{-2} in the blank KOH solution (1.0 M).
227	Specifically, the CE _{C2+} of the <i>micro</i> CuI electrode decreased from 71.9 \pm 1.6% to 51.8 \pm 1.5%
228	when the electrolysis duration was extended from 1 h to 2 h. As revealed from the XRD and
229	SEM analyses (Figure S1), the observed instability of the microCuI electrode could be
230	attributed to the decomposition of microCuI into inactive copper (II) carbonate hydroxide
231	microrods during electrolysis. The formation of copper (II) carbonate hydroxide would be a
232	result of the precipitation of Cu ²⁺ ions, generated via the spontaneous oxidation of CuI [36], in
233	the presence of carbonate ions that were generated from the dissolution of CO_2 in the electrolyte.
234	e-CO ₂ RR at high current density inevitably generates a significant amount of OH ⁻ ions at the
235	electrode surface, which results in an increase in the local pH near the electrode surface and
236	promotes the chemical reaction of dissolved CO ₂ with OH ⁻ ions to form carbonate ions. To
237	minimize the formation of copper (II) carbonate hydroxide due to the accumulation of OH-
238	ions and carbonate ions, the e-CO2RR performance of the microCuI electrode was
239	characterized by using pulse current electrolysis, which involves the periodic application of an
240	operation current density of -100 mA cm $^{-2}$ for 60 s and subsequent a regeneration current
241	density of 0 mA cm ^{-2} for 30 s. Note that the durations for the applications of regeneration
242	current and operation current were set based on the work previously reported [37]. The

243	corresponding potential fluctuations under pulse current electrolysis was shown as curve ii in
244	Figure 3a. The results (Figure 3c) show that the e-CO ₂ RR performance of the microCuI
245	electrode was significantly improved using pulse current electrolysis. Notably, the CE_{C2+} of the
246	<i>micro</i> CuI electrode remained $63.1 \pm 4.8\%$ after electrolysis for 8 h (12 h total duration). The
247	XRD and SEM analyses (Figure S2) indicate that <i>micro</i> CuI mainly converted into cuprous
248	oxide (Cu ₂ O) nanoparticle aggregates with minimal formation of copper (II) carbonate
249	hydroxide. These findings are in agreement with the previous report that pulse electrolysis
250	strategies can effectively minimize the accumulation of carbonate [37] and thus avoid the
251	formation of inactive copper (II) carbonate hydroxide. Briefly, during the application of
252	regeneration current density (0 mA cm ⁻²), the rate of e -CO ₂ RR is minimal, eliminating the
253	formation of hydroxide and carbonate ions. Meanwhile, carbonate ions, generated during the
254	application of operational current density (-100 mA cm ⁻²), are removed from the vicinity of the
255	cathode by the electrolyte flow. This dynamic cycling prevents the continuous buildup of
256	carbonate ions. Figures 3a and Figure 3d show the e-CO ₂ RR performance of the microCuI
257	electrode from the 8-h electrolysis at -100 mA cm ⁻² in the KI (0.05 M)-containing KOH
258	solution (1.0 M). It can be found that the electrolysis in the presence of KI (0.05 M) remarkably
259	enhanced the stability and CE _{C2+} of the <i>micro</i> CuI electrode. Notably, the <i>micro</i> CuI electrode
260	exhibited CE _{C2+} of 75.8 \pm 4.2% and 73.6 \pm 2.2% in the first hour and eighth hour of the
261	electrolysis. Figure S3 shows SEM and EDS analyses of the <i>micro</i> CuI electrodes after different
262	electrolysis durations. As revealed, the CuI microcrystals converted into aggregates of
263	nanoparticles, accompanied by I ⁻ leaching during e-CO ₂ RR. Further characterizations using

264	XRD, SEM, and (HR-)TEM (Figure 4) reveal CuI microcrystals were mainly converted into
265	aggregates of Cu ₂ O and Cu crystalline nanoparticles (~5 nm). Notably, the HR-TEM (Figure
266	4d) and SAED (Figure 4e) analyses indicate that the aggregate shows lattice fringes with d-
267	spacing of 2.4 Å (darker area indicated by red dashed line) and 2.09 Å (brighter area indicated
268	by yellow dashed line) corresponding to Cu ₂ O (111) (JCPDS no. 05-0667) and metallic Cu
269	(111) (JCPDS no. 85-1326), respectively. The analyses of HAADF and EDS mapping, shown
270	in Figure S4, confirm the uniform distribution of Cu ₂ O and Cu species with a small amount of
271	residual I- ion. Consequently, the observed enhanced stability would be attributed to the
272	minimization of the formation of inactive copper (II) carbonate hydroxide in the presence of I ⁻
273	ions, presumably via the redox reaction of Cu^{2+} species with I ⁻ ions (Eq. 5). In other words,
274	OS_{Cu} of the copper species in the <i>micro</i> CuI electrode can be regulated by I ⁻ ions. Besides, as
275	revealed in Figure 3a, the potential required for the <i>micro</i> CuI electrode to maintain the applied
276	current density of -100 mA cm ⁻² at the end of 8-h electrolysis in the presence of KI (0.05 M)
277	was ~ -0.74 V vs. RHE, which is about 0.02 V and 0.16 V lower than those obtained from 2-h
278	electrolysis at the constant applied current density of -100 mA cm ⁻² in the blank KOH solution
279	(1.0 M) and 8-h pulse electrolysis (12 h total duration), respectively. As revealed in Figure S5,
280	the presence of I ⁻ ions also reduced the overpotential and enhanced CE_{C2^+} in the KHCO ₃ (1.0
281	M) electrolyte solution. These findings suggest the beneficial role of I-ions played in
282	enhancing CE_{C2^+} and reducing the overpotential. Note that the CE_{C2^+} obtained from the pulse-
283	current electrolysis in the KI (0.05 M)-containing KOH (1.0 M) solution after electrolysis for
284	8 h (12 h total duration) was around 45.5%, which is lower than that obtained from the pulse-

current electrolysis in the blank KOH solution (**Figure S6**). This finding suggests that pulsecurrent electrolysis in the presence of KI (0.05 M) can't further enhance the e-CO₂RR performance of the *micro*CuI electrode. Therefore, the following sections will focus on characterizing the e-CO₂RR performance of the *micro*CuI electrode under constant-current electrolysis conditions.

