

Supporting Information for

Sustainable Conversion of Harmful Algae Biomass into a CO₂ Reduction

Electrocatalyst for Two-Fold Carbon Utilization

Xiao Hu, Wu-Jun Liu*, Lin-Lin Ma, Han-Qing Yu*

CAS Key Laboratory of Urban Pollutant Conversion, Department of Environmental
Science and Engineering, University of Science and Technology of China, Hefei,
230026, China

E-mails: liuwujun@mail.ustc.edu.cn (Liu, W.-J.), hqyu@ustc.edu.cn (Yu, H.-Q.)

Summary of the contents: 36 pages, 4 texts, 12 references, 13 tables, and 15 figures

Text S1. Synthesis of the nitrogen doped carbon materials from the algae biomass

The collected algae biomass was washed with deionized water and HCl solution (1.0 mol/L) in a row with solid to liquid ratio of 1: 100 to remove the inorganic impurities. Then, the clean biomass was filtrated and freeze-dried. For the *Enteromopha* biomass, 3.0 g of dried biomass was mixed with 25 mL of deionized water in a 50-mL autoclave, which was then sealed and heated at 180 °C for 12 h. After cooling down, the produced solid hydrochar was separated via filtration, and the filtrate was collected for further separation of value-added chemicals. The obtained hydrochar was then washed with deionized water several times and freeze-dried 48 hours to obtain carbon aerogel. The dried carbon aerogel was then annealed under a 10% NH₃ (90% argon) flow at 400 °C in the initial 2 h and then heated up to 700-1100 °C for further 2 h in a heating rate of 2.5 °C min⁻¹. After cooling down, the N-doped porous carbon material was finally obtained and denoted as E-NC. For the *Microcystis aeruginosa* biomass, 1.0 g of dried biomass was mixed with 1.5 g of NaCl via grinding, then annealed with NH₃ in the way similar to that of *Enteromopha* biomass, and finally obtained the N-doped carbon material, which was denoted as MA-NC.

Text S2. Characterizations of materials

The morphology and microstructure of the samples were characterized by SEM and TEM. The SEM images and elemental mapping of the samples were obtained using an X-650 scanning electron micro analyzer and JSM-6700F field emission SEM (JEOL Co., Japan). The TEM images (H-7650, Hitachi Co., Japan) of the samples were

recorded at an electron kinetic energy of 100 kV. The surface chemical composition and the valence states of the constituent elements were analyzed by XPS (ESCALAB250, Thermo Fisher Inc., USA). Nitrogen sorption isotherms were measured with a Tristar 3020 analyzer (Micromeritics Inc., USA) at -196 °C. The specific surface areas were calculated using the adsorption isotherms with the Brunauer-Emmett-Teller (BET) method. Pore distribution was calculated from the desorption branch of the isotherm using the Barrent, Joyner, and Halenda (BJH) method. Raman spectra were collected using a Horiba HR Evolution spectrometer (HR800UV LabRAMHR, HOBIN Co., France) with a 532 nm laser excitation. The samples for FTIR analysis were prepared by mixing the carbon materials with spectroscopy-grade KBr at a ratio of 1:100 and compressing into films. The films were analyzed using a FTIR spectrometer (EQUIVOX55, Bruker Co., Germany) with a detector at 2 cm⁻¹ resolution from 4000 to 800 cm⁻¹ and 16 scans per sample.

Text S3. Work electrode preparation

A total of 5.0 mg of carbon material (E-NC or MA-NC materials prepared under different temperatures) was dispersed into anhydrous ethanol (420 µL) and deionized H₂O (30 µL), with the addition of Nafion solution (50 µL), followed by mixing with the assistance of ultrasonication for at least 60 min to achieve a homogeneous ink. Then, 60 µL of the catalyst ink was pipetted onto a carbon paper electrode (1 cm²) to form a work electrode.

Text S4. Details of the LCA analysis

The following two objectives should be achieved in this work with LCA: (1) assess the total environmental profiles of the N-doped porous carbon materials produced from algae biomass throughout its life cycle with the thermochemical conversion approach and (2) compare the environmental profiles of thermochemical conversion with the conventional landfilling approach for algae biomass treatment. The scope of the LCA and the defined system boundary are presented in Table S6 and Figure 4, respectively.

The procedures of inventory data collection depend on the unit processes, and thorough knowledge is required to avoid gaps or double counting. In addition to the public data, expert judgments and questionnaires on the HAB presented in Figure S1, computer models and laboratory experimental data were also applied to develop the LCA inventories in this work. The methods for collecting inventory data can be found in Table S7, and the main inventory data are provided in Table S8.

LCA was performed with the methodologies available in GaBi (CML2016), and an explanation of how the LCAs were conducted is provided in Table S6. The environmental impact categories considered in the present analysis were (1) agricultural land occupation (m^2a); (2) GHG emissions ($\text{kg CO}_2\text{-eq}$); (3) fossil depletion (kg oil-eq); (4) freshwater ecotoxicity (kg 1,4-DCB-eq); (5) freshwater eutrophication (kg P-eq); (6) human toxicity (kg 1,4-DCB-eq); (7) ionizing radiation (kg U235-eq); (8) metal depletion (kg Fe-eq); (9) ozone depletion (kg CFC-11-eq); (10) particulate matter formation ($\text{kg PM}_{10}\text{-eq}$); (11) photochemical oxidant formation (kg NMVOC); (12) terrestrial acidification ($\text{kg SO}_2\text{-eq}$); (13) terrestrial ecotoxicity (kg 1,4-DCB-eq); (14)

urban land occupation (m^2a); and (15) water depletion (m^3). The various categories (1)-(15) were weighted based on the data collected in Tables S7 and S8 in Aspen Plus, relevant GaBi Professional and Ecoinvent Datasets (if available) and the literature. The distribution and use of the biofuels and chemicals produced from algae and the GHG emissions in the functionalization of the biochar materials were excluded from the impact categories.

Table S1. Important terms from the field of LCA.

| LCA items | Definitions |
|-------------------------------|--|
| Life cycle assessment (LCA) | An ISO-standardized method to quantify environmental impacts from inputs (resources used) and outputs (chemical emissions) along the life cycle of one or more defined product or service systems on a common functional basis. LCA consists of four iterative methodological phases, namely goal and scope definition, life cycle inventory analysis, life cycle impact assessment, and interpretation. |
| Life cycle stages | The stages of product or service life cycles, which mainly include raw materials extraction, manufacturing, use, and end-of-life. |
| Life cycle inventory analysis | The phase of LCA quantifying life cycle inputs and outputs for product or service systems as flows from or toward the natural environment. |
| Life cycle impact assessment | The phase of LCA characterizing life cycle inputs and outputs of product or service systems in terms of the magnitude and significance of their potential impacts on human health, ecosystem quality and natural resources. |
| Impact category | The class of impacts that represent an environmental issue of concern. Examples of impact categories are global warming, ozone depletion, human toxicity, ecotoxicity, land use, water use, and resources use, to which product system life cycle inputs and outputs may be assigned. |
| Cradle-to-gate | LCA where the product system is defined from raw materials extraction ('cradle') to factory gate, that is, not all life cycle stages are covered. |
| Cradle-to-grave | LCA where the product system is defined from raw materials extraction ('cradle') to end-of-life ('grave'), that is, all life cycle stages are covered. |
| End-of-life | The life cycle stage representing the end of the product's use. It may include processes like reuse, recycling, chemical and energy recovery, incineration, landfilling, wastewater treatment, and release of bio-based products in nature. |

Table S2. The elemental composition of the algae biomass.

| Elemental composition | <i>Enteromopha</i> | <i>Microcystis aeruginosa</i> |
|-----------------------|--------------------|-------------------------------|
| C (wt.%) | 46.3 | 49.2 |
| H (wt.%) | 5.9 | 6.2 |
| N (wt.%) | 3.2 | 3.4 |
| O (wt.%) | 41.2 | 36.5 |

Table S3. Compounds and their contents in the biodiesel obtained from the algae biomass

| | |
|---|-------------|
| C14:0 (C ₁₄ H ₂₉ COOH) | 1.19±0.001 |
| C16:0 (C ₁₆ H ₃₃ COOH) | 20.98±0.149 |
| C16:1 (C ₁₆ H ₃₃ COOCH ₃) | 9.57±0.265 |
| C17:0 (C ₁₇ H ₃₅ COOH) | 2.14±0.032 |
| C18:0 (C ₁₈ H ₃₇ COOH) | 0.63±0.006 |
| C18:1 (C ₁₈ H ₃₇ COOCH ₃) | 39.27±0.584 |
| C18:2 (C ₁₈ H ₃₆ (COOCH ₃) ₂) | 22.90±0.383 |
| C18:3 (C ₁₈ H ₃₅ (COOCH ₃) ₃) | 3.31±0.045 |
| SFAME ^a (%) | 25 |
| UFAME ^b (%) | 75 |
| a: Saturated fatty acid methyl esters/total fatty acid methyl esters. | |
| b: Unsaturated fatty acid methyl esters/total fatty acid methyl esters. | |

Table S4. The elemental composition of the algae biomass.

| Yields | <i>Enteromopha</i> | <i>Microcystis aeruginosa</i> |
|-------------------|--------------------|-------------------------------|
| Liquid-oil (wt.%) | 47.2 | 52.3 |
| Hydrochar (wt.%) | 48.6 | 47.3 |

Table S5. The comparison of biomass derived carbon materials with other reported carbon materials for the catalytic activity of CO₂ electrochemical reduction.

