



Electrosynthesis of high carbon chemicals from carbon paper†

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Accepted 1st July 2025

DOI: 10.1039/d5mh00638d

rsc.li/materials-horizons

This work presents a novel approach for synthesizing high carbon chemicals through the electrolysis process. By utilizing carbon materials as the carbon source and water as the hydrogen source, high carbon chemicals can be produced through electrolysis under normal pressure and temperature conditions. This method achieves a selectivity of 56.09% for (*Z*)-9-octadecenitrile. *In situ* Fourier transform infrared (FT-IR) spectroscopy indicates that carbon atoms and hydrogen atoms derived from water can form C–H bonds during electrolysis under reduction conditions. This study paves a new path for the electrochemical synthesis of high-carbon chemicals utilizing inorganic carbon materials and establishes a novel paradigm for organic synthesis involving the cleavage and restructuring of carbon–carbon bonds.

Introduction

High-carbon chemicals are vital raw materials in the petrochemical industry, holding significant economic value across various commercial and industrial uses. Among these, (*Z*)-9-octadecenitrile (C₁₈H₃₃N), known as a long-chain aliphatic nitrile, can be used as a starting material or intermediate in organic synthesis for the production of various organic compounds. It is usually prepared *via* the hydrogenation of related nitriles. The raw materials reported for the synthesis of (*Z*)-9-octadecenitrile are organic carbon compounds, such as linoleic acid, oleic amide, oleic acid, ethyl oleate, and so on.^{1–5} These upstream products are all high-carbon chemical raw materials. There have been no reports on the synthesis of (*Z*)-9-octadecenitrile from inorganic carbon sources.

In contrast to high carbon chemicals mainly sourced from petrochemical feedstocks, inorganic carbon can be sourced from biomass, plastics or other carbon-containing waste, providing a cost-effective and sustainable alternative.^{6,7} Therefore,

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5mh00638d>

New concepts

In this work, I introduce a novel method for synthesizing high carbon chemicals. Utilizing carbon materials as the carbon source and water as the hydrogen source, high carbon chemicals can be produced through electrolysis under normal pressure and temperature conditions. This finding not only provides valuable insights into the electrosynthesis of high-carbon chemicals through a simple and mild approach, but also establishes a new paradigm for organic synthesis involving the cleavage and restructuring of carbon–carbon bonds. The development of a technology that enables the conversion of inorganic carbon materials into high carbon chemicals such as (*Z*)-9-octadecenitrile without the need for catalysts under ambient temperature and pressure conditions has the potential to maximize the utilization of residue resources. This approach effectively addresses the issues of high raw material costs and the complex procedures involved in conventional organic synthesis routes, as well as the energy-intensive requirements and catalyst deactivation problems associated with thermal catalytic reactions.

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Electrochemical technology is an effective strategy to realize sustainable energy utilization.^{8–10} On the basis of our discovery of the carbon reduction reaction, we have developed a novel method for synthesizing high carbon chemicals using inorganic carbon materials as the carbon source and water as the hydrogen source through an electrochemical process at room temperature.¹¹ In this work, to further study the relationships between the carbon precursor and products, commercial carbon paper (CP) (TORAY, TGP-H-060, with a 20% PTFE coating) was employed as the inorganic carbon source and high-value

carbon-based chemicals were successfully synthesized under ambient conditions, including 1-octadecene, hexadecanenitrile, *cis*-9-octadecenoamide, bis(2-ethylhexyl) isophthalate and (*Z*)-9-octadecenenitrile. Among these high carbon chemicals, the selectivity of (*Z*)-9-octadecenenitrile reached 56.09%. This novel approach to synthesizing high-carbon chemicals holds promising implications for sustainable energy production and the efficient utilization of carbon resources.

Results and discussion

The diagram illustrating the preparation of high carbon chemicals is shown in Fig. 1A. To streamline the experiment, a self-supported carbon paper (CP) with dimensions of $1 \times 3 \text{ cm}^2$ was electrolyzed within a one-compartment cell containing 1 M KOH (40 ml) under a nitrogen atmosphere for 92 hours at a potential of -1.8 V vs. (RHE) (Fig. S1, ESI[†]). Throughout the extended electrolysis period, the current density was maintained at approximately 320 mA cm^{-2} (Fig. 1B). As the reaction progressed, the electrolyte was continuously consumed and required replenishment. The products extracted from the electrolyte post-electrolysis were observed as white solid deposits adhering to the interior walls of the glass bottle (Fig. S2, ESI[†]).