290 Figure S7 shows the e-CO₂RR performance of the *micro*CuI electrode in the presence of 291 different halide ions. As revealed, the e-CO2RR performance of the microCuI electrode in the 292 KOH solution containing either KBr (0.05M) or KCl (0.05 M) was inferior to that obtained 293 that in the KI (0.05 M)-containing KOH solution. Specifically, the overpotential required to sustain the applied current density of -100 mA cm⁻² was higher in the KOH solutions 294 295 containing either KBr (0.05M) or KCl (0.05 M) compared to that obtained in the KI (0.05 M)-296 containing KOH solution during electrolysis (Figure S7a). In addition, the microCuI electrode 297 exhibited a CE_{C2+} of 73.6 \pm 2.2% after 8-h electrolysis at -100 mA cm⁻² in the KI (0.05 M)-298 containing KOH solution, whereas it only exhibited CE_{C2+} of $42.2 \pm 2.0\%$ and $52.5 \pm 3.6\%$ 299 after 8-h electrolysis at -100 mA cm⁻² in the KBr (0.05 M)- and KCl (0.05M)-containing KOH 300 solution, respectively. In other words, the e-CO₂RR performance of the microCuI electrode 301 varied with different halides, following the order: Br⁻ < Cl⁻ < I⁻. The ICP-OES analyses reveal 302 that the amount of copper species on the as-prepared microCuI electrode and the microCuI 303 electrodes after 8-h electrolysis in the KI (0.05 M)-, KCl (0.05 M)-, and KBr (0.05 M)-304 containing KOH (1.0 M) solutions were 3.9 µmol cm⁻², 3.8 µmol cm⁻², 2.3 µmol cm⁻², and 2.5 305 µmol cm⁻², respectively. Therefore, the inferior e-CO₂RR performance of the microCuI

306 electrode in the KOH solution containing either KBr (0.05M) or KCl (0.05 M) would be 307 attributed to the corrosion of copper species. The minimal corrosion of copper species in the 308 KI (0.05 M)-containing KOH solution could be attributed to the redox reaction of Cu^{2+} species 309 with I⁻ ions (Eq. 5).

310
$$2Cu^{2+} + 2OH^{-} + 2I^{-} \rightarrow Cu_2O + H_2O + I_2$$
 (5)

311 The effects of I⁻ concentration on the e-CO₂RR performance of the microCuI electrode 312 were further investigated, and the results are shown in Figure 5. Compared to electrolysis in 313 the absence of I⁻ ions, the presence of I⁻ ions (0.01~0.1 M) significantly reduced the overpotential required to maintain the applied current density of -100 mA cm^{-2} (Figure 5a). 314 315 Furthermore, the electrolysis with KI also leads to a higher production rate (R_{C2+}) and higher 316 selectivity of C_{2+} products, in terms of CE_{C2+} and partial current density of C_{2+} products (J_{C2+}), during the prolonged electrolysis (Figures 5b-5d). Notably, the 8-h electrolysis in the presence 317 of 0.05 M I^- ions generated C_{2+} products at a rate of 0.22 \pm 0.01 mmol cm^{-2} h^{-1} (J_{C2+}: 73.6 \pm 318 2.2 mA cm⁻²) with a CE_{C2+} of 73.6 \pm 2.2%, whereas the electrolysis in the absence of KI 319 generated C₂₊ products at a significantly lower rate of $0.09 \pm 0.01 \text{ mmol cm}^{-2} \text{ h}^{-1}$ (J_{C2+}: 31.3± 320 5.1 mA cm⁻²) with a lower CE_{C2+} of $31.3 \pm 5.1\%$. These findings further confirm the beneficial 321 role of I⁻ ions in enhancing the C₂₊ product-selectivity and stability of the *micro*CuI electrode 322 323 at the expense of a low overpotential. It is important to note that there was an optimal 324 concentration of I⁻ ions to achieve the highest C₂₊ product selectivity and stability. The 325 electrolysis with concentrated I- ions reduced the stability of the microCuI electrode. 326 Specifically, in the presence of 0.1 M I⁻ ions, the CE_{C2+} and R_{C2+} of the *micro*CuI electrode

decreased from 75.0 \pm 2.2% and 0.23 \pm 0.01 mmol cm^-2 h^-1 to 42.2 \pm 2.9% and 0.13 \pm 0.01 327 mmol $cm^{-2}h^{-1}$, respectively, when the electrolysis duration was extended from 4 h to 8 h. The 328 329 instability of the *micro*CuI electrode observed during the prolonged electrolysis in the presence 330 of concentrated I⁻ ions could be attributed to the excessive Cu⁺ stabilization, presumably due to the strong interaction between I⁻ and Cu⁺ species [38], which in turn shifts the OS_{Cu} to the 331 332 undesired side (vide infra). The effects of I⁻ ions on the e-CO₂RR performance of the Cu 333 microcrystals modified electrode (designated as *micro*Cu for simplicity), prepared by the 334 electrochemical deposition (see Experimental Section for the details), were also investigated and the results are shown in Figure S8. The results of XRD and SEM analyses, shown in 335 336 Figure S9, confirm the successful deposition of crystalline Cu microcrystals on the *micro*Cu 337 electrode. As revealed in Figure S8, the presence of I⁻ ions also reduced the overpotential and enhanced CE_{C2+} of the *micro*Cu electrode. Specifically, the overpotential of the *micro*Cu 338 339 electrode to maintain the applied current density of -100 mA cm⁻² during the 6-h electrolysis 340 in the KI (0.05M)-containing KOH solution was about 0.2 V less than that in the blank KOH 341 solution (0.1 M). Besides, in contrast to the minimal CE_{C2+} (6.9 \pm 0.8%) of the *micro*Cu 342 electrode obtained after 6-h electrolysis in the blank KOH solution, the microCu electrode exhibited an enhanced CE_{C2+} ($30.5 \pm 5.4\%$) after 6-h electrolysis in the KI (0.05M)-containing 343 344 KOH solution. Nevertheless, even in the presence of KI (0.05 M), the CE_{C2+} ($30.5 \pm 5.4\%$ vs. 345 $73.6 \pm 2.2\%$) of the *micro*Cu electrode remains inferior to that of the *micro*CuI electrode.