| Electrocatalysts | Electrolyte | Potential (V vs. SHE) | Main products | Faradaic efficiency | Ref. |
|--|-----------------------------------|--------------------------|------------------|------------------------|------|
| Nitrogen-doped nanocarbons | 0.5 M NaHCO ₃ | -0.90 | CO | 90% | S1 |
| Nitrogen-doped carbon nanofibers | EMIM-BF ₄ ionic liquid | -0.573 | CO | 98% | S2 |
| Nitrogen-doped carbon nanotube Arrays | 0.1 M KHCO ₃ | -1.05 | CO | 80% | S3 |
| N and S Co-doping porous carbon nanotubes | 0.1 M KHCO ₃ | -0.7 | CO | 94% | S4 |
| Nitrogen-doped carbon nanotubes | 0.1 M KHCO ₃ | -0.78 | CO | 80% | S5 |
| Nitrogen-doped 3D graphene foam | 0.1 M KHCO ₃ | -0.90 | CO | 85% | S6 |
| MOF-derived nitrogen-doped carbon | 0.1 M KHCO ₃ | -0.93 | CO | 78% | S7 |
| Nitrogen-doped nano-porous carbon | 0.1 M KHCO ₃ | -0.99 | CO | 11.3% | S8 |
| C ₃ N ₄ -multiwalled carbon nanotubes | 1 M KCl | -1.46 | CO | 98% | S9 |
| 3D N-doped graphene nanoribbon network | 0.5 M KHCO ₃ | -0.49 | CO | 87.6% | S10 |
| Holey carbon layers with F engineering | 0.1 M KHCO ₃ | -0.6 | CO | 90% | S11 |
| 2D carbon nanosheets | 0.5 M KHCO ₃ | -0.36 | CO | 92% | S12 |
| <i>Microcystis aeruginosa</i> biomass derived | 0.5 M KHCO ₃ | -0.55 | CO | 96.9% | This |
| Nitrogen-doped nano-porous carbon | | | | | work |
| <i>Enteromopha</i> biomass derived Nitrogen-doped nano-porous carbon | 0.5 M KHCO ₃ | -0.60 | CO | 82.1% | This |
| | | | | | work |

References

- S1.** Xu, J., Kan, Y., Huang, R., Zhang, B., Wang, B., Wu, K.-H., Lin, Y., Sun, X., Li, Q., Centi, G., Su, D., Revealing the origin of activity in nitrogen-doped nanocarbons electrocatalytic reduction of carbon dioxide. *ChemSusChem* **2016**, 9, 1085-1089.
- S2.** Kumar, B., Asadi, M., Pisasale, D., Sinha-Ray, S., Rosen, B.A., Haasch, R., Abiade, J., Yarin, A.L., Salehi-Khojin, A., Renewable and metal-free carbon nanofiber catalysts for carbon dioxide reduction, *Nat. Commun.* **2013**, 4, 3819.
- S3.** Sharma, P.P., Wu, J., Yadav, R.M., Liu, M., Wright, C.J., Tiwary, C.S., Yakobson, B.I., Lou, J., Ajayan, P.M., Zhou, X.-D., Nitrogen-doped carbon nanotube Arrays for high-efficiency electrochemical reduction of CO₂: on the understanding of defects, defect density, and selectivity, *Angew. Chem. Int. Ed.* **2015**, 54, 13701-13705.
- S4.** Yang, H., Wu, Y., Lin, Q., Fan, L., Chai, X., Zhang, Q., Liu, J., He, C., Lin, Z., Composition tailoring via N and S Co-doping and structure tuning by constructing hierarchical pores: metal-free catalysts for high-performance electrochemical reduction of CO₂, *Angew. Chem. Int. Ed.* **2018**, 57, 15476-15480
- S5.** Wu, J., Yadav, R.M., Liu, M., Sharma, P.P., Tiwary, C.S., Ma, L., Zou, X., Zhou, X.-D., Yakobson, B.I., Lou, J., Ajayan, P.M., Achieving highly efficient, selective, and stable CO₂ reduction on nitrogen-doped carbon nanotubes, *ACS*

- Nano* **2015**, 9, 5364-5371.
- S6. Wu, J., Liu, M., Sharma, P.P., Yadav, R.M., Ma, L., Yang, Y., Zou, X., Zhou, X.-D., Vajtai, R., Yakobson, B.I., Lou, J., Ajayan, P.M., Incorporation of nitrogen defects for efficient reduction of CO₂ via two-electron pathway on three dimensional graphene foam, *Nano Lett.* **2016**, 16, 466-470.
 - S7. Wang, R., Sun, X., Ould-Chikh, S., Osadchii, D., Bai, F., Kapteijn, F., Gascon, J., Metal-organic-framework-mediated nitrogen-doped carbon for CO₂ electrochemical reduction, *ACS Appl. Mater. Interfaces* **2018**, 10, 14751-14758.
 - S8. Li, W., Seredych, M., Rodríguez-Castellon, E., Bandosz, T.J., Metal-free nanoporous carbon as a catalyst for electrochemical reduction of CO₂ to CO and CH₄, *ChemSusChem* **2016**, 9, 606-616
 - S9. Jhong, H.-R.M., Tornow, C.E., Smid, B., Gewirth, A.A., Lyth, S.M., Kenis, P.J.A., A nitrogen-doped carbon catalyst for electrochemical CO₂ conversion to CO with high selectivity and current density, *ChemSusChem* **2017**, 10, 1094-1099
 - S10. Liu, S., Yang, H., Huang, X., Liu, L., Cai, W., Gao, J., Li, X., Zhang, T., Huang, Y., Liu, B., Identifying active sites of nitrogen-doped carbon materials for the CO₂ reduction reaction. *Adv. Funct. Mater.* **2018**, 28, 1800499
 - S11. Pan, F. B. Li, X. Xiang, G. Wang, Y. Li, Efficient CO₂ electroreduction by highly dense and active pyridinic nitrogen on holey carbon layers with fluorine engineering, *ACS Catal.* **2019**, 9, 2124-2133
 - S12. Gao, T., Xie, T., Han, N., Wang, S., Sun, K., C. Hu, Z. Chang, Y. Pang, Y. Zhang, L. Luo, Y. Zhao, X. Sun, Electronic structure engineering of 2D carbon nanosheets by evolutionary nitrogen modulation for synergizing CO₂ electroreduction, *ACS Appl. Energy Mater.* **2019**, 2, 3151-3159

Table S6. Goal and scope definition for the LCA model

| Goals and scope | Definitions |
|--|--|
| Reason for conducting the LCA | To assess the sustainability and environmental impacts of harmful algae blooms and inform the research community about the state-of-the-art research outcome |
| Audiences | Environmental researchers, chemical engineering researchers, policy makers, industrial stakeholders, research and public community, sustainability evaluation researchers |
| Applications | To support interdisciplinary research development on sustainable treatments and resource recovery of the harmful algae blooms |
| Scopes | |
| Product system | Bio-fuels and chemicals, functional biochar materials |
| Function | Harmful algae blooms without treatments or treated by landfill |
| Functional unit | 1 ton of algae biomass (dried weight) |
| System boundary | See Figure 5 |
| Allocation | In the LCA, 100% of the algae will decay if it does not be treated, in which 20% of its carbon will convert into CH ₄ , and 80% will convert into CO ₂ , all the nutrition elements will return to the waterbody or release to the environment. 80% of the algae will decay if it be treated by landfill, in which 60% of its carbon will convert into CO ₂ , and 40% will convert into CH ₄ . In principle, allocation should be avoided via system expansion and subdivision, which is not possible in this study due to resources constraints. As such, a simplified LCA model is developed where input and output data are allocated based on exergy analysis performed using Aspen Plus |
| Assumptions | (I) The life span of the product system is 20 years; (II) The product system is primarily made of steel, which is 100% recycled at the end of life; (III) The carbon in the bio-fuels or chemicals finally converts into CO ₂ and releases to the environment (IV) The product system is based in China |
| Requirements on data and quality | Output data acquired from the process model simulated in Aspen Plus, relevant GaBi Professional and Ecoinvent Datasets (if available) and literature. |
| Impact categories assessed in the LCA | (1) Agricultural land occupation (m ² a) (2) GHG emissions (kg CO ₂ -eq) (3) Fossil depletion (kg oil-eq) (4) Eutrophication Potential (kg P-eq); |

| | |
|--------------------|---|
| | (5) Freshwater ecotoxicity (kg 1,4-dichlorobenzene (DCB)-eq); |
| | (6) Ionizing radiation (kg U235-eq); |
| | (7) Human Toxicity Potential (kg DCB-eq); |
| | (8) Photochemical Ozone Creation Potential (kg ethane-eq); |
| | (9) Terrestrial Ecotoxicity Potential, (kg DCB-eq); |
| | (10) Odour Potential (kg H ₂ S-eq); |
| | (11) Metal depletion (kg Fe-eq); |
| | (12) Ozone depletion (kg CFC-11-eq) |
| | (13) Water depletion (ton) |
| | (14) Natural land transformation (m ²) |
| | (15) Particulate matter formation (kg PM10-eq) |
| | (16) Urban land occupation (m ²) |
| Limitations | The following aspects are not assessed in this study |
| | (I) Distribution and use of the bio-fuel and chemical produced from algae |
| | (II) GHG emission during the functionalization of the biochar materials |

