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

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Abstract:

Several recent articles by Cui and coworkers claim syntheses of γ-graphyne, a novel sp^2/sp^1 allotrope of carbon, directly from calcium carbide. Here, we describe the replication of the key experiments from this series of articles. We did not observe the formation of γ-graphyne under the reported conditions. The characterization data from our replications are partially consistent with the results reported by Cui. However, we show that the claimed experiments produce only heavily contaminated, amorphous chars with no detectable sp^1 carbons.

Main Text:

Graphynes, carbon allotropes comprising sp^1 and sp^2 hybridized atoms, were theorized more than three decades ago [1]. Computational modeling suggests that some of these materials could feature unusual and compelling mechanical, electronic, and optical properties [2]. This has made graphynes highly attractive targets for synthesis. γ-Graphyne, an allotrope composed of a 1:1 ratio of sp^1 and sp^2 atoms, stands out due to its structural simplicity, symmetry, and expected stability, making it particularly attractive for further exploration.

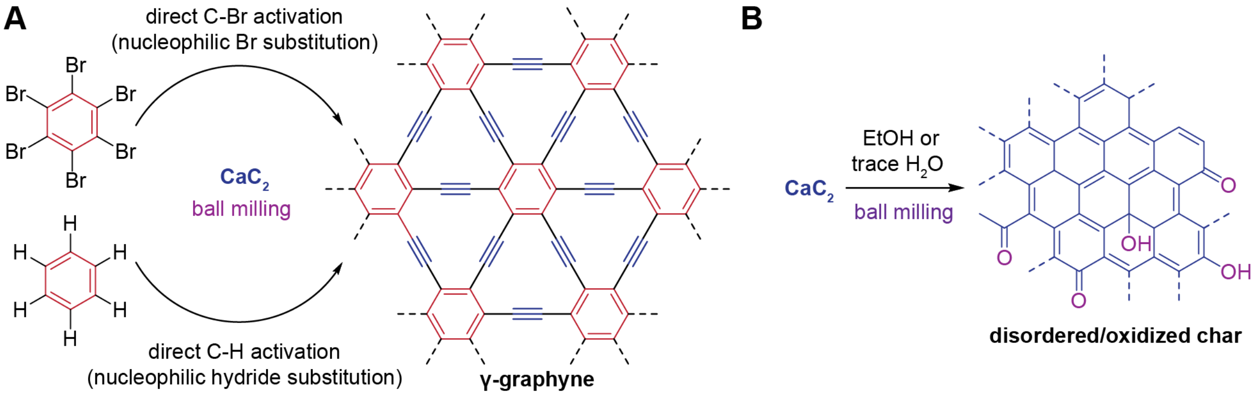

Figure 1. γ-Graphyne and its purported mechanochemical syntheses from CaC_2. (A) Direct nucleophilic substitutions at C-Br [3-8] or C-H [9, 10] sites as claimed by Cui group. The acetylenic carbons in the product originate from CaC_2, while the aromatic carbons originate from the aromatic substrates. (B) A more likely outcome of the claimed reactions. Most of the carbons in the product char are derived from CaC_2.

In a 2018 article in *Carbon* [3] and subsequent publications, Cui and coworkers claimed syntheses of macroscopic quantities of γ-graphyne through direct mechanochemical activation of calcium carbide in the presence of hexabromobenzene [4-8] or benzene [9, 10] (Fig. 1A). This body of work has been summarized in a recent review by the same authors [11]. Apart from the discovery of a novel form of carbon, the findings of Cui group could revolutionize organic chemistry. If confirmed to be true, these results would signify discovery of several entirely new reactions and end over seven decades of consensus regarding the reactivity of aromatic molecules toward nucleophiles [12-14]. This novel chemistry could render many fundamental synthetic methods, such as the Nobel-recognized Pd-mediated cross-couplings [15, 16], obsolete.