- **346 3.2 Mechanistic interpretation**
- 347

Electrochemically available surface area (ECSA) of the microCuI electrodes after 8-h

electrolysis in the blank KOH solution (1.0 M) and KI (0.05 M)-containing KOH solution was 348 349 determined using cyclic voltammetry (CV), and the result is shown in Figure S10. The doublelayer charge capacitance of the microCuI electrode after 8-h electrolysis in the presence of 0.05 350 351 M I⁻ ions was similar to that obtained after 8-h electrolysis in the absence of I⁻ ions (13.5 mF cm⁻² vs. 12.0 mF cm⁻²), which suggests that the presence of I⁻ ions did not significantly change 352 353 the ECSA of the *micro*CuI electrode during the electrolysis. On the other hand, CV analyses 354 (Figure S11 and Supporting Information: Determination of *e*-N_{Cu} and *e*-N_{Cu+}) revealed that the amount of electrochemically available Cu^0 (e-N_{Cu}) and Cu^+ (e-N_{Cu+}) species in the *micro*CuI 355 electrodes after 8-h electrolysis in the blank KOH and KI (0.05 M)-containing KOH solution 356 were 0.28 μ mol cm⁻² and 0.51 μ mol cm⁻², and 0.46 μ mol cm⁻² and 0.68 μ mol cm⁻², 357 respectively. The analyses of e-TOF_{C2+}, based on the total amount of e-N_{Cu} and e-N_{Cu+}, reveal 358 that e-TOF_{C2+} of the *micro*CuI electrode was $3.21 \pm 0.14 \text{ min}^{-1}$ when electrolysis was 359 performed in the presence of 0.05 M I⁻ ions, which is about 1.7 times higher than that obtained 360 361 in the absence of I⁻ ions. The findings from the analyses of ECSA and *e*-TOF_{C2+} suggest that 362 the remarkable enhancement in the e-CO2RR performance of the microCuI electrode in the 363 presence of I⁻ ions cannot be attributed to the differences in the electrochemically accessible 364 surface area or copper species. In other words, the restructuring of *micro*CuI was unlikely the 365 main factor in determining the overall e-CO₂RR performance of the microCuI electrode. 366 Figure 6 shows the XPS and AES analyses of the microCuI electrodes after 8-h

367 electrolysis in KOH solution (1.0 M) containing I⁻ ions of various concentrations. As revealed

368 in Figure 6a, the *micro*CuI electrode exhibited two peaks at binding energies of 931.9 eV and

369	933.6 eV in the Cu 2p region, corresponding to Cu^+/Cu^0 (2p _{3/2}) and Cu^{2+} (2p _{3/2}), respectively
370	[13, 39, 40], after 8-h electrolysis regardless of the concentration of I ⁻ ions. AES analyses in
371	Figure 6b indicates that the <i>micro</i> CuI electrode exhibited three peaks at 68.1, 570.3, and 574.4
372	eV, assignable to Cu^0 , Cu^{2+}/Cu^+ , and other transition state of the Cu LMM spectrum [13, 41].
373	Based on the results of XPS (Figure 6a) and AES (Figure 6b) analyses, the contents of Cu ⁰ ,
374	Cu ⁺ , and Cu ²⁺ species in the <i>micro</i> CuI electrodes obtained after 8-h electrolysis were then
375	deduced and summarized in Figure 6c. It was found that the <i>micro</i> CuI electrode obtained after
376	8-h electrolysis in the absence of I ⁻ ions contained 31.4% Cu^0 , 8.7% Cu^+ , and 59.9% Cu^{2+} ,
377	corresponding to an OS_{Cu} of ~1.3. In contrast, those obtained in the presence of 0.05 M and 0.1
378	M I ⁻ ions contained 49.1% Cu ⁰ , 30.0% Cu ⁺ , and 20.9% Cu ²⁺ (OS _{Cu} : ~ 0.7), and 33.6% Cu ⁰ ,
379	44.8% Cu ⁺ , and 21.6% Cu ²⁺ (OS _{Cu} : ~0.9), respectively. These findings further confirm the role
380	of I ⁻ ions in regulating the oxidation state of the surface Cu active sites. Note that the presence
381	of residual I ⁻ ions, leached from the transformation of the <i>micro</i> CuI, has been reported to be
382	beneficial in stabilizing Cu ⁺ species [12, 13]. Nevertheless, the <i>micro</i> CuI electrode obtained
383	after 8-h electrolysis in the blank KOH solution only contained a trace amount of Cu^+ (8.7%,
384	Figure 6c), which could be attributed to the rapid precipitation of copper (II) carbonate
385	hydroxide. To further discuss the role of I ⁻ ions in regulating the oxidation state of copper (II)
386	carbonate hydroxide, additional 8-h electrolysis experiments at -100 mA cm ⁻² were performed
387	with the addition of KI (0.05 M) after 2-h electrolysis. The results (Figure S12) reveal that
388	CE_{C2+} obtained from the 8-h electrolysis at -100 mA cm ⁻² , with the addition of KI (0.05 M) at
389	2^{nd} h during electrolysis, was 39.9 ± 5.7 %, which is significantly lower than that (73.6 ± 2.2%)