To determine the composition of the products, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was employed for analysis. The Py-GC-MS spectra revealed that the white solid

comprised a series of long-chain alkyl compounds, including alkanes, nitriles, amides, and esters. The primary products identified were 1-octadecene ($\text{C}_{18}\text{H}_{36}$), hexadecanenitrile ($\text{C}_{16}\text{H}_{31}\text{N}$), 9-octadecenenitrile (9*Z*)-($\text{C}_{18}\text{H}_{33}\text{N}$), *cis*-9-octadecenoamide ($\text{C}_{18}\text{H}_{35}\text{NO}$), and bis(2-ethylhexyl) isophthalate ($\text{C}_{24}\text{H}_{38}\text{O}_4$) (Fig. 1C and Fig. S3, ESI[†]). Notably, 9-octadecenenitrile (9*Z*)-($\text{C}_{18}\text{H}_{33}\text{N}$) exhibited a high selectivity of 56.09% (Fig. 1D). 9-Octadecenenitrile has not previously been reported as a product derived from inorganic carbon materials. Typically, nitriles, amides, or esters were seldom reported as products synthesized from inorganic carbon materials.

In contrast to our previous studies on polyacrylonitrile or biomass-derived carbon reduction reaction products, the nature of the carbon precursors appears to have minimal influence on the product attributes. However, electrolysis conditions, particularly the design of the electrolysis cell and the reduction atmosphere, significantly affect the types of products obtained.¹¹

To investigate the changes in carbon paper during the electrolysis process, a detailed characterization of the carbon paper was conducted both before and after electrolysis. The carbon paper that had undergone electrolysis was designated as CP-92. Scanning electron microscopy (SEM) was employed to examine the morphology of the carbon paper. As depicted in Fig. S4 (ESI[†]), the normally regular nanofibers presented before electrolysis were observed to be destroyed and to collapse into a

