

Supplementary Information accompanying:

Intense, self-induced sustainable microwave plasma using carbon nanotubes made from CO₂

Gad Licht, Kyle Hofstetter and Stuart Licht
George Washington University, Washington, DC, USA,
Carbon Corp, Calgary, Canada & Direct Air Capture LLC, Florida, USA

Elevated levels of atmospheric CO₂ are the primary driver of global warming. Historically, atmospheric CO₂ concentration fluctuated within a range of $235 \pm \sim 50$ ppm over the past several hundred thousand years, until 1850. Currently, it stands at 426 ppm and continues to increase annually, leading to widespread climate disturbances, habitat degradation, and species extinction [1-4]. The inherent chemical stability of CO₂ poses a significant challenge to its removal by conversion into a non-greenhouse material, a subject explored in our US NSF workshop on Chemical Recycling and Utilization of CO₂ [5]. However, overcoming this stability of CO₂ and utilizing it as a carbon-negative precursor for the production of valuable products provides an incentive for the reduction of this greenhouse gas.

This supplementary information includes movies of the generated plasmas as well as characterization of the C2CNT CNTs.

3200W microwave-irradiation of CNTs from CO₂

CNTs were synthesized by the electrolysis of CO₂ in 770°C Li₂CO₃ at a current density of $J=0.6$ A/cm², using Muntz Brass cathodes and 304 Stainless Steel Electrodes. Each were prepared with CO₂ from the flue gas of the Shepard natural gas power plant in Calgary, Canada.

A 3200W NE-3280 microwave was used to irradiate 1 g of CNT synthesized from CO₂ in a borosilicate (Pyrex) flask. [Movie 1](#) shows the intense plasma generated during the first minute, followed by a close-up of the post microwave red hot CNTs in the flask. [Movie 2](#) shows the same CNTs under a 2nd minute of irradiation, including the onset of visible softening of the flask. [Movie 3](#) shows a final 35 second microwave irradiation of the same sample including a melt of the flask.

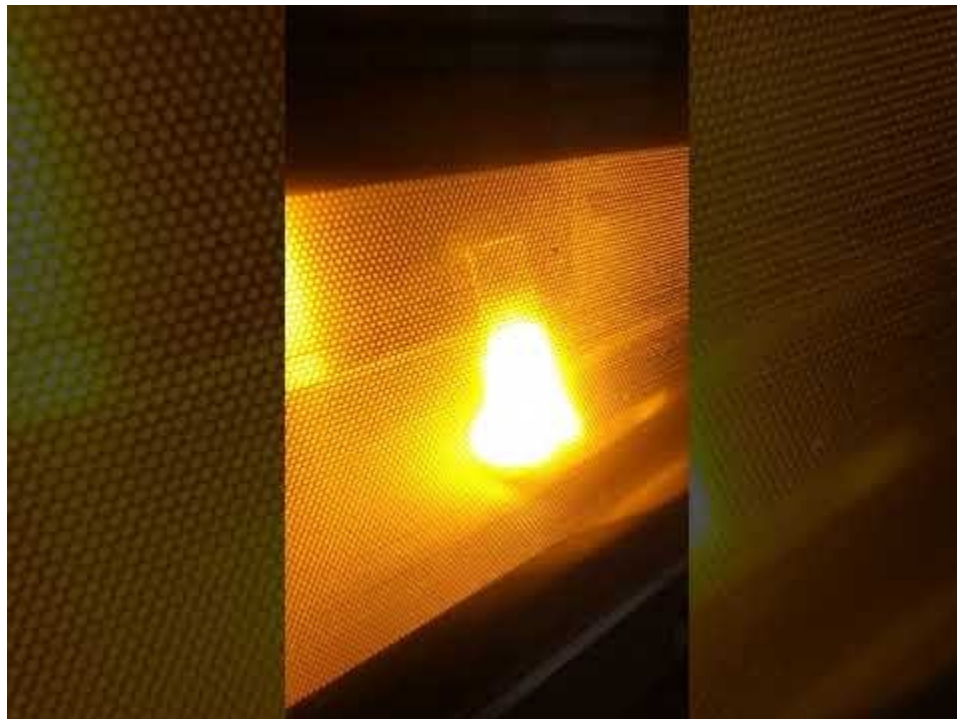
The CNTs were synthesized from the electrolysis of CO₂ in 770°C Li₂CO₃ at a current density of $J=0.6$ A/cm², and again using Muntz Brass cathodes and 304 Stainless Steel Electrodes.