In our efforts to build on this incredible innovation, we attempted to replicate the key experiments from the work of Cui group. However, we found that none of the described conditions lead to the claimed formation of γ-graphyne. Instead, the experiments produce only amorphous, highly contaminated chars with no detectable sp^1 carbons (Fig. 1B). This indicates that the purported metal-free mechanochemical activation of (Ar)C-Br and (Ar)C-H towards nucleophilic attack remains unsolved, aligning with the existing literature on the subject [17].

Table 1. Conditions of the mechanochemical syntheses of γ-graphyne reported by Cui and colleagues.

Entry	Substrate	Solvent	Conditions	Processing	Reference
1	C_6Br_6	EtOH	3:2 w/w C_6Br_6/CaC_2, ball milling, 16 h	Washed with 1 M HNO_3, H_2O, and C_6H_6. Dried at 60 °C	Li *et al.*, *Carbon*, 2018 [3]
2	C_6Br_6	EtOH	Same as Entry 1	Same as Entry 1	Wu *et al.*, *J. Mater. Chem. A*, 2018 [4]
3	C_6Br_6	none	1:8 mol/mol C_6Br_6/CaC_2, ball milling under N_2, 12 h	Calcined at 450 °C. Washed with 0.05 M HNO_3 and H_2O. Dried at 80 °C in vacuum.	Yang *et al.*, *Small*, 2019 [5]
4	C_6Br_6	EtOH	Same as Entry 1	Same as Entry 1	Yang *et al.*, *Appl. Phys. Express*, 2019 [6]
5 [a]	C_6Br_6	none	Same as Entry 3	Calcined at 600 °C in NH_3 atmosphere. Washed with 0.05 M HNO_3 and H_2O. Dried at 80 °C in vacuum.	Yang *et al.*, *Small*, 2020 [7]
6 [a]	C_6Br_6 + C_5Cl_5N	EtOH	1:8 mol/mol (C_6Br_6 + C_5Cl_5N)/CaC_2, ball milling under Ar, 12 h	Annealed at 600 °C under Ar. Washed with 0.1 M HNO_3. Dried at 60 °C in vacuum.	Lu *et al.*, *Carbon*, 2022 [8]
7	C_6H_6	EtOH	1.75:10 w/w C_6H_6/CaC_2, ball milling, 8h @ 600 rpm, 8h @ 450 rpm	Annealed at 260 °C under N_2. Washed with 0.1 M HNO_3 and 2 M AcOH [b] under sonication. Dried at 60 °C.	Li *et al.*, *J. Mater. Chem. A*, 2019 [9]
8	C_6H_6	EtOH	Same as Entry 7	Same as Entry 7	Zhang *et al.*, *Opt. Mater. Express*, 2020 [10]

[a] These studies claim syntheses of "nitrogen-doped" γ-graphyne. [b] The experimental part of this study refers to "2 M glacial AcOH". The molarity of "glacial", i.e. 100% pure, acetic acid is ~17.5 M. We chose to interpret this as 2 M aqueous acetic acid.

We categorized the diverse experimental conditions used by Cui and colleagues (Table 1) based on the substrate molecule (benzene or hexabromobenzene), reaction conditions, solvent, and post-reaction processing. For our replication study, we chose the conditions described in *Carbon* [3] (Table 1, Entry 1), *Small* [5] (Table 1, Entry 3), and *J. Mater. Chem. A* [9] (Table 1, Entry 7), as these studies appear to be most representative. In both the *Carbon* and *Small* publications, Cui and colleagues used C_6Br_6 as the substrate. They used ethanol as a solvent in the *Carbon* study, whereas the *Small* protocol was solvent-free. The procedure outlined in the *J. Mater. Chem. A* paper closely mirrors that in *Carbon*, except benzene was used instead of C_6Br_6.