Table S7. List of the parameters and assumptions for the algae treatment

| Parameters | Optimistic | Most probable | Pessimistic | Units |
|---|-------------------|-------------------|-------------------|------------------------------|
| <i>Harmful algae blooms parameters</i> | | | | |
| Algae contents in the waterbody | 1.0×10^8 | 6.0×10^7 | 3.0×10^7 | Cells/L water |
| Algae lipid contents | 45 | 35 | 25 | %(dry weight) |
| Algae settling efficiency | 0.99 | 0.95 | 0.90 | - |
| Algae ash contents | 4.0 | 7.0 | 10.0 | %(dry weight) |
| P concentration in the waterbody | 7.5 | 5.5 | 3.5 | mg/L |
| N concentration in the waterbody | 37.0 | 30.0 | 23.0 | mg/L |
| Algae molar N:P composition | 5.0 | 7.0 | 9.0 | - |
| <i>Biorefinery parameters and assumptions (Hydrothermal liquefaction (HTL) and carbonization)</i> | | | | |
| Distance to biorefinery place | 25 | 50 | 100 | km |
| Temperature for HTL reaction | 250 | 300 | 350 | °C |
| Temperature for carbonization | 1000 | 800 | 600 | °C |
| Solids content of dewatered algae | 35 | 30 | 25 | % |
| Moisture of dried algae | 5 | 7 | 10 | % |
| Liquid bio-oil yield | 30 | 25 | 20 | % |
| Solid biochar yield | 45 | 40 | 30 | % |
| C contents in the biochar | 70 | 60 | 50 | % |
| N contents in the biochar | 14 | 12 | 10 | % |
| P contents in the biochar | 5 | 3 | 2 | % |
| Biofuels yield from liquid bio-oil | 75 | 65 | 50 | % |
| Functional biochar from raw biochar | 65 | 55 | 45 | % |
| <i>CO₂/nutrition uptake and emission parameters and assumptions</i> | | | | |
| CO ₂ uptake during the algae growth | 1.75 | 1.65 | 1.50 | kg CO ₂ /kg algae |
| N uptake during the algae growth | 0.06 | 0.05 | 0.04 | kg N/kg algae |
| P uptake during the algae growth | 0.02 | 0.015 | 0.01 | kg P/kg algae |
| CO ₂ emission during algae decay | 1.10 | 1.20 | 1.25 | kg CO ₂ /kg algae |
| CH ₄ emission during algae decay | 0.15 | 0.20 | 0.25 | kg CH ₄ /kg algae |
| NO _x emission during algae decay | 0.003 | 0.005 | 0.08 | kg NO _x /kg algae |
| CO ₂ emission during algae landfill | 0.65 | 0.75 | 0.85 | kg CO ₂ /kg algae |
| CH ₄ emission during algae landfill | 0.35 | 0.45 | 0.55 | kg CH ₄ /kg algae |
| NO _x emission during algae landfill | 0.01 | 0.015 | 0.02 | kg NO _x /kg algae |

Table S8. LCA data inventory for the algae treatments (per ton dry algae biomass)

| Stage | Input/output | Utilities/materials | Units | Values |
|--|--------------|------------------------------------|-----------------------------|-----------------------|
| Harmful algae blooms and biomass harvest | Input | CO ₂ ^a | ton | 1.65 |
| | | N ^a | ton | 0.05 |
| | | P ^a | ton | 0.01 |
| | | Concrete ^b | kg | 2.2×10 ⁻⁴ |
| | | Steel ^b | kg | 7.5×10 ⁻⁷ |
| | | Plastic ^b | kg | 5.08×10 ⁻⁵ |
| | | Power ^c | kWh-electricity equivalence | 3400 |
| | Output | Algae biomass ^d | ton | 5.0 |
| Transportation (150 km) | Input | Power | kWh-electricity equivalence | 23.0 |
| Drying (From water content 80% to 2%) | Input | Power | kWh-electricity equivalence | 85.2 |
| | | Algae biomass | ton | 5.0 |
| | Output | Algae biomass | ton | 1.0 |
| Biorefining | Input | Power | kWh-electricity equivalence | 11.2 |
| | Output | Bio-oil | ton | 0.25 |
| | | Biochar | ton | 0.47 |
| Upgrading | input | Power | kWh-electricity equivalence | 22.3 |
| | | CH ₃ OH | ton | 0.13 |
| | | NH ₃ | ton | 0.05 |
| | | H ₂ | ton | 0.02 |
| | | Water | ton | 3.28 |
| | | Sulfuric acid | ton | 0.09 |
| | | Bio-fuels | ton | 0.27 |
| | Output | Biochar based functional materials | ton | 0.39 |
| | | Wastewater | ton | 3.98 |
| ^a Uptake directly from the environment | | | | |
| ^b For constructing the infrastructure | | | | |
| ^c Power for algae harvest and on-site dewater | | | | |
| ^d Water content 80% | | | | |

Table S9. Impacts results of the thermochemical conversion for the biomass treatment

| Impact category | Electricity | Transport | Water | Chemicals | Steam | Hydrogen | Total |
|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Agricultural land occupation (m ² a) | 95.3 | 0.76 | 0.87 | 12.6 | 1.32 | 1.63 | 112.48 |
| GHG emissions (kg CO ₂ -Eq) | 323.0 | 10.9 | 13.6 | 273.3 | 16.8 | 18.9 | 656.5 |
| Fossil depletion (kg oil-Eq) | 96.9 | 7.36 | 3.92 | 53.2 | 9.23 | 27.6 | 198.21 |
| Freshwater ecotoxicity (kg 1,4-DCB-Eq) | 0.14 | 1.52×10 ⁻² | 4.98×10 ⁻³ | 0.29 | 5.20×10 ⁻² | 0.16 | 0.66 |
| Freshwater eutrophication (kg P-Eq) | 1.62×10 ⁻² | 3.27×10 ⁻³ | 4.65×10 ⁻⁴ | 2.82×10 ⁻² | 1.78×10 ⁻⁴ | 2.39×10 ⁻³ | 4.49×10 ⁻² |
| Human toxicity (kg 1,4-DCB-Eq) | 2.56×10 ⁻² | 4.32×10 ⁻³ | 1.02×10 ⁻⁴ | 3.62×10 ⁻² | 2.63×10 ⁻⁴ | 1.12×10 ⁻³ | 6.21×10 ⁻² |
| Ionizing radiation (kg U235-Eq) | 1.23×10 ⁻³ | 6.35×10 ⁻³ | 1.69×10 ⁻⁵ | 2.96×10 ⁻³ | 1.52×10 ⁻⁴ | 6.36×10 ⁻⁴ | 1.06×10 ⁻² |
| Metal depletion (kg Fe-Eq) | 0.36 | 1.65 | 0.16 | 0.98 | 0.36 | 0.81 | 4.32 |
| Ozone depletion (kg CFC-11-Eq) | 1.78×10 ⁻⁵ | 3.58×10 ⁻⁶ | 9.36×10 ⁻⁷ | 7.86×10 ⁻⁵ | 2.96×10 ⁻⁶ | 1.81×10 ⁻⁶ | 9.72×10 ⁻⁵ |
| Particulate matter formation (kg PM10-Eq) | 0.59 | 1.18×10 ⁻² | 1.27×10 ⁻³ | 0.36 | 6.32×10 ⁻² | 9.65×10 ⁻² | 1.13 |
| Photochemical oxidant formation (kg NMVOC) | 0.11 | 8.86×10 ⁻³ | 7.62×10 ⁻⁴ | 5.69×10 ⁻³ | 7.96×10 ⁻³ | 8.39×10 ⁻³ | 0.13 |
| Terrestrial acidification (kg SO ₂ -Eq) | 1.38 | 0.47 | 2.31×10 ⁻² | 0.96 | 1.15×10 ⁻² | 1.03×10 ⁻² | 2.84 |
| Terrestrial ecotoxicity (kg 1,4-DCB-Eq) | 1.77×10 ⁻² | 2.08×10 ⁻³ | 2.20×10 ⁻⁴ | 2.63×10 ⁻² | 2.80×10 ⁻⁴ | 6.18×10 ⁻³ | 4.49×10 ⁻² |
| Urban land occupation (m ² a) | 7.32 | 0.16 | 0.13 | 0.26 | 0.11 | 9.36×10 ⁻² | 7.99 |
| Water depletion (m ³) | 0.62 | 1.32×10 ⁻² | 2.52×10 ⁻³ | 0.21 | 3.02×10 ⁻² | 0.11 | 0.98 |

Table S10. Impacts results of the landfilling for the biomass treatment

| Impact category | Electricity | Transport | Water | Chemicals | Steam | Landfill activity | Total |
|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Agricultural land occupation (m ² a) | 35.7 | 0.12 | 1.23×10 ⁻³ | 7.89 | 0.65 | 11.4 | 55.76 |
| GHG emissions (kg CO ₂ -Eq) | 112.6 | 1.23 | 0.58 | 156.9 | 3.62 | 1362 | 1636.93 |
| Fossil depletion (kg oil-Eq) | 26.9 | 0.98 | 0.16 | 32.5 | 2.35 | 0 | 62.89 |
| Freshwater ecotoxicity (kg 1,4-DCB-Eq) | 1.47×10 ⁻³ | 1.02×10 ⁻³ | 8.72×10 ⁻⁵ | 1.86×10 ⁻³ | 2.12×10 ⁻³ | 1.26 | 1.28 |
| Freshwater eutrophication (kg P-Eq) | 4.72×10 ⁻³ | 2.27×10 ⁻⁴ | 9.27×10 ⁻⁶ | 3.26×10 ⁻² | 3.08×10 ⁻⁵ | 0 | 3.31×10 ⁻² |
| Human toxicity (kg 1,4-DCB-Eq) | 3.79×10 ⁻³ | 5.78×10 ⁻⁴ | 7.89×10 ⁻⁶ | 4.15×10 ⁻² | 1.97×10 ⁻⁵ | 2.08 | 2.13 |
| Ionizing radiation (kg U235-Eq) | 5.78×10 ⁻⁴ | 5.23×10 ⁻⁴ | 6.32×10 ⁻⁷ | 3.21×10 ⁻³ | 3.63×10 ⁻⁵ | 0 | 6.90×10 ⁻² |
| Metal depletion (kg Fe-Eq) | 0.11 | 9.69×10 ⁻² | 1.05×10 ⁻³ | 1.03 | 0.10 | 0 | 1.25 |
| Ozone depletion (kg CFC-11-Eq) | 2.96×10 ⁻⁶ | 5.08×10 ⁻⁷ | 3.52×10 ⁻⁹ | 5.67×10 ⁻⁵ | 1.06×10 ⁻⁷ | 6.39×10 ⁻⁴ | 6.45×10 ⁻⁴ |
| Particulate matter formation (kg PM10-Eq) | 0.13 | 2.39×10 ⁻³ | 6.08×10 ⁻⁵ | 0.56 | 3.92×10 ⁻³ | 0 | 0.70 |
| Photochemical oxidant formation (kg NMVOC) | 3.93×10 ⁻⁴ | 1.06×10 ⁻³ | 2.13×10 ⁻⁶ | 1.03×10 ⁻² | 2.85×10 ⁻⁴ | 6.25×10 ⁻⁴ | 1.05×10 ⁻² |
| Terrestrial acidification (kg SO ₂ -Eq) | 0.26 | 0.10 | 1.26×10 ⁻⁴ | 1.02 | 2.30×10 ⁻³ | 1.69 | 3.09 |
| Terrestrial ecotoxicity (kg 1,4-DCB-Eq) | 2.35×10 ⁻³ | 3.45×10 ⁻⁴ | 1.08×10 ⁻⁶ | 2.13×10 ⁻² | 3.69×10 ⁻⁵ | 1.83 | 1.88 |
| Urban land occupation (m ² a) | 0.36 | 4.05×10 ⁻² | 1.29×10 ⁻³ | 0.33 | 2.96×10 ⁻³ | 13.2 | 13.93 |
| Water depletion (m ³) | 0.16 | 3.46×10 ⁻³ | 1.02×10 ⁻⁴ | 0.19 | 3.02×10 ⁻² | 0 | 0.40 |