Movie I. C2CNT CNTs from CO₂; microwaved 1 minute at 3200 W in a borosilicate (Pyrex) flask. A sustained plasma is evident. Click the video to play, available at https://youtu.be/GRzeSMIZI_c.



Movie 2. C2CNT CNTs from CO₂; continuing irradiation of the same sample as Movie 2, microwaved at 3200 W in the same borosilicate flask. A sustained plasma borosilicate substrate as well as softening of the borosilicate flask is evident, available at <https://youtu.be/1zqAYVEmFX0>.

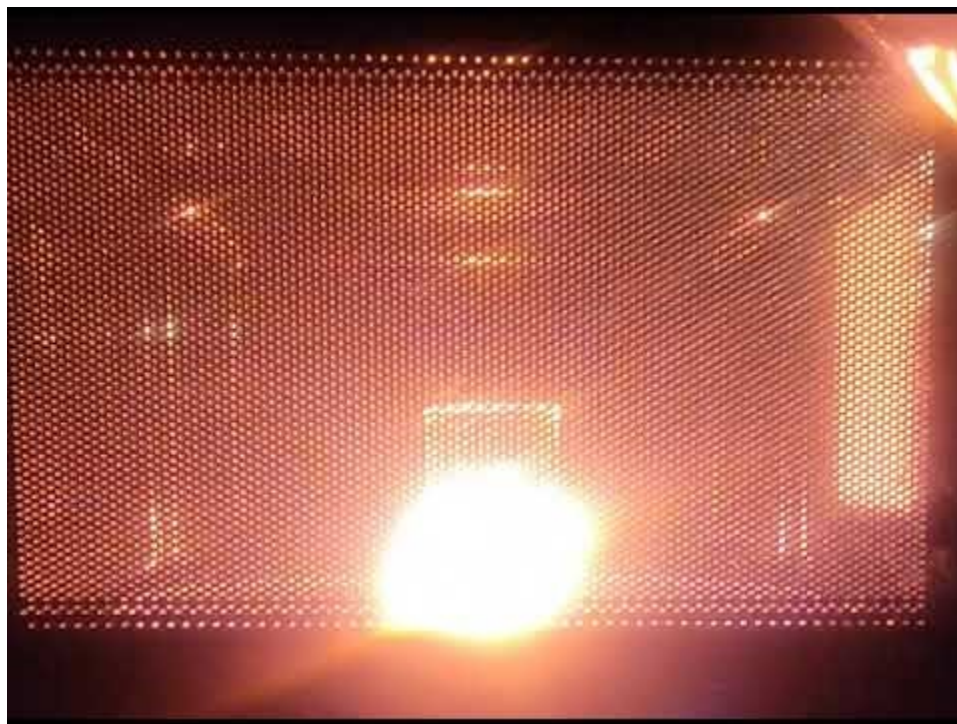


Movie 3. C2CNT CNTs from CO₂; continuing irradiation of the same sample as Movie 1, microwaved for a third minute at 3200 W in a borosilicate flask. A sustained plasma borosilicate substrate as well as melt and collapse of the borosilicate flask is evident, available at <https://youtu.be/MbUHwm0ikLY>.

650W microwave-irradiation of graphene nanocarbons (CNTs and CNOs)

Rather than the 3200W NE-3280 microwave, a variety of graphene nanocarbon (GNC) samples were also irradiated for one minute, but at a lower power of 650W in Pyrex (borosilicate) beakers in a 201 Laboratory Microwave. As seen in [Movie 4](#), 1 g of the same CNT sample that was used in Fig. 2) triggers and again sustains during the 1 minute microwave irradiation an intense plasma in the beaker, with a difference that the CNTs were observed to require a longer plasma trigger time of ~10 s, rather than ~2s occurring with the higher power microwave. The same sustained plasma was again observed in three additional CNT samples with CNTs synthesized from the electrolysis of CO₂ in 770°C Li₂CO₃ at a current density of $J=0.6 \text{ A/cm}^2$, and again using Muntz Brass cathodes and 304 Stainless Steel Electrodes. Each were prepared with CO₂ from the flue gas of the Shepard natural gas power plant in Calgary, Canada. One was prepared by electrolysis for 16 hours at 1,082 on a 1,804 cm² cathode, and analyzed with 95% SEM and TGA purity. The second was prepared by electrolysis for 16 hours at 1,584 on a 2.640 cm² cathode, with analyzed

