Supporting Information

Phosphorus-Doped Graphene Aerogel as Self-supported Electrocatalyst for CO$_2$-to-Ethanol Conversion

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Table of Contents

S1. Experimental and DFT calculation details. .......................................................... 3-7
S2. Schematic illustration of the synthesis process. ................................................. 8
S3. Textural properties of catalysts. ................................................................. 8-11
S4. Electrochemical tests for all catalysts. ......................................................... 12-15
S5. Characterization for PGA-2 after CO₂ reduction. ........................................ 15
S6. NMR characterization after electrolysis. ....................................................... 16
S7. Electrochemical behaviors analysis for all catalysts. .................................... 17-19
S8. Flow cell tests for PGA-2. ........................................................................... 20
S9. DFT calculations on P-doped graphene configurations. ............................... 21-28
S10. Electrode potentials for CO₂RR half-reactions in aqueous solution. ............ 29
S11. Comparison of catalysts performance for CO₂ reduction to EtOH .............. 30

References. ........................................................................................................... 31-34
**S1. Experimental and DFT calculation details.**

**Materials.** Graphite powder and potassium bicarbonate (KHCO₃) were purchased from Aladdin Reagent Co., Ltd. Phosphoric acid (H₃PO₄) was obtained from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were reagent grade and used as received without further purification. Carbon paper (HCP 030) and Nafion solution (5 wt%) were acquired from Shanghai Hesen Electric Co., Ltd and Sigma-Aldrich, respectively. Ultra-high purity carbon dioxide (99.999%) and argon (99.999%) were supplied from Nanchang Guoteng Gas. Co., Ltd. Ultrapure Millipore water (18.2 MΩ) was supplied by a UP water purification system.

**Sample preparation.** Graphene oxide (GO) was obtained through chemical exfoliation of graphite powders using the modified Hummer’s method.¹ P-doped graphene aerogels (PGAs) were synthesized using the hydrothermal method. Typically, a certain amount of phosphoric acid was mixed with 30 mL GO aqueous dispersion (2 mg mL⁻¹). The mixture was sonicated for 1 h to form a uniform suspension, and then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 12 h. After cooling to room temperature, the produced hydrogel was washed with water and ethanol, then freeze-dried. Finally, the product was annealed at 900 °C for 1 h under N₂ flow. The sample prepared with 1-, 2-, and 3-mL phosphoric acid loading was denoted as PGA-1, PGA-2, and PGA-3, respectively. Further improving phosphoric acid loading will cause the deformation of aerogel. For comparison, the control sample of GA was prepared without phosphoric acid *via* the same procedure.
**Electrochemical measurements.** The electrochemical performances were determined using a CHI 660E electrochemical working station with a three-electrode H-cell. The cathodic and anodic compartments were separated by the Nafion® 117 membrane. An Ag/AgCl electrode and a graphite rod are served as the reference and counter electrode, respectively. The self-supporting PGAs and GA can be cut into the desired size and directly used as the working electrode (Figure S9). All potentials were measured against the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) using the equation of $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.21 \text{ V} + 0.0591 \times \text{pH}$. The electrolysis was conducted in a CO$_2$-saturated 0.5 M KHCO$_3$ solution ($\text{pH} = 7.2$) at ambient temperature and pressure. During electrolysis, CO$_2$ was continuously bubbled into the cathodic compartment at a rate of 20 sccm. The gas products were measured using on-line gas chromatography (GC, Agilent 7890B). The electrolyte after electrolysis was collected and tested by $^{1}$H nuclear magnetic resonance (NMR, Bruker 600 MHz) using a pre-saturation method to suppress the water peak.

For the flow cell test, an Ag/AgCl electrode and Pt foil were used as the reference and counter electrode, respectively. PGA-2 was ground and loaded on a gas diffusion layer (GDL) as the working electrode and 1.0 M KOH ($\text{pH} = 14.0$) was used as the electrolyte. During the tests, the electrolyte was circulated through the cathode compartment at a rate of 12 mL min$^{-1}$, and CO$_2$ gas with a flow rate of 20 sccm was fed to the cathode GDL.

**In-situ Raman test.** In-situ Raman spectroscopy was performed using a Confocal
LabRam HR800 microscope (Horiba Jobin Yvon). Raman signals were collected based on a self-made electrochemical cell, in which graphite rod and Ag/AgCl electrode were used as the counter and reference electrode, respectively. The as-prepared PGA catalyst was used as the working electrode in 0.5 M KHCO₃ electrolyte with continuous CO₂ flowing at 20 sccm on the backside. A 50× objective lenses and a laser wavelength of 532 nm were applied.

