Generation of high-density nanoparticles in the carbothermal shock method

Ji-Yoon Song1,2†, Chansol Kim1,3†, Minki Kim1,3, Kyeong Min Cho1,3,4, Issam Gereige5, Woo-Bin Jung6*, Hyeonsu Jeong2*, Hee-Tae Jung1,3*

The carbothermal shock (CTS) method has attracted considerable attention in recent years because it enables the generation of finely controlled polyelemental alloy nanoparticles (NPs). However, fabricating high surface coverage of NPs with minimized exposure of the carbon substrate is essential for various electrochemical applications and has been a critical limitation in CTS method. Here, we developed a methodology for creating NPs with high surface coverage on a carbon substrate by maximizing defect sites of cellulose during CTS. Cu NPs with high surface coverage of ~85%, various single NPs and polyelemental alloy NPs were densely fabricated with high uniformity and dispersity. The synthesized Cu NPs on cellulose/carbon paper substrate were used in electrocatalytic CO2 reduction reaction showing selectivity to ethylene of ~49% and high stability for over 30 hours of reaction. Our cellulose-derived CTS method enables the greater availability of polyelemental NPs for a wide range of catalytic and electrochemical applications.

INTRODUCTION

Carbothermal shock (CTS) is one of the simplest synthetic methods for forming single to polyelemental metal nanoparticles (NPs). In this method, NPs are created by simply loading a metal precursor on a carbon substrate and then instantaneously raising the temperature by passing an electric current through the sample for a short time. The time during which the temperature rises and falls is very short, and so it is a very innovative way of mixing multiple metals with small and uniform NPs (1). The ability to synthesize a desired NP can open exciting new possibilities for studying polyelemental NPs, and this method has already enabled notable applications such as rechargeable energy storage systems (e.g., Li and Na ion batteries, supercapacitors, and Li-CO2 and Li-O2 batteries), electrochemical water splitting (e.g., oxygen evolution reaction), and electrocatalysis (e.g., hydrogen evolution, oxygen reduction, and carbon monoxide reduction reactions) (2–8).

Although the CTS method has been widely used with high-performance results in the various fields mentioned above, the fabrication of materials with a high surface coverage of NPs can expand applications in research fields that have previously not realized. For example, metal NPs formed through the CTS method have not been used for electrocatalytic carbon dioxide (CO2) or nitrogen (N2) reduction reactions because the hydrogen evolution reaction (HER) and unwanted reactions occur on the exposed carbon substrate as a competing reaction (9–12). To improve performance in these applications, it is necessary to increase the surface coverage of NPs. To control the surface coverage of metal NPs in the CTS method, it is important to correctly select and modify the carbon substrate because the carbon substrate offers nucleation–diffusion sites for metal NPs during the heating process (13). In particular, defects in carbon such as vacancies, dangling bonds located in the edge planes, and heteroatom-doped (e.g., O or N) sites play an important role for the formation and stabilization of metal NPs through the strong binding energy between metal atoms at high temperatures (14). This correlation was observed in previous studies, in which the metal NPs formed were small and uniform and had a high fissionability during CTS as defect sites increased in the carbon substrate (1, 13, 15). Nevertheless, it is still challenging to fabricate materials with high metal NP surface coverage by the CTS method for more expanded potential electrochemical applications.

Here, we report a methodology for fabricating materials with a high surface coverage of NPs by introducing partially carbonized cellulose as the carbon substrate on which the NPs are synthesized. The high surface coverage of NPs is made possible by a few interconnected aromatic rings with numerous edge sites including sp3 C–C bonds in the partially carbonized cellulose. As a result, we achieved an unprecedented high surface coverage of various single and copper (Cu)–based polyelemental alloy NPs with a uniform particle size distribution over a large area. In addition, we confirmed that the sum of defect sites (oxygen and sp3 bonded C–C) on the carbon substrate determine the surface coverage of metal NPs by comparing with the typical CTS carbon substrates. Moreover, we demonstrated that the material with a high surface coverage of Cu NPs can be used for electrocatalytic CO2 reduction reaction (CO2RR) in a continuous flow cell using a gas diffusion electrode (GDE). The Cu NPs on cellulose/carbon paper (Cu/cellulose/CP) showed a high ethylene selectivity of 48.92% at a potential of ~0.529 V versus the reverse hydrogen electrode (RHE) and stability over 30 hours of reaction in a 10 M KOH electrolyte. This study demonstrated how cellulose enables high surface coverage of metal NPs, which opens the possibility of applying metal NPs and multicomponent NPs to more diverse applications (7, 16–19).