390 obtained when KI was added at the beginning of the 8-h electrolysis. The lower CE_{C2+} obtained from the 8-h electrolysis at -100 mA cm⁻², with the addition of KI (0.05 M) after 2-h electrolysis, 391 could be attributed to the unsuccessful transformation of copper (II) carbonate hydroxide, 392 formed in the first 2-h electrolysis (Figure S1), to reduced copper species (i.e., Cu⁰ and Cu⁺) 393 by I⁻ ions, as evidenced by the XRD results (Figure S13). These findings suggest that the I⁻ 394 395 ions would be inactive in regulating the oxidation state of copper (II) carbonate hydroxide. 396 Figure 6d shows the correlation between CE_{C2+} and OS_{Cu} . It can be found that CE_{C2+} increased 397 with decreasing OS_{Cu} and reached its maximum 73.6 \pm 2.2% when OS_{Cu} was 0.7. This finding is in agreement with previous reports that the surface Cu active site with moderate OS_{Cu} (~ + 398 0.5) is favourable for C-C coupling [42]. In addition, this finding also confirms that the 399 presence of a suitable amount of I⁻ ions during e-CO₂RR is beneficial in regenerating Cu⁺ 400 species and thus regulating the OS_{Cu}, thereby enhancing the efficiency and selectivity of the 401 402 *micro*CuI electrode towards the generation of C_{2+} products in the prolonged electrolysis. 403 Nevertheless, the use of concentrated I⁻ ions (*i.e.*, 0.1 M KI) would result in the excessive Cu⁺ stabilization, presumably due to the strong interaction between I⁻ and Cu⁺ species [38], which 404 405 in turn shifts the OS_{Cu} to the undesired side (Figure 6d) and thus deteriorates the *e*-CO₂RR performance in prolonged electrolysis. 406

Based on the results of XPS and TEM analyses, a possible reaction pathway of I⁻ ionmediated e-CO₂RR at the developed *micro*CuI electrode was proposed and depicted in **Scheme** 1. Briefly, Cu⁰ species were generated via the electrochemical reduction of CuI under the applied cathodic current and oxidized to Cu²⁺ species [36] during e-CO₂RR. In the absence of

I⁻ ions, Cu²⁺ species precipitated with carbonate in the form of inactive copper (II) carbonate 411 hydroxide. In contrast, Cu²⁺ species can be reduced to form Cu⁺ species (i.e., Cu₂O) via the 412 redox reaction between Cu^{2+} species and I⁻ ions (Eq. 5) in the electrolyte containing I⁻ ions, 413 414 thereby limiting the formation of inactive copper (II) carbonate hydroxide. The coexistence of Cu⁰ and Cu₂O along with the presence of Cu⁰/Cu₂O interface with Cu⁰ embedded in Cu₂O 415 matrix (i.e., Figure 5d), provides dual sites for both CO₂ activation and C-C coupling [14, 15, 416 417 18, 43, 44], thereby boosting efficiency and selectivity for the generation of C_{2+} products in 418 prolonged electrolysis.

419 3.3 Electrocatalytic performance towards the conversion of low-concentration carbon 420 dioxide

421 Figure 7 shows the e-CO₂RR performance of the microCuI electrode at different applied current densities in KI (0.05 M)-containing KOH solution (1.0 M). As compared to electrolysis 422 performed at -100 mA cm⁻², electrolysis performed at -200 mA cm⁻² resulted in enhanced 423 424 selectivity of the microCuI electrode towards ethylene production (Figures 7b-7c). Notably, 2h electrolysis performed at -200 mA cm⁻² generated ethylene at a rate of 0.30 ± 0.01 mmol 425 $cm^{-2} h^{-1}$ with a current efficiency of 47.2 \pm 1.5%, whereas 2-h electrolysis performed at -100 426 mA cm⁻² generated ethylene at a rate of 0.14 ± 0.01 mmol cm⁻² h⁻¹ with a current efficiency of 427 428 44.5 \pm 2.2%. Nonetheless, the selectivity of the *micro*CuI electrode towards the generation of 429 C₂₊ products decreased with increasing applied current density and suffered instability at -300 mA cm⁻². Specifically, 2-h electrolysis performed at -100 mA cm⁻² generated C₂₊ products at 430 a rate of 0.23 \pm 0.06 mmol cm⁻² h⁻¹ with a CE_{C2+} of 76.7 \pm 2.2%, whereas those performed at 431

432	-200 mA cm ⁻² and -300 mA cm ⁻² , respectively, generated C ₂₊ products at rates of 0.42 ± 0.04
433	mmol cm ⁻² h ⁻¹ (CE _{C2+} : 69.4 \pm 1.50%) and 0.24 \pm 0.04 mmol cm ⁻² h ⁻¹ (CE _{C2+} : 25.9 \pm 4.3%).
434	To further evaluate <i>e</i> -CO ₂ RR performance of the developed <i>micro</i> CuI electrode, the cathodic
435	energy efficiencies (EE_{C2^+}) for the generation of C_{2^+} products, defined as the ratio of chemical
436	energy stored in the C_{2+} products to applied electrical energy (see Experimental Section for
437	the details), from 2-h electrolysis experiments at various applied current densities were
438	determined and summarized in Figure 7d. As revealed, the values of EE_{C2+} obtained at -100
439	mA cm ⁻² , -200 mA cm ⁻² , and -300 mA cm ⁻² were 48.8 \pm 1.8%, 39.3 \pm 1.1%, and 13.0 \pm 2.7%,
440	respectively. The excellent <i>e</i> -CO ₂ RR performance of the <i>micro</i> CuI electrode, in terms of CE_{C2+} ,
441	J_{C2+} , and EE_{ca} , at moderate J_{app} places itself among the most active Cu-based electrocatalysts
442	(Table S1). This finding indicates that regulation of OS_{Cu} by I ⁻ ions is an effective method to
443	enhance the <i>e</i> -CO ₂ RR performance of the <i>micro</i> CuI electrode. Figure S14 shows the <i>e</i> -CO ₂ RR
444	performance of the <i>micro</i> CuI electrode in the prolonged electrolysis at -100 mA cm ^{-2} in the KI
445	(0.05 M)-containing KOH solution (1.0 M). It can be found that the developed microCuI
446	electrode remained stable (CE _{C2H4} > 40%) during 12-h electrolysis at -100 mA cm ⁻² .
447	Specifically, However, the e-CO ₂ RR performance of the microCuI electrode decreased after
448	14-h operation due to the significant drop in the catholyte pH (from 13.8 to 10.4), induced by
449	dissolution of CO ₂ , as well as the flooding after 15-h operation. Reconfiguration of our
450	electrocatalytic system to improve stability is currently under investigation.

