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## 1. Introduction

The steadily rising levels of atmospheric carbon dioxide ( $CO_2$ ) are of growing concern as they are the cause of the current global climate change.<sup>1,2</sup> Although  $CO_2$  can be fixed *via* photosynthesis, the natural carbon cycle is not enough to compensate the increasing excessive  $CO_2$  emissions from fossil fuels that humans heavily rely on.<sup>3</sup> For sustainable carbon cycle, additional carbon fixation processes such as carbon capture and utilization (CCU) technology have been proposed, and electrochemical  $CO_2$  reduction reaction ( $CO_2RR$ ) has gained interest as

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# Controlling the C2+ product selectivity of electrochemical CO<sub>2</sub> reduction on an electrosprayed Cu catalyst<sup>†</sup>

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Cu catalysts prepared by modifying bulk Cu foils have achieved high performance for value-added C2+ compounds from electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>RR) but the transformation of active sites can be affected by the bulk substrate, which make it complex to design the catalyst. Herein, we newly introduce a simple electrospray pyrolysis method to take advantage of a facile wet-chemical synthesis applicable on non-copper substrates, such as a porous carbon paper, and demonstrate highly enhanced selectivity for  $C_2H_4$  production from CO<sub>2</sub>RR. The electrosprayed copper oxide on the carbon paper showed uniquely improved C2 selectivity compared with that on the copper substrate. The improved performance is proposed to be related to the presence of Cu mixed state and retention of morphology of the electrosprayed catalyst on the carbon paper, showing the importance of the substrate. In addition, the C2 product selectivity can be tuned by the electrospray synthesis time as it affects the size of the surface nanostructure as well as the porosity of the catalyst, which can provide an effective way to regulate the C2/C1 ratio.

one of these promising carbon fixation processes. CO or  $HCOO^-$  has been aimed at for obtaining promising chemicals from  $CO_2RR$  due to techno-economical analysis and life cycle assessment consideration as they can be used for Fischer-Tropsch synthesis or hydrogen storage.<sup>4,5</sup> Various metals (Ag, Au, Zn, Bi, and Pd) and modified carbon (N-doped carbon, Fe-N-C, and Ni-N-C) materials have been developed, which have high performance, product selectivity, and up to ~95% faradaic efficiency (FE).<sup>6-11</sup>

CO<sub>2</sub>RR can also be used to produce value-added multicarbon chemicals such as C<sub>2</sub>H<sub>4</sub>, which is widely used in polymer synthesis and the chemical engineering industry.12 To produce multi-carbon chemicals, understanding C-C bond formation reaction is important, and, notably, Cu is a unique single metal element that is promising in the production of C2+ compounds.<sup>13,14</sup> The activity and stability of C<sub>2</sub>H<sub>4</sub> production has been reported to be affected by sub-surface oxygen or oxidized Cu species, as with the Cu-O catalyst.15-19 C2H4 production activity can also be effectively increased by controlling the surface structure of metallic Cu or by inducing a local pH gradient by mass transfer.<sup>20-22</sup> However, because of the complexity of the CO2RR products as well as the variety of Cu-based catalyst preparation methods, extensive research is still underway to develop a coherent descriptor for selective activity. Furthermore, beyond the nature of the Cu surface, recent studies have demonstrated the importance of catalyst loading systems and electrochemical cell design to improve

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#### Paper

CO<sub>2</sub>RR activity.<sup>23</sup> The catalyst has been applied to a porous carbon electrode as a gas diffusion layer (GDL) electrode or as a specially designed flow cell system.<sup>17,24,25</sup> However, to improve the design of such catalyst systems, it is still necessary to better understand how the selectivity of C2+ products is affected by the catalyst amount.

Cu-based electrocatalysts for CO2RR have been wetchemically synthesized from metal precursor solutions to control their morphologies. A separate process is then typically employed to load the catalyst onto the electrode substrate and binder chemicals are often added, which complicates the understanding of catalytic activity as well as the preparation of the catalyst electrode. Meanwhile, many of the high performing Cu catalysts have been directly prepared by modifying the bulk Cu polycrystalline foil surface<sup>19,26,27</sup> but these catalysts on the foil are difficult to directly transfer to a porous electrode application. In addition, the morphology of the copper catalyst is known to be transformed chemically or electrochemically during CO<sub>2</sub>RR<sup>18,28,29</sup> and the effect of the underlying copper foil cannot be ignored. Given these limitations, a new and simple wet-chemical synthetic approach can allow the scalable preparation of the catalyst electrode with wide application potential.