**Characterizations.** X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with a Cu target (λ = 1.5418 Å). The spectra of X-ray photoelectron spectroscopy (XPS) were analyzed using a Thermo Fisher Scientific Escalab 250Xi system with a monochromatic Al-Kα source. The morphologies and microstructures were characterized by scanning electron microscopy (SEM, Hitachi SU800) and transmission electron microscopy (TEM, FEI Talos F200X). Raman spectra were collected using a LabRam HR800 spectrometer (Horiba Jobin Yvon) with a 532 nm laser source. N₂ and CO₂ adsorption-desorption isotherms were measured on a Micromeritics ASAP 2460 apparatus. Before each adsorption measurement, the sample was degassed at 150 °C for 12 h.

**Calculation of cathodic energy efficiency (EE).**

\[
EE = \frac{1.23 - E^0}{1.23 - E} \times FE_{\text{EtOH}}
\]

Where E is the applied potential in the experiment, FE_{\text{EtOH}} is the Faradaic efficiency of ethanol, E^0 is 0.09 V_RHE for the thermodynamic potential of CO₂ reduction to ethanol.

**DFT calculations.** DFT calculations were executed by VASP with the GGA-PBE
method (generalized gradient approximation with Perdew, Burke, and Ernzerh) functional.\cite{2-4} The cutoff energy, energy convergence, and force convergence were set as 500 eV, $1 \times 10^{-4}$ eV, and 0.03 eV/Å, respectively. Meanwhile, the gamma point is utilized in Mohkhorst-Pack (MP) grid.\cite{5} In addition, the DFT-D3 method with Becke-Jonson damping was conducted for all calculations.\cite{6}

For all absorbed intermediates of CO$_2$RR and HER, the binding energy (BE) can be written as:

$$BE = E_{\text{total}} - (E_{\text{slab}} + E_{\text{ads}})$$

Wherein, $E_{\text{total}}$ is the whole energy of intermediates absorbed on the slab, $E_{\text{slab}}$ is the energy of the basic slabs, and $E_{\text{ads}}$ represents the energy of various intermediates.

The variation of Gibbs free energy ($\Delta G$) of each reaction step refers to the calculated hydrogen electrode\cite{7} and the expression can be described as:

$$\Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_{\text{pH}} + \Delta G_U$$

$$\Delta G_U = -n e U$$

$$\Delta G_{\text{pH}} = k_B T \times \ln 10 \times pH$$

Here, the energy difference of each reaction is $\Delta E$; $\Delta ZPE$ is the zero-point energy and $\Delta S$ is the entropy difference at T=298.15 K. $\Delta ZPE$ and $\Delta S$ were obtained with displacement as 0.015 Å for all absorbed intermediates. $\Delta G_U$ is the contribution of the electrode potential to $\Delta G$. For the symbols in $\Delta G_U$ formula, $n$ represents the number of transferred electrons in each step and $U$ is the applied electrode potential. $\Delta G_{\text{pH}}$ is the correction of free energy at given pH. In this study, the environment was slightly alkaline with a pH of 7.2. All the temperature is 298.15K and $k_B$ is the Boltzmann
constant.

The energy of H\textsubscript{2}O, CO\textsubscript{2}, and H\textsubscript{2} is calculated by VASP in a vacuum. The correction of energy is obtained from vaspkit.\textsuperscript{[8]} The temperature is chosen as 298.15 K, the pressure is 0.035 atm for H\textsubscript{2}O (l) and 1 atm for CO\textsubscript{2} and H\textsubscript{2}. The energy of OH\textsuperscript{-} is derived from \(G(\text{OH}^-) = G(\text{H}_2\text{O}) - \frac{1}{2} G(\text{H}_2)\) in pH = 0. ΔZPE and TAS of absorbed intermediates are acquired from vaspkit with a temperature of 298.15 K.\textsuperscript{[8]}