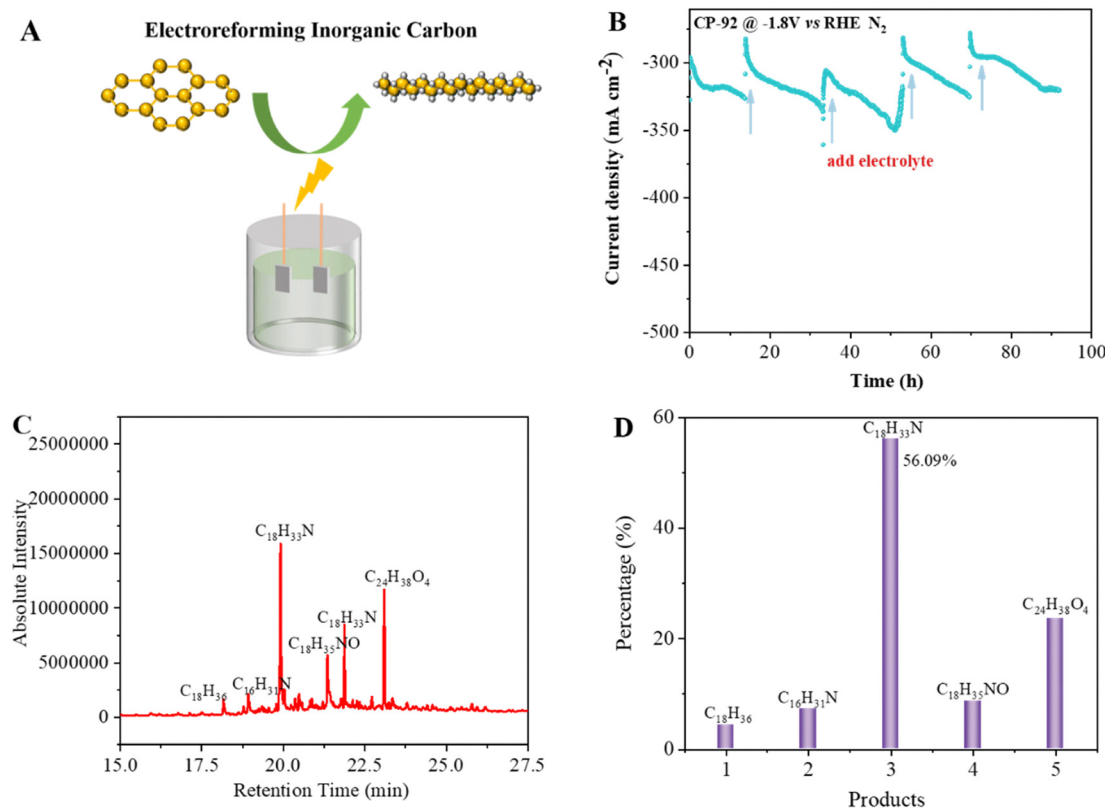


Fig. 1 (A) Illustration of the carbon paper electrolysis process. Carbon atoms, yellow; Hydrogen atoms, white. (B) Current density of carbon paper electrolyzed at -1.8 V vs. RHE in 1 M KOH under N_2 for 92 h. (C) Total ion chromatogram from Py-GC-MS analysis of the products. (D) The selectivity of the main products.

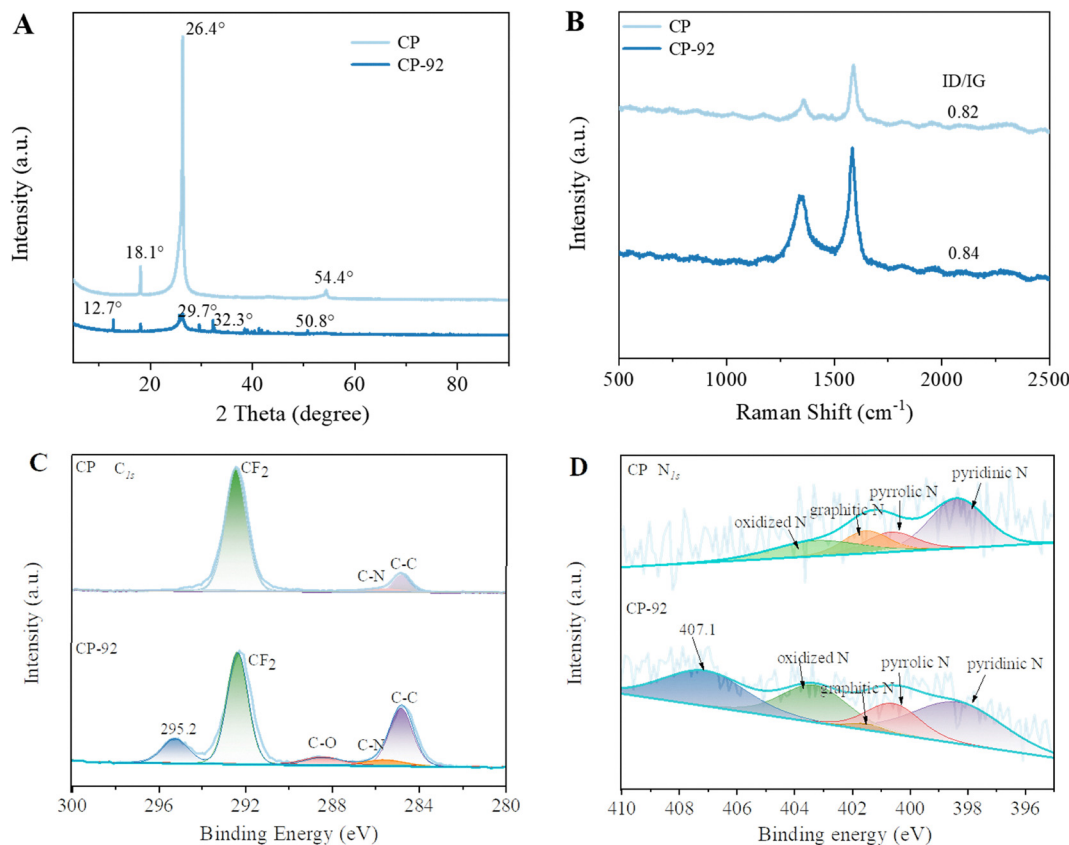


Fig. 2 XRD (A), Raman (B), XPS C 1s (C) and N 1s (D) spectra of carbon paper before and after electrolysis for 92 h.

fragmented state after electrolysis. This observed phenomenon might be caused by the destruction of the carbon network during electrolysis. The breakdown of the two-dimensional materials leads to the formation of long-chain hydrocarbons. This provides evidence for the generation of these long-chain hydrocarbon products.

