CO₂ Reduction for C₂⁺ in Seawater Using a Graphitic Frustrated Lewis Pair Catalyst

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Ocean acidification due to the absorption of 40% of the world’s anthropogenic CO₂ emissions severely affects the faltering marine ecosystem and the economy. However, there are few reports on reducing CO₂ dissolved in seawater. Herein, we introduce an electrochemical CO₂ reduction battery system for use in seawater with a graphitic frustrated Lewis pair catalytic cathode doped with boron and nitrogen (BN-GFLP). BN-GFLP converts CO₂ dissolved in seawater to multi-carbon (C₂+) products during the discharge process, thus increasing the pH of intentionally acidified seawater from 6.4 to 8.0 with more than 87% Faradaic efficiency. In computational chemistry and spectroscopy, BN-GFLP binds CO₂ in a unique manner that enables exothermic C–C coupling pathway to deliver 95% selectivity for valuable C₂, products. Based on our results, we suggest a molecular design strategy for next-generation CO₂ reduction catalysts for both green oceans and the atmosphere.
Marine life is gradually dying due to increasing amounts of carbon dioxide (CO₂) in the atmosphere caused by human activity. As the ocean absorbs ~40% of the world’s anthropogenic CO₂ emissions, ocean acidity has increased by ~26% since the pre-industrial era, a trend that is expected to continue. The impact of ocean acidification adversely affects marine calcifying organisms, such as coral, plankton, shells, and skeletons, resulting in a drastic faltering of the marine food chain and the economy. Therefore, the reduction of CO₂ in the seawater environment is a major problem that needs to be solved by mankind as it can affect climate change, employment, and food security. However, most CO₂ mitigation efforts have focused on the atmosphere and not directly on the ocean. For example, electrochemical CO₂ reduction (CO₂R) progressed significantly over the past decade in terms of the development and understanding of various catalytic materials, such as precious metals, base metals, metal oxides, covalent organic frameworks, and metal–organic frameworks. Among the developed electrocatalysts, copper-based electrocatalysts have the remarkable propensity to produce valuable multi-carbon (C₂+) products, such as ethylene and ethanol, from CO₂R. However, it is difficult to use existing CO₂R electrocatalysts in seawater because of their complexity and the presence of undesirable ionic species. Specifically, Ca²⁺ in seawater directly decreases the CO₂R activity of metallic catalysts due to the precipitation of CaCO₃ on their surfaces. Only a few reports have focused on using seawater as an electrolyte, with a poor Faradaic efficiency (FE) of 36% being reported. Nevertheless, seawater can be an extremely attractive electrolyte for CO₂R because it is abundant, can function as a sink for CO₂, and has an inherently high ionic conductivity. Therefore, systems for CO₂R in seawater are urgently needed for the marine ecosystem.

With this aim, we introduce a new CO₂R battery in seawater (CBS) system comprising a graphitic frustrated Lewis pair (GFLP) cathode, a Na metal anode, and natural seawater as the electrolyte, which can drastically recover the pH of seawater during discharging. In general, the properties of frustrated Lewis pairs (FLPs) are ideal for capturing CO₂ because the relatively constrained Lewis acid (LA) and Lewis base (LB) pair strongly binds to CO₂. Therefore, we modified the FLP system for seawater
applications using a carbon nanomaterial with an immobilised LA and LB pair on a graphitic framework, which we refer to as ‘GFLP’. The sp²-hybridised graphitic framework of GFLP can donate π-electrons to FLP sites, thereby enhancing the catalytic activity and electrochemical stability in seawater. Graphene nanopowder (GN) was used as the carbon precursor owing to its high surface area and electrical conductivity, whereas boron (B) and nitrogen (N) were selected as the LA and LB, respectively.

BN-GFLP synthesis and characterisation

We introduce the sono-cavitation and nebulisation synthesis (SNS) method for the synthesis of GFLP (Fig. 1a). A solution of GN and bis(pinacolato)diboron (a boron dopant) in N-methyl-2-pyrrolidone was passed through an ultrasonic nozzle using a syringe pump, which created vacuum bubbles inside the solution when high-frequency ultrasound (180 kHz) was applied (Fig. 1a). Acoustic cavitation creates extreme conditions inside the implosively collapsing bubbles (temperature \( \approx 5000 \) K, pressure \( \approx 1000 \) bar, and heating and cooling rates \( >10^9 \) K s\(^{-1}\))\(^{25}\), which is a well-known process in sonochemistry\(^{26}\). Such conditions permit various chemical reactions that are normally inaccessible\(^{25,27}\). The GN precursor in these bubbles can form ions or radicals that directly react with the boron dopant and even inert N\(_2\) gas in a simple, fast, and continuous manner\(^{24}\). Using this approach, we synthesized B, N, and BN co-doped GN materials, denoted as B-GN, N-GN, and BN-GFLP, respectively, and their electrodes on a carbon felt substrate (more detailed synthesis conditions are described in the Methods).