Table S11. Impacts results of the without treating for the biomass treatment

| Impact category | Electricity | Transport | Water | Chemicals | Steam | Algae emission | Total |
|--|-------------|-----------|-------|-----------|-------|-----------------------|-----------------------|
| Agricultural land occupation (m ² a) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| GHG emissions (kg CO ₂ -Eq) | 0 | 0 | 0 | 0 | 0 | 1789 | 1789 |
| Fossil depletion (kg oil-Eq) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Freshwater ecotoxicity (kg 1,4-DCB-Eq) | 0 | 0 | 0 | 0 | 0 | 23.6 | 23.6 |
| Freshwater eutrophication (kg P-Eq) | 0 | 0 | 0 | 0 | 0 | 45.3 | 45.3 |
| Human toxicity (kg 1,4-DCB-Eq) | 0 | 0 | 0 | 0 | 0 | 18.2 | 18.2 |
| Ionizing radiation (kg U235-Eq) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Metal depletion (kg Fe-Eq) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ozone depletion (kg CFC-11-Eq) | 0 | 0 | 0 | 0 | 0 | 2.91×10 ⁻³ | 2.91×10 ⁻³ |
| Particulate matter formation (kg PM10-Eq) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Photochemical oxidant formation (kg NMVOC) | 0 | 0 | 0 | 0 | 0 | 6.25×10 ⁻⁴ | 6.25×10 ⁻⁴ |
| Terrestrial acidification (kg SO ₂ -Eq) | 0 | 0 | 0 | 0 | 0 | 3.29 | 3.29 |
| Terrestrial ecotoxicity (kg 1,4-DCB-Eq) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Urban land occupation (m ² a) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Water depletion (m ³) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table S12. List of the economic parameters and assumptions for a 100 kton algae biomass treatment per year

| Economic parameters | Values |
|--|----------|
| NH ₃ (liquid) price (\$ per ton) ¹ | 300 |
| CH ₃ OH price (\$ per ton) ^{2a} | 250 |
| N ₂ (liquid) price (\$ per ton) ^{2b} | 90 |
| H ₂ price (\$ per ton) ^{2c} | 3400 |
| Fe ₂ (SO ₄) ₃ (\$ per ton) ^{2c} | 725 |
| Process water price (\$ per ton) ³ | 0.22 |
| Electricity price (\$ per kWh) ⁴ | 0.07 |
| Low pressure steam price (\$ per kWh) ⁵ | 0.021 |
| Cooling water price (\$ per kWh) ⁶ | 0.003 |
| Transportation (\$ per km per ton algae biomass) ⁷ | 0.55 |
| Economic assumptions | |
| Cost year basis ⁸ | USD-2015 |
| Operating hours (hours per year) ⁹ | 4000 |
| Equipment life span (years) ⁹ | 20 |
| Working capital (% of fixed capital investment) ⁹ | 10 |
| Equity (% of fixed capital investment) ⁹ | 40 |
| Loan interest (%) ⁹ | 8 |
| Loan terms (years) ⁹ | 10 |
| Internal Rate of Return (%) ⁹ | 10 |
| Tax rate (%) ⁹ | 35 |
| Depreciation period (years) ⁹ | 7 |
| Replacement interval (years) ¹⁰ | 7 |
| Specified yearly replacement cost (% of installed cost of electrocatalytic reactor) ¹⁰ | 15 |
| Unplanned replacement cost (% of FCI of electrocatalytic reactor) ¹⁰ | 0.5 |
| ¹ Taken from online market data (http://jiage.molbase.cn/hangqing/29119) | |
| ^{2a} Taken from online market data (http://jiage.molbase.cn/hangqing/1426584) | |
| ^{2b} Taken from online market data (http://jiage.molbase.cn/search?search_jiage=%E6%B6%B2%E6%B0%AE) | |
| ^{2c} Taken from online market data (http://jiage.molbase.cn/search?search_jiage=%E6%B6%B2%E6%B0%AE) | |
| ³ Government set industrial water price (http://tazlh.zjzfw.gov.cn/art/2014/6/16/art_30833_28099.html) | |
| ⁴ Government set electricity price (http://www.ndrc.gov.cn/gzdt/201905/t20190515_936212.html) | |
| ⁵ Taken from a book by Seider et al. (Product and process design principles : synthesis, analysis, and evaluation. 2 nd ed.; Wiley: New York, United States of America, 2004; p xviii, 802 p) | |
| ⁶ Government set industrial water price (http://tazlh.zjzfw.gov.cn/art/2014/6/16/art_30833_28099.html) | |
| ⁷ Distance is 150 km | |
| ⁸ All costs are updated to 2015 cost levels using the Chemical Engineering Plant Cost Index (CEPCI) and the average Producer Price Index (PPI) | |
| ⁹ Taken from a study by Humbird et al. (Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover; S44 National Renewable Energy Laboratory (NREL): Colorado, US, 2011) | |
| ¹⁰ Capital investment is spread over 3 years at a rate of 8%, 60%, and 32% in first, second, and third years, respectively | |

Table S13. Total direct costs, indirect cost and capital investment for a 100 kton algae biomass treatment per year

| Items | Notes | Values (\$) | |
|---------------------------------------|---|-------------------|-------------------|
| | | Landfill | Biorefinery |
| Algae biomass harvest | Harvesting the biomass from algae blooms waterbody | 635,216 | 635,216 |
| Equipment cost | The cost of equipment listed in the process flow diagram | 2,132,562 | 5,623,159 |
| Equipment installation | 0.47 * Equipment cost | 1,002,304 | 2,642,885 |
| Instrumentation and control | 0.36 * Equipment cost | 767,722 | 2,024,337 |
| Piping | 0.68 * Equipment cost | 1,450,142 | 3,823,748 |
| Electrical/heating installation | 0.19 * Equipment cost | 405,186 | 1,068,400 |
| Utility | Buildings construction + Site development + Service facilities + Delivery | 1,769,256 | 9,289,632 |
| Total Direct costs (TDC) | Sum of above items | 8,162,388 | 25,107,377 |
| Engineering and supervision | 10% of TDC | 816,239 | 2,510,738 |
| Construction fee | 10% of TDC | 816,239 | 2,510,738 |
| Legal expenses | 3% of TDC | 244,871 | 753,221 |
| Project Contingency | 10% of TDC | 816,239 | 2,510,738 |
| Construction labor cost | 15% of TDC | 1,224,358 | 3,766,107 |
| Other Costs (Start-Up, Permits) | 10% of TDC | 816,239 | 2,510,738 |
| Total Indirect Cost (TIC) | Sum of above items | 4,734,186 | 14,562,280 |
| Fixed Capital Investment (FCI) | TDC+TIC | 12,896,574 | 39,669,657 |
| Land | 10% FCI | 1,289,657 | 3,966,966 |
| Working Capital | 5% of FCI | 644,828 | 1,983,482 |
| Total Capital Investment (TCI) | FCI + Land + Working capital | 14,831,059 | 45,620,105 |
| Operating labor | Operating hours * hourly wage * workers | 2,520,000 | 2,520,000 |
| Operating supervision | 0.15 * Operating labor | 378,000 | 378,000 |
| Maintenance and repair | 0.06 * FCI | 773,794 | 2,380,179 |
| Operating supplies | 0.15 * Maintenance and repair | 116,069 | 357,026 |
| Laboratory charges | 0.15 * Operating labor | 378,000 | 378,000 |
| Royalties | 0.03 * Product sale cost | 0 | 243,256 |
| Variable operating costs | Sum of above items | 4,165,863 | 6,256,461 |
| Property tax | 0.02 * FCI | 257,931 | 793,393 |
| Insurance | 0.01 * FCI | 128,966 | 396,697 |
| Rent | 0.08 * FCI | 1,031,726 | 3,173,573 |
| Depreciation | 0.06 * FCI | 773,794 | 2,380,719 |
| Fix operating costs | Sum of above items | 2,192,417 | 6,744,382 |
| Administration | 0.20 * Operating labor + supervision + Maintenance and repair | 734,358 | 3,262,179 |

| | | | |
|----------------------------|--|------------------|-------------------|
| Distribution and selling | 0.05 * (Variable operating costs + Fix operating costs) | 317,914 | 650,042 |
| Research and development | 0.04 * (Variable operating costs + Fix operating costs) | 254,331 | 520,033 |
| General expenses | Sum of above items | 1,306,603 | 4,432,254 |
| Chemicals | NH ₃ , CH ₃ OH, H ₂ , Fe ₂ (SO ₄) ₃ | 986,325 | 10,796,258 |
| Process water | Water for the hydrothermal treatment and other reactions | 0 | 325,014 |
| Steam | For drying and dewatering | 256,982 | 812,632 |
| Cooling water | For cooling | 0 | 136,985 |
| Electricity | For all the process using electricity | 186,324 | 6,983,652 |
| Wastewater treatments | - | 169,326 | 762,589 |
| Total raw materials | Sum of above items | 1,598,957 | 19,817,130 |
| Bio-fuel revenues | Selling price * bio-fuel amount | 0 | 24,300,000 |
| Carbon materials revenues | Selling price * carbon materials amount | 0 | 35,100,000 |
| Total Revenues | Bio-fuel revenues + Carbon materials revenues | 0 | 59,400,000 |

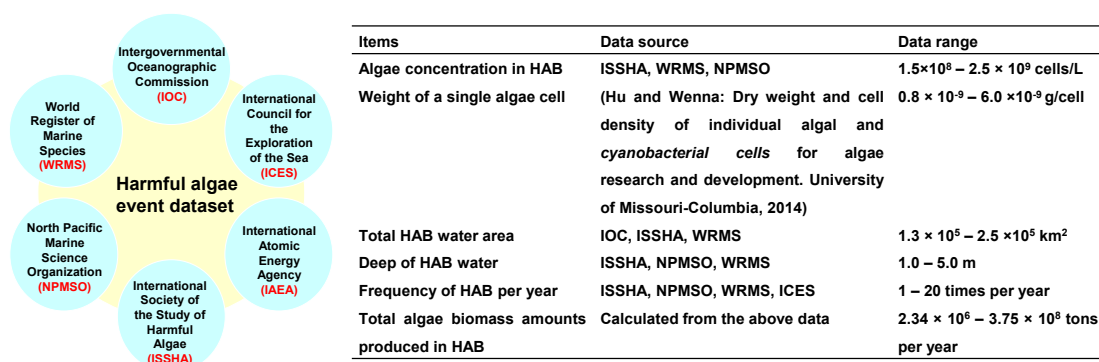


Figure S1. The data source of the current status of HAB.

