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Reactor engineering for converting CO_2 to solid carbon

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Standfirst:

Converting CO_2 into solid carbon materials provides both long-term carbon sequestration and the production of value-added products. This Comment compares reactor configurations guided by thermodynamic analysis, evaluates the market volume and morphology control of different carbon products, and identifies hurdles and opportunities for scale-up deployment.

Introduction

Achieving a carbon-neutral economy by 2050 requires a fundamental shift from fossil-based resources to renewable and circular systems. Global CO_2 emissions reached to 37.6 gigatons (Gt) in 2024[1], underscoring the urgent need for both carbon-neutral and carbon-negative technologies that reduce atmospheric CO_2 concentration. CO_2 sequestration has been widely explored in recent years, with a large focus on carbon mineralization and geological storage. Although these strategies are promising for large-scale CO_2 sequestration, the lack of economic incentives has limited their deployment[2]. Therefore, it is necessary to develop processes for carbon capture, utilization, and storage (CCUS) that yield valuable products with a longer lifetime, independent of any policy incentives[2]. Conventional CCUS approaches typically convert CO_2 into fuels and chemicals (for example, methane, methanol, long-chain hydrocarbons, oxygenates). However, these products represent only short-term fixation because they are quickly consumed and reoxidized, which results in CO_2 emissions. An alternative strategy is to convert CO_2 into solid carbon ($C_{(s)}$) materials, such as carbon nanofibers (CNFs), carbon nanotubes (CNTs), activated carbon, graphite, and carbon black, which are currently produced at tens of millions of tons (Mt) annually, almost entirely from fossil resources. Producing these materials directly from CO_2 would shift their carbon origin from fossil feedstocks to a circular pathway while providing durable carbon sequestration that enables carbon-negative outcomes.

The CO_2-to-$C_{(s)}$ conversion can be achieved through electrochemical reduction using electricity or thermochemical reduction by reacting with H_2 or light alkanes[3]. The productivity and morphology of the resulting carbon nanomaterials are governed not only by thermodynamic feasibility but also by reaction conditions, including temperature, feed composition, and catalyst structure. This Comment examines the thermodynamic feasibility of different routes for converting CO_2 into $C_{(s)}$, followed by a comparison of single versus tandem reactor configurations and a discussion of the market volume and morphology control of different carbon products.. Finally, we assess the practical potential of various carbon morphologies and highlight key hurdles and opportunities for advancing CO_2-to-$C_{(s)}$ conversion.

Thermodynamic analysis for CO_2-to-$C_{(s)}$ processes

The selection of either single or tandem reactor configurations can be guided by thermodynamic analysis. **Fig. 1** compares the CO_2-to-$C_{(s)}$ conversion using different reductants,

H_2, CH_4 and C_2H_6. As shown in **Fig. 1a**, the direct decomposition of CO_2 into $C_{(s)}$ and O_2 is not thermodynamically favorable across 200-1000 °C ($\Delta G \approx 400$ kJ/mol). Introducing molecular H_2 makes CO_2 reduction feasible, producing CO and CH_4 as possible products, with CO formation becoming more favorable above 500 °C. The resulting CO and H_2 can further produce $C_{(s)}$ through the Boudouard ($2CO \rightarrow CO_2 + C_{(s)}$) and Bosch ($CO + H_2 \rightarrow C_{(s)} + H_2O$) reactions[4,5]. In a CO-H_2 mixture, $C_{(s)}$ is thermodynamically favored below 600 °C, but becomes negligible above 700 °C (**Fig. 1c**). These results establish the thermodynamic feasibility for CO_2-to-$C_{(s)}$ through CO as the key intermediate. Practically, these sequential reactions can be realized through CO_2 hydrogenation in a single reactor within a narrow temperature window (500-600 °C), or via a tandem-reactor configuration with each being operated under optimized conditions.