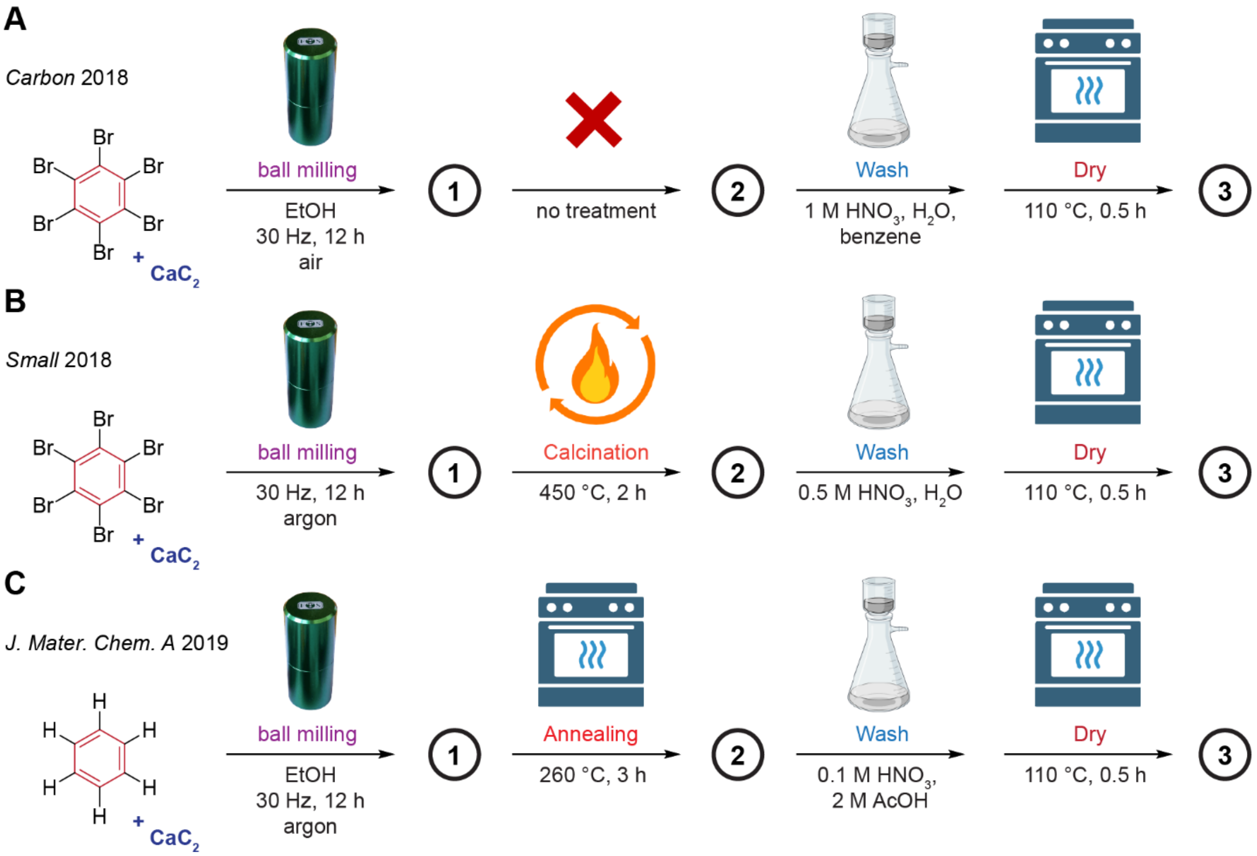

Figure 2. Experimental protocols used for the replication of the claimed mechanochemical syntheses of γ-graphyne. (A) $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{\mathrm{char}}$ from *Carbon* [3]; (B) $(CaC_2/C_6\mathbf{Br}_6)_{\mathrm{char}}$ from *Small* [5]; and (C) $(CaC_2/C_6\mathbf{H}_6/EtOH)_{\mathrm{char}}$ from *J. Mater. Chem. A* [9].