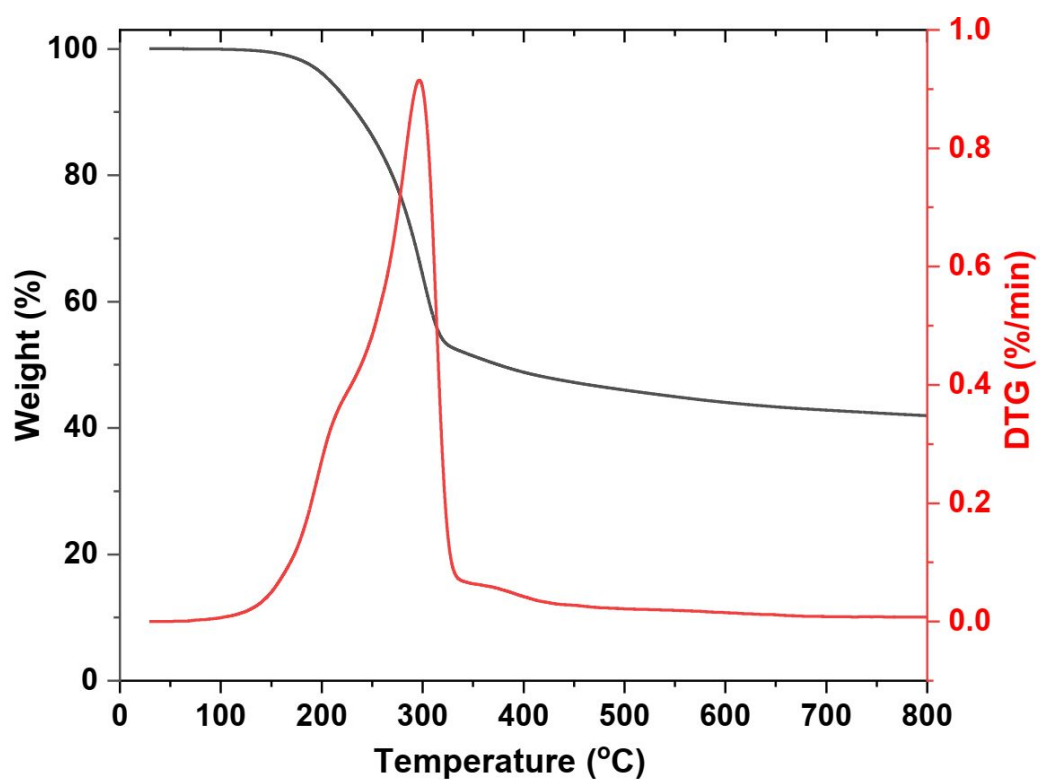


Figure S2. TG and DTG profiles for the thermochemical treatment of the NaCl-activated hydrochar.

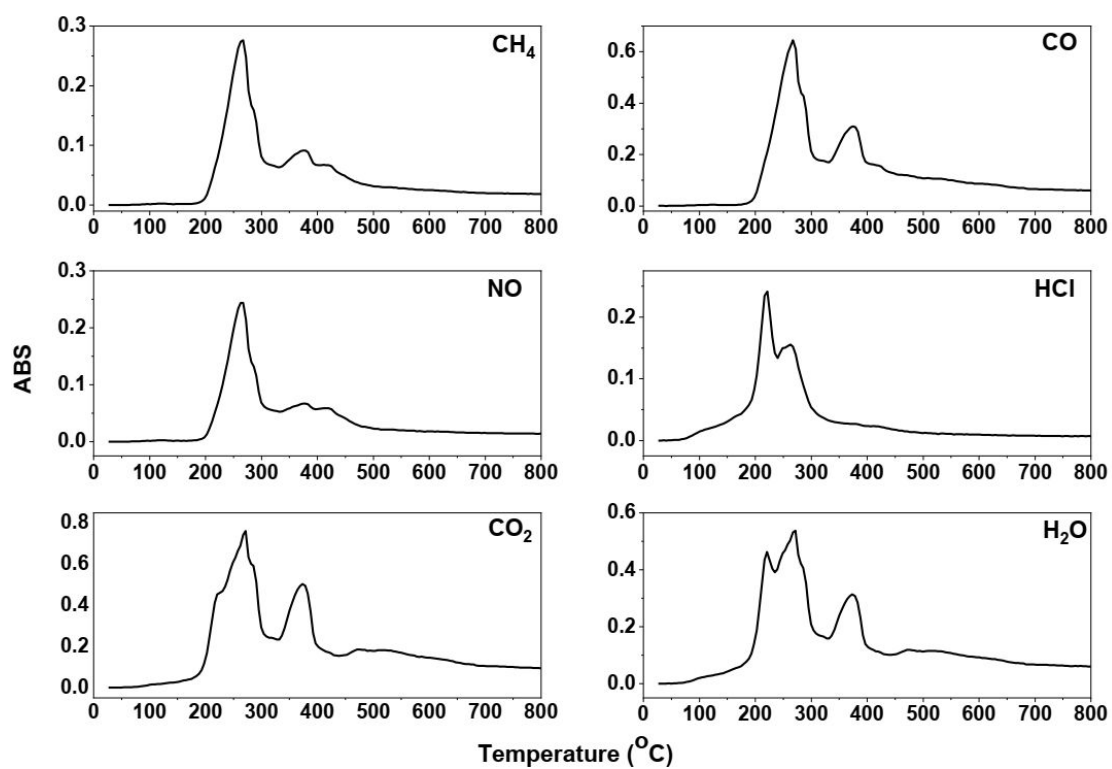


Figure S3. FTIR response of six gas compounds formed during the thermochemical treatment of the NaCl-activated hydrochar.

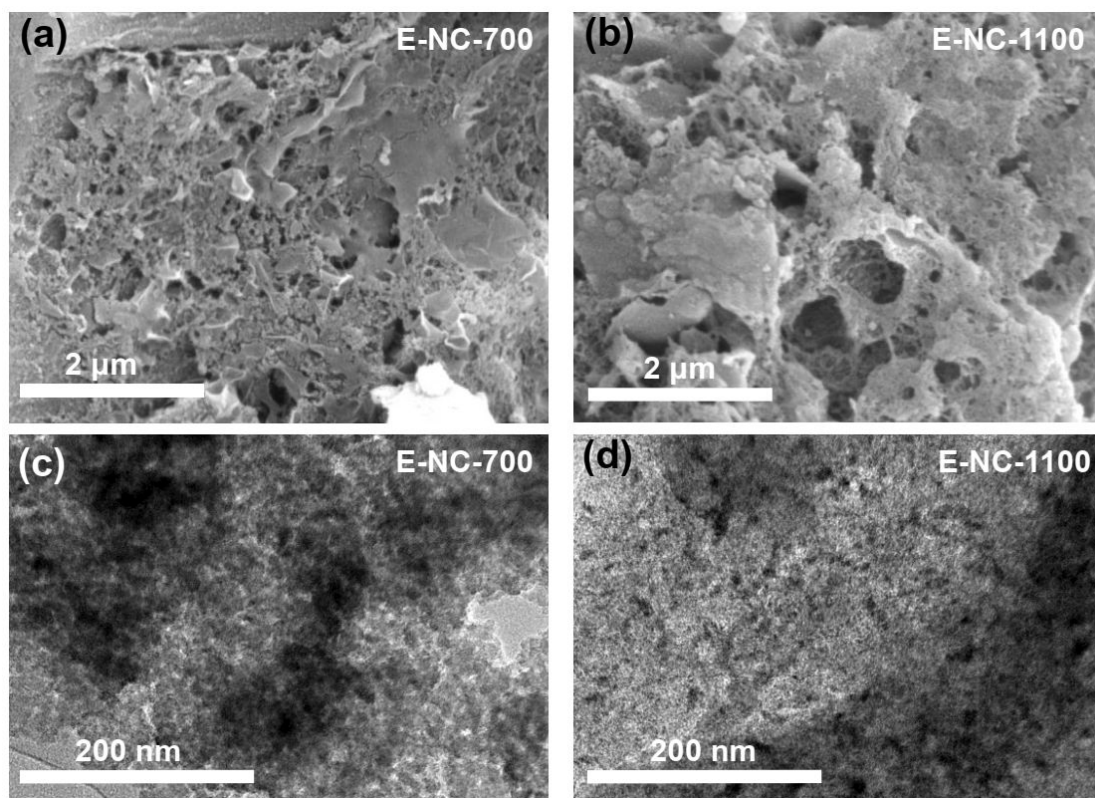


Figure S4. SEM and TEM images of the E-NC materials prepared at different temperatures.

