Supporting Information for

Replication of Mechanochemical Syntheses of γ-Graphyne from Calcium Carbide Fails to Produce the Claimed Product

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1. Nomenclature and Abbreviations

Abbreviation	Description				
AFM	Atomic Force Microscopy				
ATR	Attenuated Total Reflectance				
EDS	Energy Dispersive X-ray Spectroscopy				
EI-MS	Electron Ionization Mass Spectrometry				
FTIR	Fourier Transform Infrared Spectroscopy				
FWHM	full width at half maximum				
GC-MS	Gas Chromatography – Mass Spectrometry				
HRTEM	High-Resolution Transmission Electron Microscopy				
NMR	Nuclear Magnetic Resonance Spectroscopy				
PXRD	Powder X-ray Diffraction				
SAED	Selected Area Electron Diffraction				
SEM	Scanning Electron Microscopy				
STD	Standard deviation				
TEM	Transmission Electron Microscopy				
THF	Tetrahydrofuran				
TGA	Thermogravimetric Analysis				
TLC	Thin-Layer Chromatography				
UV-Vis	Ultraviolet-Visible Light Spectroscopy				
XPS	X-ray Photoelectron Spectroscopy				

 Table S1. Nomenclature and Abbreviations

2. Materials and Methods

Materials

All reagents and solvents were acquired from commercial suppliers (Acros Organics, MilliporeSigma, TCI Chemicals and Fisher Scientific) and used without further purification, unless otherwise noted. Benzene, ACS Grade from MilliporeSigma, was distilled over calcium hydride.

Infrared Spectroscopy

Routine small molecule FTIR spectra were collected on an Agilent Cary 630 FTIR instrument equipped with a single-reflection germanium ATR module. The instrument was calibrated before sampling against a newly cleaned (acetone) and dried crystal surface. Solid samples were placed directly on the crystal and secured with a needle press. 512 scans from 4000 to 600 cm⁻¹ were recorded. A background of 512 scans was collected for each sample.

Thermogravimetric Analysis

TGA was performed by using a TGA Q500 thermogravimetric analyzer (TA Instruments, USA). Approximately 8 mg of samples were loaded onto a Pt pan and subjected to scanning from ambient temperature (approximately 20°C) to 900°C at a heating rate of 10°C/min using nitrogen (99.99% purity) as the purge gas (flow rate 60 mL min⁻¹).

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Samples of washed and dried material were placed on conductive silver paint (Structure Probe, Inc.) on aluminum stages (Ted Pella, Inc.). The paint was brushed on the stage and a small amount of sample powder was dropped on and lightly pushed into the paint. Excess material was removed by lightly tapping the stage. Samples of $(CaC_2/C_6Br_6/EtOH)_{char}$ and $(CaC_2/C_6Br_6)_{char}$ were sputter coated with ~4 nm of palladium while $(CaC_2/C_6H_6/EtOH)_{char}$ was sputter coated with ~2 nm of gold. Samples were allowed to sit under vacuum for at least 24 hours prior to imaging.

SEM and EDS data were conllected using a Thermo Scientific Apreo 2S with an UltraDry EDS detector. Images of the EDS region were captured prior to EDS data collection. EDS collection was performed to achieve at least 10 million integral counts. For each sample, the first mapping process excluded elements not expected to be in the sample, sample coating and adhesive, sample stage, EDS detector, or ball milling equipment. A second round of mapping excluded elements present in the sample stage, sample coating and adhesive, EDS detector, and iron and alloying elements present in the ball milling equipment. Full spectrum energy and counts data were exported for plotting, while element maps were copied directly from the Pathfinder software. All peak picking and identification were performed by the Pathfinder software and reformatted upon final plotting.

X-ray Photoelectron Spectroscopy

Samples were spread onto double-sided copper tape for XPS analysis. Surveys and high-resolution spectra were acquired on a PHI VersaProbe II Scanning XPS Microprobe using a monochromatic Al X-ray at pressures of 10⁻¹⁰ to 10⁻⁷ Torr. The data was smoothed by using the Savitzky-Golay method, with a smoothing width of five, and analyzed using CasaXPS [1, 2].

Our C1s peak models were constructed based on the approach outlined by Gengenbach *et al.*, [3] with some modifications. We applied a U 3 Tougaard background [4] to each peak before deconvolution. All fits were performed using generalized Voigt-like peak shapes (LF and LA functions provided by CasaXPS) [5], which is considered best practice for fitting asymmetric XPS signals [6].