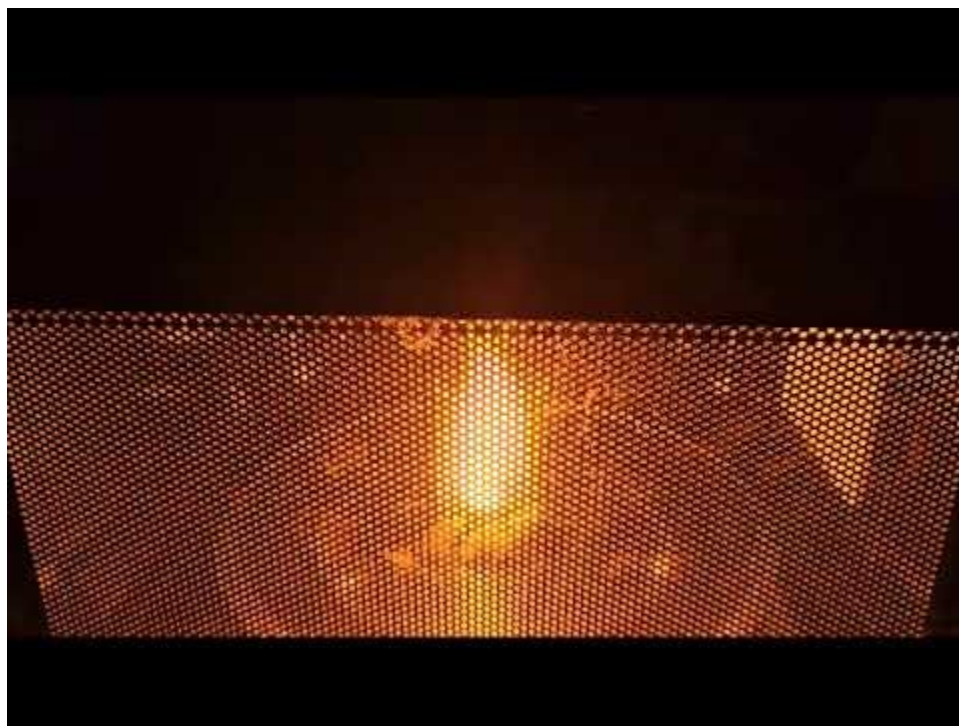
90% SEM and 97% TGA purity, and the third was prepared by electrolysis for 16 hours at 950 A on a 1,584 cm² cathode at and analyzed with 95% SEM and 97% TGA purity. Characteristics of the third sample are shown in Figure S5



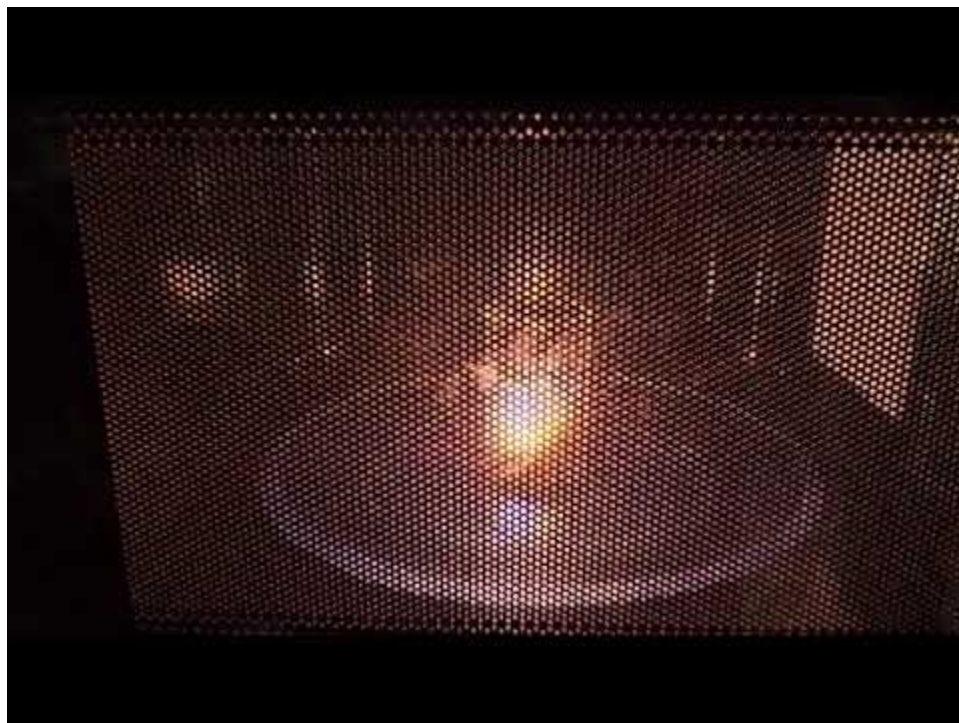
Movie 4. 1 g of C2CNT CNTs from CO₂; microwaved 1 minute at 650 W in a borosilicate (Pyrex) beaker. A sustained plasma is evident available at <https://youtu.be/rosw5xtymHg>

