

Tuning reaction pathways via acetylene recycling to synergistically boost solid carbon yield in methane plasma pyrolysis

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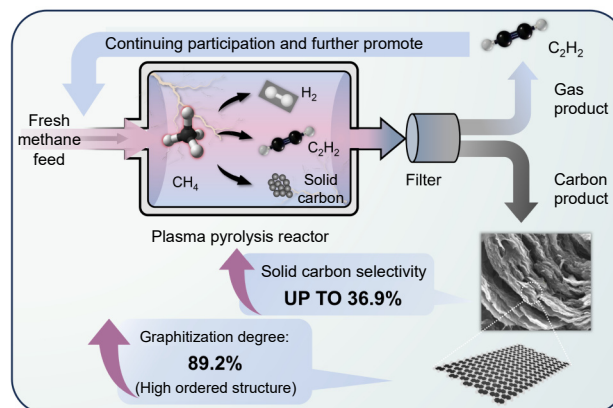


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ABSTRACT: Methane plasma pyrolysis represents a promising clean technology for solid carbon production, enabling simultaneous hydrogen generation without direct CO₂ emissions. Current research primarily focuses on single-feed methane processes, yet the strategic utilization of byproduct acetylene to enhance reaction efficiency and product value remains underexplored. This study systematically optimized key parameters—including plasma power, methane flow rate, and nozzle design—achieving a methane conversion rate of 91.3% and a solid carbon selectivity of 21.9%. Furthermore, an innovative cyclic feeding strategy combining methane and *in-situ*-generated acetylene was proposed. This approach significantly boosted solid carbon selectivity to 36.9%, outperforming conventional pure methane feeding. Mechanistic analysis revealed that acetylene not only redirects reaction pathways toward solid carbon formation but also acts as an efficient carbon source and template, promoting the synthesis of highly graphitized solid carbon with a graphitization degree of 89.2%. These findings provide critical insights into plasma-driven carbon material synthesis and establish a foundation for sustainable manufacturing through byproduct valorization.



KEYWORDS: methane pyrolysis, plasma technology, solid carbon, acetylene recycling, graphitization, hydrogen production

1 Introduction

Solid carbon materials, which mainly include carbon black, graphitic carbon, carbon nanotubes, and graphene, among various forms, are indispensable key raw materials in fields such as energy, electronics, chemical engineering, and advanced manufacturing, with extremely high industrial value and economic significance¹. Currently, mainstream production methods (e.g., coal

carbonization and oil furnace process) often rely on high-temperature pyrolysis or combustion of fossil fuels, resulting in high energy consumption during the production process and accompanied by substantial greenhouse gas emissions^{2,3}. Methane plasma pyrolysis ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) has attracted considerable attention as a promising alternative process, owing to its green characteristics of utilizing methane as the feedstock, the high economic value of its products, and its advantages of low carbon emissions^{4,5}. However, the practical application of this technology still faces critical challenges in product control, primarily manifested as complex reaction pathways and the high dependence of product distribution and carbon black properties on reaction conditions^{6,7}.

The primary challenge lies in the control of product selectivity. In the plasma pyrolysis of methane for solid carbon production, acetylene (C_2H_2) serves as the primary byproduct of the reaction and possesses certain economic value. However, its applications are largely limited to fields such as metal cutting and welding, as well as

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chemical synthesis, resulting in a market scale and added value substantially lower than those of solid carbon^{8,9}. Therefore, how to engineer the reaction pathway to balance the selectivity between solid carbon and gaseous acetylene, thereby maximizing the overall value of the products, constitutes a key scientific question that must be addressed for the industrial adoption of this technology¹⁰. Secondly, controlling the morphology and properties of solid carbon is essential. Current research has largely focused on the preparation of solid carbon, while systematic studies on the precise control of its micro-morphology (such as spherical¹¹, layered¹², or capsule¹³), particle size distribution, and degree of graphitization are still relatively lacking. These microstructural characteristics directly determine the reinforcing and conductive properties of solid carbon in applications^{14,15}.

To address the aforementioned issues, this study proposes an innovative C_2H_2 recycling strategy, which involves separating C_2H_2 from the reaction outlet gas stream and partially recycling it back to the reactor inlet^{16,17}. This strategy is expected to optimize the process in two ways: first, regarding reaction distribution, the recirculation of C_2H_2 is anticipated to alter the chemical equilibrium and radical concentration within the reaction zone, thereby suppressing certain side reactions and optimizing solid carbon selectivity^{18,19}. Second, in terms of controlling the morphology of solid carbon, varying atmospheric conditions can control the microstructure and properties of solid carbon^{20,21}.

This study aims to systematically investigate the effects of different reaction conditions on the methane plasma pyrolysis process for solid carbon production, focusing on the following aspects: (1) optimizing key process parameters such as input power, CH_4 feed flow rate, and the gas nozzle specifications of the plasma torch to achieve high CH_4 conversion rate and solid carbon selectivity; (2) examining the impact of the C_2H_2 recycling strategy on reaction performance, including CH_4 conversion rate and solid carbon selectivity; (3) elucidating the effects of C_2H_2 recycling on the micro-morphology, crystalline structure, and surface chemical properties of the resulting solid carbon. This study aims to establish a theoretical foundation and technical pathways for developing highly efficient and controllable low-carbon solid carbon production processes.

2 Experimental methods

2.1 Experimental procedure

The experimental equipment for plasma assisted methane pyrolysis used in this work is shown in Fig. 1a and is composed of the

following parts: gas supply system, plasma torch, cooling system, carbon powder filter, and online analysis system. The gas supply system manages the routing of the input gases used in this work: CH_4 , Ar, and N_2 . N_2 is used as an internal standard for calculating the carbon and hydrogen balance before and after the reaction. Methane and argon gas are controlled into the electrolytic generator through the flow meter, and plasma methane cracking reaction occurs in an oxygen-free atmosphere. The generated hydrogen and hydrocarbon substances are partially drained through the high point of the exhaust pipe, with the remaining portion directed to an online detection system. The generated solid carbon is collected through the dust filtration system.