In this study, we developed a one-step synthesis method to prepare oxidized Cu catalysts using electrospray pyrolysis on porous carbon papers (Scheme 1). This method has the advantages of simultaneous catalyst synthesis from the precursor solution and electrode fabrication. It also eliminates



Scheme 1 One-step Cu-based electrode preparation *via* electrospray pyrolysis method.

the need for a separate process to spray the catalyst onto the substrate after the synthesis. Compared with a Cu foil catalyst, the prepared CuO catalyst-porous carbon support showed threefold enhanced CO<sub>2</sub>RR performance, especially for C<sub>2</sub>H<sub>4</sub> production. These results suggest that the interaction of both the catalyst and the substrate is important in  $CO_2RR$ . We also observed that the synthesized nanoparticles enlarged and their shape changed with increasing reaction time, and this enlargement was related to a decrease in the C<sub>2</sub>H<sub>4</sub> selectivity. The ratio of  $C_2H_4/CH_4$  could be controlled by adjusting the amount of the sprayed catalyst. With this structural improvement and chemical state changes, our catalyst showed a FE of C<sub>2</sub>H<sub>4</sub> up to 52% and also showed higher than 70% selectivity for C2+ compounds. In addition, the FE for the hydrogen evolution reaction (HER) was significantly suppressed, *i.e.*, down to 10%. Our synthetic method can be widely applied to other conductive substrates and CO<sub>2</sub>RR reactor systems, including the fabrication of porous electrodes.

## 2. Experimental section

## One-step synthesis of CuO catalyst-substrate by electrospray pyrolysis

The CuO spray nanoparticle (CSNP) catalyst was synthesized using an electrospray system (Nano NC, NNC-ESP 200T; Korea) on a porous carbon paper substrate (Toray, TGP-H-120). The precursor solution for electrospray deposition was prepared using 0.03 M copper(II) nitrate trihydrate (77-80%  $Cu(NO_3)_2 \cdot 3H_2O$  assay, Shinyo Pure Chemical) dissolved in ethanol (99.8%, Sigma-Aldrich) and was sprayed through a stainless steel needle tip (27 G; 13 mm) using a syringe pump system (NORM-JECT®; Luer Lock; Henke Sass Wolf Germany). During the electrospray pyrolysis, the carbon paper substrate (4 cm  $\times$  4 cm) was heated to 350 °C on a temperature control plate (TZ4M, Autonics) and the high direct current (DC) voltage between the nozzle and the carbon paper substrate was adjusted to 20 kV to change the solution droplets to an aerosol, which was then sprayed. The distance from the needle tip to the substrate was fixed at 9 cm and the spray precursor solution was pumped at the rate of 15  $\mu$ L min<sup>-1</sup>. To ensure the uniformity of electrospray on the substrate, the substrate was placed between PTFE masks with a hole of dimensions 5.5 cm  $\times$  5.5 cm. For the control sample, CSNP was prepared on a Cu foil (Alfa Aesar, 99.9999%) under the same conditions, except Cu foil was used as the substrate.

#### Electrochemical measurement of the CO<sub>2</sub> reduction reaction

The performance of the prepared catalysts for CO<sub>2</sub>RR was measured in an electrochemical cell divided into two sections by an anion exchange membrane (Selemion AMV) to avoid the crossover of gaseous products as well as liquid products. This electrochemical cell was made of polyether ether ketone (PEEK), which has strong chemical resistance. A CSNP sample working electrode and an Ag/AgCl reference electrode (Basi, 3 M NaCl) were placed in the cathode section, and a platinum counter electrode was put in the other part. The geometrical areas of all the samples were fixed as 0.503 cm<sup>2</sup> for better comparison. All the electrochemical potentials and currents were measured by a potentiostat (Ivium technology). To prevent contamination, all the apparatus were washed prior to CO<sub>2</sub>RR and 0.1 M KHCO<sub>3</sub> (Sigma-Aldrich, 99.95%) electrolyte solution was prepared with deionized water (18.2 M $\Omega$  cm). At every applied potential, the working electrode sample was replaced with a fresh one to prevent unpredictable contamination and surface state change. For long-term stability, CO<sub>2</sub> RR was conducted at one fixed potential. The measured potential values were converted to reversible hydrogen electrode (RHE) values using the equation below.

$$E_{\rm R}$$
 (vs. RHE) =  $E_{\rm A}$  (vs. Ag/AgCl) + 0.209 V + 0.05916 × pH

To compensate for resistance loss, solution resistance ( $R_s$ ) was analyzed by electrochemical impedance spectroscopy (EIS) in the range from 1000 to 0.1 Hz; the general values of  $R_s$  were fitted and found to be 75–80  $\Omega$  in CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub>, whose pH was measured to be 6.8.