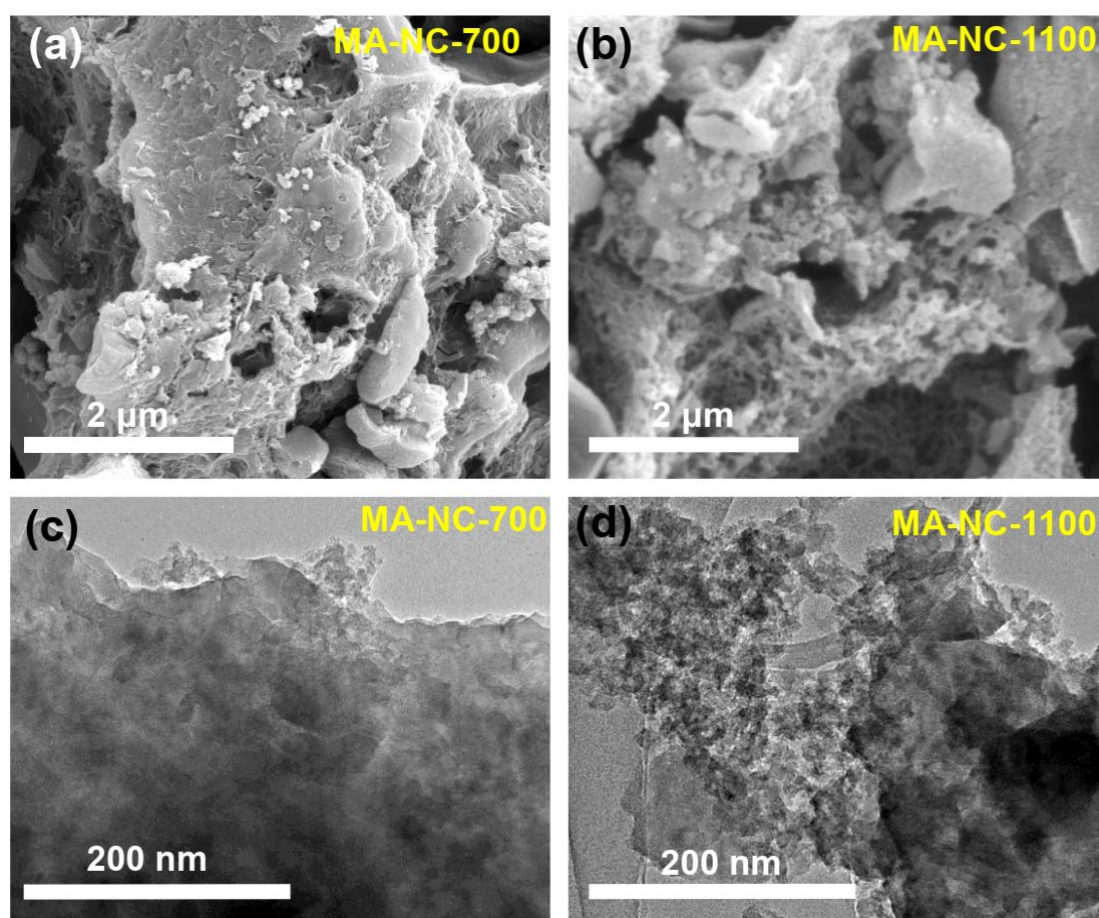


Figure S5. SEM and TEM images of the MA-NC materials prepared at different temperatures.

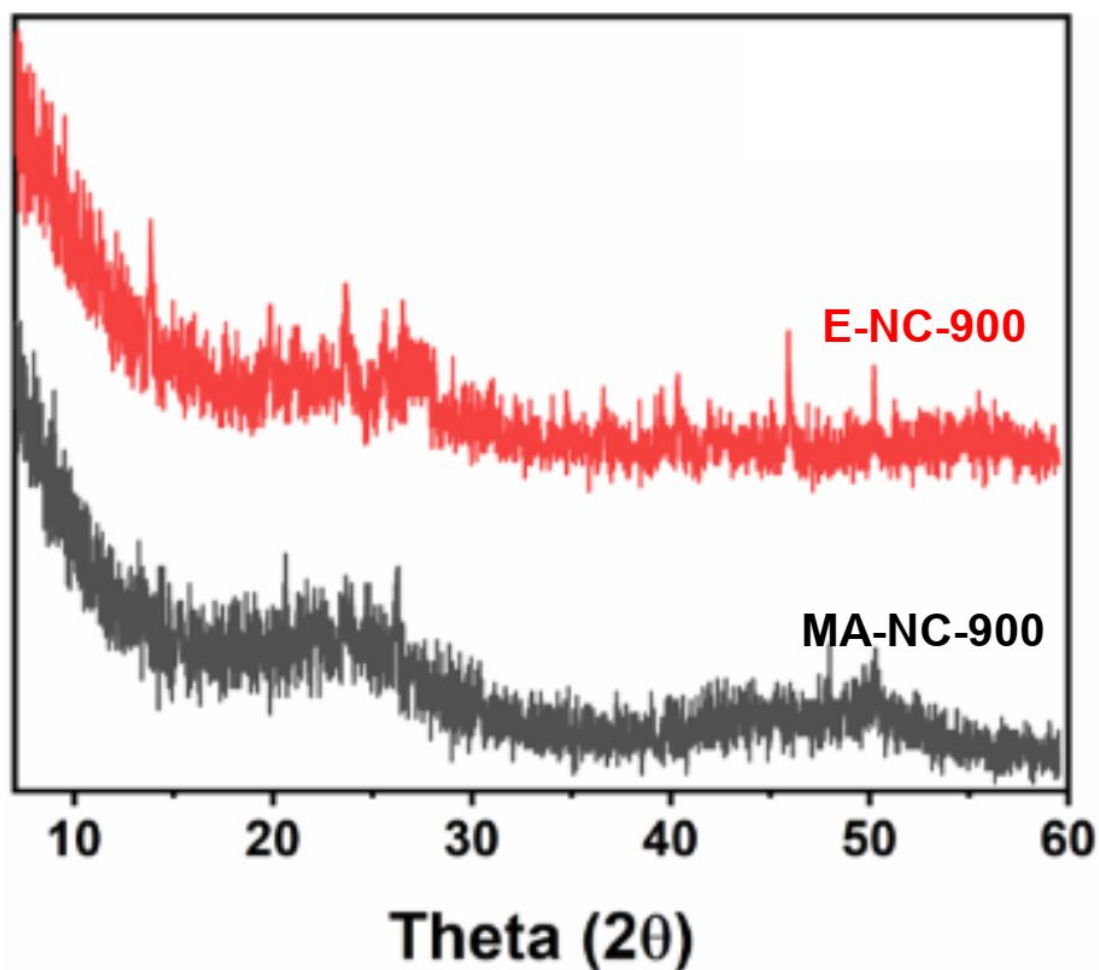


Figure S6. XRD patterns of the E-NC-900 and MA-NC-900 carbon materials. The XRD patterns of E-NC-900 and MA-NC-900 materials show two broad peaks at 25° corresponding to the (002) characteristic peak of carbon. The broad peaks of two samples display obviously low intensity, which is indicative of low crystallinity and high degree of structural disorder due to the etching of NH_3 and NaCl .

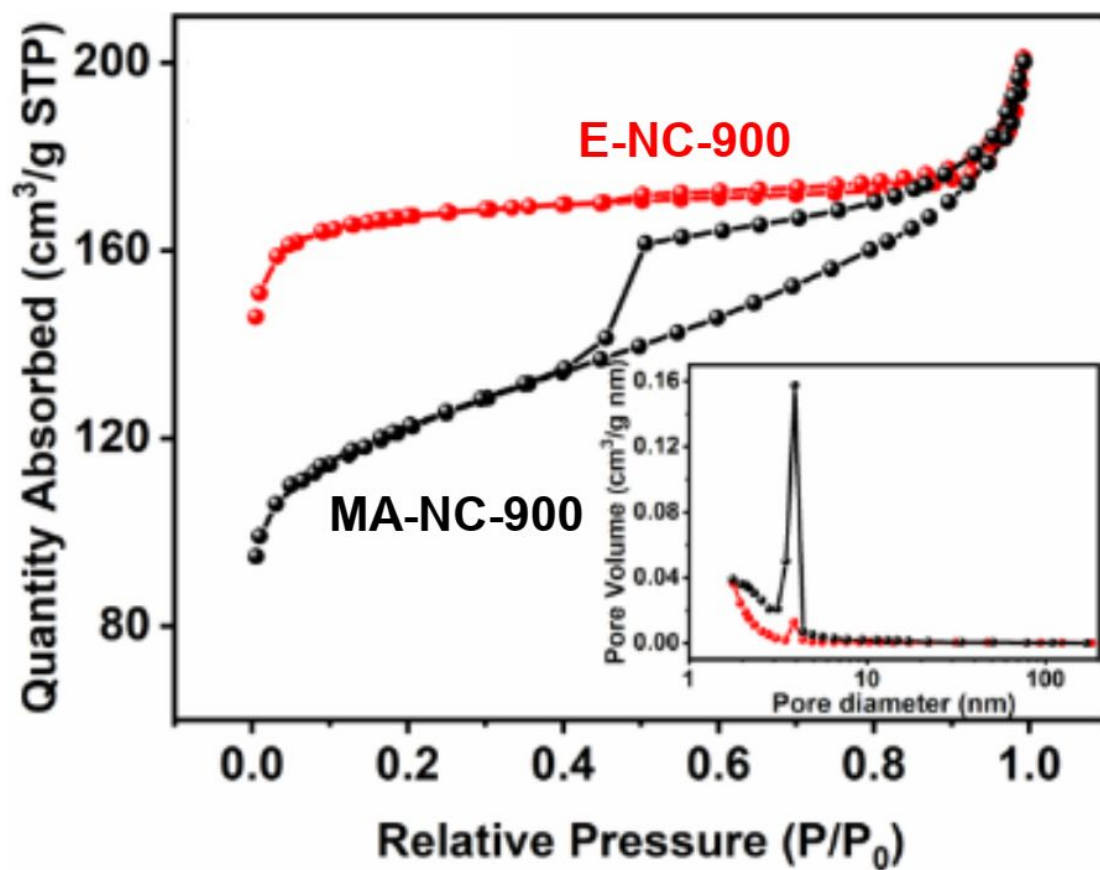


Figure S7. N₂ adsorption-desorption isotherms of the E-NC-900 and MA-NC-900 carbon materials