In this study, the plasma generator employed is an arc plasma system²², utilizing tungsten for the cathode and copper for the anode. The tungsten electrode functions as the electron emission source, while the copper electrode's structure serves as the nozzle for the plasma torch gas, acting as the attachment point for the arc and the chamber for the formation of the plasma jet. The schematic diagram of the plasma torch gas nozzle is shown in Fig. 1b.

Prior to each experiment, the reactor was purged with high-purity argon for 10 min to remove air. Subsequently, a gas mixture—composed of the reactant gas (CH_4 , C_2H_2 , or a mixture thereof) and the diluent gas (Ar)—was introduced and allowed to stabilize under flow for 5 min before plasma ignition. The plasma was then generated by applying a 380 V AC voltage, which created a stable, high-temperature jet within the gas mixture. After ignition, the system was allowed to stabilize for approximately 15 min, after which data acquisition was initiated and lasted for a minimum of 15 min. During the experiment, the following parameters were recorded: the power of the plasma torch, the flow rates of CH_4 , C_2H_2 , and Ar, and the length and diameter of the plasma torch gas nozzle.

2.2 Characterization methods

Following each synthesis conducted with the reactor illustrated in Fig. 1(a), the solid carbon powder collected on the filter was subjected to analysis. The morphology and microstructure of the solid carbon were characterized using scanning electron microscopy (SEM, Verios 5UC) and transmission electron microscopy (TEM, JEM-2010). The crystalline structure of the solid carbon was examined using Raman spectroscopy (Raman, LabRAM HR), with a 532 nm helium-neon laser line serving as the excitation source, and Raman spectra were measured within the range of 1000 to 3000 cm^{-1} . The crystalline structure of the solid carbon was also analyzed by X-ray diffraction (XRD, D8 ADVANCE), determining the proportion of graphitized carbon in

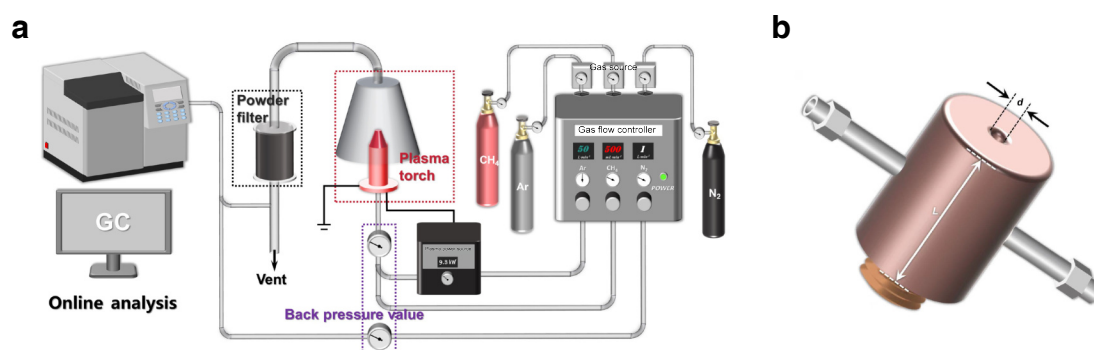


Fig. 1. Schematic of the plasma-assisted methane pyrolysis setup and the plasma torch nozzle: a, Pyrolysis device; b, Plasma torch nozzle.

the product using Cu K α radiation over a 2θ range of 10–70°. The surface elemental composition and chemical states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The binding energy was calibrated using the C1s peak of surface adventitious carbon, and peak deconvolution was performed to quantitatively analyze the content of each chemical state. The specific surface area and pore structure of the samples were determined by low-temperature N₂ adsorption-desorption measurements (MICROTRAC MRB MAX X) by using Brunauer-Emmett-Teller (BET) method. Prior to testing, the samples were degassed under vacuum at 150 °C for 6 h to remove surface adsorbates. The thermal stability of the samples was characterized by thermogravimetric analysis (TGA, METTLER TOLEDO TGA/DSC 3+). The test was conducted under an air atmosphere (flow rate of 20 mL/min), with the temperature increased from room temperature to 900 °C at a heating rate of 10 °C/min.

Gas chromatography (GC, GC-990, Agilent) equipped with a dual thermal conductivity detector (TCD) was used to analyze the composition of the exhaust gas, allowing for rapid and accurate analysis of a sample within 4 min.

2.3 Chemical reaction analysis

The reacted gas enters the gas chromatography inlet for product detection. Based on the chromatographic data and calculation formulas, the methane conversion rate and the selectivity of various products were determined. The formulas for the CH₄ conversion rate (X_{CH_4}) and the selectivity (S) of each product are shown in Eqs. 1–4:

$$X_{CH_4} (\%) = \frac{\text{Moles of CH}_4 \text{ converted}}{\text{Moles of CH}_4 \text{ input}} \times 100 \quad (1)$$

$$S_{C_xH_y} (\%) = \frac{x \times \text{Moles of C}_x\text{H}_y \text{ produced}}{\text{Moles of CH}_4 \text{ converted}} \times 100 \quad (2)$$

$$S_{H_2} (\%) = \frac{\text{Moles of H}_2 \text{ produced}}{2 \times \text{Moles of CH}_4 \text{ converted}} \times 100 \quad (3)$$

$$S_C (\%) = \{1 - S_{C_xH_y} (\%) \} \times 100 \quad (4)$$

Energy efficiency (η_{Energy}) is defined as the ratio of the chemical energy contained in all output products (e.g., H₂, C₂H₂, and solid carbon) to the total energy input to the process. The chemical energy of the products and the methane feedstock is calculated based on their respective lower heating values (LHV). The efficiency is expressed as²³:

$$\eta_{\text{Energy}} = \frac{\sum m_i \times \text{LHV}_i}{m_{CH_4} + \text{LHV}_{CH_4} + P_{\text{Plasma}}} \times 100 \% \quad (5)$$

where m_i and LHV_i are the mass flow rate and lower heating value of product i , m_{CH_4} and LHV_{CH_4} are the mass flow rate and lower heating value of the input methane, and P_{Plasma} is the electrical power input of the plasma.