#### Analysis of CO<sub>2</sub> reduction reaction products

The gaseous products at each fixed potential were quantitatively detected using a gas chromatograph (GC, Agilent 6890N), which was directly linked to the top of the cathode. The sample injection was controlled by a six-port valve. During CO<sub>2</sub>RR, high purity CO<sub>2</sub> gas ( $\geq$ 99.999%) was continuously flowed without interruption in each compartment of the electrochemical cell. The CO<sub>2</sub> gas flux was regulated with a mass flow meter to maintain the flow rate of 20 mL min<sup>-1</sup>, which was measured at an outlet by a universal flow meter (Agilent, AMD 2000 and ADM Flow meter). A Carboxen 1000 (15 ft, Supelco) packed column was installed in the GC to separate H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The GC had two detectors, namely, a thermal conductivity detector (TCD) and a flame ionization detector (FID) with a methanizer for measuring H<sub>2</sub> and others carbon based gases (CH<sub>4</sub>, CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>), respectively. The carrier gas was Ar ( $\geq$ 99.999%).

$$i_{\rm x} = \frac{C_{\rm x} \times q \times p}{RT} \times n_{\rm x}F \tag{1}$$

$$FE(\%) = \frac{i_x}{i_{\text{total}}} \times 100\%$$
(2)

Eqn (1) was used to calculate the partial current ( $i_x$ ) of each of the products ( $x = H_2$ , CH<sub>4</sub>, CO, C<sub>2</sub>H<sub>4</sub>, or C<sub>2</sub>H<sub>6</sub>).  $C_x$  is the volumetric concentration of the products, q is the gas flux, p is the pressure, R is the ideal gas constant (8.314 m<sup>3</sup> Pa K<sup>-1</sup> mol<sup>-1</sup>), Tis the temperature,  $n_x$  is the equivalent number of electrons required by CO<sub>2</sub> RR for each product x, and F is the Faraday constant (96 485 s A mol<sup>-1</sup>). Then, the faradaic efficiency (FE) was obtained from eqn (2), where  $i_{\text{total}}$  is the total current density measured by chronoamperometry during CO<sub>2</sub>RR. The <sup>13</sup>CO<sub>2</sub> (Cambridge Isotope Laboratories, Inc.; 99%) isotope experiments were performed using gas chromatography-mass spectroscopy (GC-MS; Agilent) composed of a 6890 GC system and a 5973 mass selective detector. The liquid products were collected at the catholyte after bulk electrolysis and quantified by nuclear magnetic resonance (NMR; DD2, Agilent, 600 MHz). The formate ion (HCOO<sup>-</sup>) was quantitatively analyzed using the phenol internal standard and the other liquid products were analyzed with the DMSO internal standard. The FE of each liquid product was calculated using eqn (3).

$$FE_{liquid}(\%) = \frac{L_{c} \times V_{catholyte} \times n_{y}F}{C_{total}}$$
(3)

where,  $C_{\text{total}}$  is the total charge during bulk electrolysis and  $L_{\text{c}}$  is the detected liquid product concentration. The catholyte volume is expressed as  $V_{\text{catholyte}}$  and the electron demand of each liquid product (y = HCOO<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>OH, and C<sub>3</sub>H<sub>7</sub>OH) is expressed as  $n_{\text{y}}$ .

#### Material characterization

The surface morphology of each working electrode was analyzed by field emission scanning electron microscopy (FE-SEM, FEI, Inspect F) and the morphology was analyzed in more detail by transmission electron microscopy (TEM, Titan<sup>TM</sup> and Technai<sup>TM</sup>). The crystal structure was confirmed by grazing incidence X-ray diffraction (GI-XRD, Rigaku corporation, D/Max 2500). The differences in the chemical state of the catalyst were analyzed by high-performance X-ray photoelectron spectroscopy (HP-XPS, Thermo-Fisher Scientific, K-Alpha XPS system) equipped with an Al K $\alpha$  monochromator (1486.6 eV).

#### Measurement of in situ/operando XAS

Cu K-edge X-ray absorption spectroscopy (XAS) was performed using hard X-rays at the 1D beamline of the Pohang Accelerator Laboratory (PAL) to characterize the Cu status *in situ/operando* CO<sub>2</sub>RR condition. The X-ray adsorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were employed to analyze the standard samples, and the catalyst was also analyzed through the measured spectra.