RESULTS

Cellulose, earth-abundant organic polymer consisted of linear chain of several hundreds to many thousands linked d-glucose units (20)...
was used as the key material for the high surface coverage NP synthesis through CTS method (Fig. 1A). It can provide numerous sp³ carbon and oxygen content regarding carbon defects by partial carbonization to carbon nanoclusters, which consist of many edge sites. To generate a high surface coverage of metal NPs using cellulose as the substrate, we used the detailed fabrication scheme described in Fig. 1 (B to D). Since the cellulose has too low electrical conductivity to flow the current for Joule heating, it needs to be loaded on the CP, which allows current flow and can emit the heat for the carbonization of the cellulose and the simultaneous synthesis of NPs. To load cellulose layer on CP, cellulose is dispersed in distilled water, and the dispersion is vacuum-filtrated on CP that plays the role of filter membrane and cellulose is filtered on CP forming thin layer. A cellulose layer loaded onto the CP (cellulose/CP) is then cut into specimens with a width of 3 mm and a length of 20 mm. The Cu precursor, CuCl₂ dissolved in ethanol, is loaded onto the cellulose/CP by drop casting to form the CuCl₂/cellulose/CP. It showed a pale green color, as shown in the photo image in Fig. 1B. CTS was used by applying a high electrical current of ~1 A to induce Joule heating through the CP, which resulted in the emission of red light at ~830°C (fig. S1), and the heat was radiated to the cellulose layer (Fig. 1C). After CTS, Cu NPs were densely formed by the reduction of the CuCl₂ precursor. The photo image shows that the color of the cellulose layer changed from pale green to a copperish color after 1.5 s of CTS, implying the transition of the cast CuCl₂ into Cu metal, called Cu/cellulose/CP (Fig. 1D). Partially carbonized cellulose during

Fig. 1. Preparation process and surface structural characterizations of Cu NPs on cellulose-loaded CP (Cu/cellulose/CP). (A to E) Schematic illustration of the preparation [inset: photo images before CTS in (B) and after CTS in (D); photo credit: J.-Y.S., KAIST]. (F) Low-magnification scanning electron microscopy (SEM) image of Cu/cellulose/CP [inset: SEM–energy-dispersive x-ray spectroscopy (EDS) mapping of Cu and particle size distribution].
CTS offered enormous defect sites, including high levels of sp\(^3\) carbon and oxygen through the maximal formation of carbon nanoclusters, which are composed of polycyclic aromatic hydrocarbon and inner bridged oxygen dopant. The formation of the nanoclusters enabled the high surface coverage of Cu NPs by even dispersion and stabilization of the liquid Cu after CTS (Fig. 1E).

The surface of Cu/cellulose/CP was densely covered by Cu NPs of uniform size (35 ± 3.3 nm), as shown in the low-magnification scanning electron microscopy (SEM) image in Fig. 1F. It showed the formation of finer and denser non-noble metal NPs as compared with previous reports that used the CTS method (1, 13). Cu NP formation on the carbon substrate was confirmed using an SEM–energy-dispersive x-ray spectroscopy (SEM-EDS) mapping image (inset of Fig. 1F) and 0.21 nm of lattice spacing corresponding to Cu(111) in the high-resolution transmission electron microscopy (TEM) images (Fig. S2). The successful reduction of CuCl\(_2\) to Cu NPs can be further supported by elemental analysis according to the change of Cu and Cl atomic ratio of Cl on the cellulose layer. The Cl content decreased from an atomic % (at %) of 8.86 to 0.85, while the content of Cu increased from 8.14 to 18.71 at % during the CTS process (fig. S3). In addition, the Cu 2p and Auger Cu LMM x-ray photoelectron spectroscopy (XPS) spectra analyses further prove the complete transition of Cu\(^{2+}\) in CuCl\(_2\) to Cu(0) (fig. S2, C and D). Moreover, the cellulose/CP substrate had a high surface coverage not only for Cu but also for other metals (Ni, Co, Pd, Pt, Ru, and Au) (fig. S4).

Although only single-metal NPs are shown in Fig. 1, the biggest advantage of the CTS method is that it can easily mix various metal elements. Therefore, when we demonstrated the synthesis of NPs in the same way in our cellulose-based method, we were able to synthesize alloys with high surface coverage (Fig. 2). The SEM and high-angle annular dark-field scanning TEM (HAADF-STEM) images show elemental compositions of the exemplary metal-alloy NPs that were successfully synthesized on the cellulose via CTS. We confirmed the uniform formation with a high surface coverage of metal alloys using SEM analysis when binary (CuPd in Fig. 2A), ternary (CuPdPt in Fig. 2B), and quaternary (CuPdPtNi in Fig. 2C) metal NP alloys formed. Furthermore, the EDS mapping via STEM reveals that the NPs are completely alloyed metals including all components with no segregated regions of specific elements. Therefore, even with the cellulose-based CTS method in this study, it was possible to synthesize metal alloys at the level implemented in the previously reported CTS method with an even larger surface coverage.