High-resolution transmission electron microscopy images showed that the two-dimensional BN-GFLP structures contain substantial wrinkles and scrolls, which are characteristic of graphene (Supplementary Fig. 1). Energy-dispersive X-ray spectroscopy revealed clear and uniform distributions of B and N, implying that the LA and LB sites in BN-GFLP may be on the molecular scale (Supplementary Fig. 2). X-ray photoelectron spectroscopy (XPS) confirmed that the prepared carbon nanomaterials are doped at high heteroatom concentrations, i.e. 3.1 at% B in B-GN, 4.1 at% N in N-GN, and 6.8 at% B and 4.2 at% N in BN-GFLP (Fig. 1b). Furthermore, the heteroatom-doping contents of the GN materials can be controlled by the N\(_2\) pressure (Supplementary Fig. 3) and concentration of the B dopant (Supplementary...
The B 1s high-resolution spectrum of BN-GFLP was deconvoluted into four component peaks, revealing the presence of B–C (188.7 eV), sp²-C–B–N (189.8 eV), sp²-BN (191.5 eV), and B–O (193.1 eV) bonds (Supplementary Fig. 5a). The N 1s high-resolution spectrum of BN-GFLP also showed noticeable pyridinic (398.6 eV), pyrrolic (399.5 eV), and graphitic (401.2 eV) N peaks (Supplementary Fig. 5b). Although the SNS process randomly inserted heteroatoms into GN, three types of heteroatom configuration were present in the BN-GFLP structure according to XPS (Supplementary Fig. 5c). These heteroatom-doping characteristics were also evidenced by a higher D-to-G band Raman intensity ratio \( \frac{I_D}{I_G} \) than that of the control GN (Supplementary Fig. 6). Furthermore, the heteroatom doped-GN materials exhibited paramagnetic properties below 10 K due to the presence of radical defects from the doped B and N, as determined by electron paramagnetic resonance spectroscopy (Fig. 1c). In contrast, bare GN is strongly diamagnetic, similar to graphite. The radical defects in BN-GFLP contribute to accelerating the first CO₂ surface-adsorption step.

**Structural understanding of BN-GFLP**

The LA and LB in BN-GFLP were characterised by magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (Figs. 1d,e). Acidity was first determined by \(^{31}\)P MAS NMR spectroscopy using the \(^{31}\)P-trimethylphosphine (TMP) \(^{23,30}\) phosphorus probe adsorbed on a BN-GFLP sample (Fig. 1d). A \(^{31}\)P peak at 35.47 ppm was observed for BN-GFLP, which is attributable to the physical adsorption of TMP oxide (TMPO) on the BN-GFLP surface by the reaction of TMP with oxygen functional groups \(^{30–32}\). A \(^{31}\)P peak at 55.04 ppm appeared when TMPO was chemisorbed at the LA boron sites of BN-GFLP (Fig. 1d), which corresponds to Lewis acidities in the 50–55 ppm range \(^{30–32}\). It is worth noting that weak Brønsted acid peaks for TMP-adsorbed BN-GFLP appear at −8.79 and −15.69 ppm \(^{30}\). Then, to determine basicity, pyrrole was used as the probe for \(^1\)H MAS NMR spectroscopy (Fig. 1e) \(^{23,33,34}\). The intense peak at 5.95 ppm is assigned to the protons of aromatic pyrrole ring. Unlike the normal peak of NH group in pyrrole (8.26 ppm), the pyrrole adsorbed on the BN-GFLP sample exhibited a large \(^1\)H chemical shift in
the shoulder peak at approximately 13.89 ppm owing to hydrogen bonding interactions\textsuperscript{33} with the LB nitrogen in BN-GFLP (Fig. 1e). This result is similar to the chemical shifts observed in corresponding KX zeolites, which are known as super basic materials\textsuperscript{34}. It is also noteworthy that the broadened peaks of the LA and LB sites in the \textsuperscript{31}P and \textsuperscript{1}H MAS NMR results are caused by the $\pi$-electron donating ability of the sp$^2$-hybridised framework of BN-GFLP (Figs. 1d,e).