451 Figure S15 and Figure 8 show the *e*-CO₂RR performance of the *micro*CuI electrode 452 towards the conversion of low-concentration CO₂ gas (40%) in the simulated biogas

453	atmosphere. It can be found that the <i>micro</i> CuI electrode exhibited negligible activity towards
454	electrocatalytic reduction of low-concentration CO_2 in the absence of I ⁻ ions (Figure S15). In
455	contrast, the presence of $I^{\scriptscriptstyle -}$ ions significantly enhanced the selectivity and $\mathrm{EE}_{\mathrm{C2^+}}$ of the
456	microCuI electrode towards the generation of C2+ products from the electrocatalytic reduction
457	of low-concentration CO_2 in the simulated biogas atmosphere, generating C_{2+} products at a rate
458	of 0.15 ± 0.01 mmol cm $^{-2}$ h^{-1} with a CE $_{C2^+}$ of 47.7 \pm 7.5% and a EE $_{C2^+}$ of 27.1 \pm 4.1% after 2-
459	h electrolysis at -100 mA cm ⁻² . This finding highlights the beneficial role of I ⁻ ions in
460	regulating OS_{Cu} and creating abundant Cu^0/Cu^+ interface for both CO_2 activation and
461	stabilization of *CO intermediates, boosting the e-CO2RR performance of the microCuI
462	electrode towards the conversion of low-concentration CO_2 in the simulated biogas atmosphere.
463	As the presence of CO_2 (35-45%) significantly diminishes the heating value of the biogas [45,
464	46], the removal of CO_2 to upgrading biogas is of great importance. The acceptable CE_{C2+} and
465	EE_{C2^+} of the developed <i>micro</i> CuI electrode in the presence of a suitable amount of I ⁻ ions
466	suggest its potential application for the simultaneous electrochemical upgrading of biogas and
467	mitigating carbon emissions. It is important to note that the electrolysis in the presence of KI
468	(0.05 M) under the simulated biogas atmosphere yielded a lower CE_{C2^+} compared to that under
469	the concentrated CO_2 atmosphere. This decrease in CE_{C2^+} obtained under the simulated biogas
470	atmosphere was attributed to the significant loss in the current efficiency for the liquid C_{2^+}
471	products (i.e., ethanol and 1-propanol). For instance, the current efficiency for the generation
472	of C ₂ H ₄ remained similar (37.5 \pm 6.0% vs. 42.9 \pm 1.7%) when the CO ₂ concentration was
473	reduced from 98% to 40%, but the current efficiency for liquid C_{2+} products decreased

significantly from $32.2 \pm 1.6\%$ to $10.1 \pm 3.1\%$. While the mechanism behind is unclear at this 474 stage, the change in the ethylene/alcohol selectivity could be attributed to mass-transport 475 limitations induced by the use of the low-concentration CO₂ as the mass transport of CO₂ and 476 H₂O was reported to played an important role in regulating the relative surface coverage of 477 478 adsorbed CO and H atom and thus tuning the ethylene and ethanol pathways [47]. It is also important to note that the relative humidity of the simulated biogas atmosphere was ~33%, 479 480 which is higher than that ($\sim 14\%$) of the concentrated CO₂ atmosphere. To further investigate 481 the effects of humidity on the e-CO₂RR performance of the microCuI electrode towards the conversion of low-concentration CO₂ gas, additional electrolysis experiments were performed 482 483 under the humidified simulated biogas atmosphere (relative humidity: ~81%). As revealed in Figure 9, the CE_{C2+} of the *micro*CuI electrode decreased from $47.7 \pm 7.5\%$ to $30.3 \pm 2.4\%$ 484 when the relative humidity of the biogas was increased from 33% to 81%. This drop in CE_{C2+} 485 486 could be attributed to the reduced CO₂ availability, resulting from the blockage of pores of the 487 gas diffusion layer on the gas-diffusion electrode due to water accumulation under high-488 humidity conditions [48]. The impact of humidity on the product selectivity becomes more 489 significant when the concentration of CO₂ in the CO₂ gas feed was low since the mass transport 490 of CO₂ and H₂O had an important role in regulating the relative surface coverage of adsorbed 491 CO and H atom and thus tuning the reaction pathways [47]. The negative impact of humidity 492 on the CE_{C2+} could be minimized by the integration of the microCuI electrode with a 493 permselective membrane, such as Zn-based Metal-organic framework (Calgary Framework-20 [48]) that enables the selective permeation of CO₂ to the CuI electrocatalyst. 494