Since this study was the first to use cellulose for the CTS method, it was necessary to understand the cause of the formation of NPs with a high surface coverage. For this, we investigated the relationship among the chemical state of cellulose, surface coverage and size uniformity of single-metal (Cu) NPs, and heating time (Fig. 3). Cu NPs after CTS showed particles with different size, uniformity, and surface coverage depending on the heating time, as shown in Fig. 3A. NPs formed at the heating time of 0.4 s had an average particle size of 52 nm, and they were hardly visible on the surface, indicating no substantial changes in the cellulose layer. Until 1.5 s of the CTS process, the particle size decreased while the uniformity and the surface coverage improved; the smallest average size was 35 nm ± 3.3 nm, and Cu/cellulose/CP had the highest surface coverage at this stage. The size of the NPs began to increase again, accompanied by a decrease in surface coverage and the uniformity, with CTS times greater than 1.5 s.

In previous studies, the mechanism of cellulose carbonization has been studied extensively (21–22). On the basis of the mechanism, we could predict how cellulose changes during the CTS process and how it affects NP formation. Generally, cellulose carbonization proceeds from the formation to the growth of carbon nanoclusters that are intermediates of the carbonization process (Fig. 3B) (21–25). Conductive carbon nanoclusters begin formation from the decomposition of glucose, which is formed after depolymerization of cellulose (26, 27). The number of edge sites (sp\(^3\) C—C bond is mostly located at the edge of aromatic rings) increases because of the continuous formation of carbon nanoclusters during the early stages of carbonization from 0.4 to 1.5 s. The carbon nanoclusters then condensed through growth as the edge defects decreased with an increase in electrical conductivity over 1.75 s.

Microstructural analyses of the cellulose during the CTS process were performed to verify our hypothesis. First, carbonization of the cellulose layer according to the CTS time was confirmed by the ex situ Raman spectra (Fig. 3C). Before CTS, cellulose consisted of

---

*Fig. 2. Characterizations of polyelemental alloys.* SEM and HAADF-STEM images and EDS elemental mapping of alloyed compositions corresponding to (A) CuPd, (B) CuPdPt, and (C) CuPdPtNi.

---
aliphatic carbon (without the benzene ring), and so the D-band (~1350 cm\(^{-1}\)) and G-band (~1580 cm\(^{-1}\)) peaks were absent from the Raman spectrum (fig. S5) (28). D- and G-band peaks arising from the vibration of the benzene ring appeared after CTS for 0.4 s, indicating the initiation of the formation of carbon nanoclusters composed of a few aromatic rings (29). After that time, the carbonization of cellulose proceeds up to 3 s. That is supported by the intensity of D- and G-band peak ratio (\(I_D/I_G\)). Gradually increasing \(I_D/I_G\) means the formation of polycyclic aromatic carbons over CTS time (26).

Furthermore, the carbonization process of the cellulose layer during CTS from 0.4 to 3 s can be confirmed by calculating the sp\(^3\)/sp\(^2\) carbon ratio from the XPS C1s spectra (Fig. 3D and fig. S6). The change in the sp\(^3\)/sp\(^2\) carbon ratio while the total content of the C–C bond was maintained reflects the change in the chemical structure of cellulose between aliphatic (sp\(^3\)) and aromatic (sp\(^2\)) carbon without loss during the carbonization process (26, 28). The sp\(^3\)/sp\(^2\) ratio increased up to 1.5 s and decreased sharply between 1.5 and 1.75 s. The increase in the sp\(^3\)/sp\(^2\) ratio over time until 1.5 s means that carbon nanoclusters containing numerous edge sites consisting of sp\(^3\) carbon are maximally formed at 1.5 s and begin growth over 1.5 s, as shown in Fig. 3B (28).

Last, a strong relationship between the total amounts of defect and the NP size and uniformity is shown in Fig. 3E. Since oxygen defects exist in the cellulose in addition to the sp\(^3\) defects, we analyzed the total amount of defects by summing the atomic % of sp\(^3\) carbon and oxygen from XPS. At 0.4 s, low amounts of defect sites due to the initial carbonization step of the cellulose layer caused low dispersity for the metal NPs on the carbon substrate; the particles were large and nonuniform (Fig. 3A). Afterward, the size of Cu NPs gradually became uniform and fine with increasing surface NP coverage until 1.5 s, the point at which the defects acting as nucleation and diffusion sites reach 62.8 at %. From 1.75 s, the NPs became larger, and the uniformity decreased because of the sharp decrease in defect sites because of carbon nanocluster condensation. Therefore, we could verify that the quantity of defects in the cellulose reached a maximum at 1.5 s of CTS and decreased afterward, a phenomenon that can govern the morphological trend in the Cu NP formation.