**Electrocatalytic CO$_2$R activity of BN-GFLP in CBS system**

Then, we fabricated a gas-tight Swagelok-type CBS system consisting of a modified 2465-type coin cell comprising a BN-GFLP cathode, Na metal anode, natural seawater as the electrolyte, and superionic conductor membrane, which enables the formation of an aprotic electrolyte-based seawater hybrid system\textsuperscript{35} (Supplementary Fig. 7). The CBS was connected to a pressure measuring system that consecutively measures the changes in inner CO$_2$ gas pressure during the discharge process. We then quantitatively verified the CO$_2$R selectivity of BN-GFLP from the hydrogen evolution reaction (HER) in situ experiments using a home-built differential electrochemical mass spectrometry (DEMS) system. The pressure decay of the Swagelok-type CBS cell filled with pure CO$_2$ gas was monitored during the electrochemical discharge process. Figures 2a and c show the galvanostatic discharge voltage profiles and the corresponding CO$_2$ reduction results, respectively, of the prepared catalytic electrodes at a fixed current density of 0.13 mA cm$^{-2}$. The observed stable voltage plateau with a linear drop in consumed CO$_2$ gas revealed that the co-doped BN-GFLP delivered a lower CO$_2$ reduction overpotential and significantly enhanced CO$_2$ reduction performance compared with the GN, N-GN, and B-GN catalysts (Fig. 2a, red line). It should be noted that the single-heteroatom-doped B-GN catalyst showed high CO$_2$ reduction but a similar overpotential to that of the control (GN), whereas the N-GN single catalytic electrode had a lower overpotential but similar CO$_2$ consumption to that of the control. These results agree with the theoretical explanation that the LA enhances catalytic activity, whereas LB increases the reaction rate\textsuperscript{36}. Therefore, BN-GFLP, with its FLP structure, increases CO$_2$R efficiency through synergism between LA and LB. Notably, the physically mixed N-GN and B-GN showed different CO$_2$R performance than that
shown by BN-GFLP (a detailed explanation of the mixed N-GN and B-GN is shown in Supplementary Fig. 8). The two-electrode Swagelok-type CBS system was also subjected to linear sweep voltammetry (LSV) under various gas atmospheres to further confirm CO$_2$R selectivity versus HER (Figs. 2b,d). As shown in Fig. 2b, the LSV curves of BN-GFLP exhibited significant differences in onset potential for CO$_2$R (2.6 V vs. Na/Na$^+$) under CO$_2$ saturation and HER (1.7 V vs. Na/Na$^+$) under Ar saturation in the seawater electrolyte. In particular, inner pressure decay and real-time DEMS measurements of the gas-tight Swagelok-type CBS system revealed that CO$_2$ was reduced at potentials up to 2.0 V and that H$_2$ gas was evolved from a sweep voltage of 1.8 V (Fig. 2d); these results are well matched with the onset potential for galvanostatic discharge (Fig. 2a) and LSV curves (Fig. 2b). Thus, we confirmed that BN-GFLP exhibits reliable CO$_2$R selectivity versus HER.

We performed $^{11}$B and $^{15}$N NMR spectroscopy to validate the capacity of BN-GFLP to bind CO$_2$ (Figs. 2e,f). Prior to CO$_2$ gas stimulus, BN-GFLP showed broad $^{11}$B peaks due to inhomogeneous boron doping in the graphitic framework (Fig. 2e). In contrast, a remarkably intense $^{11}$B signal at 27.58 ppm associated with BO bonds was observed for BN-GFLP with CO$_2$.$^{37}$ For $^{15}$N NMR spectroscopy, $^{15}$N urea was used as the $^{15}$N dopant in BN-GFLP (synthesis details are given in the Methods). Without CO$_2$, the $^{15}$N NMR spectrum showed a broad peak at 64.41 ppm from $^{15}$N in the graphitic framework of the BN-GFLP sample (Fig. 2f). In contrast, in BN-GFLP with CO$_2$, two sharp peaks at 71.05 and 91.72 ppm appeared due to two possible N–C interaction modes (Fig. 2f, inset). We assumed that the bidentate coordination of N–C and B–O corresponded to the more downshifted peak (at 91.72 ppm) due to charge localisation effects, compared with monodentate N–C coordination (at 71.05 ppm)$^{38}$. This hypothesis was supported by Raman spectroscopy (Supplementary Fig. 9), temperature programmed desorption (Supplementary Fig. 10), and the subsequent computational study. These NMR results confirm that CO$_2$ adsorbs on BN-GFLP through boron binding as the LA to the oxygen of CO$_2$, with nitrogen binding as the LB to the carbon$^{21}$ (Fig. 1a).