Compared to molecular H_2, which is still largely derived from fossil fuels and often results in net CO_2 emissions, the rapid development of shale gas has provided abundant light alkanes (CH_4 and C_2H_6) as alternative reductants, offering the potential for net-zero or even net-negative CO_2 emissions[6]. Using CH_4 as the reductant (**Fig. 1b**), the CO_2-to-$C_{(s)}$ pathway proceeds through dry reforming of methane to generate CO and H_2, followed by the Boudouard reaction that produces $C_{(s)}$. As shown in **Fig. 1b**, dry reforming is endothermic and becomes favorable only at temperatures above 600 °C whereas the Boudouard reaction is exothermic and preferred below 600 °C, suggesting potential advantages of using tandem reactors[7]. In comparison, using C_2H_6 as the reductant provides more favorable thermodynamics for carbon formation through combined dry reforming and ethane decomposition (**Fig. 1b**). Although the temperature-dependent trends for carbon formation in CO_2-C_2H_6 systems are similar to those in CO_2-CH_4 (**Fig. 1b**), the higher reactivity of ethane makes the process more practical. Based on the thermodynamic equilibrium compositions for CO_2-CH_4 and CO_2-C_2H_6 mixtures (**Fig. 1d, e)**, carbon formation remains thermodynamically feasible up to 1000 °C[8,9]. This broader temperature windows, compared with the CO-H_2 system (**Fig. 1c**), allow control of $C_{(s)}$ morphology, which is temperature-dependent.