X-ray diffraction (XRD) was utilized to analyze the structural changes in the carbon paper. Prior to electrolysis, the carbon paper was predominantly composed of graphite carbon (PDF 41-1487). Several new peaks emerged at 12.7°, 29.7°, 32.3°, and 50.8° in the XRD spectra following electrolysis. These peaks were not characteristic of potassium, nor of any carbon-, nitrogen-, or oxygen-containing compounds, suggesting that they might stem from alterations in the carbon structure, consistent with observations from SEM images (Fig. 2A).¹² Raman spectroscopy was employed to characterize the defects in the carbon paper. As shown in Fig. 2B, two peaks around 1350 and 1590 cm⁻¹ could be attributed to the D band and G band, respectively. The Raman I_D/I_G ratios (where I_D and I_G were the D band and G band Raman intensities) were widely used to assess the quality of the carbon materials.¹³ The relative intensity (I_D/I_G) ratio of CP and CP-92 was 0.82 and 0.84, respectively, suggesting a decrease in the degree of graphitization after electrolysis (Fig. 2B).

The elements in the carbon paper before electrolysis were firstly detected by XPS. XPS survey spectra revealed that the main elements in the carbon paper were F (61.43 at%) and C

(38.46 at%). The F element was introduced by polytetrafluoroethylene (PTFE). In addition, there were also a small amount of N (0.1 at%) and O (0.01 at%) elements, which were further evidenced by element analysis (Fig. S5 and Table S1, ESI†). To analyze the state of carbon and nitrogen before and after electrolysis, the C 1s and N 1s spectra of the original carbon paper (CP) and the electrolyzed carbon paper (CP-92) were examined. The C 1s peak of CP comprised three distinct peaks corresponding to C-C bonds at 284.8 eV,¹⁴ C-N bonds around 285.6 eV,¹⁴ and C-F₂ bonds around 292.4 eV.¹⁵ However, two new peaks emerged at 288.4 eV and 295.2 eV, which could be attributed to C-O bonds¹⁴ and the carbon of long-chain alkyl groups,¹⁶ respectively. The formation of the C-O bond may be due to the incorporation of oxygen from the environment during the electrolysis process. The peak at 295.2 eV suggested that the graphitic carbon in the carbon paper had been converted to alkyl carbon, which provided evidence for the conversion of inorganic carbon to organic carbon through the electrolysis process.

The high-resolution XPS analysis of the N 1s signals for both CP and CP-92 revealed the presence of four distinct nitrogen species: pyridinic N at 398.3 eV, pyrrolic N at 400.8 eV, graphitic N at 401.5 eV, and oxidized N at 403.5 eV.¹⁷ Notably, a new peak at 407.1 eV appeared in the N 1s spectra of CP-92, which could be attributed to nitrogen atoms attached to alkyl groups, further confirming the transformation of carbon from inorganic to hydrocarbon forms (Fig. 2D).¹⁸

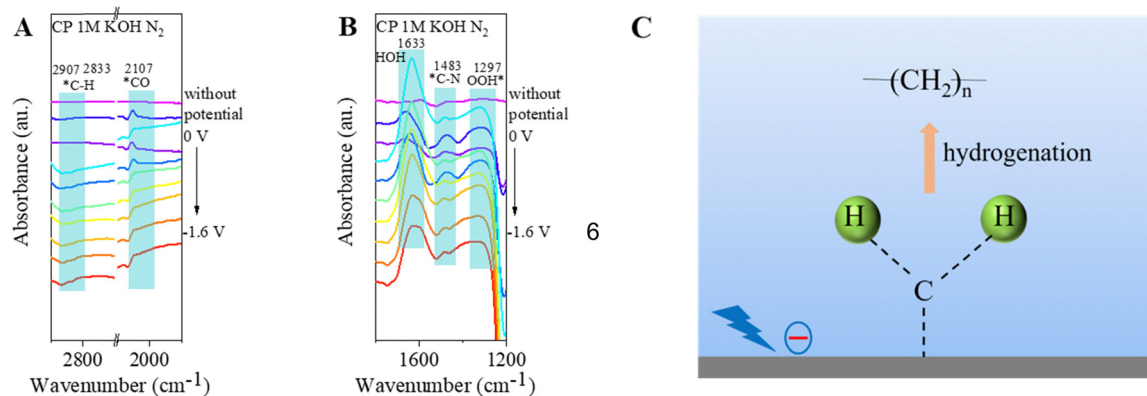


Fig. 3 (A) and (B) *In situ* attenuated total reflection infrared (ATR-IR) spectra recorded during CP electrolysis in 1 M KOH saturated with N₂ at different applied potentials. (C) Schematic of the mechanism for the formation of C–H bonds.