**Performance of CBS cell in anthropogenic acidified seawater**
For actual CO₂R operation in a seawater environment, we fabricated the zig-type CBS cell shown in Fig. 3a. The zig-type CBS cell with CO₂ bubbling provided sufficient electrical energy to operate a light-emitting diode (LED) device (Fig. 3b). In addition, to reflect natural ocean acidification by anthropogenic CO₂ emissions, we intentionally prepared CO₂-saturated seawater by bubbling CO₂ for 2 h, resulting in a drastic decrease in pH to 6.4. This acidified seawater electrolyte was restored by the CO₂R activity of the BN-GFLP cathode, resulting in a gradual increase in pH from 6.4 to 8.0 after 90 h of CBS discharging (Fig. 3c). The charge–discharge cycling stability of the CBS cell under a CO₂ atmosphere was well retained for 200 h with lower discharge–charge overpotentials than the GN catalyst (Fig. 3d).

The unusual multi-carbon liquid products (C₂⁺), such as ethanol, n-propanol, and a small amount of methanol, from CO₂R were collected and identified by electrospray ionisation mass spectrometry (Supplementary Fig. 11) and high-performance liquid chromatography (Supplementary Fig. 13). At 0.13 mA cm⁻², the total CO₂R FE on BN-GFLP was 87.6% and selectivity for C₂⁺ (ethanol and n-propanol) was 95.0% in the seawater electrolyte (Supplementary Fig. 15). The detailed mechanism for C₂⁺ alcohol production from CO₂R will be discussed in the computational chemistry study. Furthermore, during the CO₂R process in seawater, calcite (CaCO₃) precipitates in response to a local increase in pH, which is a major stability issue with metallic CO₂R catalysts. This calcification is generally related to the existence of Ca²⁺ in seawater. However, no CaCO₃ was detected on the surface of BN-GFLP in our CBS system, even after intentionally adding 0.5 M CaCl₂ to the seawater electrolyte; only C₂⁺ products were detected, similar to those observed in pure seawater (Supplementary Figs. 12, 13, and 15). Moreover, the dissolved CO₂ in seawater is converted at equilibrium into bicarbonate (HCO₃⁻) at neutral pH, hence, we also analysed the products of CO₂R with BN-GFLP in a 0.5 M NaHCO₃ saline electrolyte, instead of saturated CO₂ and confirmed the formation of the same C₂⁺ products (Supplementary Figs. 12, 13, and 15). When combined, these results show that BN-GFLP is highly reactive toward HCO₃⁻ and CO₂ reduction prior to the formation of CaCO₃. In addition, the BN-GFLP cathode showed unprecedented and persistent catalytic performance for up to 100 h (Supplementary Fig. 17) without significant calcification.
This improved electrochemical stability might be related to \( \pi \)-electron donation from the graphitic framework.

**DFT calculations for mechanistic insights of BN-GFLP**

We used density functional theory (DFT) to elucidate the unique features of the BN-GFLP catalyst for CO\(_2\)R and suggest a plausible C\(_2^+\) production mechanism (Fig. 4a). BN-GFLP was found to bind to CO\(_2\) more strongly in a bidentate structure involving N–C and B–O than in a monodentate structure involving N–C, which agrees with the \(^{11}\)B and \(^{15}\)N MAS NMR studies (Fig. 2e,f). Furthermore, the bidentate structure favours the formation of the carbon monoxide (CO) intermediate from both CO\(_2\) and HCO\(_3^-\), with a favourable Gibbs energy (\(\Delta G\)) of -1.4 eV. Subsequently, direct C–C bond formation between the CO intermediate and another CO\(_2\) results in the favourable formation of C\(_2\)O\(_3\) with a \(\Delta G\) of approximately -3.2 eV (Fig. 4a).