Under the same microwave conditions sustained plasma were not generated by either in-house synthesized 90% SEM purity 99% TGA purity carbon nano-onions ([Movie 5](#)), or, similar dimensioned, commercial CVD 98% purity M8 MWCNTs (Timesnano, China ([Movie 6](#)) or commercial CVD 87% purity thinner NC7000 MWCNTs (nanocyl, Belgium). As seen in [Movie 5](#) (for the 1g of CNOs) and [Movie 6](#) (for the 1 g of M8s) intermittent sporadic plasmas and flames were observed during the one minute of 650 W microwave irradiation. The nanocyl CNTs (not shown) exhibited no observable consistent plasma and occasional sparking.

A fascinating phenomenon was observed, seen [Movie 7](#), in a second microwave irradiation of 1 minute, following the run in [Movie 4](#), of the microwave irradiation of an in-house CNT from CO₂ sample in a beaker. In this case, the triggering of the plasma split the beaker, and the plasma escaped intact, and migrated intact to the top of the microwave where it continued as a bright, continuous oval-shaped plasma throughout the full minute of irradiation, only extinguishing with the end of the microwave irradiation. Stainless steel 304 is resistant to oxidation to 925°C, and the lack of oxidation as the microwave SS304 ceiling establishes this maximum temperature of the plasma. Hence the plasma, which can soften borosilicate is within the temperature range of 820-925 °C.



Movie 5. 1 g of C2CNT carbon nano-onions from CO₂; microwaved 1 minute at 650 W. A sustained plasma does not occur, available at <https://youtu.be/VXYRFQeLs9A>.



Movie 6. 1 g commercial M8 CNTs; microwaved 1 minute at 650 W. A sustained plasma does not occur, available at <https://youtu.be/Pg0BEALfnuE>.



Movie 7. 1 g of C2CNT CNTs from CO₂; 2nd run, microwaved 1 minute at 650 W. Beaker breaks, but plasma is sustained, escaping as an undulating, intense plasma at the top of microwave. A sustained plasma, becoming fully dissociated from the borosilicate substrate is evident, available at <https://youtu.be/wsdw5TaIMfg>.

High resolution TEM, XRD and Raman characterization of C2CNT CNTs

In 2015, it was shown that the growth of transition metal nuclei during this electrolysis process leads directly to the conversion of CO₂ into pure graphene nanocarbons, including carbon nanofibers and carbon nanotubes (CNTs) [6]. This transformation of the greenhouse gas CO₂ into valuable GNC products offers a chance to convert CO₂ into a form of carbon stabilized by graphene, thus aiding in mitigating climate change. Graphite is an analogous macroscopic form of layered graphene, and as a mineral graphite has an established geologic (hundreds of millions of years) lifetime.

The high electrical conductivity character of the graphene nano-allotropes supports continuous growth during the CO₂ molten electrolysis at low electrolysis voltage. This cathode product grows as an interconnected matrix with electrolyte in the matrix pores. Deriving its name from aerogels, this matrix containing carbonate electrolyte has been termed a carbanogel. Some of the electrolyte in this matrix is rather loosely bound. For example, a post-electrolysis cathode lifted out of the molten electrolyte can release over 30% of the bound electrolyte by gravitational drip.