495 **4.** Conclusions

496 microCuI was successfully synthesized via the SILAR method, and its application as an efficient electrocatalyst for the selective generation of C₂₊ products (*i.e.*, ethylene, ethanol, and 497 498 1-propanol) from e-CO₂RR was thoroughly investigated. The microCuI electrode exhibited high selectivity for the generation of C_{2+} products but suffered instability due to the formation 499 of inactive copper (II) carbonate hydroxide within 2-h electrolysis at -100 mA cm⁻². The 500 501 presence of I⁻ ions effectively regulated the OS_{Cu} of surface active sites via its redox reaction with Cu²⁺ species, and thus minimized the formation of inactive copper (II) carbonate 502 503 hydroxide in the prolonged electrolysis. As compared to other halide ions, the presence of a 504 suitable amount of I⁻ ions not only minimized the corrosion, but also maintained OS_{Cu} at ~ 0.7 and facilitated the formation of Cu⁰/Cu₂O interfaces with Cu⁰ embedded in Cu₂O matrix, which 505 506 provides dual sites for both CO₂ activation and C-C coupling, resulting in the significantly enhanced stability in the prolonged electrolysis at -100 mA cm⁻². Notably, the high CE_{C2+} of 507 $73.6 \pm 2.2\%$ and high EE_{C2+} of $48.8 \pm 1.8\%$ of the *micro*CuI electrode at -100 mA cm⁻² in the 508 509 presence of I⁻ ion (0.05 M) places itself among the most active Cu-based electrocatalysts. The 510 I⁻ ion-mediated *e*-CO₂RR scheme was proposed and demonstrated to be an effective strategy 511 to enhance the CE_{C2+} and EE_{C2+} of the *micro*CuI electrode towards the generation of C_{2+} 512 products from the electrocatalytic reduction of low-concentration CO₂ in the simulated biogas 513 atmosphere. The microCuI electrode exhibited deteriorated performance towards the 514 conversion of low-concentration CO₂ in the humidified simulated biogas atmosphere, likely attributed to the limited CO2 availability. Efforts are underway to address the adverse effects of 515

516	impurity gas components (e.g., moisture, H ₂ S) in biogas by incorporating a permselective
517	membrane with the <i>micro</i> CuI electrode that enables the selective permeation of CO ₂ to the CuI
518	electrocatalyst are under investigation. Overall, the present contribution provides an effective
519	strategy for the efficient and selective production of C ₂₊ products via <i>e</i> -CO ₂ RR at the copper-
520	based electrocatalysts.

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- 734 Scheme caption
- 735

736 Scheme 1 The proposed reaction scheme of I^- ion-mediated *e*-CO₂RR at the developed 737 *micro*CuI electrode.

- 738 Figure captions
- 739 Fig. 1 Physical characterizations of the as-prepared microCuI electrode: (a) XRD pattern, (b-
- c) Top-view SEM images at 2,000X (b) and 10,000X (c) magnifications, (d) TEM
- 741 image, (e, f) HR-TEM image (e) and SAED pattern (f) of circled part of (d), (g)
- HAADF image, and (h, i) EDS elemental mapping images for Cu (h) and I (i).
- 743 Fig. 2 XPS spectra (a: Cu 2p region; b: I 3d region) of the as-prepared *micro*CuI electrode.

Fig. 3 (a) Potential transients obtained from (i) the 2-h electrolysis at -100 mA cm⁻² in blank
KOH solution (1.0 M), (ii) the pulsed electrolysis in blank KOH solution (1.0 M), and

(iii) the electrolysis at -100 mA cm^{-2} in KI (0.05M)-containing KOH solution (1.0 M).

(b) CEs of generated products obtained during electrolysis at -100 mA cm⁻² in blank
KOH solution. (c) CEs of the products obtained during pulsed electrolysis in blank
KOH solution (1.0 M), and (d) CEs of the products obtained during the electrolysis at
-100 mA cm⁻² in KI (0.05M)-containing KOH solution (1.0 M). The standard deviation

of the reported data was determined from a minimum of three repeated experiments.

Fig. 4 (a) GI-XRD patterns and (b) SEM image, (c) TEM image, (d) HR-TEM image, and (e)
SAED pattern of the *micro*CuI electrodes obtained after 8-h electrolysis at -100 mA
cm⁻² in KOH solution (1.0 M) containing KI (0.05M). The peaks assigned for CuI,
graphite/C, and Cu₂O are referred to JCPDS no. 06-0246, JCPDS no. 41-1487, and
JCPDS no. 05-0667, respectively.

757 Fig. 5 The *e*-CO₂RR performance of the *micro*CuI electrodes obtained from 8-h electrolysis

758	at -100 mA cm ⁻² in KOH solution (1.0 M) containing KI of various concentrations (i:
759	0 M; ii: 0.01 M; iii: 0.05 M; iv: 0.1 M): (a) Potential transients, (b) CEs of generated
760	products, (c) J_{C2+} , and (d) product generation rate (R). The standard deviation of the
761	reported data was determined from a minimum of three repeated experiments.
762	Fig. 6 (a) Cu 2p spectra and (b) Cu LMM spectra of the <i>micro</i> CuI electrode after 8-h <i>e</i> -CO ₂ RR

- 763in KOH solution (1.0 M) containing I⁻ ions of various concentrations (i: 0 M; ii: 0.05764M; 0.1 M). Peak A in (b) stands for other transition state of the Cu LMM spectrum. (c)765Content of Cu species deduced from XPS and AES analyses. (d) Correlation between766 CE_{C2+} and OS_{Cu} .
- 767Fig. 7The *e*-CO2RR performance of the *micro*CuI electrodes obtained from 2-h electrolysis768in KOH solution (1.0 M) containing KI (0.05 M) at different applied current densities769(i: -100 mA cm⁻²; ii: -200 mA cm⁻²; iii: -300 mA cm⁻²): (a) Potential transients, (b) CEs770of generated products, (c) R, and (d) EEc2+. The standard deviation of the reported data771was determined from a minimum of three repeated experiments.
- 772Fig. 8The e-CO2RR performance of the *micro*CuI electrodes obtained from 2-h electrolysis773at -100 mA cm⁻² in KI (0.05 M)-containing KOH solution (1.0 M) under simulated774biogas atmosphere with (i) 33% relative humidity and (ii) 81% relative humidity: (a)775Potential transients, (b) CEs of generated products, (c) product generation rate (R), and776(d) EE_{C2+}. The standard deviation of the reported data was determined from a minimum777of three repeated experiments.



