To elucidate the reaction pathways of the transformation from inorganic carbon to hydrocarbon *via* electrolysis, *in situ* infrared (IR) absorption spectroscopy was employed to monitor the intermediates formed during the process (Fig. S6, ESI†). Fig. 3A presents potential-dependent absorption spectra for CP in N₂-saturated 1 M KOH, displaying bands ranging from 3000 to 1800 cm⁻¹. The peaks at 2907 and 2833 cm⁻¹ were attributed to the asymmetric and symmetric stretching vibrations of the C–H group, respectively, indicating the formation of C–H bonds during electrolysis.^{19,20} A band at 2107 cm⁻¹ was assignable to a line-bound CO (CO_L), which shifted to lower energies at negative scans, consistent with the appearance of a Stark effect, as previously reported.^{21,22} The band at 2107 cm⁻¹, assigned to the intermediates of *CO, may result from the adsorption of OOH* onto the carbon surface, which was consistent with the XPS results showing the emergence of a C–O peak after prolonged electrolysis.

As depicted in Fig. 3B, the band at 1633 cm⁻¹ was attributed to the O–H bending mode of H₂O, indicating the presence of water molecules.²³ The band at 1483 cm⁻¹ was assigned to *C–N, suggesting the formation of nitrogen-containing functional groups.²¹ The band at 1297 cm⁻¹ represented the bond stretching of OOH*, which was likely generated by the oxygen evolution reaction (OER) at the anode.²⁴ Comparing the *in situ* FT-IR spectra recorded without an applied potential, it is evident that increasing the electrode potential negatively accelerated the appearance of the intermediates' peaks.

There have been many investigations on porous electrodes and the electrode/electrolyte interface, however, there are few studies on the hydrogenation of carbon electrodes.^{25–27} On the basis of the key intermediates identified in the *in situ* FT-IR spectra and the experimental results, we propose a “hydrogen dissociation-delocalized π -electron synergy” model and establish a new paradigm for organic synthesis involving the cleavage and restructuring of carbon–carbon bonds (Fig. 3C).¹¹

Graphite carbon featured sp² hybridized orbitals with delocalized π bonds between carbon atoms, making it electron-rich due to the σ bonds of C–C.^{28,29} When graphite carbon was connected to the cathode, it became electron-rich and negatively charged. Concurrently, the oxygen evolution reaction

(OER) at the anode produced a high concentration of protons in the solution.³⁰ The negatively charged carbon atoms were surrounded by positively charged protons. The interaction between the negatively charged carbons and the positively charged protons in the aqueous solution disrupted the extended π delocalization of the graphite carbon, ultimately leading to the formation of long-chain hydrocarbons. Additionally, the intermediate OOH* generated by the OER and the introduction of nitrogen from the environment could potentially contribute to the formation of high carbon chemicals with oxygen or nitrogen-containing functional groups.¹¹

Conclusions and prospects

This work introduces a novel approach for synthesizing high-carbon chemicals *via* the electrolysis of carbon materials under ambient conditions. By utilizing carbon materials as the carbon source and water as the hydrogen source, this method yields a series of high-carbon materials, achieving a selectivity of 56.09% for (*Z*)-9-octadecenitrile. *In situ* FT-IR spectroscopy confirmed the formation of C–H bonds during electrolysis. Furthermore, this study proposes a “hydrogen dissociation-delocalized π -electron synergy” model, establishing a new paradigm for organic synthesis centered on carbon–carbon bond cleavage and restructuring. This represents a novel strategy for synthesizing industrially significant high-carbon chemicals, such as pharmaceuticals, pesticides, and perfumes, which possess considerable application potential.

Author contributions

H. C.: conceptualization, funding acquisition, investigation, methodology, data curation, formal analysis, visualization, writing – original draft, review & editing.

Conflicts of interest

A patent application titled “A method for electrosynthesis of high carbon chemicals” (application no. 202410764010.6) was

submitted on 14 June 2024. The author declares no other competing interests.

Data availability

All data are available in the main text or the ESI.†

Acknowledgements

Dr Hongyuan Chuai acknowledges Dr Sheng Zhang for his support and also acknowledges the support of the Seed Foundation of Tianjin University (Grant number 2022XJS-0051).

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