---

**Fig. 3. High surface coverage for the Cu NP formation mechanism with carbonization of cellulose.** (A) SEM images of Cu/cellulose/CP depending on CTS time from 0.4 to 3 s. (B) Proposed cellulose carbonization process. (C) Raman spectra, (D) sp\(^3\)/sp\(^2\) C–C ratio, and (E) defects of the cellulose layer and mean particle size with respect to CTS time from 0.4 to 3 s. a.u., arbitrary units.
To compare how cellulose is different from other carbon materials and to identify its advantages, Cu NPs were synthesized on various carbon substrates, such as bare CP, carbon nanotubes (CNTs), graphene oxides (GOs), and carbon nanofibers (CNFs) through the CTS method (Fig. 4). Each carbon material includes different defect density on surface and was representatively used in CTS as carbon substrate (1, 6, 30–32). The atomic ratios of the total defect sites were determined by summing sp$^3$ C–C and O from XPS; these were 10.1 at % in bare CP, 12.4 at % in CNT, 22.7 at % in GO, 49.0 at % in CNF, and 62.8 at % in partial carbonized cellulose (Fig. 4A). The quantified amount of defect in carbon substrates was only used for relative comparison because of the influence of trace amount of carbon contaminant.

Because of different defect densities, Cu NPs showed prominent differences in the morphology and surface coverage (Fig. 4B). Unlike the cellulose system, SEM images of the Cu/CP and Cu/CNT/CP show that no prominent Cu NPs were observed on the surface of the bare CP and CNT layer (Fig. 4B and figs. S7 and S8). In addition, Cu contents of Cu/CP and Cu/CNT/CP that cross-checked by the XPS and SEM-EDS quantification were very low because of low total defect sites for NP formation (Fig. 4A and fig. S8). In the case of GO, which has a similar oxygen content (30 O at %) as cellulose (43 O at %), an irregular distribution of Cu NPs and low Cu content after CTS was observed. Cu/GO/CP had the same O content (O/C ratio of 0.16 from XPS) as Cu/cellulose/CP after CTS; however, after CTS, GO contained significantly lower levels of sp$^3$ carbon species (9 at %). The discrepancy in NP formation between GO and the cellulose was observed. Cu/GO/CP because of its low total defect sites.

Among the carbon substrates, CNFs, which are widely used as the carbon substrate for CTS, were also investigated. CNF has low O content on surface (9.7 O at %); however, high content of sp$^3$ hybridized C–C bonds (39.4 at %) in Fig. 4A. Accordingly, the Cu NPs synthesized on the CNF showed higher Cu content than did the bare CP, CNT, and GO on CP. Nevertheless, the Cu NPs on CNF (Cu/CNF) showed lower Cu content as compared with Cu/cellulose/CP. In addition, Cu/cellulose/CP showed high surface coverage on the exposed surface, as observed by SEM, in which the surface coverage was ~85%, 6.5 times greater than the surface coverage of Cu/CNF, 13% (fig. S10). This phenomenon is directly related to the photo images in the inset in Fig. 4B, which shows that only the Cu/cellulose/CP changed into a copperish color after CTS, unlike the other carbon substrates. In the case of cellulose, unlike other carbon materials, defect sites increase as the CTS process progresses (Fig. 4A). During heating process of CTS, as carbons are graphitized, sp$^3$ defect sites are eliminated, and oxygen content is reduced, so defect sites are inevitably reduced. However, it is only possible for cellulose to increase the amount of defect sites because cellulose undergoes the process of making carbon nanoclusters before graphitization during CTS. As a result, the comparison showed that Cu/cellulose/CP enabled the formation of dense metal NPs by numerous defect sites for broadening CTS applications.