The CSNP/CP working electrode was masked with Kapton polyamide tape and installed in the electrochemical cell facing the backside of the electrode in the window of the electrochemical cell to prevent interruption by the aqueous electrolyte. The synchrotron radiation beam was positioned to illuminate the backside of the working electrode and XAS was measured using a fluorescence detector. Identical  $CO_2RR$  conditions were applied during the XAS measurements. High purity (99.999%)  $CO_2$  gas was continuously flowed into the 0.1 M KHCO<sub>3</sub> electrolyte. A Pt coil and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. A potentiostat (Ivium Vertex) was used to generate a potential difference of -1.0 V vs. RHE at the working electrode. Under the  $CO_2RR$ conditions, the X-ray absorption spectra were measured at 5, 35, 65, and 105 min. Each spectrum measurement took 30 min.

### 3. Results and discussion

The catalyst synthesized with electrospray pyrolysis on carbon paper was the shape of a cluster of nanoparticles that grew well



Fig. 1 SEM image, XRD pattern, and *ex situ* Cu K-edge XANES spectra of the (a and b) CSNP/CP; (c) XRD pattern of CSNP/CP and carbon paper; (d) Cu K-edge XANES spectra of CSNP/CP and the reference material.

on the carbon fiber of the carbon paper and had a size in the range of 30 to 40 nm (Fig. 1a and b). An XRD and Cu K-edge XANES analysis was conducted to confirm the crystal structure and chemical composition of copper electrospray nanoparticle (CSNP) catalyst synthesized on carbon paper. The crystal structure of the CSNP catalyst could be estimated as the CuO crystal structure (JCPDS #05-0661) through the CuO main peak at 35.6 and 38.8 degrees, excluding the peak from carbon paper

using XRD analysis (Fig. 1c). In addition, the XANES spectra of CSNP was similar to the XANES fingerprint of CuO when compared with the Cu K-edge XANES spectra of Cu-foil, Cu<sub>2</sub>O, and CuO reference materials (Fig. 1d). These results confirm that the initial state of the synthesized CSNP catalyst was CuO.

When the CuO spray-nanoparticles were prepared on carbon paper (CSNP/CP) and linear sweep voltammetry (LSV) in CO<sub>2</sub>- or Ar-saturated electrolyte condition was carried out, the current density became larger in CO2-saturated electrolyte under high overpotential ranges (Fig. S1<sup>†</sup>). This might be because CSNP catalyze HER in the absence of CO<sub>2</sub> but when CO<sub>2</sub> is present, CO2 or CO2RR intermediates adsorb on the catalyst surface, which block the HER active sites. So, it significantly increases the C<sub>2</sub>H<sub>4</sub> production selectivity and suppressed the HER compared to bare Cu-foil in high overpotential region (Fig. 2a). In the Cu foil case, the selectivity for C<sub>2</sub>H<sub>4</sub> was poor  $(FE_{C,H_{c}} = 13.6\%)$  but a further disadvantage was that almost half of the total reaction current was used for HER ( $FE_{H_{a}} =$ 46.7%). In contrast, CSNP/CP reduced the HER selectivity by 19.8% but C<sub>2</sub>H<sub>4</sub> generation selectivity increased to 48.7%. We performed <sup>13</sup>CO<sub>2</sub> isotope experiment to confirm that the carbon origin of the CO<sub>2</sub>RR products is indeed the CO<sub>2</sub> molecule (Fig. S2<sup>†</sup>). When normal CO<sub>2</sub> was used, a major signal was observed at MW = 28 and no signal was observed at MW = 30 in the typical  ${}^{12}C_2H_4$  spectrum. Meanwhile, in the  ${}^{13}CO_2$  experiment, the signal in the mass spectrum was shifted by two at MW = 30 (*i.e.*,  ${}^{13}C_2H_4$ ). In addition, we also confirmed that when only carbon paper was used as the cathode, only H<sub>2</sub> was produced and no CO<sub>2</sub>RR production was observed, indicating that CSNP catalyses the reduction reaction of  $CO_2$  (Fig. 4b).



Fig. 2 Characterization of CSNP and Cu foil sample; (a) comparison of each sample's performance; (b) stability of gaseous products of CSNP Cu; SEM images of (c) 2 hours post CO<sub>2</sub>RR sample of CSNP/CP and (d) 30 hours post CO<sub>2</sub>RR sample of CSNP/CP.