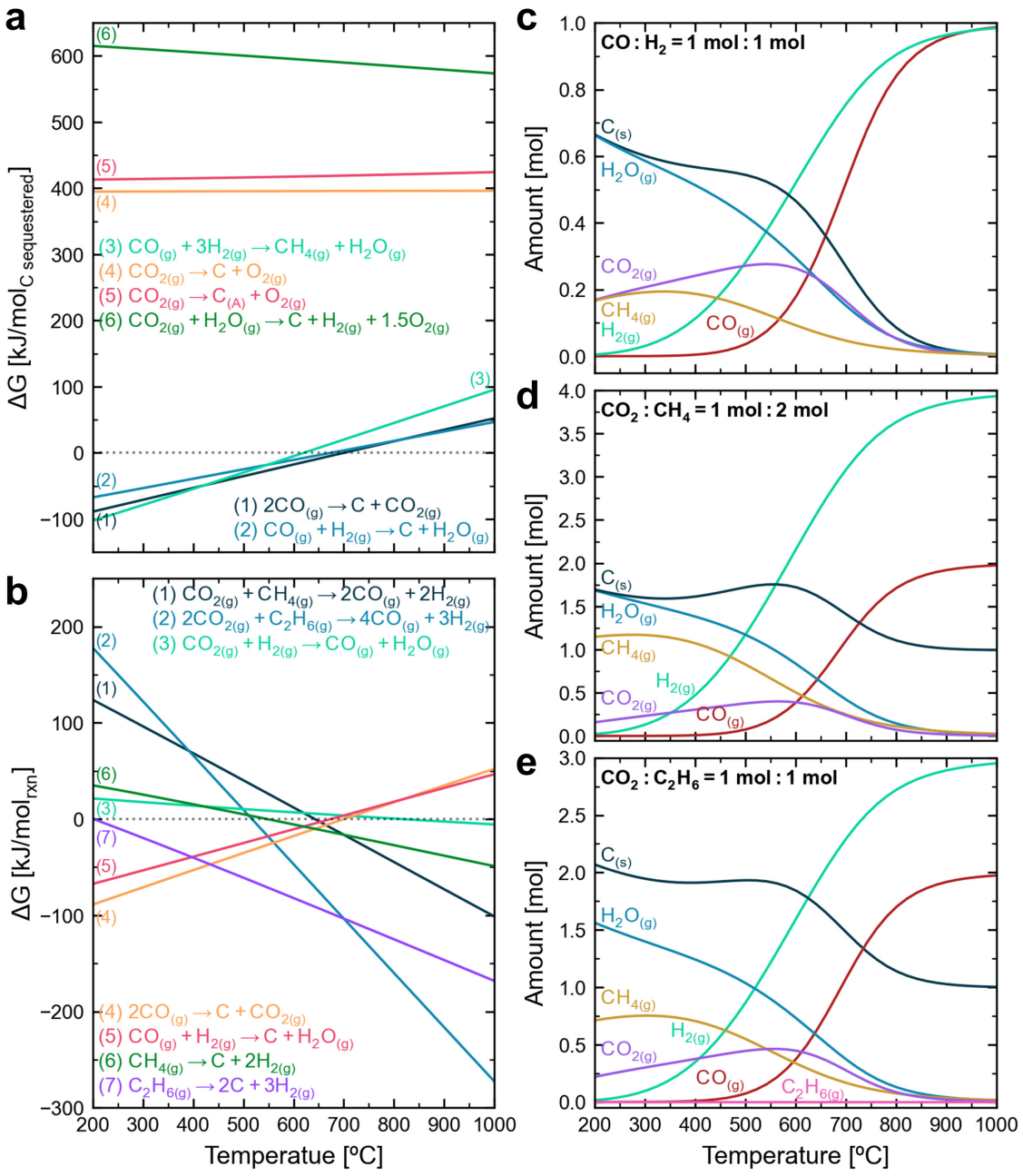

Fig. 1| Thermodynamic analysis of H_2 and alkane-assisted CO_2 sequestration into $C_{(s)}$. a-b, Gibbs free energy change of reaction (ΔG) as a function of temperature for the possible reactions involved in CO_2 using (**a**) H_2 and (**b**) alkanes as reductants. **c-e**, Equilibrium composition as a function of temperature for the reactions of (**c**) CO + H_2, (**d**) CO_2 + CH_4, and (**e**) CO_2+C_2H_6. Thermodynamic parameters for graphitic carbon were used for $C_{(s)}$ in all calculations unless amorphous carbon ($C_{(A)}$) is specified. Calculations were performed using the HSC Chemistry 6.0 software package.

CO_2-to-$C_{(s)}$ using single reactors

Single reactor systems enable the direct conversion of CO_2 into $C_{(s)}$ through either electrochemical or thermochemical pathways, although multiple sequential reactions may occur within the same unit. Electrochemical methods have emerged as an attractive route for CO_2 sequestration into $C_{(s)}$ due to the relative ease of using renewable electricity to overcome the thermodynamic barriers to CO_2 fixation. In a single electrochemical cell, alkali molten salts are gaining traction as they readily react with CO_2 to form carbonates[10], which can subsequently be decomposed into $C_{(s)}$ at the cathode and O_2 at the anode. This process requires a narrow operating window: temperatures should be high enough to liquefy alkali carbonates (for example, Li_2CO_3 melts at 723 °C) but below ~800 °C to avoid the competing CO_2-to-CO pathway[11]. Demonstrations have shown that amorphous carbon can be produced using stainless steel cathodes. However, scaling this process requires optimized electrolytes with lower melting points, higher ionic conductivity, and the ability to promote CNF or CNT growth at intermediate temperatures in the range of 200–600 ºC.

Thermochemical conversion of CO_2 has attracted considerable attention due to its scalability and compatibility with existing industrial infrastructure. Using a single-reactor system, CO_2 and C_2H_6 can be converted into CNTs at 750 °C and CNFs at 450 °C over earth-abundant transition metal catalysts (Fe, Co, Ni)[8]. The process simultaneously generates syngas (H_2/CO = 1.0-2.0) as co-products. A follow-up study demonstrated bimetallic CoFe catalysts can increase CNT production by an order of magnitude[9]. However, because C_2H_6 is a valuable feedstock, identifying alternative reductants that are abundant and inexpensive, such as CH_4, remains an important consideration. In a single-reactor configuration, converting CO_2 and CH_4 into $C_{(s)}$ typically requires high temperatures of 600-800 °C. At 600 °C, Ni/Al_2O_3 catalyst[12] produced CNFs with a carbon yield of 12.8% (based on total carbon fed) and a productivity of 2.1 $g_C \cdot gmetal^{-1} \cdot h^{-1}$, accompanied by syngas with H_2/CO = 1.2. At 800 °C, NiMo/MgO catalysts[13] generated CNTs at 8.7 $g_C \cdot gmetal^{-1} \cdot h^{-1}$ and syngas with H_2/CO = 1.1. Overall, although these processes yield both valuable carbon and syngas, the total carbon yield remains low, and the H_2/CO ratio is restricted to approximately 1.0, due to the distinct optimal temperatures of the dry reforming and Boudouard reactions (**Fig. 1b**).

CO_2-to-$C_{(s)}$ using tandem reactors

Tandem reactors decouple CO_2-to-$C_{(s)}$ conversion into two distinct processes, using separate units optimized for each reaction step. As shown in **Fig. 1a**, direct conversion of CO_2 and H_2O to $C_{(s)}$ is thermodynamically unfavorable. Such thermodynamic limitations can be circumvented by tandem electrochemical-thermochemical (EC-TC) reactors, in which CO_2 and H_2O are first electrochemically reduced to CO and H_2 over a Pd/C electrocatalyst, with subsequent thermochemical conversion to $C_{(s)}$ over an Fe_3Co_6/CeO_2 catalyst at 450 °C without any intervening separation step. This configuration has been demonstrated to produce high-quality CNFs at a rate of 2.5 $g_C \cdot gmetal^{-1} \cdot h^{-1}$, with H_2 as a valuable co-product[4]. The bimetallic FeCo catalyst exhibits strong tolerance to varying H_2/CO ratios during CNF growth, providing flexibility for the upstream electrochemical cell to generate syngas with different compositions.