In this work, the reaction mechanism can be described as,

\[
* + 2\text{CO}_2 (g) + \text{H}_2\text{O} + e^- \rightarrow *\text{COOH} + \text{CO}_2 (g) + \text{OH}^- \\
*\text{COOH} + \text{CO}_2 (g) + e^- \rightarrow *\text{CO} + \text{CO}_2 (g) + \text{OH}^- \\
*\text{CO} + \text{CO}_2 (g) + \text{H}_2\text{O} + e^- \rightarrow *\text{CHO} + \text{CO}_2 (g) + \text{OH}^- \\
*\text{CHO} + \text{CO}_2 (g) + \text{H}_2\text{O} + 2e^- \rightarrow *\text{COCHO} + 2\text{OH}^- \\
*\text{COCHO} + \text{H}_2\text{O} + e^- \rightarrow *\text{CHOCHO} + \text{OH}^- \\
*\text{CHOCHO} + \text{H}_2\text{O} + e^- \rightarrow *\text{CH}_2\text{CHO} + \text{OH}^- \\
*\text{CH}_2\text{CHO} + \text{H}_2\text{O} + e^- \rightarrow *\text{CH}_2\text{CHOH} + \text{OH}^- \\
*\text{CH}_2\text{CHOH} + \text{H}_2\text{O} + e^- \rightarrow *\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \\
*\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} + e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{OH}^- \\
\]

Besides, the HER reaction mechanism in alkaline condition is as follows:

\[
* + \text{H}_2\text{O} \rightarrow *\text{H} + *\text{OH} \\
*\text{H} + *\text{OH} + e^- \rightarrow *\text{H} + \text{OH}^- \\
\]

7
$*H + OH^- \rightarrow \frac{1}{2} H_2 + OH^-$

**S2. Schematic illustration of the synthesis process.**

![Schematic illustration of the synthesis process](image)

**Figure S1.** Schematic illustration of P-doped hydrogel preparation.

**S3. Textural properties of catalysts.**

![Textural properties of catalysts](image)

**Figure S2.** SEM and TEM images of (a and d) GA, (b and e) PGA-1, (c and f) PGA-3.
Figure S3. Raman spectra of all samples.

Figure S4. N\textsubscript{2} adsorption-desorption isotherms for all samples.
**Figure S5.** Pore size distribution for all samples.

**Figure S6.** XPS survey for all samples.
Figure S7. High-resolution C 1s XPS spectra for all samples.

Figure S8. High-resolution O 1s XPS spectra for all samples.
**S4. Electrochemical tests for all catalysts.**

**Figure S9.** Image of (a) PGA-2 electrode and (b) assembled in H-cell.

**Figure S10.** LSV curves in CO$_2$- and Ar-saturated 0.5 M KHCO$_3$ electrolyte on (a) PGA-1, (b) PGA-2, (c) PGA-3, and (d) GA.
Figure S11. EtOH partial current densities of all samples.

Figure S12. Comparison of EtOH FE on different state-of-the-art catalysts.
**Figure S13.** FE of all products at different applied potentials in CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte on GA.

**Figure S14.** Energy efficiency at different applied potentials for all samples.
Figure S15. EtOH yields at different applied potentials for all samples.

**S5. Characterization for PGA-2 after CO$_2$ reduction.**

Figure S16. (a) SEM and (b) TEM images, (c) EDS mappings, (d) XRD patterns, and high-resolution XPS spectra of (e) C 1s and (f) P 2p of PGA-2 after duration test.
**S6. NMR characterization after electrolysis.**

**Figure S17.** $^1$H NMR results of the liquid product of PGA-2 in CO$_2$ and Ar-saturated 0.5 M KHCO$_3$ electrolyte after electrolysis.

**Figure S18.** (a) $^1$H NMR and (b) $^{13}$C NMR spectra of the catholyte after electrolysis using $^{13}$CO$_2$ and $^{12}$CO$_2$ as feeding gas on PGA-2 at -0.8 V.
**S7. Electrochemical behaviors analysis for all catalysts.**

**Figure S19.** Cyclic voltammetry (CV) results of (a) PGA-1, (b) PGA-2, (c) PGA-3, and (d) GA.

**Figure S20.** Charging current densities plotted against scan rates for all samples.
**Figure S21.** Relationship between $C_{dl}$ and BET specific surface areas.

**Figure S22.** Adsorption (solid) and desorption (open) isotherms of CO$_2$ at 298 K and 1.0 bar on all samples.
Figure S23. Tafel plot for all samples.

Figure S24. Electrochemical impedance spectroscopy of all samples.
S8. Flow cell tests for PGA-2.

Figure S25. FE of products at different applied potentials on PGA-2 in flow cell.
S9. DFT calculations on P-doped graphene configurations.