Control of the electrode and electrolyte composition, and CO₂ electrolysis splitting temperature and current density tunes the decarbonization process to form a range of high purity graphene nanocarbon products, including carbon nanotubes. Typical SEM, TEM and HAADF (High Angle Annular Dark-Field TEM) elemental analysis imaging of the CNTs are presented in Figure S1, and have been extensively detailed [7].

Control of the CO₂ electrolysis conditions is used to tune the specific GNC generated by control of the temperature, current density, and the composition of the electrolyte [8]. For example, a lower temperature (725°C) is typically used in the electrolytic growth of carbon nano-onions, while higher temperature (750 to 770°C) is used in the electrolytic growth of carbon nanotubes. Lithium carbonate, a typical electrolyte, has a melting point of 723°C. Binary lithium carbonate mixtures have a lower melting point. A high sodium carbonate content in a mixed sodium/lithium carbonate electrolyte and a lower electrolysis temperature (670°C) drive the formation of a graphene scaffold nanocarbon product formation. Applied electrolysis current densities generally range from 0.03 to 0.6 A cm⁻². High current density (0.6 A cm⁻² or over) is one of the principal conditions driving the formation of fascinating helical, rather than straight, carbon nanotubes.

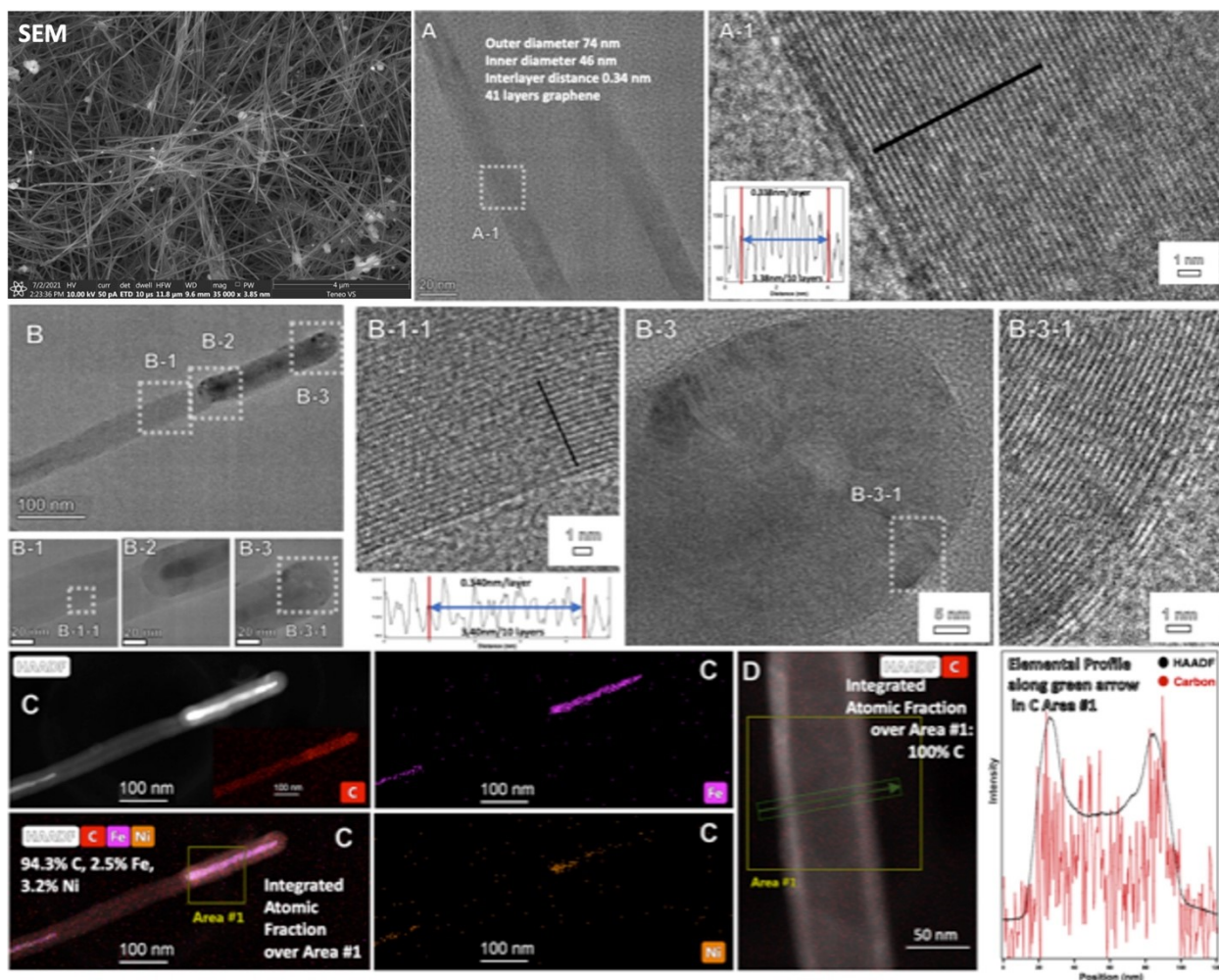


Figure S1. SEM TEM and HAADF of the synthesis product of high purity, high yield carbon nanotubes by electrolytic splitting of CO_2 in 770°C Li_2CO_3 . The SEM has a scale bar of $5\ \mu\text{m}$. Panels B are TEM with scale bars decreasing from 100, 20 nm, 5 and 1 nm. Bottom rows panels C are HAADF elemental analyses with scale bars decreasing from 100 to 50 nm, and in the bottom right a HAADF elemental carbon profile analysis of the carbon nanotube cross section.

Electrode (and electrolyte additive) composition variation has been used to grow a number of other GNC allotropes from CO_2 . These include carbon nanobamboo, carbon nanopearl, graphene from nanocarbon platelets, carbon nanofiber, carbon nanobelt, carbon nanotree, and other specific carbon allotrope morphologies. SEM of a range of these GNC products is presented in Fig. S2, and XRD and Raman spectra of the products are presented in Figs. S3 and S4 as previously detailed [8]. The solid graphene nanocarbon product from CO_2 grows as a matrix directly on the cathode. Under constant current electrolysis conditions, the product formation is continuous, and the growth occurs in the direction towards the anode.