The observed unusual formation of C\(_2\)O\(_3\) can be explained by the sp\(^2\)-type electronic structure of CO bonded to BN-GFLP, resulting in a single electron occupying the antibonding molecular orbital of CO (Supplementary Fig. 25), which increases the electron population on C and weakens the CO bond. Specifically, the triple bond of molecular CO induces a formal negative charge on C\(^{41}\). Furthermore, based on Bader charge analysis, the population of the C atom of CO bound to BN-GFLP is greater than that of a CO molecule by 0.28 electrons (Fig. 4b and Supplementary Fig. 26), which enhances C–C coupling between the negative C of the CO and positive C of a CO\(_2\), resulting in C\(_2\)O\(_3\) formation. Moreover, according to density of states (DOS) calculations, the antibonding state of the CO DOS in the -1 eV region is reduced through attachment to another CO\(_2\) (Supplementary Fig. 25). This change in DOS makes CO\(_2\) attachment favourable, which explains the marked decrease in Gibbs free energy when CO\(_2\) bonds to CO. This thermodynamically favourable C\(_2\)O\(_3\) formation contributes to the activation of subsequent hydrogenation steps and selectivity towards C\(_2^+\) products. It is noteworthy that the present exothermic formation of C\(_2\)O\(_3\) by CO–CO\(_2\) bonding is completely different from previously reported mechanisms that have endothermic CO–CO coupling steps for C\(_2^+\) production\(^{5,11,12,42-44}\). The exothermic formation of
C$_2$O$_3$ is derived from the cooperative effects of the enhanced negative Bader charge on C and the antibonding dangling-bond electrons on the CO intermediate from the dual FLP binding sites on BN-GFLP, whereas the mono-binding B-GN and N-GN sites result in endothermically unfavourable C$_2$O$_3$ formation. Furthermore, the dual binding mode on BN-GFLP highly stabilises the C–O bonds of H$_3$CH$_2$CO$^*$ (ethanol intermediate) and H$_3$CH$_2$CH$_2$CO$^*$ (n-propanol intermediate), which leads to suppressed deoxygenation (Supplementary Fig. 27). Therefore, the BN-GFLP catalyst showed high alcohol selectivity in the C$_2$+ product distribution (Supplementary Fig. 15) over hydrocarbon products in the CO$_2$R process.$^{45}$ (Supplementary Fig. 27). Moreover, the energetic levels of all the species on BN-GFLP show favourable Gibbs free binding energies for conversion from CO$_2$ into C$_2$+ (ethanol and n-propanol). The potential-determining step for the overall reaction is the initial formation of CO ($^*$CO$_2$H + H$^+$ + e$^-$ → $^*$CO + H$_2$O), which was calculated to be uphill by 1.57 eV at $U = 0$ V. With an onset potential of -1.57 V$_{RHE}$ at pH 6.8, all proton–electron transfer steps have exothermic pathways. Thus, the DFT-calculated free energetics of CO$_2$R on BN-GFLP rationalise the experimental results for C$_2$+ production from CO$_2$ in seawater.

**Conclusions**

In summary, we developed a CBS system to reduce CO$_2$ dissolved in seawater using a BN-GFLP catalytic cathode, resulting in the recovery of acidified seawater at a 87% FE. The unique features of BN-GFLP afford a novel dual CO$_2$ binding mode, which enables exothermic C–C coupling to deliver 95% selectivity for valuable multi-carbon products from CO$_2$R. This state-of-the-art molecular design strategy for CO$_2$R catalysts will contribute to saving the oceans and the atmosphere and to overcoming the current limitations of electrochemical catalytic performance in various fields.
Methods

Materials. N-methylpyrrolidone (NMP), pyrrole bis(pinacolato)diboron, CaCl₂, TMP, ¹⁵N urea were purchased from Sigma-Aldrich, USA, and used as received. Graphene nanopowder (multi-flakes) was obtained from Graphene Supermarket, USA. Other reagents and solvents were of analytical or high-performance liquid chromatography grade and used without further purification.

Synthesis of heteroatom doped GN by sono-cavitation and nebulization synthesis (SNS).

Preparation of precursor solutions: GN powders (15 mg) were added to NMP (30 mL) and dispersed by sonication for 2 hours with an ultrasonic probe (750 W, 20 kHz, Sonics and materials Inc., USA) to form a 0.5 mg mL⁻¹ spray solution. The solution was directly used to synthesize the N-GN with N₂ gas via SNS. To synthesize the both of B-GN and BN-GFLP, bis(pinacolato)diboron (30 mg) as boron dopant was added to the prepared GN solution (0.5 mg mL⁻¹, 30 mL,) and sonicated for 1 hour.

Sono-cavitation and nebulization synthesis: The concurrently pumped spray coating was performed with an ExactaCoat system fixed with an impact ultrasonic nozzle (Sono-Tek Co.). The prepared precursor solutions were sequentially fed into the ultrasonic nozzle (180 kHz) system at the spray rate of 0.3 mL min⁻¹. The nozzle-to-substrate distance (10 cm) and the compressed N₂ or Ar gas pressure (3.0 psi) were used to spray the gas diffusion layer substrate (carbon felt, area: 5 cm × 5 cm, thickness: ~4.1 mm) at a spray speed of 20 mm s⁻¹ on a temperature-controlled (150 °C) stage. The resulting products were cool to room temperature and washed with water, ethanol, and acetone to remove the unreacted precursor and impurities. The residual solvent was evaporated in a vacuum oven at 200 °C for 24 hours. As a result, the SNS process with GN solution synthesized the GN (with Ar gas carrier) and the N-GN (with N₂ gas carrier) catalytic cathodes. The SNS process with boron dopant mixed GN solution synthesized the B-GN (with Ar gas carrier) and the BN-GFLP (with N₂ gas carrier) catalytic cathodes.
**Surface chemistry analysis.** The structure and doping of the carbon materials treated by the SNS were analyzed using high-resolution transmission electron microscopy (TEM, JEOL JEM-2100F (Cs), operating at 200 kV), Raman spectroscopy (Alpha 300R, WITec GmbH), X-ray photoelectron spectroscopy (Thermo Fisher, K-alpha), and energy dispersive spectroscopy (resolution: 128 eV, Oxford, x-Max T-80). Raman spectra and images for the samples were obtained with a micro-Raman system with a 532 nm laser. In order to avoid the laser-induced thermal effects or damage to the samples, the incident laser power was controlled to below 4 mW.