To overcome the intrinsic limitation of narrow operating windows in CO_2-CH_4 conversion to $C_{(s)}$, tandem reactor strategies have been developed to decouple dry reforming and the Boudouard reaction into thermochemical-thermochemical (TC-TC) reactors, each operated under optimized conditions. For example, dry reforming of methane at 600 °C over a Ni/MCM-41 catalyst generates CO and H_2, which are subsequently fed into a second reactor at 450 °C containing a $Co_{12}K_5/CeO_2$ catalyst[7]. This TC-TC tandem configuration significantly improves carbon fixation efficiency, as confirmed by both thermodynamic analysis and experimental data: the ratio of catalyst weight gain to the initial catalyst weight (CWG/Initial) increases to 7, compared with only 1.1 using a single reactor at 600 °C. Operating at lower temperatures also yields syngas with higher H_2/CO ratios (2-3 versus <1.5 in single-reactor systems). Overall, these findings highlight the potential of using either EC-TC or TC-TC tandem reactor systems for efficient conversion of CO_2 into $C_{(s)}$.

Solid carbon morphology and applications

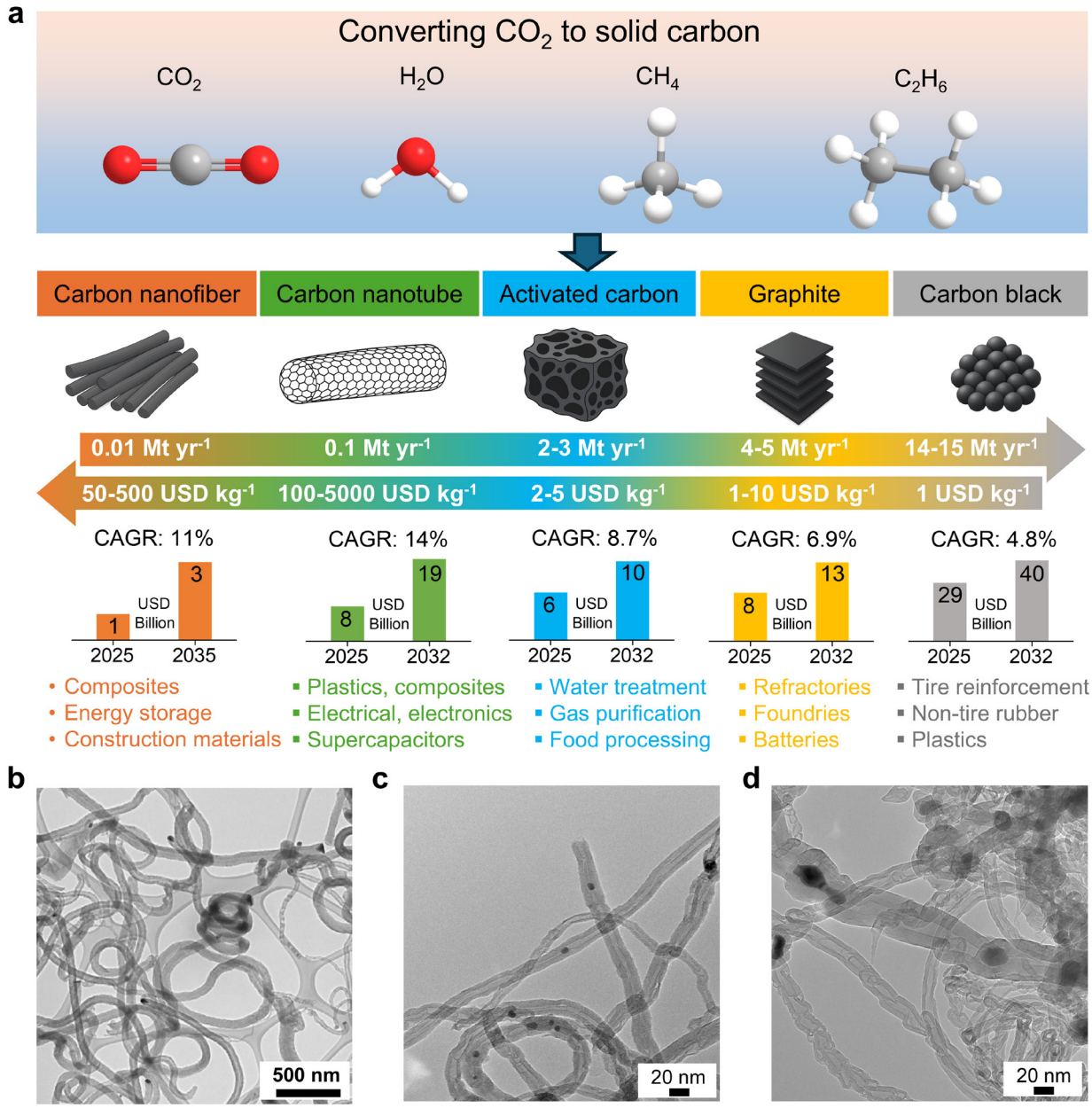

Fig.2| Converting CO_2 into multiple solid carbon materials. a, Schematic illustration of converting CO_2 into solid carbon, with the co-feeding of H_2O or light alkanes (CH_4, C_2H_6) depending on the reaction pathway. Five representative carbon materials are shown with their approximate production volume, market value, and major industrial applications. Mt denotes million tons. CAGR denotes compound annual growth rate. Data are primarily sourced from Market Research Future[14] for CNFs and from Fortune Business Insights[15] for CNTs, activated carbon, graphite, and carbon black. Typical industrial price ranges are compiled from publicly

accessible market information. **b**, TEM image of CNFs obtained from the $Co_{12}K_5/CeO_2$ catalyst in the second reactor (450 °C) of the tandem CO_2-CH_4 system. Reprinted with permission from ref.[7]. Copyright 2025 Springer Nature. **c**-**d**, TEM images of CNT produced from the CO_2-C_2H_6 reaction at 750 °C over CoFe(5:1)/Al_2O_3 (**c**) and Fe/Al_2O_3 (**d**). Reprinted with permission from ref.[9]. Copyright 2025 Elsevier Inc.