3 Results and discussion

3.1 Process parameter optimization

To achieve efficient pyrolysis of methane in the plasma reactor and obtain highly selective solid carbon products, this study employed a controlled variable experimental approach. The process parameters,

including CH₄ flow rate, Ar flow rate, and power, were systematically adjusted²⁴. Additionally, the specifications of the plasma torch gas nozzle were optimized²⁵.

To investigate the influence of power on the conversion rate and product distribution of methane, under constant conditions of Ar flow rate at 50 L/min, CH₄ flow rate at 500 mL/min, and a gas nozzle specification of 25 mm length and 7 mm inner diameter, the input power of the plasma torch was increased from 6.5 kW to 13.0 kW. The CH₄ conversion rate increased from 75.1% to 83.4%. The selectivity of the product solid carbon varied within the range of 13.9%–15.2%, the selectivity of the product C₂H₂ ranged from 74.6%–78.0%, and the selectivity of the product H₂ ranged from 75.2%–76.8% (Fig. 2a).

When the input power was doubled, the CH₄ conversion rate increased significantly, while the product selectivity showed only a minor variation. The increased power created a reaction environment with higher energy and a greater abundance of active species²⁶, enabling more methane molecules to acquire sufficient energy to overcome the energy barrier and undergo cracking reactions, thus leading to a substantial rise in CH₄ conversion. At 6.5 kW, the system already possessed sufficient conditions for the reaction to proceed along the CH₄ $\rightarrow$ C₂H₂ $\rightarrow$ C pathway²⁷. Increasing the power to 13 kW merely accelerated the reaction rate along the same pathway, without opening a new and more advantageous reaction route. Consequently, the selectivity exhibited a narrow variation.

When the input power was increased, the methane conversion rate showed a significant rise. Besides input power, the CH₄ flow rate is another critical parameter. We further investigated its effect on performance under specific power conditions (Fig. 2b). At an Ar flow rate of 50 L/min, an input power of 13.0 kW, and a gas nozzle specification of 25 mm in length with an inner diameter of 7 mm, the CH₄ flow rate was adjusted. When the CH₄ flow rate was set at 500 mL/min, the conversion rate was 83.4%. However, the short residence time of 0.115 s at this flow rate rapidly purged methane molecules from the high-temperature core, thereby preventing them from acquiring sufficient energy for cracking reactions before exiting the reaction zone. In contrast, when the CH₄ flow rate was reduced to 125 mL/min, the residence time increased to 0.461 s, allowing the molecules ample time to react in the plasma zone. Nevertheless, the conversion rate at this flow rate was only 75.5%. This was attributed to the energy dilution effect. A fixed input power (such as 13 kW) is required to crack a certain number of CH₄ molecules. This is attributed to the energy dilution effect. Under a fixed input power, a low methane flow rate increases the specific energy input (SEI, defined as input power (kW)/gas flow rate (L/min))²⁸. However, an excessively high SEI means that a portion of the energy cannot be effectively utilized by the reactants for the cracking reaction, thus resulting in energy waste and a reduction in the energy efficiency of the process.

The experiments revealed that the methane conversion rate did not show a monotonic increase with reduced flow rate but exhibited a distinct optimum. When the CH₄ flow rate was set at 250 mL/min, with a residence time of 0.231 s, the conversion rate of CH₄ reached a maximum of 91.2%.

To achieve efficient methane pyrolysis and high selectivity for solid carbon production in the plasma, this study optimized the design of the plasma reactor by refining the dimensions of the plasma nozzle gas outlet^{25, 29}. Under experimental conditions of an Ar flow rate of 50 L/min, a CH₄ flow rate of 500 mL/min, and a power of 13 kW, a controlled variable method was employed to test