**Nuclear magnetic resonance (NMR) spectroscopy.** All the NMR experiments were performed on a Varian VNMRS 600 MHz spectrometer at resonance frequencies of 599.83, 242.82, 192.45, and 60.79 MHz for $^1$H, $^{31}$P, $^{11}$B, and $^{15}$N nucleus, respectively. The NMR spectra were recorded using a 1.6 mm HXY fast MAS triple resonance probe and a spinning rate of 35, 25, and 20 kHz. A π/2 pulse lengths of 1.33, 1.55, 4.80, and 2.70 μs, and a recycle delay of 5, 3, 3, and 200 s were used for the $^1$H, $^{31}$P, $^{11}$B, and $^{15}$N MAS NMR experiments, respectively. The chemical shifts of $^1$H, $^{31}$P, $^{11}$B, and $^{15}$N were externally referenced to hexamethylbenzene, 1 M H$_3$PO$_4$ in D$_2$O, 15% BF$_3$·O(C$_2$H$_5$)$_2$ in CDCl$_3$, and $^{15}$N labeled glycine, respectively.

Lewis acidity and Lewis basicity: Prior to the adsorption of probe molecules, the samples were placed in glass tubes and then connected to a vacuum line for dehydration. The temperature was gradually increased at a rate of 1 K/min, and the samples were kept at a final temperature of 453 K at a pressure below 10^-3 Pa over a period of 10 hours and then cooled. After the samples cooled down to the room temperature, sufficient pyrrole molecules were introduced into the activated samples and then frozen by liquid N$_2$. Subsequently, the samples were evacuated at 333 K for 2 hours on the vacuum line to eliminate physisorbed pyrrole molecules after the adsorption was equilibrated. Finally, the sample tubes were flame-sealed. The similar approaches were also employed in the preparation of trimethylphosphine.
(TMP) adsorbed samples. Prior to NMR experiments, the sealed sample was transferred into a ZrO2 rotor with a Kel-F end-cap under a dry nitrogen atmosphere in a glovebox.

B–O and N–C interaction between BN-GFLP and CO2: $^{11}$B NMR and $^{15}$N NMR spectra of graphitic frustrated Lewis pair (GFLP, BN-GFLP) before and after external gas stimuli were tested by VRMS 600 MHz of Varian Instrument. For the synthesis of $^{15}$N labeled BN-GFLP, $^{15}$N urea was used as N dopant, and Ar carrier gas was used in SNS process. Into 60 mL vial were added GN precursor (15 mg), bis(pinacolato)diboron (30 mg), $^{15}$N urea (30 mg), and 30 mL of N-methyl-2-pyrrolidone. The prepared precursor solution was fed into the ultrasonic nozzle (180 kHz) at the 0.3 mL/min of flow rate through syringe pump. The ultrasonic nozzle-to-substrate distance (10 cm) and the compressed Ar gas pressure (3.0 psi) were used to spray deposition to the substrate (SUS plate) on a temperature-controlled (150 °C) heating stage. The resulting products were washed and the residual solvent was evaporated with same procedure of SNS method. Furthermore, to quantitatively control the CO2 aeration amount to a given BN-GFLP sample, we used a microflow-pump GHN-1 (CHIYODA SEIKI Co.) connected into a gas cylinder (10 L), and the gas flow rate was fixed at 50.0 mL s$^{-1}$ and the gas pressure was constant at 1.0 bar.

**Electron paramagnetic resonance (EPR) spectroscopy.** The X-band continuous wave electron paramagnetic resonance spectroscopy signals were collected by EMX plus 6/1 spectrometer (Bruker BioSpin, MA, USA). The radical defects of heteroatom doped graphene nanopowders were recorded by X-band CW-EPR (Bruker EMX plus 6/1 spectrometer equipped with Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller). These analyses were progressed at Western Seoul Center, Korea Basic Science Institute (KBSi).

**Temperature programmed desorption (TPD).** TPD measurements were made on the AutoChem l 2920 instrument. For CO2-TPD measurement, 200 mg of catalyst powder was put into quartz tube and
adsorption of CO₂ was performed in 10%CO₂/He gas flow for 3 h at 50 °C. After 0.5 hours of purging with He (99.999%) gas to remove residual CO₂, it was heated from 50 °C to 400 °C at a rate of 10 °C min⁻¹. The TPD signal was recorded using a thermal conductivity detector.