The carbon materials produced from CO_2 span a broad spectrum, including CNFs, CNTs, activated carbon, graphite, and carbon black. These products serve distinct application areas, and their market sizes differ by several orders of magnitude in both production volume and commercial value (**Fig. 2a**)[14,15].

CNFs are fiber-like graphitic structures produced on relatively small scales (~0.01 Mt yr^{-1}) but with high market value (>50 USD kg^{-1}) and strong projected growth (11%)[14]. Industrial CNFs are typically synthesized via catalytic chemical vapor deposition (CVD) of hydrocarbons or CO at over Fe-, Co-, or Ni-based catalysts, where reaction temperature, metal particle size, and support structure strongly influence fiber diameter and purity. CNFs are widely used in composite materials, energy-storage and construction materials. Instead of using hydrocarbons as feedstock, CO_2-derived CNFs can be produced using a tandem process in which CO_2 is first reduced to CO via electrochemical reduction or thermoreduction and subsequently converted to CNFs through the Boudouard reaction (**Fig. 2b**)[4,5,7]. Bimetallic catalysts, such as CoFe and CoK, enhance CNF productivity and suppress CH_4 formation.

CNTs are hollow graphitic cylinders with exceptional electronic, thermal, and mechanical properties, enabling applications in plastics and composites, electrical and electronic devices, and supercapacitors[15]. Although the global CNT market remains small (~0.1 Mt yr^{-1}), it is high value (100-5000 USD kg^{-1}) and is projected to grow at ~14% compound annual growth rate (CAGR), with single-wall or few-wall CNTs representing the most valuable products. Industrial CNTs are typically produced by CVD, where hydrocarbons decompose on transition-metal catalysts. The emerging CO_2-to-CNT pathways offer an attractive alternative to using hydrocarbons alone as feedstock In CO_2-C_2H_6 co-conversion[8,9], catalyst composition strongly governs productivity and morphology: face-centered cubic (fcc) monometallic Co and Co-rich CoFe catalysts (Co/Fe ≥ 5) promote cylindrical CNTs via surface-mediated carbon diffusion (**Fig. 2c**), while body-centered

cubic (bcc) monometallic Fe and Fe-rich CoFe catalysts (Co/Fe ≤ 2) convert to metal carbides and yield bamboo-like CNTs through bulk diffusion (**Fig. 2d**).