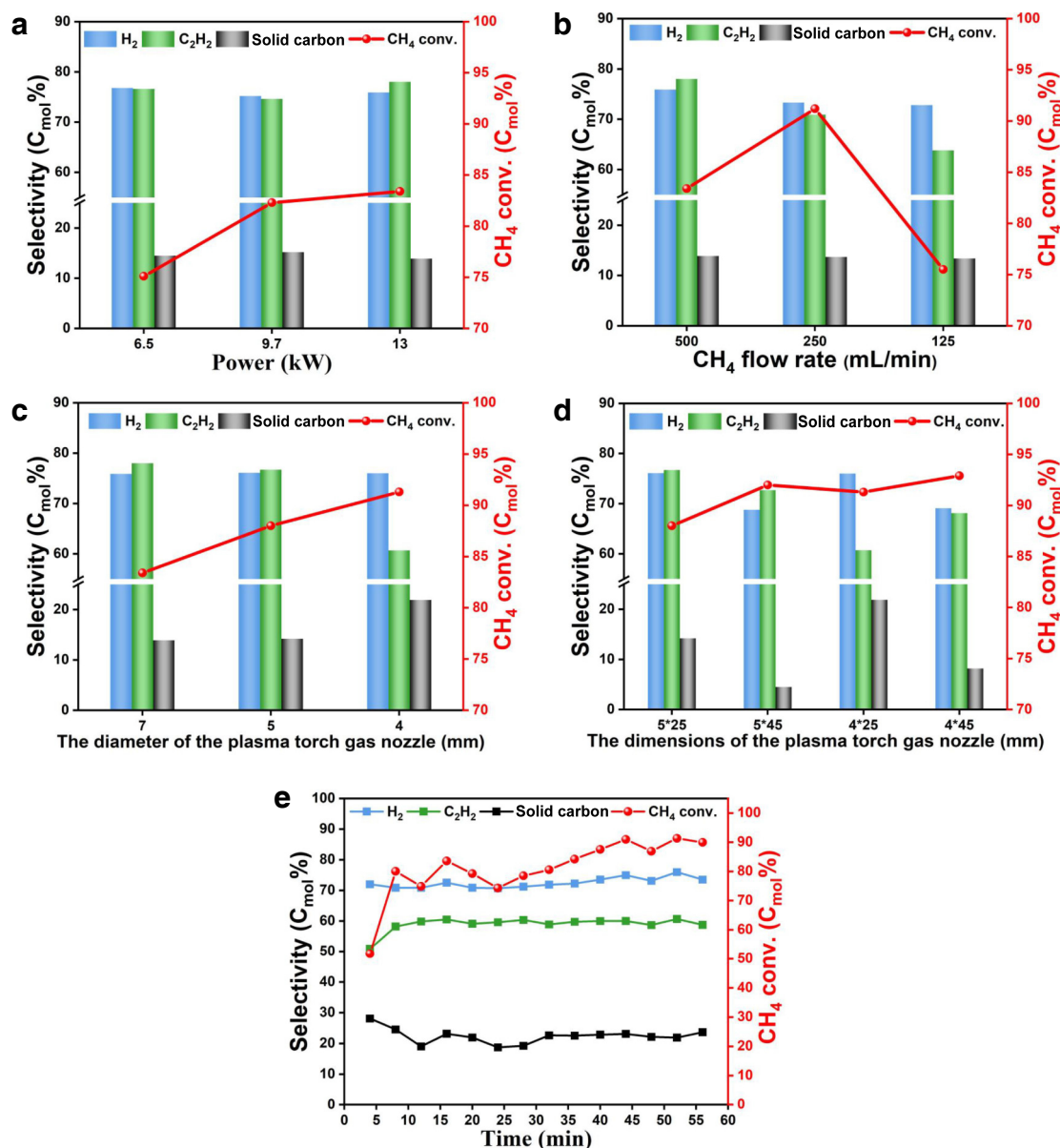


Fig. 2. The influence of the process conditions on the performance of plasma decomposition of methane: a, Power; b, CH_4 flow rate; c, The diameter of the plasma torch gas nozzle; d, The dimensions of the plasma torch gas nozzle; e, Stability test.

different gas nozzle inner diameters (7, 5, and 4 mm) and lengths (25 and 45 mm). The experimental results are shown in Figs. 2c and 2d.

As the diameter of the gas nozzle decreases, the CH_4 conversion rate increases, and the selectivity for solid carbon improves. A smaller nozzle diameter provides a high-temperature, high-speed reaction environment³⁰, which not only facilitates the initial cracking of methane but also accelerates the conversion rate of the intermediate product, C_2H_2 , to the final product, solid carbon. However, from the perspective of pure mass transfer or flow velocity, a smaller nozzle diameter promotes the reaction process. Yet, considering the inherent limitations of the upstream reactor and the potential risk of clogging by solid products, we cannot indefinitely reduce the diameter. The optimized nozzle size adopted currently represents the optimal design choice that achieves the best overall performance while ensuring the continuous and stable operation of the plasma process.

Conversely, as the length of the gas nozzle decreases, the CH_4 conversion rate decreases while solid carbon selectivity increases. A longer nozzle allows for a longer residence time, leading to a higher CH_4 conversion rate, whereas a shorter nozzle create conditions for rapid quenching, reducing the occurrence of secondary reactions and thereby enhancing solid carbon selectivity.

Therefore, an optimal nozzle length strikes the best balance between high conversion and high solid carbon selectivity. The current optimal experimental results indicate that when the Ar flow rate is 50 L/min, the CH_4 flow rate is 500 mL/min, the power is 13 kW, and the gas nozzle has an inner diameter of 4 mm and a length of 25 mm, the CH_4 conversion rate can reach 91.3%, with the highest selectivity for solid carbon at 21.9%. Additionally, the selectivity for the byproduct C_2H_2 in the product reaches 60.7%.

Stability tests were conducted under the aforementioned experimental conditions for 56 min. The results are presented in Fig. 2e. After a reaction time of 40 min, the CH_4 conversion rate

fluctuated between 87% and 92%. The selectivity fluctuated within the following ranges: H_2 73%–76%, C_2H_2 58%–61%, and carbon 21%–24%.

Based on the stability test data, we conducted an analysis of the energy efficiency. Using the measured average conversion (90%) and product selectivity (H_2 : 74.5%, C_2H_2 : 59.5%, carbon: 22.5%), the process energy efficiency was calculated via Eq. 5. The result is 2%–3%. This low value is attributed to the fact that the input electrical energy is primarily used to generate a highly reactive environment and drive the reaction pathway ($\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 \rightarrow \text{C}$), rather than being stored in the products. Consequently, a significant portion of the energy is dissipated as waste heat via the reactor cooling system and exhaust gases.

This result highlights that improving overall energy efficiency remains a primary challenge for scaling this technology. The most promising route for substantial efficiency gains lies in the integration of a heat recovery system to capture and repurpose the waste heat (e.g., for feedstock preheating, power generation, or external heating purposes). Such an integration would significantly enhance the process's economic viability and environmental sustainability, moving it closer to practical industrial application. Future work will focus on system-level thermal integration and optimization to address this key challenge.

3.2 Plasma pyrolysis with co-feed of CH_4 and C_2H_2

Based on the above experimental results, it can be seen that plasma decomposition of methane not only produces solid carbon but also generates a large amount of C_2H_2 . From the perspective of improving the overall economic efficiency and carbon utilization rate of the entire process, a cyclic strategy of feeding the byproduct C_2H_2 together with CH_4 can be adopted.

Therefore, we selected conditions for high CH_4 conversion rate (92.9%), specifically with an Ar flow rate of 50 L/min, a CH_4 flow rate of 500 mL/min, a power of 13 kW, and a gas nozzle with an inner diameter of 4 mm and a length of 45 mm. Under these experimental conditions, the composition of the feed gas was

varied, leading to three sets of experiments. The feed gas compositions were 99% N_2 + 1% CH_4 , 98% N_2 + 1% CH_4 + 1% C_2H_2 , and 99% N_2 + 1% C_2H_2 . The performance results are shown in Fig. 3a.

When pure methane is involved in the plasma cracking process, the reaction performance exhibits a high CH_4 conversion rate (92.9%) and low solid carbon selectivity (8.2%). In contrast, when pure C_2H_2 is fed, the experimental results show a low C_2H_2 conversion rate (39.0%) but a high solid carbon selectivity (69.3%). Under the experimental conditions of co-feeding CH_4 and C_2H_2 , the selectivity for solid carbon significantly increases compared to feeding methane alone, rising to 36.9%. At the same time, the CH_4 conversion rate decreases but remains at 64.0%, while the selectivity for H_2 can also reach 53.1%. This indicates that the presence of C_2H_2 during co-feeding can improve the product distribution and enhance solid carbon selectivity, without significantly reducing the CH_4 conversion rate.