**CO₂ reduction battery in seawater (CBS) system components preparation.** Coin-type CBS system consists of Na-metal anode with aprotic electrolyte (1 M sodium trifluoromethanesulfonate (NaCF₃SO₃) in tetraethylene glycol dimethyl ether (TEGDME)), carbon felt-support current collector with seawater cathode, and the Na super ion conductor (NASICON) separate. The carbon felt substrate (XP–30A, Toyobo Co., Ltd) was heat-treated at 500 °C in ambient atmosphere for 4 hours with the ramping ratio of 5 °C min⁻¹ to enhance the hydrophilicity, before the aforementioned SNS process. The thickness of heat-treated carbon felt is ~4.1 mm. Natural seawater was collected from the Ilsan beach, Ulsan, Republic of Korea (GPS: 35.497005, 129.430996). NASICON ceramic solid electrolyte (Na₁⁺ₓZr₂Si₃P₃ₓO₁₂, x=2) was purchased from 4TOONE Energy Co., Ltd¹⁷. All chemicals are purchased from Sigma Aldrich and used without any purification.

**Electrochemistry.** All electrochemical evaluations of CBS system were performed by using a battery measurement system (VMP3 Multichannel Workstation, BioLogic). For the CO₂ reduction electrocatalytic activity, the 2-electrode gas-tight Swagelok type CBS system (Extended Data Fig. 3) was connected to linear sweep voltammetry (LSV) and lab-built pressure monitoring system. The hydrogen evolution of GFLP was measured by using lab-built in situ differential electrochemical mass spectroscopy (DEMS). The details of DEMS systems are described elsewhere⁴⁶. The LED panel was prepared by connecting the 36 LED (5 mm, green color) onto the Arduino Breadboard (MB-102) in parallel. To monitoring the pH (Five Easy FE20, Mettler Toledo) of seawater, the flowable zig type CBS system (4TOONE Energy Co., Ltd) was placed into the plastic container. The pH of seawater was controlled by bubbling the CO₂ gas before discharge.
**Product analysis.** Quantitative analysis of the liquid products formed during electrolysis was performed with high performance liquid chromatography (HPLC). After electrolysis, aliquots of the catholyte were collected and analyzed with HPLC (Agilent, 1200 series). Sample vials were placed in a chilled autosampler and 10 μL of each sample was injected onto the column. Synergi Polar C18 column (4 μm, 150 × 4.6 mm) placed in series were used to obtain satisfactory product separation. During analysis the column oven was maintained at a steady temperature of 25 °C, with a steady flow rate of 0.800 mL/min of 100% H2O (isocratic) as eluent. The effluent stream coming from the column was passed through a refractive index detector (RID) for product detection. Standard calibrations were performed using dilute solutions of the expected products, methanol, ethanol, n-propanol, and formic acid. Reported Faradaic efficiencies were averaged from at least three different electrolysis experiments. Electrospray ionization mass spectroscopy (ESI-MS) was carried out on a AccuTOF 4G+ DART (JEOL) for confirming the molecular weight of all the samples. Samples containing 10-100 μg of an analyte were introduced using direct injection to mass spectrometer with a flow rate of 3 μl/min. The potential between the spray needle and the orifice was set to 2.0 kV. The detector potential was 2.5 kV. The AccuTOF 4G+ DART instrument equipped with an ESI source with ion funnel, was operated in the positive or negative ion mode and calibrated before each analysis with the Tunemix mixture (Agilent) by a quadratic method.

**Evaluation of CO2R performance.** For liquid products, the following method was used for the calculation of Faradaic efficiency. The concentration of species \( l (c_l \text{ (mol L}^{-1})\) was calculated from the HPLC with internal standard method. With \( z_l \), Faraday constant and the electrolyte volume \( (V \text{ (L)})\), the partial charge to produce species \( l (q_l \text{ (C)})\) was calculated. The Faradaic efficiency for species \( l (FE_l)\) is the percentage of the partial charge in the total charge passed \( (q_{tot} \text{ (C)})\):
\[ FE_l = \frac{q_l}{q_{tot}} = \frac{96485 \times c_l \times V \times z_l}{q_{tot}} \times 100\% \]

Formation rate (R) for each species and C₂⁺ selectivity were calculated using the following equations:

\[ R_l = \frac{q_{tot} \times FE_l}{96485 \times z_l \times t \times S} = \frac{c_l \times V}{t \times S} \]

where \( t \) was the electrolysis time (h) and \( S \) was the geometric area of the electrode (cm²).

\[ C_{2+} \text{ selectivity (\%)} = \frac{2R_{ethanol} + 3R_{propanol}}{R_{methanol} + 2R_{ethanol} + 3R_{propanol}} \times 100\% \]