In addition, CSNP/CP was able to maintain high  $C_2H_4$  selectivity and suppressed the HER activity for 20 h but after some time,  $C_2H_4$  selectivity slowly decreased and HER was increased (Fig. 2b). In this stability experiment, CSNP/CP showed that the particle shape and size changed with reaction time. After 2 hours of CO<sub>2</sub>RR, it is not much different from the initial morphology (Fig. 2c). However, after 30 hours of reaction, the structure of the catalyst was electrochemically reconstructed, and small nanoparticles of 30 to 40 nm in size almost disappeared and changed into large particle of various shapes (Fig. 2d).

To understand why C2 selectivity was increased and HER was suppressed in CSNP/CP compared to Cu foil, CSNP was also synthesized on Cu foil (CSNP/Cu) to compare the CO2RR performance (Fig. S3<sup>†</sup>). Our expectation was that CSNP/Cu would have high C<sub>2</sub>H<sub>4</sub> selectivity and HER suppressed effects. CSNP/Cu, however, had high selectivity for C2H4 in CO2RR products but also had high hydrogen selectivity ( $FE_{H_2} = 56.6\%$ ) (Fig. 3a). When electrospraying the same volume of precursor solution (2 mL), the catalyst amount of CSNP/Cu (59.2  $\mu$ g cm<sup>-2</sup>) was higher than that of CSNP/CP (38.4  $\mu$ g cm<sup>-2</sup>) but CSNP/CP showed better performance. The difference in HER performance in CSNP according to these substrates was presumed to be because the HER activity of carbon paper was much lower than that of the Cu foil (Fig. S4<sup>†</sup>). In a previous study, when copper oxide catalysts were electrodeposited on the Cu-foil substrate,<sup>30,31</sup> it was ambiguous whether or not the bottom Cu foil affected CO<sub>2</sub>RR. In our comparison, CO<sub>2</sub>RR to C<sub>2</sub>H<sub>4</sub> production was greatly enhanced when the CSNP was loaded on carbon paper, suggesting that is Cu foil is inferior to carbon paper as a CO<sub>2</sub>RR support.

In addition, the morphology change in CSNP/CP by reaction time was observed through SEM (Fig. S5<sup>†</sup>); the particle size increased to more than 100 nm after 15 hours of CO<sub>2</sub>RR and at that moment, the C2 selectivity began to decrease (Fig. S5b† and 2b). After 30 hours, particles of size 200 nm and cubes of sizes 300-400 nm were formed (Fig. S5c<sup>†</sup>), and after 60 hours, only 300-400 nm sized-cubes remained (Fig. S5d<sup>+</sup>). Therefore, maintaining the initial morphology of the catalyst may be an important factor in C-C coupling. However, in CSNP/Cu, the shape of the catalyst changed rapidly after CO<sub>2</sub>RR for 2 hours (Fig. S6<sup>†</sup>). Also, the typical oxygen-Cu combination catalysts exhibited a relatively rapid surface reconstruction within a few hours ( $\sim$ 2 hours) due to the reductive potential of CO<sub>2</sub>RR.<sup>18,28,29</sup> On the other hand, CSNP/CP well maintained the initial morphology after 2 hours (Fig. 2c). This result suggests that carbon paper may be a better support than Cu foil in terms of catalyst stability and performance.

Nevertheless, both CSNP/CP and CSNP/Cu showed good C–C coupling ability in  $CO_2RR$  (Fig. 3a). The HR-TEM images of the pre-/post- $CO_2RR$  sample simply showed that the overall dimension of the nanostructures were similar and the post- $CO_2RR$  sample had defective structures (Fig. S7†) both on the porous carbon substrate and on the Cu-foil. Although we also do not believe that the defect sites were identically maintained, the nanostructure and defective structure of the as-sprayed CSNP sample could contribute to the transformation of the catalyst having defects. Because only the TEM images are not enough to characterize the details of the defective sites and compare their nature on the porous carbon and Cu-foil, it is difficult to clarify that the defect sites are the only origin of the high  $C_2H_4$  production activity of CSNP/CP. However, we believe



Fig. 3 The CSNP/Cu and CSNP/CP performance compared and Cu  $2p_{3/2}$  XPS peak in the CSNP/CP catalyst, Cu K-edge *in situ/operando* X-ray absorption spectroscopy analysis; (a) FE compared with CSNP/Cu and CSNP/CP; (b) Cu  $2p_{3/2}$  XPS peak deconvolution for pre-CO<sub>2</sub>RR CSNP sample; (c) Cu K-edge EXAFS spectra of the Cu foil and *in situ/operando* CSNP/CP data; (d) Cu K-edge XANES spectra of the Cu foil and Cu<sub>2</sub>O, and the *in situ/operando* CSNP/CP data.

that the interaction between CSNP and carbon support can affect the formation of defective structures. Recent studies have demonstrated that the initial copper oxide nanoparticles can have morphology transformation and form defective sites on the carbon support,<sup>32,33</sup> which contribute to enhancement of  $CO_2RR$ -to- $C_2H_4$  conversion.