Figure 5



Figure 6



Figure 7



Figure 8

Electronic Supporting Information

Iodide-mediated electroreduction of carbon dioxide for efficient and selective electrosynthesis of multicarbon products over copper iodide microcrystals

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References

Determination of e**-TOF**_{C2+}**.** To access the intrinsic e-CO₂RR activity of the *micro*CuI electrode, the turnover frequency (e-TOF_{C2+}), based on the total amount of electrochemically available Cu⁰ (e-N_{Cu}) and Cu⁺ (e-N_{Cu+}) species, was determined using Eq. S1.

$$e \text{-TOF}_{C2+} = \frac{R_{C2+}}{e N_{Cu} + e N_{Cu^{+}}}$$
(S1)

where e-N_{Cu} and e-N_{Cu+} in the *micro*CuI electrodes were determined, after 8-h electrolysis at -100 mA cm⁻², using cyclic voltammetry (CV) at a scan rate of 10 mV s⁻¹ in NaOH solution (1.0 M, pH 14) (**Figure S11**). Briefly, e-N_{Cu} and e-N_{Cu+} were determined, respectively, by estimation of the charges responsible for the oxidation of Cu⁰ to Cu₂O (A₁ peak in **Figure S11**; Eq. S2), Cu⁰ to CuOH (A_{2a} peak in **Figure S11**; Eq. S3), and CuOH to Cu(OH)₂ species (A_{2b} peak in **Figure S11**; Eq. S4), and subsequent conversion with Faraday's law [1]. Note that the C₁, C_{2a}, and C_{2b} cathodic peaks were assigned, respectively, to the electrochemical processes listed in Eqs. S5-S7 [1]:

$$2\mathrm{Cu} + 2\mathrm{OH}^{-} \rightarrow \mathrm{Cu}_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} + 2e^{-} \qquad (S2)$$

$$Cu + OH^{-} \rightarrow CuOH + e^{-}$$
 (S3)

$$CuOH + OH^{-} \rightarrow Cu(OH)_{2} + e^{-}$$
 (S4)

 $2CuO_2^{2-} + 2e^- + 3H_2O \rightarrow Cu_2O + 6OH^-$ (S5)

 $CuO + H_2O + e^- \rightarrow CuOH + OH^-$ (S6)

$$CuOH + e^{-} \rightarrow Cu + OH^{-}$$
(S7)

Catalyst	Electrolyte	CEc2+ (%)	Jc2+ (mA cm ⁻²)	EEc2+ (%)	Ref.
E-Copper iodide-derived Cu	0.1 M KHCO3	74.96	-251.8 (at -1.2 V vs. RHE)	38.4	[2]
CuI-derived Cu nanofibers	1 M KHCO ₃	57.2	~ -14.3 (at -0.73 V vs. RHE)	32.5ª	[3]
Cu-CuI composite	1 M KOH	71	-591 (at -1 V vs. RHE)	39.1ª	[4]
CuI	0.1 M KHCO3	32	~ -3.3 (at -1 V vs. RHE)	16.7ª	[5]
CuI	0.1 M KHCO3	65.21	~ -26.1 (at -1.74 V vs. RHE)	28.1ª	[6]
Cu@CuI composite	1 M KOH	75.7	-288 (at -1.57 V vs. RHE)	31.8 ^a	[7]
Cu5Ga1	1 M KOH	~80%	~ -800 (at ~ -0.65 V vs. RHE)	>50	[8]
Nafion [®] -modified iodide-derived Cu	0.1 M KHCO3	~40% (C ₂ H ₆)	~ -3.4 (at -0.7 V vs. RHE)	24.3ª	[9]
Mixture of fluorinated carbon black and Cu nanoparticles	0.1 M KHCO3	55.6 (C ₂ H ₄)	-175.7 (C ₂ H ₄ ; at -3.7 V)	17.6 (Full cell EE)	[10]
diethanolamine-modified Cu	2 M KCl	50.5 (C ₂ H ₄)	-155.7 (C ₂ H ₄ ; at -1.1 V vs. RHE)	24.9	[11]
Cu NCs@Cu-BTC	1 M KCl	92.3	- 276.9	46.9 ^a	[12]
NiCu-SACs/N-C	0.5 M KHCO3	~92 (Ethanol)	~11 (Ethanol; at -0.6 V vs. RHE)	57	[13]
CuPOF-Bpy/Cu2O@CNT	0.5 M KHCO3	71 (C ₂ H ₄)	~ -31 (C ₂ H ₄ ; at -1.1 V vs. RHE)	35 ^a	[14]
H–Cu ₂ O@C/N	0.1 M KHCO3	59.2	~ -27.4 (at -0.9 V vs. RHE)	33.1 ^a	[15]
Fluorine-modified copper	2.5 M KOH	84	-800 (at -0.54 V vs. RHE)	55	[16]
O ₂ -plasma-oxidized Cu foil	0.1 M KHCO ₃ +0.3 M KI	61.7	\sim -58 ^b (at -1 V vs. RHE)	33.7 ^a	[17]
KI-pretreated Cu foil	0.1 M KHCO3	80	-31.2 (at -0.9 V vs. RHE)	45.5ª	[18]
CuCl-assisted reconstructed Cu	3 M KOH	84	-336 (at -0.68 V vs. RHE)	50	[19]

Table S1 Comparison of the e-CO₂RR performance of the developed *micro*CuI electrode with those reported previously.

Dodecanethiol-modified CuBr	0.5 M KCl	35.9	~-4.5 (Ethanol; at -1.25 V vs. RHE)	32.7ª	[20]
AgI–CuO	1 M KHCO ₃	63.2	-86.4 (at -1.05 V vs. RHE)	30.6 ^a	[21]
Fluorine-doped Cu single-atom catalyst	1 М КОН	50.8	~-450 (at -1 V vs. RHE)	26.2 ª	[22]
<i>micro</i> CuI	1 M KOH containing 0.05M KI (98% CO ₂)	$73.6\pm2.2^{\rm c}$	-73.6 ± 2.2 ^c (~ -0.74 V vs. RHE)	$48.8 \pm 1.8^{\rm c}$	This work
		$69.4 \pm 1.5^{\circ}$	$-138.8 \pm 3.0^{\circ}$ (~ -0.82 V vs. RHE)	$39.3\pm1.1^{\circ}$	
	1 M KOH containing 0.05M KI (40% CO ₂)	$47.7\pm7.5^{\rm c}$	-47.7 ± 7.5° (~ -0.71 V vs. RHE)	$27.1 \pm 4.1^{\circ}$	

^{a:} Based on the readings of the presenting curves and/or information on the applied current density/potential and CE_{C2+} ; ^b: J_{total}; ^c: The standard deviation of the reported data was determined from a minimum of three repeated experiments.