Among the other three types of solid carbon in **Fig. 2a**, activated carbon is a high-surface-area adsorbent produced at 2-3 Mt yr^{-1} with a moderate price of 2-5 USD kg^{-1} and a projected CAGR of ~8.7%[15]. Industrial production typically involves pyrolyzing biomass, coal, or synthetic polymers followed by steam or chemical activation. Activated carbon is widely used in water purification, gas adsorption, and food processing. Graphite has a global output of 4-5 Mt yr^{-1} and a market price of 1-10 USD kg^{-1} depending on purity and whether it is natural or synthetic. Synthetic graphite is prepared by high-temperature graphitization of petroleum coke and is used in high-temperature applications, foundries, and lithium-ion battery anodes[15]. Carbon black is the largest-volume carbon materials, produced at 14-15 Mt yr^{-1} with a low cost near 1 USD kg^{-1}. It is manufactured by partial combustion or thermal cracking of hydrocarbons and is essential for tire reinforcement, rubber additives, and plastics[15]. Although direct CO_2 conversion to activated carbon, graphite, or carbon black has not yet been demonstrated at industrial scale, these products represent large markets that offer significant opportunities for future CO_2-to-$C_{(s)}$ development.

Key hurdles and opportunities

Overall, CO_2-to-$C_{(s)}$ conversion is a promising strategy for long-term carbon sequestration that also creates pathways to value-added materials. Recent advances in catalyst design, reactor engineering, and process integration have enabled significant progress, yet several hurdles remain for scalable deployment.

Morphology control. The value of CNTs and CNFs strongly depends on diameter, with smaller-diameter and better-graphitized structures commanding higher commercial value. Continued progress therefore requires strategies that enable precise diameter control. Expanding CO_2 conversion to other carbon allotropes, including activated carbon, graphite, and carbon black, would further enhance industrial relevance due to their large-volume markets. Achieving selective morphology will require coordinated control of feed composition, catalyst structure, and reaction environment. Promising directions include tandem reaction schemes and catalyst design approaches that promote more selective and scalable carbon growth under mild conditions.

Catalyst recovery and durability. Current post-processing methods, such as acid leaching or repeated catalyst re-synthesis, generate substantial chemical waste and require significant

energy input. Developing alternative recovery approaches, including magnetic separation, selective dissolution, and physical detachment, will be essential for improving the economic and environmental sustainability of CO_2-to-$C_{(s)}$ processes. Equally importantly, catalyst durability under reaction conditions remains insufficiently understood, and mechanistic studies will be essential to guide effective catalyst design for continuous long-duration operation.

Carbon purification. As-produced carbon often contains catalyst particles and amorphous carbon that limit its utility in high-value applications. Conventional purification approaches rely on strong acids or oxidative treatments that are costly and environmentally burdensome. Future work should target milder purification strategies, physical separation techniques, or the design of systems that inherently reduce downstream purification requirements.

Integration with real process streams. Industrial deployment will require CO_2-to-$C_{(s)}$ technologies that operate with diluted or impure CO_2 feedstocks, such as flue gas from steel, cement, or chemical plants. These streams contain impurities such as SO_x, NO_x, and steam, and have fluctuating CO_2 concentrations, all of which complicate reaction control and catalyst stability. Developing reactors and catalysts that can tolerate or utilize these impurities would reduce pre-treatment needs and improve overall process viability.

In the meantime, the CO_2-to-C(s) technologies also offer unique opportunities to advance reactor engineering, catalysis, and sustainable materials development.

Advanced reactor configurations and catalyst discovery. Improving CO_2-to-$C_{(s)}$ efficiency will benefit from exploring advanced tandem configurations, including solar-thermal and plasma-thermal systems. Fluidized bed and molten metal reactors offer strong heat management and allow continuous removal of solid carbon, which mitigates catalyst deactivation and supports long-duration operation. In parallel, coupling computationally-guided alloy discovery with *in-situ* characterization should accelerate the identification of catalytic phases that control carbon nucleation and diffusion under realistic feed conditions.