Cui and colleagues claim that all three methods we reproduce here yield pure γ-graphyne. While we did not expect the products to be analytically pure, we reasonably anticipated that they would contain detectable γ-graphyne and be consistent with each other. To preempt any broad argument from the authors suggesting that minor impurities or imperfections are responsible for deviations in our findings, we established relatively modest criteria for assessing successful replication: (1) The sp^1 carbons in the synthesized materials must be detectable by vibrational spectroscopy; (2) X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) must confirm that the materials are primarily carbonaceous; (3) The materials should contain at least a fraction of a crystalline, layered phase, consistent with expectations for γ-graphyne; and (4) The spectroscopic signatures and chemical properties of the synthesized materials should be similar between experiments, and independent of the synthetic protocol.

All three replication attempts yielded black substances, which we designate $(\mathrm{CaC_2/C_6}\mathbf{Br}_6\mathrm{/EtOH})_{\mathrm{char}}$, $(\mathrm{CaC_2/C_6}\mathbf{Br}_6)_{\mathrm{char}}$, and $(\mathrm{CaC_2/C_6}\mathbf{H}_6\mathrm{/EtOH})_{\mathrm{char}}$ based on the protocol (Fig. 2). Due to the uncertainty regarding the nature of the reactions, we quantified the outcomes by mass recovery relative to the purported reactants (C_6Br_6 or C_6H_6, and CaC_2), rather than using what would be an arbitrary stoichiometric yield. Mass recoveries assessed this way ranged between approximately 27% and 60%. However, for the $(\mathrm{CaC_2/C_6}\mathbf{Br}_6\mathrm{/EtOH})_{\mathrm{char}}$, only about 4% of the mass could be recovered from the filter. The particle size was small, and most of the products appeared to be soluble in benzene and were removed during the indicated wash steps.

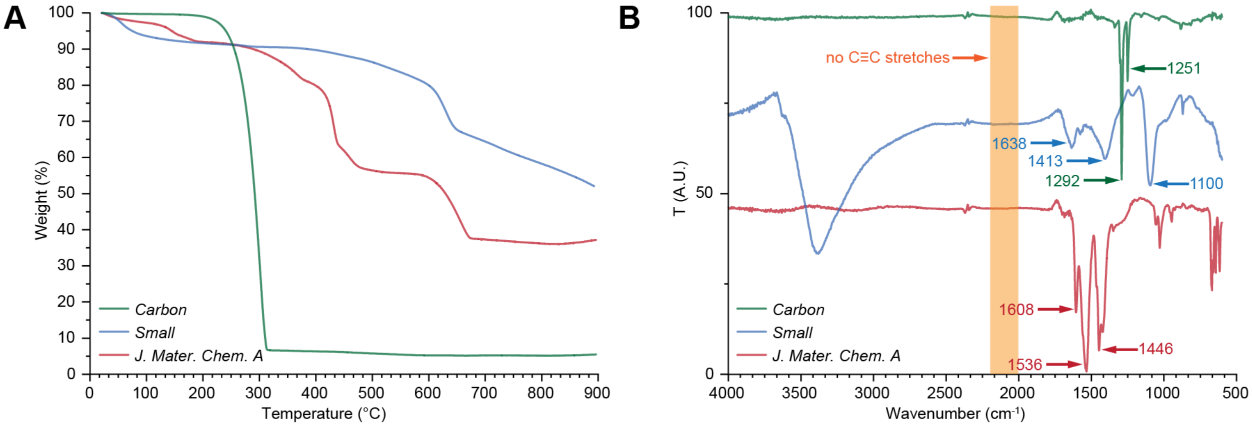

Figure 3. Initial characterization of the products of ball milling. (A) Thermogravimetric analysis and (B) IR spectra of $(\mathrm{CaC_2/C_6}\mathbf{Br}_6\mathrm{/EtOH})_{\mathrm{char}}$ from *Carbon* [3], $(\mathrm{CaC_2/C_6}\mathbf{Br}_6)_{\mathrm{char}}$ from *Small* [5], and $(\mathrm{CaC_2/C_6}\mathbf{H}_6\mathrm{/EtOH})_{\mathrm{char}}$ from *J. Mater. Chem. A* [9].