Acetylene molecules are the most direct precursors for the formation of carbon nuclei. They can rapidly polymerize to form polycyclic aromatic hydrocarbons (PAHs), which, upon reaching a critical size, precipitate to form carbon black particles^{31, 32}. The addition of C_2H_2 significantly accelerates the nucleation and growth processes of carbon black particles, allowing the reaction pathway to quickly and efficiently progress towards the final product—nanostructured solid carbon with a high degree of graphitization. Furthermore, the energy provided by the plasma is sufficiently high to simultaneously crack both CH_4 and C_2H_2 , ensuring that the conversion rate of CH_4 does not decrease significantly.

The solid carbon products generated under three different atmospheric conditions were characterized using SEM, as shown in Figs. 3b–3d. The solid carbon produced from pure CH_4 and pure C_2H_2 feedstock exhibited a morphology characterized by spherical shapes with a minor presence of layered structures. In contrast, the solid carbon produced from the co-feeding of CH_4 and C_2H_2 displayed a morphology consisting of stacked layered structures.

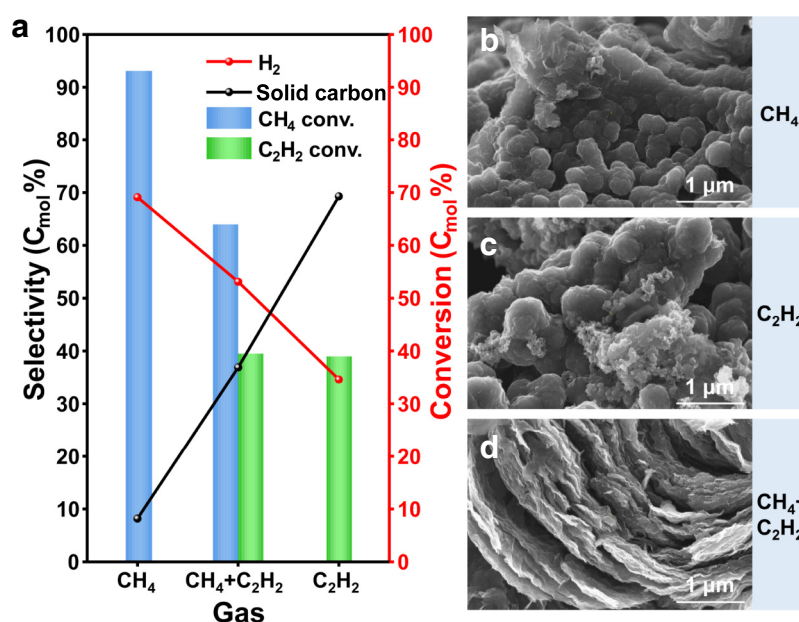


Fig. 3. Methane pyrolysis performance and carbon product morphology under different gas atmospheres: a, Methane pyrolysis performance; b–d, SEM images of carbon products.

This study, supported by the literature³³, demonstrates that the morphology of carbon nanostructures is governed by two key parameters: the local C_2 molecular concentration, where a high concentration favors the formation of ordered structures, and the effective hydrogen-to-carbon atomic ratio (H/C). When $H/C > 1$, hydrogen atoms effectively passivate the growing edges of graphene sheets, suppressing their curling or closure and thereby promoting two-dimensional planar growth.

Based on this framework, the morphological differences under the three feed conditions can be clearly explained: (1) CH_4 feed: The low efficiency of C_2 generation results in an insufficient local concentration. Carbon clusters thus form spherical solid carbon via isotropic coalescence. (2) C_2H_2 feed: Although providing a high C_2 concentration, the very low H/C ratio leads to a lack of edge passivation. The reactive edges rapidly curl, again leading to dense spherical solid carbon through isotropic growth. (3) $CH_4 + C_2H_2$ co-feed: Acetylene ensures a rich supply of C_2 , while methane co-cracking elevates the H/C ratio above 1. The sustained hydrogen passivation inhibits edge curling and drives the lateral expansion of the carbon network, ultimately yielding flake-like graphene nanoflakes. Therefore, the transition from “spheres” to “flakes” clarifies how precursor composition — by tuning both the C_2 concentration and the H/C ratio—provides a fundamental basis for the directed synthesis of target carbon materials.

3.3 Characterization and analysis of solid carbon

The content of amorphous carbon and graphite carbon in the solid carbon materials was quantitatively assessed using XRD. As depicted in Fig. 4a, the XRD pattern for the solid carbon materials reveals two diffraction peaks at approximately $2\theta = 26^\circ$ and $2\theta = 43^\circ$, which correspond to the (002) and (100) diffraction peaks, respectively. Generally, the intensities of the (002) and (100) peaks

serve as indicators of graphite structure, with the fitted area of the (002) peak reflecting the relative proportions of the graphite and disordered structures^{34, 35}. Regarding carbon phases, graphite carbon possesses a higher degree of crystallinity and narrower interlayer spacing, whereas amorphous carbon has slightly broader interlayer spacing³⁶. Thus, Peak 1 denotes the relative content of amorphous carbon, while Peak 2 signifies the relative content of graphite carbon. The fitting analysis results reveal that the carbon nanomaterials synthesized in a co-feeding atmosphere of CH_4 and C_2H_2 exhibit the highest content of graphite carbon (89.2%). In the atmospheres where CH_4 and C_2H_2 were fed separately, the graphite carbon contents in the synthesized carbon nanomaterials were found to be 84.1% and 83.4%, respectively.

All Raman spectra contain three distinctive peaks: the D band at 1350 cm^{-1} , the G band at 1580 cm^{-1} , and the 2D band at 2700 cm^{-1} , which signify the presence of sp^2 nanocarbon. The ratio of the D band intensity to the G band intensity (I_D/I_G) is frequently utilized to evaluate the defect level within the sample; a lower ratio suggests a reduced defect density^{37, 38}. The Raman spectral analysis presented in Fig. 4b indicates that the I_D/I_G ratio is minimized (0.28) under the co-feeding conditions of CH_4 and C_2H_2 , reflecting an improved crystallinity of the carbon nanomaterials.