Interestingly, the total current density of CSNP/Cu and CSNP/CP was similar, compared to the significant difference in HER performance of the substrate (Fig. S8<sup>†</sup>). We conducted further analysis to determine the difference between the porous carbon substrate and the Cu-foil substrate. Therefore, we additionally performed XPS analysis to understand the Cu states. High performance XPS analysis before and after the CO2RR of CSNP/Cu and CSNP/CP was compared. CSNP/CP had a Cu  $2p_{3/2}$  peak at the binding energy of 934.5 eV before CO<sub>2</sub>RR, which was 0.2 eV higher than that for CSNP/Cu (Fig. 3b). Even after CO<sub>2</sub>RR, these binding energy differences were observed to be maintained (Fig. S9<sup>†</sup>). These binding energy differences can be induced because carbon has higher electronegativity than Cu. Similarly, in other electrocatalyst cases, the chemical states of the metal element were reported to have changed as a result of the interaction between the catalyst and the support.<sup>34-36</sup> These results suggest that each substrate influences the chemical state of the CSNP catalyst. It is also assumed that the CSNP catalyst is more electron deficient on carbon paper than on Cufoil.

Using in situ/operando Cu K-edge extended X-ray absorption fine structure (EXAFS) analysis, it was confirmed that the defect site in CSNP/CP mentioned above was maintained during CO<sub>2</sub>RR (Fig. 3c). The ex situ EXAFS of the reference material was assigned to the Cu-O characteristic at 1.5 Å and the Cu-Cu feature at 2.2 Å, respectively, similar to that in previous reports (Fig. S10<sup>†</sup>).<sup>26,37</sup> The in situ/operando EXAFS results showed that the Cu-O characteristics at 1.5 Å were retained after the initial 5 min reaction but the subsequent EXAFS measurement showed a decrease in Cu-O and only the Cu-Cu feature remained. These results are consistent with the previously reported studies that showed the Cu metallic state under CO<sub>2</sub>RR conditions.<sup>38,39</sup> However, CSNP/CP maintained a lower intensity of the Cu-Cu feature at 2.2 Å than that of the Cu foil during CO<sub>2</sub>RR. This result means that the average coordination number of CSNP/CP during CO<sub>2</sub>RR was less than 12 for Cu foil. If there are many defect sites in the catalyst, the coordination number of Cu-Cu will decrease. Therefore, it could be assumed that CSNP/CP maintained the defect site well for 105 min during the reaction.

However, in the *in situ/operando* Cu K-edge X-ray absorption near edge structure (XANES) analysis, the chemical state of CSNP/CP during the reaction was different than that of the conventional Cu metal reference (Fig. 3d). CSNP/CP showed a different XANES fingerprint pattern from Cu foil even in a strong reduction environment (-1.0 V vs. RHE) where CO<sub>2</sub>RR occurs. The XANES spectra of the Cu foil reference material showed a characteristic peak at 8988 eV, 8998 eV, and 9019 eV. These characteristic peaks were also observed in CSNP/CP but compared to the Cu foil spectra, the position and shape were slightly different. When compared with the XANES spectra of bulk Cu<sub>2</sub>O reference material, we could estimate the peaks of CSNP/CP that overlap with the characteristic peaks of  $\rm Cu_2O$  (red arrow in Fig. 3d).

This result indicated that CSNP/CP may have an oxidized state during the reaction. In order to accurately estimate the degree of oxidation, linear combination fitting (LCF) was carried out on the in situ/operando data of CSNP/CP. The LCF results for each in situ/operando data were fitted with the mixed state of Cu<sup>0</sup>, Cu<sub>2</sub>O, and CuO (Fig. S11<sup>†</sup>). In the 5 min data, the oxidized species exceeds 40% (Cu<sub>2</sub>O: 28.7% and CuO: 12.9%) but after 35 min, the CuO ratio slowly decreased while maintaining about 70% metallic Cu and 25% Cu<sub>2</sub>O (Table S1<sup>+</sup>). This data was related to our previous report that C2 selectivity and stability were improved when Cu<sup>0</sup>, Cu<sup>+</sup>, and Cu<sup>2+</sup> exist in the metastable mixed state.<sup>19</sup> Because of this previous report, the Cu mixed state in CSNP/CP may be the cause of improved C<sub>2</sub>H<sub>4</sub> selectivity. In other studies, the association between Cu<sup>+</sup> species and C2 selectivity has also been suggested.15-18,40 However, the oxidized species seen during the reaction may be due to the oxide domain being isolated from the reaction surface of the catalyst. Alternatively, the origin of high selectivity in CSNP/CP may be due to the formation of a defect site in the oxidized phase and the reduced Cu domain, and the deactivation factor of the catalyst may be due to reconstruction into metallic Cu cube during the reaction time.