To prove that our cellulose-derived CTS method can broaden applications in fields that require high surface coverage of NPs, we applied the Cu/cellulose/CP electrode for electrocatalytic CO$_2$RR. We used Cu NPs because they are the only metals capable of producing C$_2$ products including ethylene and ethanol, which exhibit high energy densities for efficient renewable electricity storage and feedstock for chemical production. Under moderate applied potential, CO$_2$ adsorption and CO formation followed by C–C dimerization on Cu metal surface can reduce CO$_2$ to C$_2$ products (33–35). No previous studies have reported the CTS method for electrocatalytic CO$_2$RR because of the low surface coverage of NPs and the severe competitive HER and unwanted reactions on the exposed carbon support (9–12). Moreover, it is much more challenging to use Cu NPs because non-noble metals tend to have low surface coverage properties. In this study, the electrocatalytic CO$_2$RR performance of the Cu/cellulose/CP electrode in a continuous flow cell reactor with a GDE system was investigated (Fig. 5). Figure S11 shows the structure of the cathode compartment in the GDE cell with an assembled electrode that is introduced between the flow of CO$_2$ and the electrolyte. Hydrophobic CP and Cu/cellulose/CP were assembled using a hand press, which allowed the hydrophobic layer of the CP to come into contact with the Cu NPs. An alkaline electrolyte (1 M KOH) was used to suppress the HER and to provide a high hydroxide (OH$^-$) ion concentration for efficient C$_2$ production (36, 37). The CO$_2$RR performance was optimized by changing the CTS time and the cellulose loading (fig. S12).
Figure 5A shows the Faradaic efficiency (FE) of the CO$_2$RR products with Cu/cellulose/CP (1.5 s of CTS) at an applied potential ranging between −0.576 and −0.976 V versus a reversible hydrogen electrode (V$_{RHE}$). The highest FE for ethylene and ethanol was 32.51 and 15.20% with suppressed HER to 23.01% at −0.776 V$_{RHE}$. At a less negative applied potential, HER and the formation of C$_1$ products increased with FE of hydrogen and C$_1$ products (FE$_{H2}$ and FE$_{C1}$) to more than 40 and 25%, respectively. Furthermore, CO$_2$RR performance for various alloys on cellulose/CP has been investigated in fig. S13. CuPd, CuAu, CuPdPt, and CuPdPtNi/cellulose/CP showed CO as a main CO$_2$RR product with relatively high FE to hydrogen. Among these, CuPd/cellulose/CP exhibited the highest selectivity to CO of 55.67% at −0.575 V$_{RHE}$.

To demonstrate the distinction of Cu/cellulose/CP as an electrocatalyst for CO$_2$RR, we compared the CO$_2$RR performance of our Cu/cellulose/CP with other samples of Cu NPs on typical CTS substrates (Fig. 5B). The optimization for each substrate was conducted by comparing the CO$_2$RR performance with changing CTS time in the range of 0.3 to 1.5 s (fig. S14). Among various samples, Cu/cellulose/CP showed the highest FE of C$_2$H$_4$ (FE$_{C2H4}$) over a wide potential window. Because of the low surface coverage of Cu NPs on typical CTS substrates, the highest FE$_{C2H4}$ values were only 1.983, 11.34, 17.24, and 13.91% at −0.776 V$_{RHE}$ for bare CP, CNT, GO, and CNF, respectively. Cu/cellulose/CP showed an FE$_{C2H4}$ that was 1.8 times higher relative to all the other typical substrates. This could be attributed to the high surface coverage of uniform Cu NPs.
on cellulose, which can suppress unwanted HER on the exposed carbon substrate. Other typical carbon substrate–based samples are excessively covered by relatively catalytically inactive sites that derived poor selectivity and activity to CO₂RR. Furthermore, we observed efficient production of C₂ products, including C₂H₄ and ethanol, with the suppression of other C₁ products and HER, as shown in Fig. 5C, which displays the FE of C₂ products (FE C₂) and the partial current density for the C₂ products (J C₂) at −0.776 V RHE. Cu/cellulose/CP exhibited the highest selectivity to C₂ products, with an FE C₂ of 47.71%, which is 3.43 and 3.46 times higher than FE C₂ of CNF and the GO substrate, respectively. In particular, J C₂ reached 48.80 mA/cm², which is 5.47 times that of the GO substrate. This high selectivity and productivity for C₂ products can be attributed to the large active-site density for electrocatalytic CO₂RR, a result of the high surface coverage of uniform Cu NPs.

The electrocatalytic CO₂RR performance of Cu/cellulose/CP in a continuous flow cell was also investigated using a highly alkaline electrolyte, which can induce a much more efficient C–C dimerization and HER suppression at a more positive potential because of the impact of concentrated hydroxide ions. FE C₂H₄ and total current density (J total) of Cu/cellulose/CP with increasing of KOH concentration from 1 to 10 M are shown in Fig. 5 (D and E). FE C₂H₄ reached 48.92% at −0.529 V RHE when a 7 M KOH electrolyte was used. With the 10 M KOH electrolyte, the selectivity to ethylene slightly decreased compared with the 7 M KOH electrolyte. The potential with the highest ethylene selectivity and onset potential for the CO₂RR shifted remarkably to a less negative potential with increasing KOH concentration, consistent with previous reports (Fig. 5D). At the same time, J total increased markedly because of the high concentration of KOH electrolyte. In particular, current density and FE C₂H₄ reached 220.5 mA/cm² at −0.717 V RHE and 45.6% at −0.517 V RHE, respectively, in a 10 M KOH electrolyte environment (Fig. 5E).