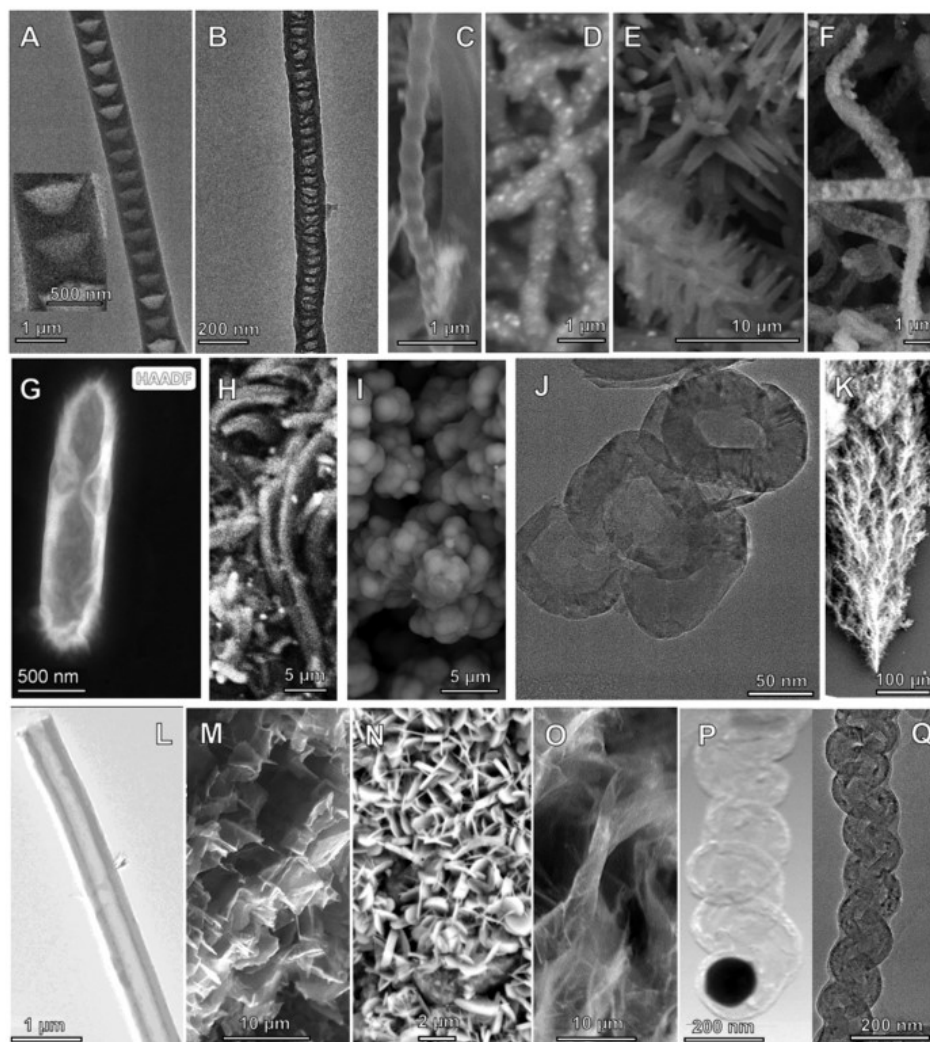


Figure S2. SEM of nanocarbon allotropes synthesized by the electrolytic splitting of CO_2 in molten carbonate. Top row (from A to F) conical CNF, nano-bamboo, nano-pearl, Ni coated CNT, nano-flower, nano-dragon. Middle row (from G to K): nano-rod, nano-belt, nano-onion, hollow nano-onion, and nano-tree. Bottom row (from