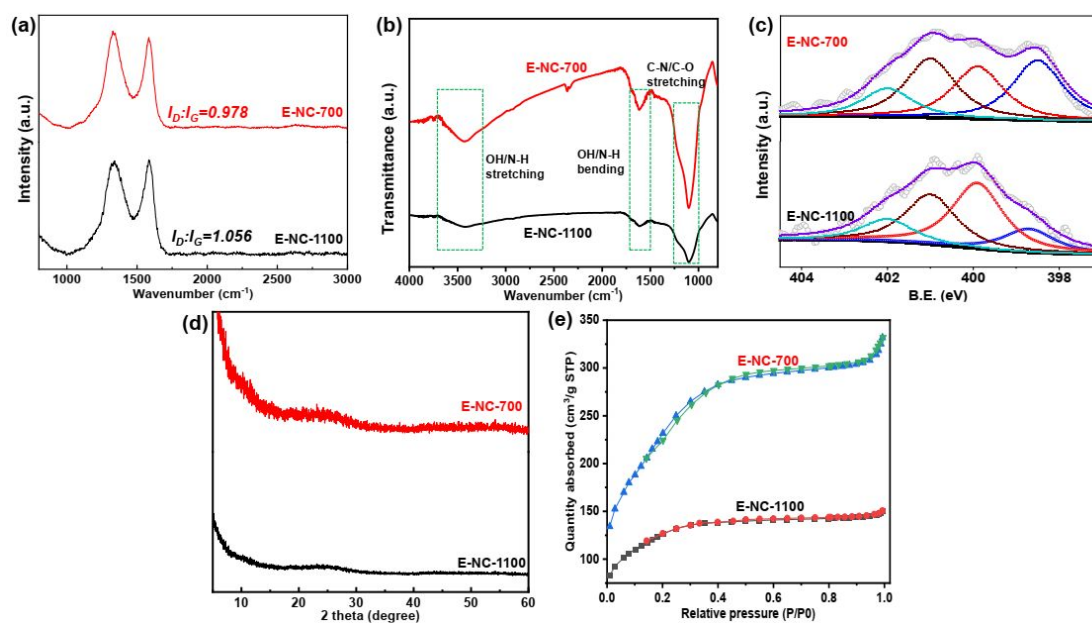


Figure S8. Structure features of the E-NC materials prepared at different temperatures.

(a) Raman spectra; (b) FTIR spectra; (c) XPS spectra; (d) XRD patterns; (e) N_2 adsorption-desorption isotherms.

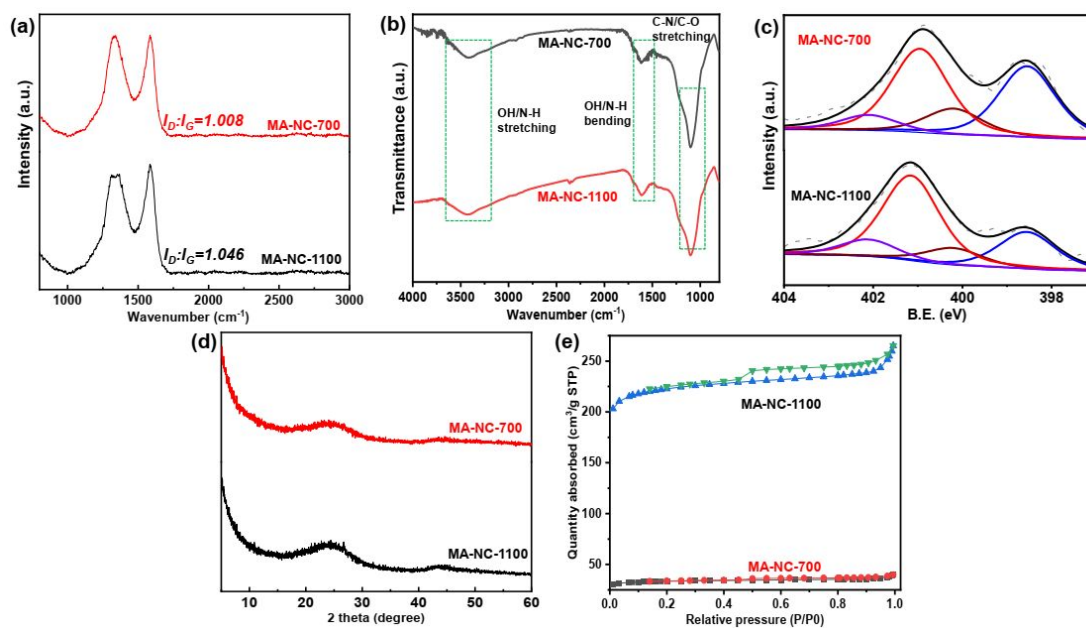


Figure S9. Structure features of the MA-NC materials prepared at different temperatures. (a) Raman spectra; (b) FTIR spectra; (c) XPS spectra; (d) XRD patterns; (e) N_2 adsorption-desorption isotherms.

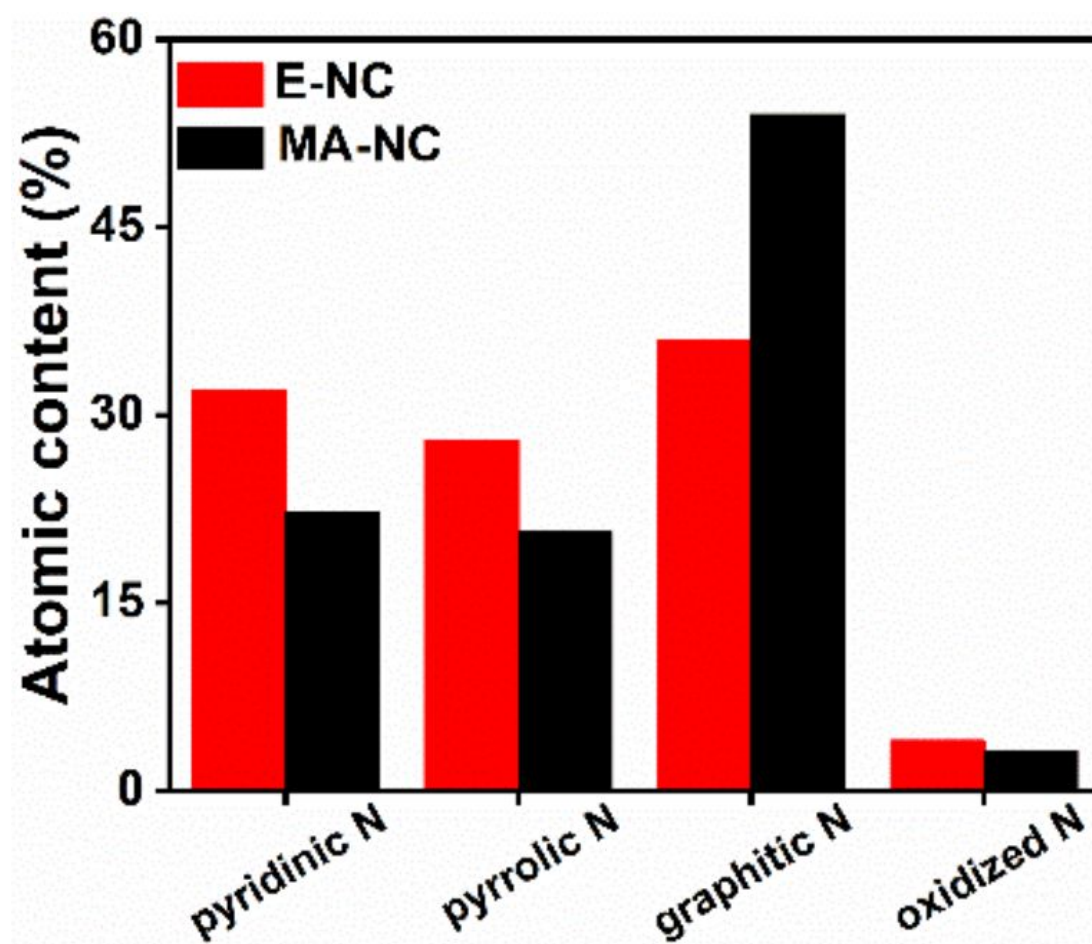


Figure S10. Contents of the four types of nitrogen species in E-NC-900 and MA-NC-900.

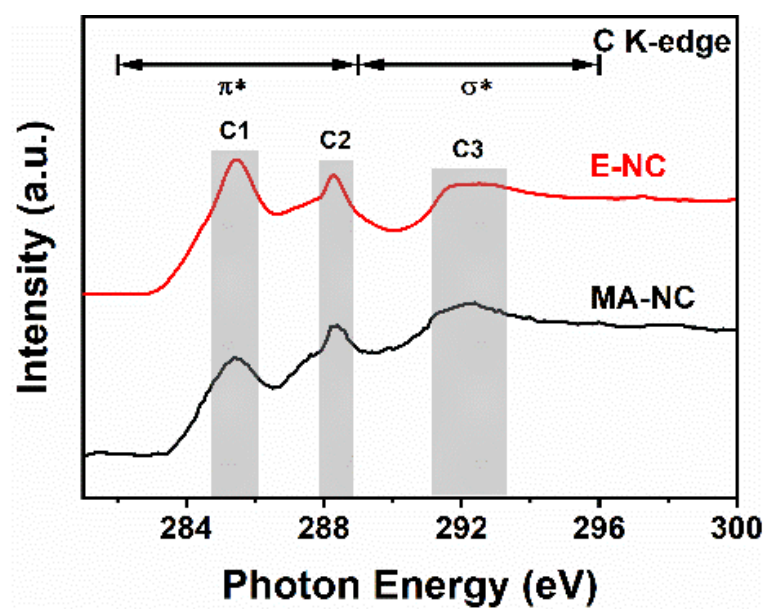


Figure S11. C K-edge NEXAFS spectra of E-NC-900 and MA-NC-900.