Cu/cellulose/CP had extraordinary stable properties for electrocatalytic CO₂RR under harsh conditions at high concentrations of KOH (Fig. 5F). We applied Cu/cellulose/CP to an electrode configuration that was composed of a porous polytetrafluoroethylene (PTFE) membrane used as a hydrophobic layer and Cu/cellulose/CP used as a catalyst layer. FE C₂H₄ and J total almost maintained their initial value of ~45%, showing a slight decrease after 31 hours of CO₂RR at −0.517 V RHE in 10 M KOH electrolyte. Cross-sectional SEM and inset EDS mapping images of the electrode after 31 hours CO₂RR show a well-maintained PTFE/Cu/cellulose/CP configuration without detachment and reconstruction (Fig. 5G). In previous studies, only a few CO₂ conversion electrocatalysts demonstrated stability over 30 hours in highly alkaline electrolyte (table S1). In addition, the morphology of Cu NPs was almost maintained, with no serious restructuring and aggregation even after a long electrocatalytic reaction under harsh conditions. We suggest that this highly stable property can be mainly attributed to the protective effect of the cellulose/CP layer at which the Cu NPs were located, which can stabilize the Cu catalyst surface while preventing restructuring and contamination (38). At the same time, an independent PTFE hydrophobic layer that is separate from a conventional carbon-based GDE could more stably inhibit flooding during the long-term reaction (36). Consequently, we proved that the cellulose-based CTS method can be used for efficient electrocatalytic CO₂RR applications; this suggests the applicability to numerous research fields that require minimized exposure of carbon support.

DISCUSSION

In summary, we synthesized Cu NPs with high surface coverage (~85%) and uniformity by facile radiation CTS method by introducing cellulose. The maximal formation of carbon nanoclusters from partial carbonized cellulose during CTS enables the formation of numerous defect sites, resulting in a high metal NP surface coverage for single and polyelemental alloy metal NPs. Through a comparison with other carbon materials, we also confirmed that the defect density, including the sp²-hybridized C–C bonds and the doped heteroatom, O, is important for determining the amount of metal on the surface. Moreover, cellulose is only possible for increasing the amount of defect sites CTS. To our knowledge, there are no other studies that created this high surface coverage of metal NPs in CTS that can be widely used in various applications. Moreover, we expanded the application area of CTS method to electrocatalytic CO₂RR in a continuous flow cell using GDE. Through this property, Cu/cellulose/CP showed a maximum ethylene FE of 48.92% at an applied potential of −0.529 V RHE. At the same time, we showed highly stable properties over 30 hours in electrocatalytic CO₂RR through the protective effect of the cellulose/CP layer that inhibit restructuring and contamination. Furthermore, our successfully synthesized polyelemental alloy NPs made our cellulose/CP with high surface coverage an appealing carbon support for many future electrocatalytic applications using the CTS method.

MATERIALS AND METHODS

Preparation of Cu/cellulose/CP

Cellulose (4 mg) was dispersed in distilled water, and the dispersion was weakly vacuum-filtered on CP (Sigraet 39 AA, Fuel Cell Store). CP played the role of the filter membrane, and the cellulose filtered on the CP formed a thin layer. Cellulose-loaded CP was stabilized at 240°C with a ramping rate of 3°C/min and kept for 1 hour to enhance the thermal stability of cellulose layer, termed cellulose/CP. Cellulose/CP was cut into pieces, and CuCl₂/ethanol solution (48 µl, 0.1 M) was drop-casted onto the cellulose/CP and dried at 50°C oven for 1 hour to prepare CuCl₂/cellulose/CP. It was fixed on a quartz plate and connected with Cu tape with a length of 20 mm. It was then loaded in a vacuum chamber with 500 standard cubic centimeter per minute (sccm) of argon gas flow. The electrode was Joule-heated by applying 1 A for 0.3 to 3 s through a connected power source (Keithley 2461).