Figure S26. Models of P-doped graphene configurations. (a) P[OH]$_2$O-doped graphene; (b) P[OH]-doped graphene (OH terminated is due to the slightly alkaline environment); (c) P replaces one carbon atom at the boundary; (d) P replaces one carbon atom in the center; (e) P-chain doped graphene; (f) P atom connected at the boundary of graphene (P$_1$@ZZG). Color code: P, pink; H, white; O, red; C, grey.
Figure S27. Binding energy of *COOH absorbed at different sites of various configurations. (a) P[OH]$_2$O-doped graphene; (b) P[OH]-doped graphene; (c) P replaces one carbon atom at the boundary of graphene; (d) P replaces one carbon atom in the center of graphene; (e) P-chain doped graphene; (f) P atom connected at the boundary of graphene. Color code: P, pink; H, white; O, red; C, grey.
Figure S28. Absorbed situation of *CO at different sites of various configurations. (a) P[OH]2O-doped graphene; (b) P[OH]-doped graphene; (c) P replaces one carbon atom at the boundary of graphene; (d) P replaces one carbon atom in the center of graphene; (e) P-chain doped graphene; Color code: P, pink; H, white; O, red; C, grey.

The absorbed sites on different models for *CO are chosen from the most possible absorbing sites of *COOH. However, *CO cannot be absorbed on models displayed in Figure S26a-d. The binding energies of *CO on the two P sites were all positive as 0.13 and 0.21 eV (Figure S28e). The high *CO binding energies indicated that the process of *COOH conversion to EtOH cannot be conducted. Besides, the *CO absorbed on the slab in Figure S26f was shown in the rightmost picture in Figure S29.
Figure S29. Reaction pathway from CO$_2$ to *COOH to *CO on P$_1$@ZZG structure.

Figure S30. Two P-doped graphene model (P$_2$@ZZG): the initial constructed structure (left) and the final optimized structure (right).

Figure S31. Bader charge analysis around P atoms in P$_2$@ZZG.
Figure S32. The reaction pathway from \(^{*}\)CO to the first C-C coupling intermediates:
path I: \(^{*}\)CO \(\rightarrow\) \(^{*}\)CHO \(\rightarrow\) \(^{*}\)COCHO; path II: \(^{*}\)CO \(\rightarrow\) \(^{*}\)COCO; path III: \(^{*}\)CO \(\rightarrow\) \(^{*}\)OCCO. Here, the denoted energy barriers are divided by two, because these steps included two transferred electrons.

Figure S33. Symbolic element model for the overall pathways (the grey bottom line represents graphene and P atom is the purple circle).
Figure S34. Free energy diagram of two optimal reaction pathways for CO$_2$ reduction to EtOH on P$_2$@ZZG at U = -0.86 V.
Figure S35. (a) Schematic illustration of *CH$_2$CHO transformation process on P$_2@$ZZG. (b) The comparison of energy barrier from *CH$_2$CHOH to *CH$_2$CH$_2$OH or *CH$_2$CH.

C$_2$H$_4$ and EtOH share most reaction intermediates until *CH$_2$CHO (or *CH$_2$CHOH), which could transform to EtOH through further protonation to *CH$_2$CHOH (or *CH$_2$CH$_2$OH/*CH$_3$CHOH), or to C$_2$H$_4$ via *CH$_2$CH$_2$O $\rightarrow$ *O + CH$_2$CH$_2$ (or *CH$_2$CHOH $\rightarrow$ *CH$_2$CH + OH$^-$). The *CH$_2$CH$_2$O intermediate will spontaneously transform to *CH$_2$CHOH after optimization, implying the favorable EtOH generation (Figure S35a). For *CH$_2$CHOH, the energy barrier towards *CH$_2$CH is 1.37 eV, much higher than that of *CH$_2$CH$_2$OH (0.45 eV, Figures S33 and 35b). The value is also lower than that of *CH$_3$CHOH (0.69 eV). Therefore, the whole reaction prefers processing to EtOH rather than C$_2$H$_4$. 

**Figure S36.** Free energy diagram (left) and corresponding stick-ball models (right) of HER at three different pathways (color code: P, purple; H, white; O, red; C, grey).