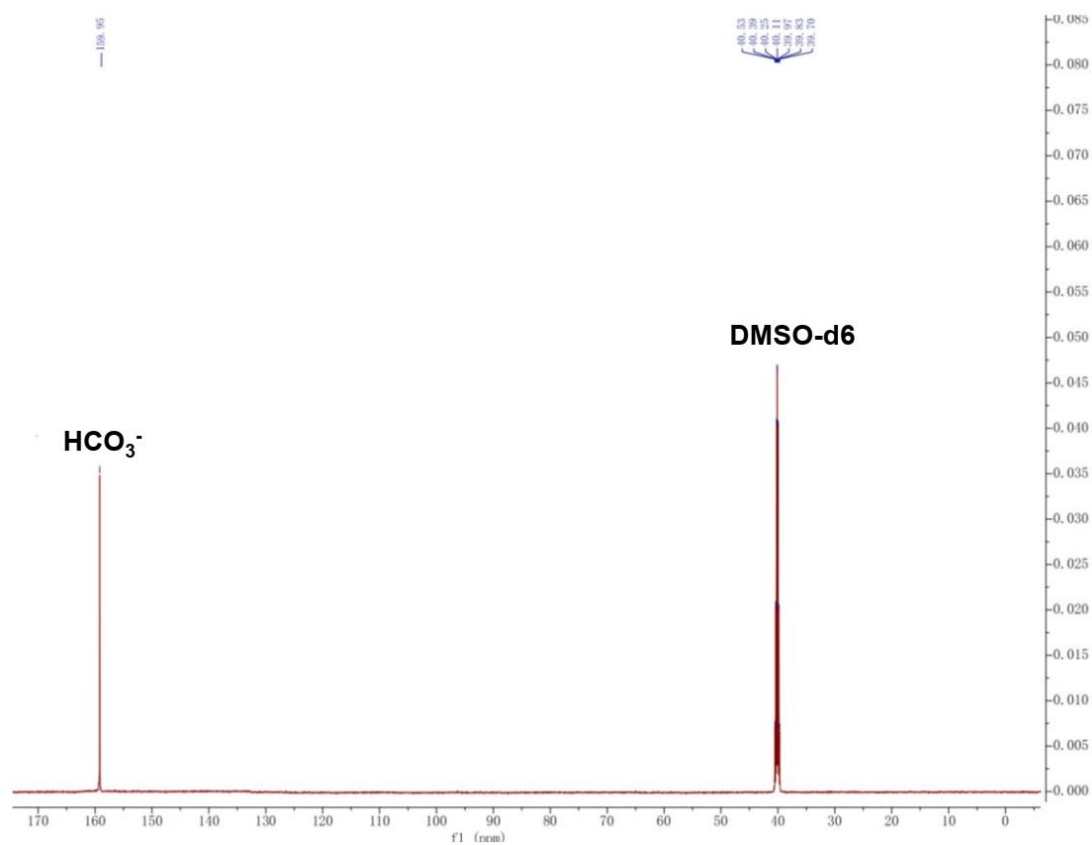


Figure S12. ^{13}C -NMR of the electrolyte after electrocatalytic CO_2 reduction with the catalysis of E-NC-900 material.

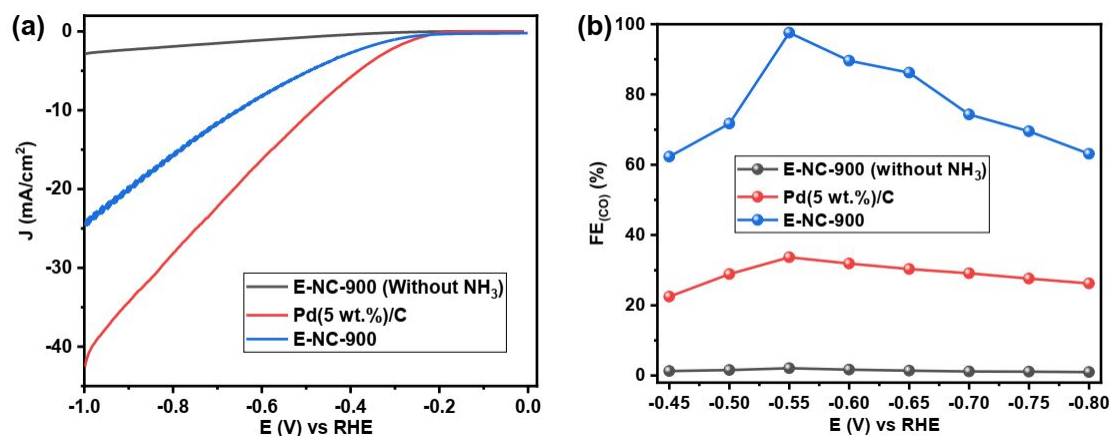


Figure S13. (a) LSV curves of E-NC-900 materials with and without NH₃ activation, as well as the benchmark Pd/C catalyst acquired in CO₂-saturated 0.5 M KHCO₃ solution. (b) Faradaic efficiency (FE) of the E-NC-900 materials with and without NH₃ activation, as well as the benchmark Pd/C catalyst at different potentials.

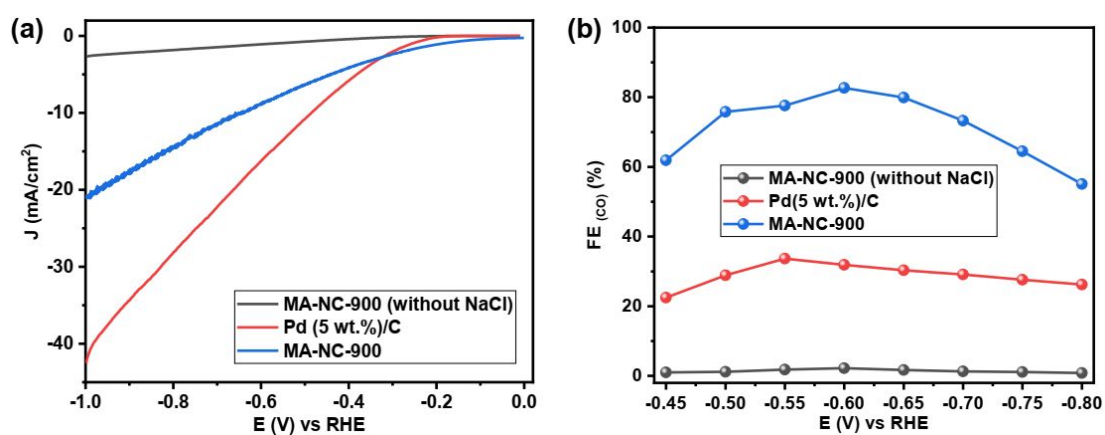


Figure S14. (a) LSV curves of MA-NC-900 materials with and without NH₃ activation, as well as the benchmark Pd/C catalyst acquired in CO₂-saturated 0.5 M KHCO₃ solution. (b) Faradaic efficiency (FE) of the MA-NC-900 materials with and without NH₃ activation, as well as the benchmark Pd/C catalyst at different potentials.

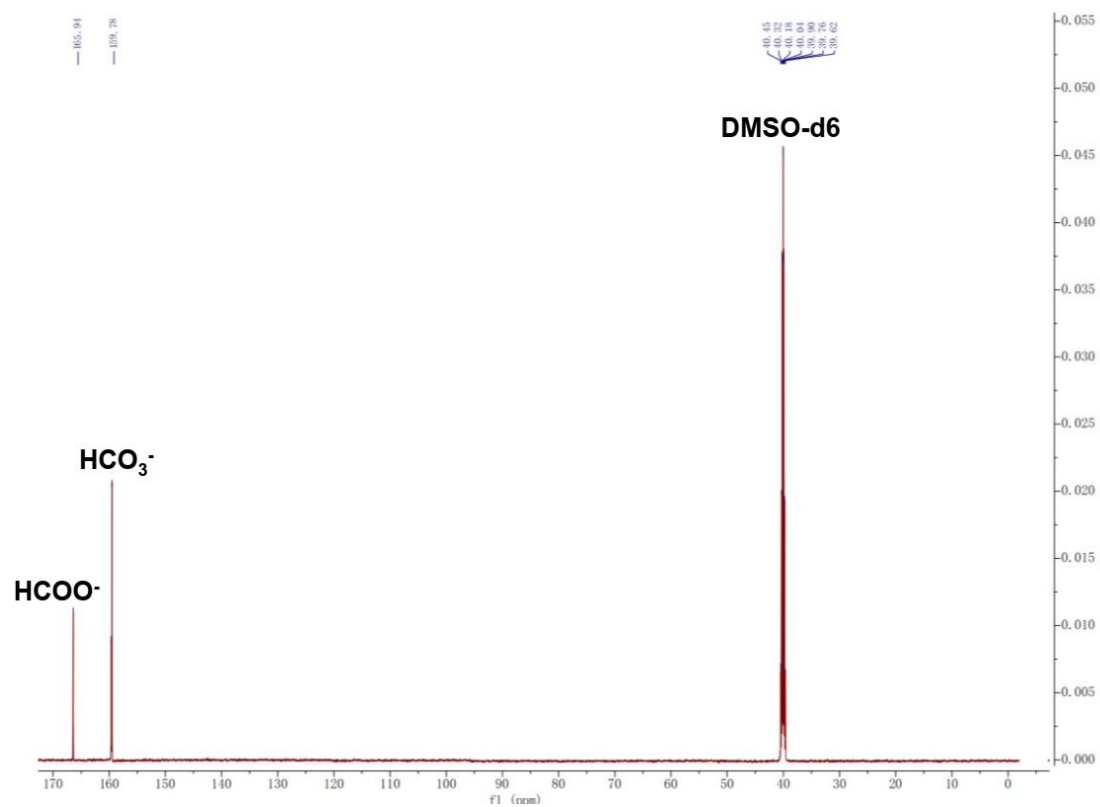


Figure S15. ^{13}C -NMR of the electrolyte after electrocatalytic CO_2 reduction with the catalysis of Pd/C material.