Preparation of the working electrode

The working electrodes for the CO₂RR performance test were prepared by hand pressing various fabricated Cu NP/carbon support–based catalysts and PTFE-coated hydrophobic CP with a microporous layer (Sigraet 39 BC, Fuel Cell Store) used as a GDE. The hydrophobic layer of CP and Cu NPs was in contact through this process. For the stability test, a porous PTFE membrane (Fuel Cell Store) was used as a hydrophobic layer instead of microporous CP.

Electrochemical measurements

Electrochemical tests were performed in a continuous flow cell reactor composed of polyetherether ketone and a silicone gasket for sealing. E-beam–evaporated Pt on GDE was used as the counter electrode, and Ag/AgCl (3 M KCl saturated) was used as the working electrode. The gas flow rate was controlled at 10 sccm using a mass flow controller. CO₂ gas flowing at the back side of the cathode
GDE was connected to the GC, and the back side of the anode GDE was exposed to air. The catholyte and anolyte were separate, and the flow rate was 2 ml/min. KOH solutions with a concentration ranging from 1 to 10 M were used as the electrolyte with a Nafion proton exchange membrane.

During the constant potential with iR correction, the gas products were detected by a gas chromatography (Agilent 7890 GC), which was connected to the reactor. Liquid products were quantified using 1H nuclear magnetic resonance (NMR Bruker Avance III HD). After electrolysis, 630 μl of electrolyte was mixed with 70 μl of deuterated water (D2O), 35 μl of 50 mM phenol, and 10 mM dimethyl sulfoxide for reference. The potential was converted to RHE using the following equation

$$E_{\text{RHE}} = E_{\text{AgCl}} + 0.059 \text{pH} + 0.209 \text{V}$$

The FE for the products was calculated using the following equation

$$\text{FE} (%) = \frac{nFxV \times 100}{I_{\text{total}}}$$

where \(n\) is the number of electrons transferred, \(F\) is Faraday’s constant, \(x\) is the molar fraction of product, \(V\) is the total molar flow rate of gas reactant, and \(I_{\text{total}}\) is the total current applied during the CO2RR.

Characterizations

The morphology and surface atomic composition of films were observed by SEM (FEI Magellan 400 and Versios 460). Raman spectra were confirmed by InVia Reflex using a 514-nm laser. TEM was performed to show lattice d-spacing for a metal NP under 200 kV, using a Tecnai G2 F20. HAADF-STEM and elemental mapping images of the NPs were obtained using a Titan G2 Cube at 80 kV. XPS analyses were performed using a K-Alpha spectrometer.
33. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* 3, 1311–1315 (2010).

34. Y. Lum, J. W. Ager, Evidence for product-specific active sites on oxide-derived Cu catalysts for electrochemical CO2 reduction. *Nat. Catal.* 2, 86–93 (2019).

35. C. Kim, K. M. Cho, K. Park, J. Y. Kim, G. T. Yun, F. M. Toma, I. Gereige, H. T. Jung, Cu/Cu2O interconnected porous aerogel catalyst for highly productive electrolysissynthesis of ethanol from CO2. *Adv. Funct. Mater.* 31, 2102142 (2021).

36. C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. G. de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E. H. Sargent, CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* 360, 783–787 (2018).

37. K. M. Cho, W.-B. Jung, D. Kim, J. Y. Kim, Y. Kim, G. T. Yun, S. Ryu, A. Al-Saggaf, I. Gereige, H. T. Jung, Confined cavity on a mass-producible wrinkle film promotes selective CO2 reduction. *J. Mater. Chem. A* 8, 14592–14599 (2020).

38. T. Burdyny, W. A. Smith, CO2 reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy Environ. Sci.* 12, 1442–1453 (2019).

39. P. Grosse, D. F. Gao, F. Scholten, L. Jin, L. Zhang, Y. Yang, P. Kerns, B. Liu, S. Li, J. He, Hierarchically porous Cu/Zn bimetallic catalysts for highly selective CO2 electroreduction to liquid C2 products. *Appl. Catal. B-Environ.* 269, 118800 (2020).

40. H. Jung, S. Y. Lee, C. W. Lee, M. K. Cho, D. H. Won, C. Kim, H. S. Oh, B. K. Min, Y. J. Hwang, Electrochemical fragmentation of Cu2O nanoparticles enhancing selective C-C coupling from CO2 reduction reaction. *J. Am. Chem. Soc.* 141, 4624–4633 (2019).

41. Z.-Q. Liang, T.-T. Zhuang, A. Seifitokaldani, J. Li, C.-W. Huang, C.-S. Tan, Y. Li, P. De Luna, C. T. Dinh, Y. Hu, Q. Xiao, P.-L. Hsieh, Y. Wang, F. Li, R. Quintero-Bermudez, Y. Zhou, P. Chen, Y. Pang, S.-C. Lo, L.-J. Chen, H. Tan, Z. Xu, S. Zhao, D. Sinton, E. H. Sargent, Copper-on-nitride enhances the stable electrolysissynthesis of multi-carbon products from CO2. *Nat. Commun.* 9, 3828 (2018).