In Path 1, water was directly split to *OH and *O on different P atoms with an overall energy barrier of 1.82 eV. In path 2, after adsorbing *COOH onto the single-bond P atom, the overall HER progressed around the neighboring P atom with a lower energy barrier of 1.28 eV that was still higher than that of CO$_2$RR (0.86 eV). Thus, HER was greatly depressed on P$_2$@ZZG with the applied voltages around -0.86 V.
**S10. Electrode potentials for CO₂RR half-reactions in aqueous solution.**

**Table S1.** Electrode potentials for CO₂RR half-reactions in aqueous solution.[9]

| CO₂RR half-reactions | Electrode potentials (V<sub>RHE</sub> at pH = 7) |
|----------------------|-----------------------------------------------|
| CO₂ + 2H⁺ + 2e⁻ → CO + H₂O | -0.11 |
| CO₂ + 2H⁺ + 2e⁻ → HCOOH | -0.22 |
| CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O | 0.17 |
| 2CO₂ +12H⁺ + 12e⁻ → C₂H₄ + 4H₂O | 0.08 |
| 2CO₂ + 12H⁺ + 12e⁻ → C₂H₅OH + 3H₂O | 0.08 |
| 3CO₂ + 18H⁺ + 18e⁻ → C₃H₇OH + 5H₂O | 0.09 |
### S11. Comparison of catalysts performance for CO\(_2\) reduction to EtOH.

**Table S2.** Comparison of catalytic performances for CO\(_2\) electroreduction to EtOH.

| Catalyst                      | Electrolyte       | \(E^a\)  | \(\text{FE}_{\text{EtOH}}^a\) | \(\text{Yield}^a\) | \(j_{\text{EtOH}}^a\) | \(\text{EE}^a\) |
|-------------------------------|-------------------|----------|-------------------------------|--------------------|-----------------|----------|
| PGA-2                         | 0.5 M KHCO\(_3\) | -0.8     | 48.7                          | 14.62              | 4.7             | 27.3     |
| Fe\(_2\)P\(_2\)S\(_6\) nanosheet\(^{[10]}\) | 0.5 M KHCO\(_3\) | -0.2     | 23.1                          | 1.096              | 0.01            | 18.4     |
| Cu\(_4\)Zn\(^{[11]}\)       | 0.1 M KHCO\(_3\) | -1.05    | 29.1                          | 25.45              | 8.2             | 14.6     |
| Ag-Cu\(_2\)O\(_{pb}\)\(^{[12]}\) | 0.2 M KCl         | -1.2     | 34.15                         | 2.15               | 1.02            | 16.0     |
| CuAu NWA\(^{[13]}\)         | 0.1 M KHCO\(_3\) | -0.7     | 45                            | 3.156              | 0.4             | 26.6     |
| OD-Cu/C\(^{[14]}\)          | 0.1 M KHCO\(_3\) | -0.5     | 34.8                          | 1.12               | 0.4             | 21.7     |
| GO-VB\(_6\)-Cu\(^{[15]}\)   | 0.1 M KHCO\(_3\) | -0.25    | 56.3                          | 8.08               | 2.55            | 43.4     |
| BND\(_3\)\(^{[16]}\)        | 0.1 M KHCO\(_3\) | -1.0     | 93.2                          | 5.2                | 0.58            | 47.6     |
| MNC-5\(^{[17]}\)            | 0.1 M KHCO\(_3\) | -0.56    | 78                            | 1.3                | 0.39            | 49.7     |
| c-NC\(^{[18]}\)             | 0.1 M KHCO\(_3\) | -0.63    | 77                            | 0.38               | 0.13            | 47.2     |
| GB-Cu\(^{[19]}\)            | 1 M KOH           | -1.3     | 31.7                          | 44.388             | 45              | 14.3     |
| Cu nanocube\(^{[20]}\)      | 0.1 M KHCO\(_3\) | -1.0     | 22                            | 21.91              | 6.89            | 11.2     |
| Cu-Cu\(_2\)O\(^{[21]}\)     | 0.1 M KCl         | -0.4     | 32                            | 11.47              | 3.68            | 22.4     |
| a-Cu\(^{[22]}\)             | 0.1 M KHCO\(_3\) | -0.8     | 22                            | 0.40               | 0.91            | 12.4     |
| GO-VB\(_6\)-4\(^{[23]}\)    | 0.1 M KHCO\(_3\) | -0.4     | 36.4                          | 1.014              | 0.43            | 25.5     |
| Ag\(_{13}\)Cu\(_{88}\)\(^{[24]}\) | 0.5 M KHCO\(_3\) | -1.0     | 33.7                          | 26.97              | 8.67            | 17.2     |

\(^a\) The data were obtained at the potential of maximum EtOH FE achieved.
Reference.

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