Thermogravimetric analysis (TGA) of the three substances revealed extremely different mass loss profiles (Fig. 3A), indicating that the obtained substances were chemically different. $(\mathrm{CaC_2/C_6}\mathbf{Br}_6\mathrm{/EtOH})_{\mathrm{char}}$ experienced a rapid, single-step weight loss event at ~250°C, retaining less than 10% of the original weight when heated past 300°C. In contrast, both $(\mathrm{CaC_2/C_6}\mathbf{Br}_6)_{\mathrm{char}}$ and $(\mathrm{CaC_2/C_6}\mathbf{H}_6\mathrm{/EtOH})_{\mathrm{char}}$ exhibited complicated weight loss profiles, with main loss events between 400 and 600°C. Both materials retained 40-50% of the initial weight when heated to 900°C. These results directly contradict one of the key claims of the 2018 *Carbon* paper [3], which declared the $(\mathrm{CaC_2/C_6}\mathbf{H}_6\mathrm{/EtOH})_{\mathrm{char}}$ material to be "incombustible" even in pure oxygen at 1000°C (though Cui and colleagues failed to provide any experimental data supporting this extraordinary claim).

We then characterized the materials by infrared (IR) spectroscopy. The C≡C stretch is IR-inactive for symmetric alkynes, and an ideal infinite crystal of γ-graphyne would not possess this band. However, idealized γ-graphyne is not indicated by any of the other data, and the inevitable symmetry breaking in microcrystalline and/or defected powders must activate this absorption, analogous to the activation of the D band in Raman spectra of finely milled graphite [18]. The expected absorption band structure for graphyne in this C≡C stretch region is very particular, since the frequency and intensity for the IR C≡C stretch peaks are sensitive to the substitution pattern. Terminal aryl alkynes Ar-C≡C-H show a moderately-intense peak at 2100-2115 cm^{-1} accompanied with an intense, sharp (sp^1)C-H stretch peak near 3300 cm^{-1}, while unsymmetric internal diaryl alkynes Ar-C≡C-Ar' feature a weak absorption at 2190-2200 cm^{-1}. Thus, an authentic sample of microcrystalline graphyne would exhibit a weak, broad band close to 2200 cm^{-1}. For materials with significant content of C≡C-H edge or defect groups, peaks at ~2100 and 3300 cm^{-1} must appear.

The IR spectra provided further evidence for the structural differences between the three products of ball milling (Fig. 3B). The spectrum of $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ was uncannily similar to that of hexabromobenzene [19], while the spectrum of $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ contained peaks at 1426 and 1446 cm^{-1} consistent with $CaCO_3$ (*vide infra*). Further direct assignment of the peaks was not feasible. The only clear commonality between the three spectra was the complete lack of any absorption between 2100 and 2200 cm^{-1}, the diagnostic region for C≡C stretches. Alkyne-specific stretches were also absent from the IR spectra of all the intermediates, before anenaling, calcination, drying, or washing (Fig. 2 and S1-S6, SI)

Our IR spectra for $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ and $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ had no features in common with the corresponding spectra reported by Cui. However, the spectra in the surveyed articles also entirely lack IR absorption peaks that could be reasonably attributed to C≡C stretches. In the *Appl. Phys. Express* paper [6], the purported spectrum of $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ has a peak that roughly aligns with the alkyne window. However, its exceptionally high intensity and a frequency of ~2150 cm^{-1} indicate it is unlikely to be a C≡C stretch. The "peaks" at 2139 and 2150 cm^{-1} claimed by Cui in the spectrum of $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ [9] are artifactual, as their intensities are clearly below the experimental noise floor. The authors failed to provide IR data for the $(CaC_2/C_6\mathbf{Br}_6)_{char}$, but a spectrum for a closely related material was reported in their subsequent 2020 *Small* paper [7]. While that spectrum broadly agrees with our result for $(CaC_2/C_6\mathbf{Br}_6)_{char}$, neither ours nor theirs exhibits a characteristic C≡C stretch.