42. M. Luo, Z. Wang, Y. C. Li, J. Li, F. Li, Y. Lum, D.-H. Nam, B. Chen, J. Wicks, A. Xu, T. Zhuang, W. R. Leow, X. Wang, C.-T. Dinh, Y. Wang, S. Zhao, D. Sinton, E. H. Sargent, Hydroxide promotes carbon dioxide electroreduction to ethanol on copper via tuning of adsorbed hydrogen. *Nat. Commun.* 10, 5814 (2019).

43. F. Li, Y. C. Li, Z. Wang, J. Li, D.-H. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S.-F. Hung, B. Chen, Y. Wang, J. Wicks, Y. Xu, Y. Li, C. M. Gabardo, C.-T. Dinh, Y. Wang, T.-T. Zhuang, D. Sinton, E. H. Sargent, Cooperative CO2-to-ethanol conversion via enriched intermediates at molecule–metal catalyst interfaces. *Nat. Catal.* 3, 75–82 (2020).

44. X. Su, Y. Sun, L. Jin, L. Zhang, Y. Yang, P. Kerns, B. Liu, S. Li, J. He, Hierarchically porous Cu/Zn bimetallic catalysts for highly selective CO2 electroreduction to liquid C2 products. *Appl. Catal. B-Environ.* 269, 118800 (2020).

45. T.-T. Zhuang, Z.-Q. Liang, A. Seifitokaldani, Y. Li, P. De Luna, T. Burdyny, F. Che, F. Meng, Y. Min, R. Quintero-Bermudez, C. T. Dinh, Y. Pang, M. Zhong, B. Zhang, J. Li, P.-N. Chen, H. Liang, W.-N. Ge, B.-J. Ye, D. Sinton, S.-H. Yu, E. H. Sargent, Steering post-C-C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. *Nat. Catal.* 1, 421–428 (2018).

46. Y. Wang, Z. Wang, C.-T. Dinh, J. Li, A. Ozden, M. G. Kibria, A. Seifitokaldani, C.-S. Tan, C. M. Gabardo, M. Luo, H. Zhou, F. Li, Y. Lum, Y. Calcellum, Y. Xu, M. Liu, A. Proppe, A. Johnston, P. Todorovic, T.-T. Zhuang, D. Sinton, S. O. Kelley, E. H. Sargent, Catalyst synthesis under CO2 electroreduction favours faceting and promotes renewable fuels electrosynthesis. *Nat. Catal.* 3, 98–106 (2020).

47. H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y. W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Stasser, B. Roldan Cuenya, Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. *Nat. Commun.* 7, 12123 (2016).

48. Y. Peng, T. Wu, L. Sun, J. M. V. Nsanzimana, A. C. Fisher, X. Wang, Selective electrochemical reduction of CO2 to ethylene on nanopores-modified copper electrodes in aqueous solution. *ACS Appl. Mater. Interfaces* 9, 32782–32789 (2017).

Acknowledgments

Funding: This study was supported by the grants from open research program of the Korea Institute of Science and Technology and National Research Foundation of Korea (NRF-2020R1A2C2014235) and the Saudi Aramco-KAIST CO2 Management Center. In addition, this research was supported by a grant from the National Research Foundation of Korea and funded by the Ministry of Science, ICT, and Future Planning (grant no. 2021K1A4A01079356). This research was supported by KAIST Institute for the NanoCentury. Author contributions: J.-Y.S. and C.K. contributed equally to this work, came up with the design concept, and cowrote the manuscript. J.-Y.S. mostly synthesized and conducted structural analyses. C.K. tested electrocatalytic performances and analysis after electrocatalysis. M.K. offered CNF for control and C.K. contributed equally to this work, came up with the design concept, and cowrote the manuscript. J.-Y.S. mostly synthesized and conducted structural analyses. C.K. tested electrocatalytic performances and analysis after electrocatalysis. M.K. offered CNF for control synthesis. C.K. and K.M.C. designed the continuous flow cell for electrocatalytic CO2 reduction. I.G. supported the design and concept for electrocatalyst. W.-B.J. designed the schematic figure. W.-B.J., H.J., and H.-T.J. edited the manuscript and guided the work and co-supervised this project. Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 5 July 2021
Accepted 4 October 2021
Published 24 November 2021
10.1126/sciadv.abk2984