L to Q) Carbon nanotube, nano-scaffold [8], nano-platelet, graphene, nano-helices.

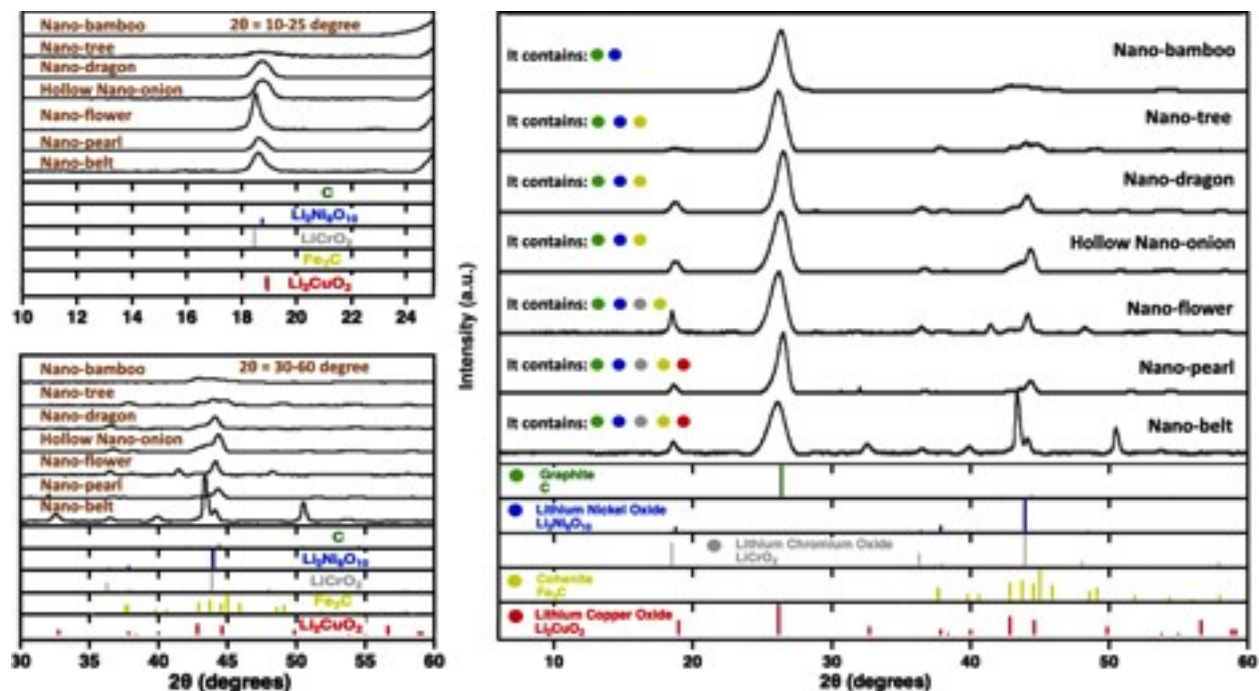


Figure S3. XRD of the synthesis product consisting of various labeled unusual nanocarbon morphologies synthesized by the electrolytic splitting of CO_2 in 770°C Li_2CO_3 with a variety of systematically varied electrochemical conditions.