Figs. 4c–4h shows TEM test results. The solid carbon synthesized via the plasma pyrolysis of CH_4 predominantly comprises graphene nanoflakes (GNF)³⁹. Figs. 4c and 4d clearly depict that the GNF contains several layers of graphite structure, exhibiting a certain degree of distortion, which suggests the presence of some disorder within the GNF. Conversely, the solid carbon derived from the plasma pyrolysis of C_2H_2 is mainly composed of spherical carbon nanoparticles (SCN)³³. Figs. 4e and 4f demonstrate that the SCN possesses multiple nuclei with a characteristic concentric structure, along with numerous distorted graphite layers encircling these nuclei. The solid carbon obtained from the co-feeding of CH_4 and

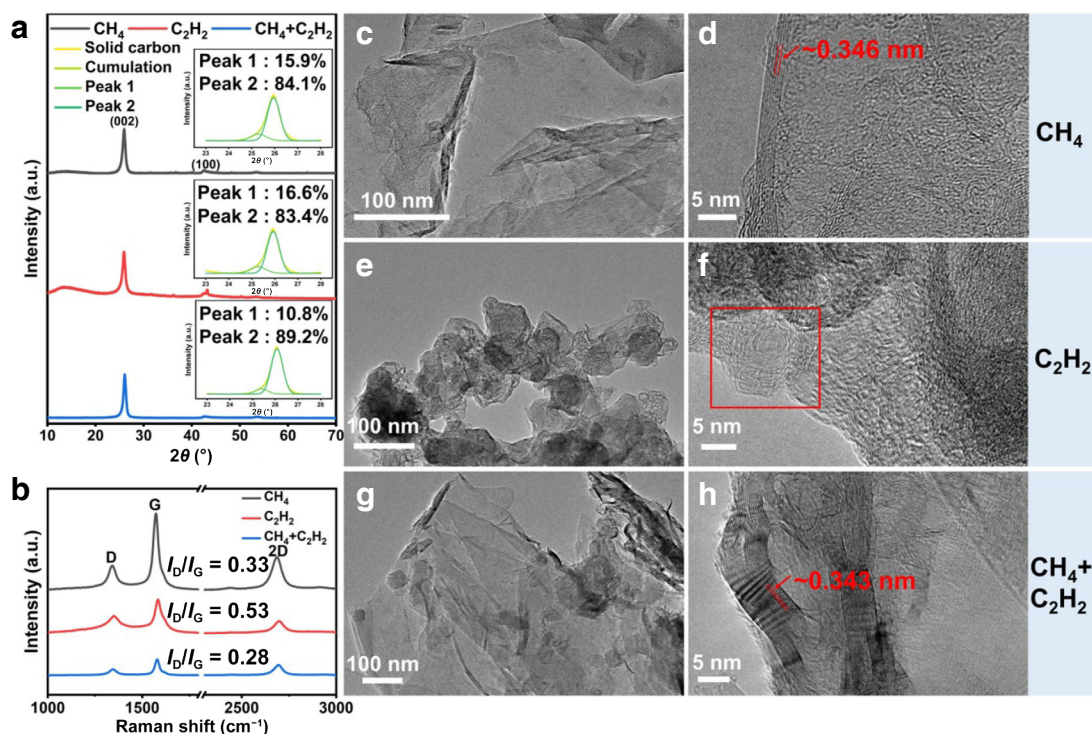


Fig. 4. Characterization of solid carbon obtained under different atmospheres: a, XRD pattern; c, e, g, TEM images of solid carbon; d, f, h, HRTEM images of solid carbon.

C_2H_2 during plasma pyrolysis primarily consists of both GNF and graphitic nanocapsules (GNC)¹³, as observed in Figs. 4g and 4h.

XRD quantitative analysis demonstrates that the co-feed samples possess the highest graphite carbon content, which is highly consistent with the high graphitization degree and low defect density indicated by the lowest I_D/I_G value observed in the Raman spectroscopy. TEM observations offer direct visual evidence of morphology: distinct graphene nanosheets and graphite nanoplatelet structures were identified in the co-feed samples with elevated graphitization levels, supporting the findings from XRD and Raman analyses.

The introduction of acetylene significantly increases the local C_2 concentration in the reaction zone, providing abundant aromatic precursors for the rapid nucleation of graphitic crystallites. Meanwhile, the continuous cracking of methane not only contributes active small carbon species (e.g., C_2 and CH_3) but, more critically, elevates the effective H/C ratio of the system above 1, enabling sustained passivation of the growing edges. This synergy between “high C_2 concentration-driven rapid nucleation” and “appropriate H/C ratio-guided two-dimensional growth” creates a near-equilibrium dynamic growth environment. As a result, carbon atoms have sufficient time to migrate to the lowest-energy lattice sites and undergo ordered stacking. Consequently, not only are highly graphitized GNF generated, but unique morphologies such as GNC is also promoted, which can release strain energy by forming closed structures under curved stress fields. Thus, the essence of the co-feeding strategy lies in simultaneously optimizing both the concentration of key precursors (C_2) and the chemical environment (H/C ratio) within the reaction zone, thereby precisely

regulating the carbon atom assembly pathway from the gas phase to the solid phase and promoting the formation of more stable graphitic structures.

The surface chemical states of the solid carbon samples synthesized from different precursors were analyzed by XPS (Fig. 5a). Carbon and oxygen elements were detected on the surface of all samples. The carbon element primarily exists as the C1s peak at a binding energy of 284.5 eV, corresponding to graphitic carbon (sp^2 and sp^3) or surface adventitious carbon. The oxygen element is present as the O1s peak at 532.5 eV, originating from airborne contamination or surface oxidation^{20,22}.

The analysis of the high-resolution C1s spectra (Fig. 5b) reveals that the solid carbon derived from the CH_4/C_2H_2 co-feeding exhibits the highest sp^2 -C content (81.0%) and the lowest sp^3 -C content (13.2%). This finding is consistent with its highest degree of graphitization observed in XRD and Raman analyses. Although a certain amount of oxygen-containing functional groups (C–O, 5.8%) is present on its surface, the content is significantly lower than that of the pure C_2H_2 -derived sample (6.7%). This indicates that the co-feeding strategy not only significantly enhances the graphitic ordering of the solid carbon's bulk structure but also effectively suppresses excessive oxidation caused by highly reactive surfaces, resulting in a solid carbon material with a more stable surface chemical state.