**DFT calculation method.** Spin-polarized Density Functional Theory calculations were performed by using Vienna Ab-initio Simulation Package (VASP) code⁴⁷. The plane wave cutoff energy of 400 eV was employed with PBE parameterization of GGA exchange-correlation functional⁴⁸. We adopted the ribbon structure model with the lattice parameter \( a = 17.04 \) Å, \( b = 25.00 \) Å, \( c = 20.00 \) Å, where the ribbon is extended along the a-direction and sufficient vacuum regions greater than 15 Å are inserted along the other directions to minimize the unphysical interaction between periodic images. All structures were fully optimized in the 1x1x1 k-mesh until the force is less than 0.01 eV/Å with van der Waals correction by Grimme’s scheme, D3 method⁴⁹. In HCO₃⁻ calculation, we constructed cell with different length, and extrapolated their energy to get appropriate binding energy without unphysical interactions in periodic boundary condition. For density of states (DOS) calculation, 8x1x1 k-mesh was used. We calculated the Gibbs free energy by the equation, \( \Delta G = \Delta E^{DFT} + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}^{50} \). \( \Delta E^{DFT} \) refers to the calculated adsorption energy difference between subsequent intermediates proposed by Norskov et al.⁵¹. Zero-point energy and vibrational entropy, \( \Delta ZPE \) and \( T\Delta S \), were calculated by vibrational frequencies of each intermediates. Under the applied electrode potential \( U \), \( \Delta G_U = -eU \) correction was added to the total Gibbs free energy. \( \Delta G_{pH} \) denotes correction of solution acidity by \(-k_B T \ln [H^+]\). We performed the Bader charge analysis for CO and C₂O₃ structure to figure out the effect of electrostatic interaction between adsorbed CO and CO₂ molecule to form C₂⁺ product⁵².
Data availability

The authors declare that all data supporting the findings of this study are available in the paper and Supplementary Information. Additional datasets related to this study are available from the corresponding authors on reasonable request.


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Author contribution


Competing financial interests

The authors declare no competing financial interest.

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Fig. 1: Sono-cavitation and nebulisation synthesis (SNS) process and BN-GFLP structure characterisation. (a) Schematic of the SNS process for BN-GFLP synthesis and molecular interactions between BN-GFLP and CO₂. (b) Survey XPS spectra (normalised to C₁s) and (c) EPR spectra of GN, N-GN, B-GN, and BN-GFLP at 10 K. (d) \(^{31}\)P MAS NMR spectrum of TMP on BN-GFLP. (e) \(^{1}\)H MAS NMR spectrum of pyrrole adsorbed on BN-GFLP.
Fig. 2: Electrochemical CO₂ reduction on the BN-GFLP electrode in seawater. (a) Galvanostatic discharge voltage profiles of the CBS system with the prepared catalysts at a fixed current density of 0.13 mA cm⁻² and (b) LSV profiles of the BN-GFLP catalyst under various system atmospheres in the 3.0–1.0 V voltage window at a sweep rate of 0.1 mV s⁻¹. (c) Quantitative CO₂ gas consumption during the galvanostatic discharge process in (a). (d) Inner pressure decay (red) and complementary DEMS (black) results corresponding to the LSV profiles in (b). (e) ¹¹B and (f) ¹⁵N MAS NMR spectra of BN-GFLP with (red) and without (black) CO₂ stimulus. Possible binding configurations between BN-GFLP and CO₂ are shown in the insets of (e) and (f).
Fig. 3: Electric energy harvesting and stability of the CBS system with the BN-GFLP cathode during CO$_2$R. (a) Schematic of the zig-type CBS system. (b) Digital photograph of 36 LEDs powered by the CBS system. (c) Seawater pH as a function of time during CO$_2$R with a fixed current density of 0.13 mA cm$^{-2}$. The pH was controlled by bubbling CO$_2$ into the seawater. (d) Galvanostatic charge-discharge voltage plots of zig-type CBS cells with BN-GFLP and control GN cathodes.
Fig. 4: DFT calculations of the BN-GFLP catalyst for CO₂R. (a) Gibbs free energy diagram for CO₂R reaction to C₂+ products on the BN-GFLP electrode. The red lines show the optimal mechanism for C₂⁺ product formation at an applied potential of -1.57 V. According to the reaction path at 0 V applied potential (black lines) CO–CO₂ coupling (4 → 5) is highly favourable, with a Gibbs free energy difference of -3.2 eV. (b) Bader charges (e⁻) of the active sites in BN-GFLP and the reaction-path intermediates corresponding to (a). The Bader charge of each atom is shown in the same color as the corresponding atom: hydrogen (black), nitrogen (blue), boron (purple), carbon (grey), and oxygen (red).