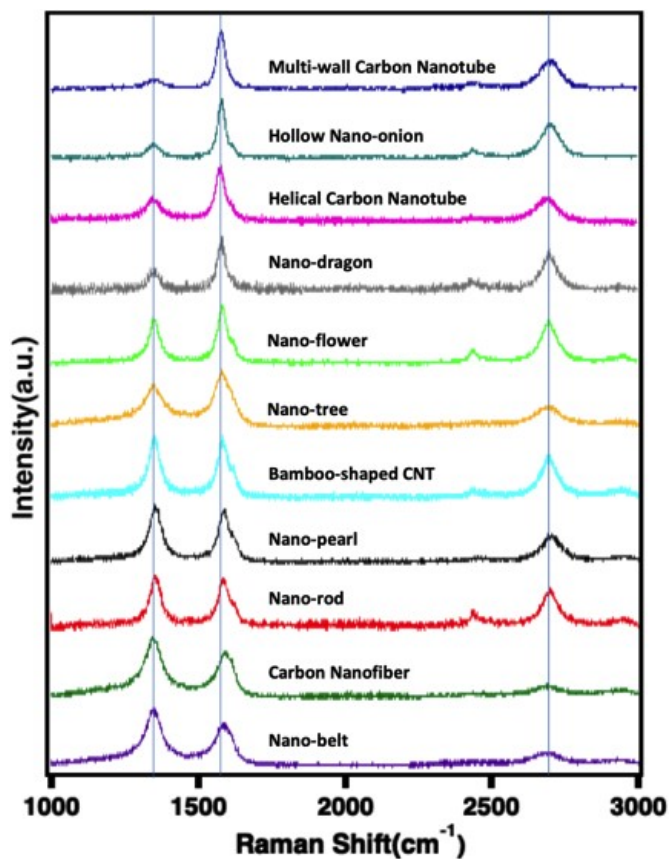


Figure S4. Raman of the synthesis product consists of various labeled GNCs and packed carbon nanotube assemblies synthesized by the electrolytic splitting of CO_2 in 770°C Li_2CO_3 with a variety of systematically varied electrochemical conditions.

References

- [1] CO₂-Earth: Daily CO₂ Values. Available online: <https://www.CO2.earth/daily-CO2> (accessed on 6 June 2024).
- [2] NASA: Global Climate Change: The Relentless Rise of Carbon Dioxide. Available online: https://climate.nasa.gov/climate_resources/24/ (accessed 6 June 2024).
- [3] M. C. Urban, Accelerating extinction risk from climate change, *Science* 348 (2015) 571–573. <https://www.science.org/doi/10.1126/science.aaa4984>.
- [4] S. L. Pimm, Climate disruption and biodiversity, *Curr. Biol.* 19 (2009) R595–R601. <https://doi.org/10.1016/j.cub.2009.05.055>.
- [5] G. K. Praksh, G. A. Olahn, S. Licht, N. B. Jackson, Reversing Global Warming: Chemical Recycling and Utilization of CO₂; Report of 2008 NSF Workshop; University of Southern California: Los Angeles, CA, USA, 2008. https://www.nsf.gov/mps/che/workshops/2008_ReversingGlobalWarming_NSF_Workshop.pdf (accessed 6 June 2024).
- [6] J. Ren, F.-F. Li, J. Lau, L. Gonzalez-Urbina, S. Licht, One-pot synthesis of carbon nanofibers from CO₂. *Nano Lett.* 15 (2015) 6142–6148. DOI: [10.1021/jp9044644](https://doi.org/10.1021/jp9044644).
- [7] X. Liu, G. Licht, S. Licht, Controlled Transition Metal Nucleated Growth of Carbon Nanotubes by Molten Electrolysis of CO₂ Catalysts 12 (2022) 137. <https://doi.org/10.3390/catal12020137>.
- [8] X. Liu, G. Licht, X. Wang, S. Licht, Controlled Growth of Unusual Nanocarbon Allotropes by Molten Electrolysis of CO₂. *Catalysts* 12 (2022) 137. <https://doi.org/10.3390/catal12020125>.
- [9] G. Licht, K. Hofstetter, S. Licht, Separation of molten electrolyte from the graphene nanocarbon product subsequent to electrolytic CO₂ capture. *Decarbon* 4 (2024) 100044. <https://doi.org/10.1016/j.decarb.2024.100044>.