Fig. 5c presents the TGA results of solid carbon prepared from different precursors. All samples exhibit a single-stage weight loss in an air atmosphere, corresponding to the complete oxidation of the carbon matrix. The temperature at which the most rapid oxidation occurs for all three solid carbon materials exceeds 700 °C, far surpassing that of most disordered carbon materials (typically

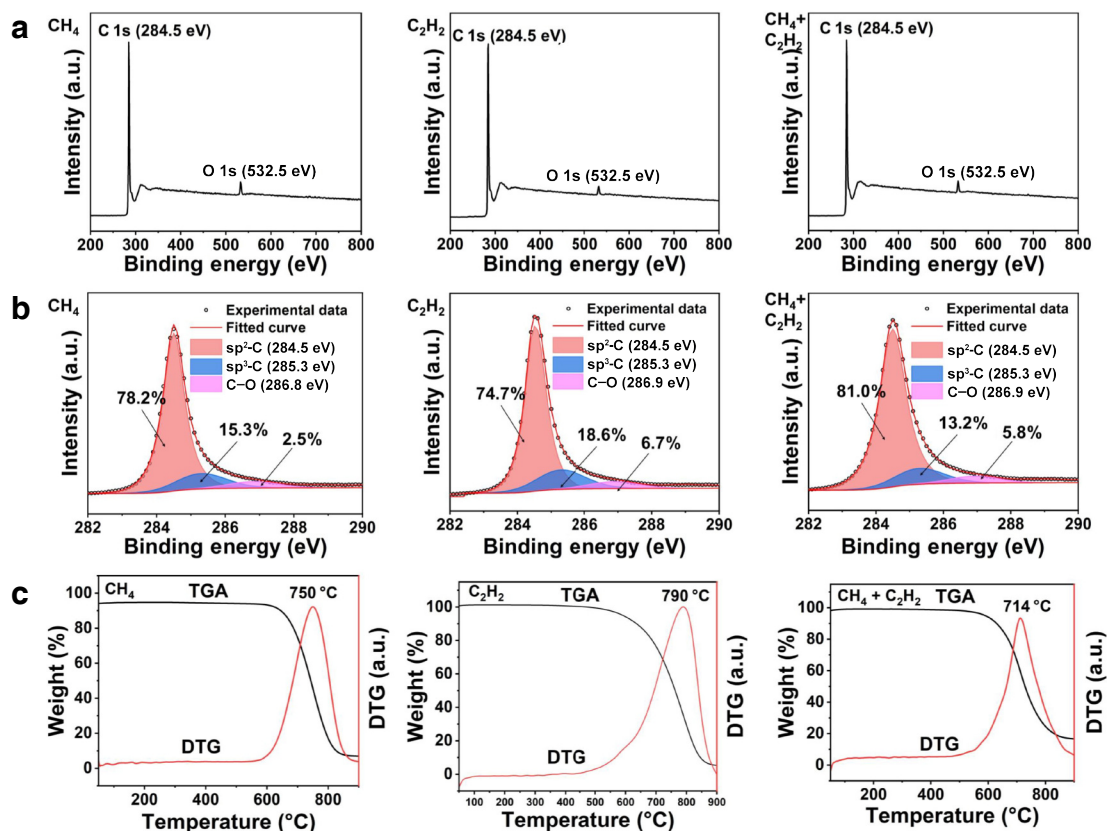


Fig. 5. XPS and TGA/DTG characterization of solid carbon synthesized under different gas atmospheres: a, XPS full survey spectra; b, C1s XPS spectra; c, TGA/DTG curves.

oxidized between 400–600 °C¹⁶). This demonstrates that, regardless of the precursor variation, the carbon products synthesized in the high-temperature plasma environment possess a highly stable carbon skeleton and a robust carbon-carbon network.

Fig. 6 displays the nitrogen adsorption–desorption isotherms and pore size distributions of solid carbon samples synthesized from different precursor atmospheres. All isotherms exhibit Type IV behavior with H3-type hysteresis, indicative of slit-shaped pores formed by plate-like particle stacking²⁰. Pore size distributions confirm that while all samples possess mesopores, their pore development varies notably. The co-feed sample shows a shift toward smaller mesopores.

The specific surface area of the co-feed solid carbon (6.24 m²/g) lies between those of the CH₄-derived (3.97 m²/g) and C₂H₂-derived (7.06 m²/g) samples, yet its pore volume (0.03 m³/g) is markedly lower than both (CH₄: 0.05 m³/g; C₂H₂: 0.07 m³/g). The extremely low specific surface area indicates that the material has an overall “poor” surface and does not fall into the category of high-surface-area porous materials. This is highly consistent with its highest degree of graphitization and lowest defect density observed

in XRD and Raman spectroscopy, as highly ordered and complete graphite lattices tend to minimize surface energy through tight stacking. The very low pore volume indicates that the total internal pore space of the material is minimal. This is because the GNC structures formed under co-feeding conditions are more enclosed and complete, and the stacking of GNF is more compact and ordered, resulting in reduced pore space available for nitrogen filling both within and between particles.

Therefore, the co-feeding strategy results in a unique structure characterized by a surface composed of highly graphitized crystalline domains and internally compacted porosity. This material is more suitable for applications requiring high electrical conductivity, high thermal conductivity, and structural stability (such as composite reinforcements and conductive fillers).

3.4 Comparative analysis and discussion of comprehensive performance

To systematically evaluate the performance of the “acetylene recycling co-feeding strategy” proposed in this study, we have compared its key performance metrics with those from important recent peer research^{8, 20, 29}. Table 1 summarizes and contrasts the critical data across different plasma processes, including feedstock composition, experimental conditions, conversion rate, the yield or selectivity of solid carbon, and product quality.