In the Lorentzian finite LF(α , β , w, n, m) function, the first three parameters (α , β , w) influence the Lorentzian line shape and its asymmetry, while the final two parameters (n, m) affect the Gaussian function's width and the number of convolutions with the Lorentzian component. CasaXPS implements the LA asymmetric Lorentzian lineshape with an additional parameter specifying the width of the Gaussian used to convolute the Lorentzian curve, denoted as LA(α , β , m), where m is an integer between 0 and 499 that defines the Gaussian's width.

An asymmetric line shape described by LF(0.65,1.17,550,180,2) was assumed for the aromatic sp² species. The shake-up features were modeled as LA(1.53,243) based on best fit to data. The remaining subpeaks were modeled with the symmetric LF(1,1,255,360,6) line shape. All sub-peak widths, except for the shake-up feature, were constrained to FWHM of 1.6 eV or less. The peak components included were: 284.3 eV (aromatic sp²), 290 eV ($\pi \rightarrow \pi^*$ shake-up), 284.8 eV (aliphatic sp³), 286.9 eV (aromatic C-Br), 286.2 (aliphatic C-O), and 288.5 eV (carbonyl C=O) [7]. The shake-up feature and aliphatic C-O peak positions were allowed a padding of ± 0.4 eV, while the padding for the other peaks was set at ± 0.2 eV.

We obtained low residual STD values for all the fits: 0.95 for $(CaC_2/C_6Br_6/EtOH)_{char}$ (Fig. 4B), 1.58 for $(CaC_2/C_6Br_6)_{char}$ (Fig. 4D), and 1.66 for $(CaC_2/C_6H_6/EtOH)_{char}$ (Fig. 4F). However, it's important to note that fitting models with more than 3–4 components inevitably involve some degree of arbitrariness. We found that capturing the asymmetry of the observed peaks required the use of at least 5 components, strongly suggesting complex speciation of carbon in our samples.

SAED and PXRD Simulations

The lattice parameters and bond lengths for γ -graphyne were obtained from a previously published computational study [8]. SAED and PXRD simulations were performed using the CrystalMaker software suite [9]. A model of a single γ -graphyne sheet was built in CrystalMaker using a hexagonal P6 lattice with parameters *a* and c set to 6.86 Å and 3.4 Å, respectively. The asymmetric unit comprised four atoms placed at 0.208, 0.412, 0.589, 0.795 along the hexagonal P6 *x* axis. The basic models corresponding to various sheet stacking modes were constructed using Vesta [10].

3. Replication of the Purported Mechanochemical Syntheses of γ -Graphyne

General Protocols

All ball milling was conducted using a Retsch MM 400 Mixer Mill (Haan, North Rhine-Westphalia, Germany) equipped with 5 ml stainless steel (SS) jars charged with a single 5 mm SS ball. All reactions were all run at 30 Hz for the total run time with 15 min cool-down breaks every 90 min; these cool down periods are in addition to the stated run time. The temperature was not actively increased through external heating, but the process does tend to equilibrate at an approximately 45 °C internal temperature [11]. The jars were allowed to sit for at least 30 minutes at ambient temperature (~23 °C) at the end of the process before being opened and the sample removed and treated according to the specific protocols described.

All filtrations were conducted using Fisherbrand filter paper (P8 coarse porosity, Fisher Scientific Canada, Ottawa ON) supported by a coarse sintered glass filter. All process drying was conducted at 110 °C in a Fisher Scientific Isotemp microbiological incubator working as an oven. Calcination was conducted at 260 °C in a SHEL Lab SMO high performance oven. Specific details of the reaction conditions and isolation protocols are detailed below.

We do not provide stoichiometric yields, as the nature and purity of the products are unclear. Instead, we report the mass recovery relative to the original mass of the non-solvent reagents. We caution that the solvents may participate in the reaction and could be incorporated into the products, potentially leading to an underestimation of the actual yields, as solvent mass was not included in our calculations. While the mass recovery is primarily of academic interest and not directly relevant to the replication study, it is noteworthy that some processes exhibited low mass recovery, which could be expected based on the protocol.

Whenever possible, samples were collected from each step of every process for characterization. The characterizations of the final samples are presented in the main article, and the characterization of intermediate samples is included here in the Supporting Information to assist others in replicating the results. The samples collected include: '*ball mill crude*' (immediately after ball milling), '*after heating, before washing*', and the final sample, '*post-washing and drying*'. The reported mass recovery reflects the total non-solvent mass obtained at each step, used to calculate the final percentage.