Scheme S1 Schematic illustration of the developed three-electrode two-compartment flow type electrolyzer.





Figure S1 (a) GI-XRD patterns of the as-prepared *micro*CuI electrode (i) and the *micro*CuI electrodes obtained after 1-h (ii) and 2-h (iii) electrolysis at -100 mA cm⁻² in KOH solution (1.0 M). The peaks assigned for CuI, graphite/C, Cu₂CO₃(OH)₂, and Cu₂O are referred to JCPDS no. 06-0246, JCPDS no. 41-1487, JCPDS no. 76-0660, and JCPDS no. 05-0667, respectively. (b) SEM image of the *micro*CuI electrode obtained after 2-h electrolysis at -100 mA cm⁻² in KOH solution (1.0 M).



Figure S2 (a) GI-XRD patterns and (b) SEM image of the *micro*CuI electrodes obtained after
8-h pulse electrolysis at -100 mA cm⁻² (12 h total duration) in blank KOH solution (1.0 M).
The peaks assigned for CuI, graphite/C, and Cu₂O are referred to JCPDS no. 06-0246, JCPDS
no. 41-1487, and JCPDS no. 05-0667, respectively.



Figure S3 (a-d) SEM images of the as-prepared *micro*CuI electrode (a) and the *micro*CuI electrodes obtained after electrolysis at -100 mA cm-2 in KOH (1.0 M) solution containing KI (0.05 M) for different durations (b: 2 h; c: 6 h; d: 8 h). (e) EDS-determined I⁻ content (atomic %) of the *micro*CuI electrodes.



- **Figure S4** (a) HAADF image and (b-d) EDS elemental mapping of aggregated nanoparticles.
- 36 Scale bar: 50 nm.





Figure S5 The *e*-CO₂RR performance of the *micro*CuI electrodes obtained from 8-h 41 electrolysis at -100 mA cm⁻² in KHCO₃ (1.0 M) solution containing KI of various 42 concentrations (i: 0 M; ii: 0.05 M): (a) Potential transients and (b) CEs of generated products. 43 The standard deviation of the reported data was determined from a minimum of three repeated 44 experiments.





Figure S6 The *e*-CO₂RR performance of the *micro*CuI electrode obtained from pulse-current
electrolysis in KOH (1.0 M) solution containing KI (0.05 M): (a) Potential transients and (b)
CEs of generated products.





Figure S7 The *e*-CO₂RR performance (a: Potential transients; b: CEs of generated products)
of the *micro*CuI electrodes obtained from 8-h electrolysis at -100 mA cm⁻² in KOH (1.0 M)
solution containing (i) KCl (0.05 M), (ii) KBr (0.05 M), and (iii) KI (0.05 M). The standard
deviation of the reported data was determined from a minimum of three repeated experiments.



Figure S8 The *e*-CO₂RR performance (a, c: Potential transients; b, d: CEs of generated products) of the *micro*Cu electrode obtained from 6-h electrolysis at -100 mA cm⁻² in (a, b) the blank KOH (1.0 M) solution, and (c, d) KI 0.05 M-containing KOH (1.0 M) solution. The standard deviation of the reported data was determined from a minimum of three repeated experiments.



S9 (a) GI-XRD pattern and (b) top-view SEM image of the *micro*Cu electrode.



Figure S10 (a, b) CVs of the *micro*CuI electrode after 8-h electrolysis in (a) blank KOH solution (1 M) and (b) KI (0.05M)-containing KOH solution (1 M) recorded at various scan rates (i: 10 mV s⁻¹; ii: 30 mV s⁻¹; iii: 50 mV s⁻¹; iv: 75 mV s⁻¹; v: 100 mV s⁻¹) in KHCO₃ solution (1 M). (c) Corresponding plots of ΔJ vs. scan rate. ΔJ is the sum of the anodic and cathodic current densities measured at open-circuit potential (OCP) from (a-b). (i) Blank KOH solution (1 M); (ii) KI (0.05M)-containing KOH solution (1 M).



Figure S11 CVs of the *micro*CuI electrodes obtained after 8-h electrolysis (i) in the blank KOH solution and (ii) in the KI (0.05 M)-containing KOH (1.0 M) solution. The CVs were performed at a scan rate of 10 mV s⁻¹ in NaOH solution (1.0 M).





94 Figure S12 The *e*-CO₂RR performance of the *micro*CuI electrodes obtained from 8-h 95 electrolysis at -100 mA cm⁻² in KOH (1.0 M) solution with the addition of KI (0.05 M) at 2nd 96 h during the electrolysis: (a) Potential transients and (b) CEs of generated products. The 97 standard deviation of the reported data was determined from a minimum of three repeated 98 experiments. 99



Figure S13 GI-XRD patterns of the *micro*CuI electrode obtained after 8-h electrolysis at -100
mA cm⁻² in KOH solution (1.0 M) with the addition of KI (0.05 M) at 2nd h during electrolysis.
The peaks assigned for CuI, graphite/C, Cu₂CO₃(OH)₂, and Cu₂O are referred to JCPDS no.
06-0246, JCPDS no. 41-1487, JCPDS no. 76-0660, and JCPDS no. 05-0667, respectively.



Figure S14 The *e*-CO₂RR performance of the *micro*CuI electrodes obtained from 15-h 109 electrolysis at -100 mA cm⁻² in KOH (1.0 M) solution containing KI (0.05 M): (a) Potential 110 transients and (b) CE_{C2H4} and R_{C2H4} traces.



Figure S15 The *e*-CO₂RR performance of the *micro*CuI electrodes obtained from 2-h
electrolysis at -100 mA cm⁻² in KOH solution (1.0 M) under simulated biogas atmosphere.

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