Analysis of the data in Table 1 reveals that the “cyclic co-feeding strategy” employed in this study exhibits significant comprehensive advantages. (1) In terms of methane conversion rate, this study (~91.3%) has achieved an excellent level comparable to state-of-the-art thermal plasma processes. (2) Regarding solid carbon selectivity, the 36.9% selectivity achieved through our acetylene recycling strategy is significantly higher than most reported studies that primarily produce gaseous hydrocarbons or disordered carbon. This directly demonstrates the unique efficacy of our strategy in steering the reaction pathway towards high-value solid carbon. (3) In terms of product quality, the graphitization degree of the solid carbon produced in this work (89.2%) is at a relatively high level. This indicates that we have not only increased the yield of

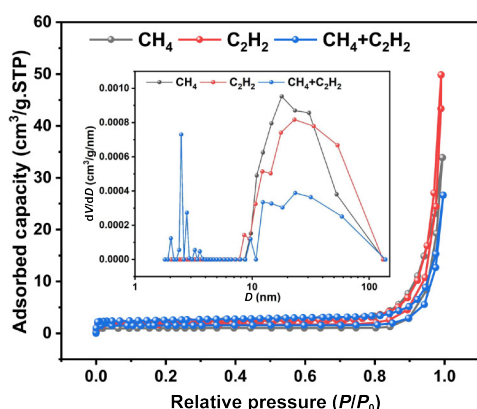


Fig. 6. N₂ adsorption–desorption isotherms and BJH pore size distribution of solid carbon samples.

Table 1 Benchmarking of methane conversion performance and solid carbon characteristics

Plasma type	Feedstocks	Experimental conditions	Conversion rate	Solid carbon selectivity or yield	Graphitization degree	Primary product morphology	Ref.
Arc thermal plasma	CH ₄	CH ₄ : 500 SCCM Power: 13 kW	91.3%	21.9%	Graphitization degree ~89.2%	Graphite nanoflakes (GNF)	This work
Arc thermal plasma	CH ₄ +C ₂ H ₂	CH ₄ : 250 SCCM C ₂ H ₂ : 250 SCCM Power: 13 kW	64.0%	36.9%	Graphitization degree ~89.2%	GNF and graphitic nanocapsules (GNC)	This work
Magnetically rotating arc	CH ₄	CH ₄ : 3.6 SLM, H ₂ : 3.6 SLM, Ar: 1 SLM; Current: 60 A, 80 A, 100 A (low/med/high SEI); CH ₄ /H ₂ = 1:6	Low SEI: 98.35%; Med SEI: 98.90%; High SEI: 99.16%	The article does not cover this aspect	Low SEI: CNSs ≈ 37.57%, GNFs ≈ 29.88%; Med SEI: GNFs ≈ 42.01%; High SEI: GNFs ≈ 51.23%	Low SEI: Mixture of CNSs & GNFs; Medium/high SEI: Increased proportion of GNFs with larger size (50–300 nm) and higher crystallinity.	[8]
Magnetically stabilized gliding Arc discharge	CH ₄	CH ₄ : 0.2 SLM, Current: 0.3 A, Voltage: 420–850 V, Power: 126–255 W	Not explicitly given; Product yield ranges 3–13%	Synthesis rate: 3.6–13.7 mg/min; Yield: 3.4–12.8%	CH ₄ : I _D /I _G = 0.757	Pure CH ₄ & Ar: Mixture of SCNs & GNFs	[20]
Nanosecond pulsed discharge (NPD) plasma	CH ₄	Pure CH ₄ , flow rate: 50–1000 sccm; Voltage amplitude: 50% or 99% of nominal;	82%	The article does not cover this aspect	XRD: unresolved peaks, indicating highly amorphous carbonaceous material.	Amorphous carbon deposits	[29]

solid carbon but also concurrently enhanced the microstructural order, which is crucial for its performance in high-end applications such as conductivity.

In summary, compared to previous studies, the “acetylene recycling co-feeding strategy” employed in this work achieves better synergy and balance among the three typically competing parameters of methane conversion rate, solid carbon selectivity, and product graphitization degree. This represents a significant advancement in the field of plasma-driven carbon material synthesis.

4 Conclusions

This study systematically optimized the process conditions, including power, CH₄ feed flow rate, and the gas injection specifications of the plasma torch, achieving both a high CH₄ conversion rate and high selectivity for solid carbon. The influence of feed gas composition on the performance, crystallinity, and microstructure of the solid carbon materials produced through plasma pyrolysis of methane was investigated. By comparing three strategies—pure CH₄, pure C₂H₂, and co-feeding of CH₄ and C₂H₂—it was found that the co-feeding approach optimizes the reaction pathway and serves as an effective method for producing high-performance graphitized solid carbon, with a graphitization degree reaching 89.2%, which is close to the level of commercial conductive solid carbon⁴⁰. This approach provides a technologically viable route for the scalable and low-cost production of high-performance carbon materials, demonstrating significant potential for industrial applications.

1. By precisely optimizing the input power, methane feed flow rate, and gas nozzle specifications in a coordinated manner, the goals of achieving high methane conversion rate and high selectivity in solid carbon production can be successfully accomplished.

2. The addition of C₂H₂ improves the product distribution of methane plasma pyrolysis and enhance the selectivity of solid carbon.

3. The introduction of C₂H₂ provides the most direct and efficient material and template for constructing layered structures within the reaction system, thereby influencing and altering the final morphology of the solid carbon.

This study offers essential theoretical and experimental foundations for the plasma production of high-performance carbon materials. Future investigations will concentrate on optimizing the parameters for co-feeding CH₄ and C₂H₂, aiming to further unveil the underlying reaction mechanisms. Furthermore, the application of these highly graphitized carbon materials in areas such as electrochemical energy storage and efficient catalysis will be pursued to assess their practical performance.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript. Additional data related to this paper may be requested from the corresponding author upon request.

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Author contributions

F. W. and X. C. conceived the concept; X. C. also reviewed and edited the manuscript; Z. F. N., M. Y. Z., and B. C. Z. designed and conducted the experiments, and wrote the original draft; H. X. revised the manuscript with critical input; V. V., W. S., A. A., B. S., A. J., and O. S. contributed to resources and supervision; all authors discussed the results and commented on the final manuscript.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article. Author Fei Wei is the Editor-in-Chief of this journal, but he is not involved in the peer review or decision of this article.

Use of AI statement

None.



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