Replication of the Synthesis from Li et al., Carbon 2018 [12]

The milling jar was charged with hexabromobenzene (300 mg, 0.54 mmol, 1 equiv.), calcium carbide (200 mg, 3.12 mmol, 5.8 equiv.), anhydrous ethanol (2 ml), and a 5 mm stainless steel ball. The sample was milled for 12 hours and allowed to cool for 30 minutes before opening. Once opened, a grey slush was obtained which continued to produce gas for 30 minutes after opening (or 1 hour after the end of the milling process). At this 1 hour mark, the slush was poured into a sintered glass Büchner funnel with filter paper, and the residual solvent sucked away. The solid residue was then sequentially washed and physically agitated (vigorous stirring with a glass rod for 5 minutes) with 1 M nitric acid (5 ml x2), benzene (4 ml x 2) and distilled water (4 ml x 2). The washes were removed by vacuum filtration after each intervention. The remaining solids, sitting on the filter paper, were then dried in an oven at 110°C for 0.5 h to obtain a grey solid. The excess mass of the filter paper above that of the filter paper alone was 137 mg, suggesting a mass

yield of 27.4%, but only 21.1 mg (4.2%) of the mass could be recovered as a free powder and transferred into a vial for storage and further processing. It appears that most of the mass has been lost during benzene washes. The IR spectrum of the corresponding fraction (Fig. S2) appears largely identical to that of hexabromobenzene.

Replication of the Synthesis from Yang et al., Small 2018 [13]

The milling jar was charged with calcium carbide (279 mg, 4.35 mmol, 8 equiv.) and hexabromobenzene (300 mg, 0.54 mmol, 1 equiv.) along with a single 5 mm stainless steel ball, all under a nitrogen atmosphere. The jar was flushed repeatedly with argon before being sealed. The reaction jar was ball-milled for 12 h under the general protocol. Following a 30-minute latency period, the container was opened to reveal black solid powder. This was immediately transferred to a 10 mL round-bottomed flask equipped with a Teflon stir bar and flushed under a continuous low flow of argon gas from a Schlenk line. This material was then heated at 450°C for 2 h under the argon flow. The temperature was maintained using a heat gun, and temperature was monitored using an IR thermometer. After cooling, the material remained black powder. It was transferred to a sintered glass Büchner funnel with filter paper, and sequentially washed and agitated (for 5 minutes per treatment) with 0.05 M HNO₃ (5 ml x 3) and then water (5 ml x 3). After each intervention, the washes were removed by vacuum filtration. After the final wash, the filter paper was dried in an oven at 110 °C for 0.5 h. The resulting 220 mg of black solids were transferred into a glass vial implying a mass recovery of 38%. The material was free flowing, unlike the material obtained in the *Carbon 2018* replication above.

Replication of the Synthesis from Li et al., J. Mater. Chem. A 2019 [14]

The milling jar was charged with benzene (40 μ l, 0.45 mmol, 35 mg, 1 equiv.), calcium carbide (200 mg, 3.1 mol, 6.8 equiv.), anhydrous ethanol (700 μ l), and a 5 mm stainless steel ball. This was flushed with argon, then sealed. The reaction jar was ball-milled for 12 h following the general protocol. Following a 30 min latency period, the container was opened to reveal a dark grey slurry. The mixture was transferred to a vial, then placed open in an oven at 260°C for 3 h. The resulting deep grey solid was then transferred to a sintered glass Büchner funnel equipped with filter paper, and sequentially washed and agitated (for 5 minutes per treatment) with 0.1 M nitric acid (5 mL x 3) and 2M glacial acetic acid (5 mL x 3). After each intervention, the washing solvent was removed through vacuum filtration. After the final wash, the filter paper was dried in an oven at 110 °C for 0.5 h. The filter paper weighed 159 mg more than the original filter paper implying a 68% mass recovery. 140 mg of deep grey powder could be recovered from the filter paper for a 60% net mass recovery.

4. Characterization Data



Figure S1. IR spectrum of (CaC₂/C₆Br₆/EtOH)_{char} ball mill crude.







Figure S4. IR spectrum of (CaC₂/C₆H₆/EtOH)_{char} after heating, before washing.





Figure S6. IR spectrum of $(CaC_2/C_6Br_6)_{char}$ after heating, before washing.



Figure S7. TGA of (CaC₂/C₆Br₆/EtOH)_{char} ball mill crude.





Figure S9. TGA of (CaC₂/C₆H₆/EtOH)_{char} after heating, before washing.



Figure S10. TGA of (CaC₂/C₆Br₆)_{char} ball mill crude.



Figure S11. TGA of (CaC₂/C₆Br₆)_{char} after heating, before washing.



Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Figure S12. SEM and EDS elemental mapping of the products of ball milling. The samples correspond to Fig. 5, Main Text. (A) $(CaC_2/C_6Br_6/EtOH)_{char}$ replicated from *Carbon* 2018 [12], (B) $(CaC_2/C_6Br_6)_{char}$ replicated from *Small* 2019 [13], and (C) $(CaC_2/C_6H_6/EtOH)_{char}$ replicated from *J. Mater. Chem. A* 2019 [14].



5. Summary of Characterization Data from Cui Group Papers

Figure S13. Summary of Raman data from Cui group papers. (A) Carbon 2018 [12], (B) J. Mater. Chem. A 2019 [14], (C) J. Mater. Chem. A 2018 [15], (D) Carbon 2022 [16], (E) Appl. Phys. Express 2019 [17], (F) Small 2019 [13], (G) Small 2020 [18], and (H) Opt. Mater. Express 2020 [19].

2500



Figure S14. Summary of survey XPS data from Cui group papers. (A) *Carbon* 2018 [12], (B) *J. Mater. Chem. A* 2019 [14], (C) *J. Mater. Chem. A* 2018 [15], (D) *Small* 2019 [13], and (E): *Small* 2020 [18].



Figure S15. Summary of high resolution C1s XPS data from Cui group papers. (A) *Carbon* 2018 [12], (B) *J. Mater. Chem. A* 2019 [14], (C) *J. Mater. Chem. A* 2018 [15], (D) *Carbon* 2022 [16], (E) *Small* 2019 [13], and (F) *Small* 2020 [18].



Figure S16. Summary of solid-state NMR data from Cui group papers. (A) *Small* 2019 [13] and (B) *Small* 2020 [18].



Figure S17. Summary of X-ray powder diffraction data from Cui group papers. (A) *Carbon* 2018 [12], (B) *J. Mater. Chem. A* 2018 [15], (C) *Carbon* 2022 [16], and (D) *Small* 2019 [13].



Figure S18. SAED diffractograms reproduced from (A) *Carbon* 2018 [12] and (B) *J. Mater. Chem. A* 2019 [14] papers, claimed by Cui and colleagues to be the same material. The images have been scaled to ensure the scale bars have the same pixel length.



Figure S19. Correct indexing of the reflections in the SAED pattern from *J. Mater. Chem. A* 2019 paper [14]. (A) Authentic SAED diffractogram of graphene (orange) overlaid with "graphyne" diffractogram from *J. Mater. Chem. A* 2019 paper [14]. (B) The (110) plane set of graphene.

Entry	Reference	IR	Raman	Survey XPS	C1s XPS	EDS	NMR	PXRD	SAED
1	Li et al., Carbon, 2018 [12]	-	Fig. 1b	Fig. 1a	Fig. 1c	Fig. S1	-	Fig. 2d2	Fig. 3a
2	Wu et al., J. Mater. Chem. A, 2018 [15]	Fig. S2ª	Fig. 2ª	Fig. S4	Fig. 4a	Fig. S3b ^a	-	Fig. 1ª	Fig. 3c ^a
3	Yang <i>et al.</i> , <i>Small</i> , 2019 [13]	-	Fig. 4f	Fig. 4d	Fig. 4e	Fig. 2c,d	Fig. 4b	Fig. 4c	Fig. 1d inset
4	Yang <i>et al.</i> , <i>Appl. Phys.</i> <i>Express</i> , 2019 [17]	Fig. 1c ^b	Fig. 1a	-	-	-	-	-	-
5°	Yang <i>et al.</i> , <i>Small</i> , 2020 [18]	Fig. 2b	Fig. 2c	Fig. S3	Fig. 2e	Fig. S1b	Fig. 2d	-	Fig. 2h
6	Lu <i>et al.</i> , <i>Carbon</i> , 2022 [16]	-	Fig. 2f ^d	-	Fig. 2a ^d , Table S1 ^e	Fig. S2-S4	-	Fig. S6	Fig. 1h inset
7	Li et al., J. Mater. Chem. A, 2019 [14]	Fig. 2c	Fig. 2b	Fig. S1	Fig. 2d	Fig. 2a	-	-	Fig. 2h
8	Zhang et al., Opt. Mater. Express, 2020 [19]	-	Fig. 1f	-	-	-	-	-	-

Table S2. Summary of Key Characterization Data from Cui Group Papers.

^a The IR, Raman, and EDS spectra, as well as PXRD and SAED patterns are reported for a "nanocomposite" with TiO₂ rather than pure graphyne. ^b Vis-NIR spectrum between 500-2500 nm. ^c All the characterization *except* EDS is for purported "nitrogen doped" graphyne. ^d Data for "nitrogen doped" graphynes. ^e Fitting parameters in Table S1 do not match Fig. 2a. For instance, FWHMs appear dramatically different.

6. References

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