In order to investigate the effect of selectivity on the surface structure of these catalysts, the surface structure was controlled by adjusting the amount of catalyst sprayed on the carbon paper substrate. The amount of catalyst spray was adjusted from 4  $\mu$ g cm<sup>-2</sup> to 60.8  $\mu$ g cm<sup>-2</sup>. The SEM images confirmed that the surface morphology greatly changed, depending on the spray amount (Fig. S12†). The product distribution during CO<sub>2</sub>RR varied greatly even at the same biased potential, depending on the amount of catalyst sprayed but the total current densities had similar values except for the sample sprayed with 4  $\mu$ g cm<sup>-2</sup> (Fig. 4a). The 4  $\mu$ g cm<sup>-2</sup> sample was exceptional presumably because the amount of CSNP was too small to cover most of the carbon surface compared with the other samples.

The FE of each product changed significantly, especially between  $CH_4$  and  $C_2H_4$ , depending on the transition of surface morphology of the 4, 8, 12.8, and 19.2 µg cm<sup>-2</sup> sprayed samples (Fig. 4b). As the amount of the applied catalyst decreased,  $CH_4$  formation increased and  $C_2H_4$  production decreased (Fig. 4c). The FE ratio of  $C_2H_4/CH_4$  was adjustable from 1.0 to 21 (Fig. S13a†).

Several studies have reported that the production selectivity of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> is affected by the local pH due to the pH dependence of each reaction.<sup>20–22</sup> Similarly, our catalysts presumably had different product distributions due to the difference in local pH produced by the porous catalyst surfaces. Through SEM analysis, we found that nanoparticles of the 4 µg cm<sup>-2</sup> deposited sample were well dispersed and showed a morphology of relatively low porosity. On the other hand, the nanoparticles of the samples sprayed with more than 19.2 µg cm<sup>-2</sup> were well clustered with each other and the porosity was increased (Fig. S12†).

We compared the partial current density of  $C_2H_4$  and  $CH_4$  production depending on the spray amount, which shows



Fig. 4 The catalyst spray amount control results: (a) total current density for each sample, (b) product selectivity change by spray amount; (c)  $C_2H_4$  and  $CH_4$  selectivity change.

a distinct trend (Fig. S13b<sup>†</sup>). The partial current density for CH<sub>4</sub> production decreased as the spray amount increased, while that of C<sub>2</sub>H<sub>4</sub> was more or less the same in the same ranges. The previous studies have reported that C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> production ratio are sensitively affected by the electrolyte pH because of their different pH dependence and the porous catalyst can tune the CO<sub>2</sub>RR product distribution by inducing a local pH increase at high current density condition due to the unbalanced proton supply.<sup>20-22,41</sup> It is proposed that the protonation process is involved in the rate determining step of CH<sub>4</sub> production to form the \*CHO intermediate and the CH<sub>4</sub> production rate decreases at high pH.<sup>42</sup> On the other hand, in the case of C<sub>2</sub>H<sub>4</sub>, the C-C coupling step is proposed as the rate determining step in which the proton is not involved,<sup>41</sup> and thus, has constant C<sub>2</sub>H<sub>4</sub> production rate at different pH of the electrolyte. Thus, CH<sub>4</sub> production depends on the pH of the electrolyte while C<sub>2</sub>H<sub>4</sub> production shows pH independence. Taken together, increasing the pH near the catalyst surface can induce decrease in CH<sub>4</sub> production rate while the same also causes constant C<sub>2</sub>H<sub>4</sub> production rate. Therefore, we proposed that a higher spraying amount forms a more porous surface and a higher local pH increase near the catalyst surface decreases CH<sub>4</sub> production.