Morphology diversity and materials valorization. CO_2 conversion can yield a variety of solid-carbon materials, each with different industrial applications. Carbon morphology is strongly influenced by feed composition, reaction atmosphere, catalytic phase, and reactor environment. These dependencies create opportunities for morphology-selective carbon formation directly from mixed CO_2 or industrial waste streams, potentially without requiring extensive pretreatment.

Integrated process design and multifunctional transformation. Beyond producing solid carbon, CO_2-to-C(s) systems can be coupled with upstream or downstream steps to produce gas or liquid byproducts without additional separation. Tandem CO_2-conversion schemes can generate solid carbon while also producing H_2-rich syngas for on-site fuel synthesis. Because each reaction step operates under its own optimized temperature and flow conditions, tandem configurations should also provide improved heat management and reduced mass-transfer limitations.

Compact and modular deployment. Compact and modular CO_2-to-$C_{(s)}$ reactor units provide a practical route for industrial adoption. Deploying these units directly at major CO_2 point sources, including steel, cement, and chemical plants, reduces gas-transport and compression needs while enabling integration with existing utilities. Their flexible architecture supports rapid replication across production sites and allows future incorporation of emerging catalytic platforms such as biocatalysis and photocatalysis.

Data availability

Source data are provided with this paper.

References

1. CO_2 Emissions – Global Energy Review 2025 – Analysis. *IEA* https://www.iea.org/reports/global-energy-review-2025/co2-emissions.
2. Bui, M. *et al.* Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **11**, 1062–1176 (2018).
3. Xie, Z. & Chen, J. G. Comparison of approaches for CO_2 sequestration as solid carbon products. *CCS Chem.* **6**, 2855–2865 (2024).
4. Xie, Z. *et al.* CO_2 fixation into carbon nanofibres using electrochemical–thermochemical tandem catalysis. *Nat. Catal.* **7**, 98–109 (2024).
5. Crandall, B. S. *et al.* Transforming CO_2 into advanced 3D printed carbon nanocomposites. *Nat Commun* **15**, 10568 (2024)
6. Biswas, A. N., Xie, Z. & Chen, J. G. Can CO_2-assisted alkane dehydrogenation lead to negative CO_2 emissions? *Joule* **6**, 269–273 (2022).
7. Xie, Z. *et al.* Biogas sequestration to carbon nanofibers via tandem catalytic strategies. *Nat. Chem. Eng.* **2**, 118–129 (2025).

8. Yuan, Y., Huang, E., Hwang, S., Liu, P. & Chen, J. G. Converting carbon dioxide into carbon nanotubes by reacting with ethane. *Angew. Chem. Int. Ed.* e202404047 (2024).
9. Yuan, Y. *et al.* Enhancing carbon nanotube production from carbon dioxide and ethane using bimetallic catalysts. *Chem Catal.* **5**, 101428 (2025).
10. Jia, Y. *et al.* Recent advances in molten salt CO_2 capture and electrochemical conversion to functional carbon materials. *J. Ind. Eng. Chem.* **134**, 17–27 (2024).
11. Chery, D., Lair, V. & Cassir, M. CO_2 electrochemical reduction into CO or C in molten carbonates: a thermodynamic point of view. *Electrochim. Acta.* **160**, 74–81 (2015).
12. Pinilla, J. L., de Llobet, S., Moliner, R. & Suelves, I. H_2-rich gases production from catalytic decomposition of biogas: viability of the process associated to the co-production of carbon nanofibers. *Int. J. Hydrog. Energy* **42**, 23484–23493 (2017).
13. Saconsint, S. *et al.* Development of high-performance nickel-based catalysts for production of hydrogen and carbon nanotubes from biogas. *Sci. Rep.* **12**, 15195 (2022).
14. Market Research Future. *Carbon nanofibers market research report*. Available at: https://www.marketresearchfuture.com/reports/carbon-nanofibers-market-55358.
15. Fortune Business Insights. *Market reports for carbon nanotubes, activated carbon, graphite, and carbon black*. Available at:https://www.fortunebusinessinsights.com/carbon-nanotubes-cnt-market-102700, https://www.fortunebusinessinsights.com/activated-carbon-market-102175, https://www.fortunebusinessinsights.com/graphite-market-105322, https://www.fortunebusinessinsights.com/industry-reports/carbon-black-market-101718.

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Competing interests

Columbia University, representing some of the co-authors in this article, has filed two patent applications regarding the conversion of CO_2 and biogas to carbon nanofibers.