In addition, we observed that the catalytic activity of CSNP/ CP is affected by the cation type (Fig. S15 and S16<sup>†</sup>), which is consistent with the previous study. It suggests that as the cation size increases, the hydrated alkali metal cation forms a dipole field in the outer Helmholtz plane, which stabilizes the adsorbed intermediates (i.e., \*CO<sub>2</sub>, \*CO, and \*OCCO), thus effectively increasing C-C coupling and CO2RR on flat Cu electrodes. It is also proposed that a large size cation reduces \*CHO formation by stabilizing \*CO, which reduces the formation of \*CHO, which is an important rate determining intermediate in CH<sub>4</sub> formation.<sup>43</sup> Thus, we tested the performance of CSNP in Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> electrolytes (Fig. S14<sup>+</sup>). As reported in the paper mentioned, HER increased and CO<sub>2</sub>RR decreased in Na<sup>+</sup> electrolytes with small cation sizes. As the size of the cation increased, \*CO and \*OCCO were stabilized and C2H4 production increased. The observed Tafel slope is 98.1 mV  $dec^{-1}$  in 0.1 M KHCO3 and similar values were obtained both in NaHCO3 and CsHCO<sub>3</sub> electrolytes, as shown in Fig. S17.<sup>†</sup> These values are also similar to the recently reported values (75–97 mV dec $^{-1}$ ,

depending on the Cu-based catalysts).<sup>44</sup> Although it is difficult to determine the electrokinetics based on simple Tafel slope measurement, it suggests that the electrokinetics of  $C_2H_4$ production on our catalysts are similar to those on others. The turn over frequency (TOF) of the CSNP was is estimated in 0.1 M KHCO<sub>3</sub>. The deposited Cu amount was calculated by measuring the mass of the deposited catalyst and the lower bound value was calculated by assuming that all the Cu atoms are involved on the active sites. Our estimated TOF value for  $C_2H_4$  production was 0.05 S<sup>-1</sup> at -1.05 V *vs.* RHE (Fig. S18†), which is comparable to the previously reported TOF of 0.01 s<sup>-1</sup> (32.6 h<sup>-1</sup>) at the optimum potential in the half cell.<sup>45</sup>

Using the catalyst synthetic method proposed in this study, a difference in the porosity, which can induce a local pH gradient, can be easily achieved just by controlling the amount of the catalyst spray without a complicated catalyst design process. The optimal  $C_2H_4$  FE was 51% when a 12.8 µg cm<sup>-2</sup> spray amount was applied (Fig. 4c) but the CH<sub>4</sub> selectivity was still about 10%. When K<sup>+</sup> was replaced with Cs<sup>+</sup>, 12.8 µg cm<sup>-2</sup> CSNP/CP decreased the HER at lower overpotentials and decreased the C1 gas products in all the potential ranges, and a maximum of 52% of  $FE_{C_2H_4}$  was achieved (Fig. S15 and S16†). In particular, the partial current density of  $C_2H_4$  production was greatly increased up to ~21 mA cm<sup>-2</sup> (Fig. S16b†). The faradaic efficiency of the liquid products according to the amount of CSNP catalyst is shown in Fig. S19.†

#### 4. Conclusions

We developed a high-performance catalyst–substrate system by electrospraying copper-based catalyst on a porous carbon substrate and demonstrated enhanced  $C_2H_4$  production compared to Cu-foil, with 3.8 times greater selectivity and 20fold higher production rate. Notably, this catalyst–substrate system was synthesized by a very simple one-step electrospray pyrolysis method, unlike the conventional method of loading onto the substrate after catalyst synthesis. Also, it was confirmed that the activity of the C2 product was different depending on the type of substrate, even for catalyst synthesized by the same method. Also, it was confirmed that  $CO_2RR$  activity was affected by the type of the support, even if the same method was applied for Cu-catalyst synthesis, thus indicating the importance of proper substrate material as it can affect multiple parameters such as morphology, defect sites, and electronic structures. The morphology of the catalyst was retained longer on the carbon substrate than on the Cu-foil, which contributes to long-term C<sub>2</sub>H<sub>4</sub> selectivity and stability. In addition, in situ/ operando XAS experiments showed that the Cu mixed state (Cu<sup>0</sup>, Cu<sub>2</sub>O, and CuO) coexisted during CO<sub>2</sub>RR. This mixed state was also suggested to play an important role in C-C coupling. The nanostructure porosity of this catalyst was very easily controlled by the amount of catalyst sprayed and a local pH gradient was induced to precisely control the C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> ratio. As a result of this study, we are able to propose effective methods for synthesizing C2 products using Cu catalysts and to explain some causes of selectivity of some products. Our study can also be applied in the future to easily synthesize catalysts on gas diffusion porous electrode and the enhanced performance produced by the catalyst-substrate interaction provides insights into the research on catalyst-substrate system.

## Conflicts of interest

The authors declare no conflict of interest.

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