In addition to the IR spectra, many of the papers by Cui also include Raman spectra of purported γ-graphynes. Surprisingly, every single one of these Raman spectra is materially different. For example, Cui and colleagues reported the A_{1g} Raman mode (Y band) to have shifts of either 2095 and 2250 cm^{-1} [3], or

1950 and 2200 cm^{-1} [5], or 2072 and 2171 cm^{-1} [6], or 2021 cm^{-1} [7], or 2080 cm^{-1} [8], or 1928 and 2221 cm^{-1} [9], or 1946 and 2181cm^{-1} [10]. Such variability in what should be a diagnostic Raman peak for γ-graphyne is concerning. The underlying cause of the observed variability is that *none* of the spectra reported by Cui exhibit a genuine Y band. Every purported peak falls below the noise floor or is clearly artifactual (Fig. S13, SI).

The interpretations of the Raman spectra provided by Cui and colleagues are also consistently and demonstrably incorrect. The splitting of the A_{1g} mode in γ-graphyne is a physical impossibility. Moreover, the intensity of this band, which corresponds to the in-plane stretching of the acetylenic bonds, must be comparable to or higher than the intensity of the aromatic A_{1g} and E_{2g} modes [20]. If the authors struggle to locate this band below the baseline noise (as noted above), their material cannot possibly be γ-graphyne. Additionally, most surveyed papers from the Cui group refer to the breathing mode of the aromatic rings at ~1350 cm^{-1} as an indicator of defects and disorder. While such interpretation has some validity for the graphite/graphene system [21], it is manifestly erroneous for γ-graphyne. Because the lattice of γ-graphyne is less symmetric compared to graphene, this band is always active in Raman spectra of γ-graphyne and is absolutely unrelated to lattice defects [20, 22]. Considering the absence of C≡C or (sp^1)C-H stretches in our IR spectra of the CaC_2-derived chars, and the absence of the true Y bands in all the Raman spectra reported by Cui and colleagues, we found it unnecessary to acquire Raman spectra of these materials.

While it was evident that the three synthesized materials differed chemically and had no sp^1 carbons detectable by vibrational spectroscopy, we found it necessary to establish their elemental composition and determine how much, if any, of the purported mechanochemical aromatic substitution chemistry was occurring. XPS spectra (Fig. 4) further confirmed that the three chars had different composition. The surfaces of $(CaC_2/C_6\mathbf{Br}_6)_{char}$ from *Small* [5] and $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ from *J. Mater. Chem. A* [9] were heavily contaminated by calcium (Fig. 4C, E). Additionally, and unsurprisingly, spectra for $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ and $(CaC_2/C_6\mathbf{Br}_6)_{char}$ revealed significant amounts of residual bromine (Fig. 4A, C). High-resolution spectra of the C1s region indicated the presence of multiple species inconsistent with γ-graphyne. This speciation was considerably different between the samples (compare Fig. 4B, D, F). The C1s peak for $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ was broadly consistent with expectations for hexabromobenzene contaminated with adventitious carbon, while the C1s for $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ indicated contamination with carbonate (CO_3^{2-}). All three materials appeared to contain a significant sp^3 component, suggesting highly disordered amorphous structures. We would also like to note that the survey XPS spectra reported by Cui and colleagues (Fig. S14, SI) do not appear to show the level of contamination with Ca that we observed, even though we followed the washing protocols described by the authors.

Cui and colleagues failed to provide full XPS datasets with all of the surveyed papers, which precludes a detailed quantitative analysis of their data. However, like the vibrational spectroscopy, the XPS spectra reported by them are inconsistent between publications (Fig. S14-S15, SI). The authors neglected to detail the exact procedures for fitting the C1s peaks, which is poor practice. Assumptions regarding peak shape, background model, subpeak chemical shifts, and full width at half maximum (FWHM) of the subpeaks should be documented and justified. Incorrect values consistently lead to arbitrary and inaccurate interpretation of XPS data [23].

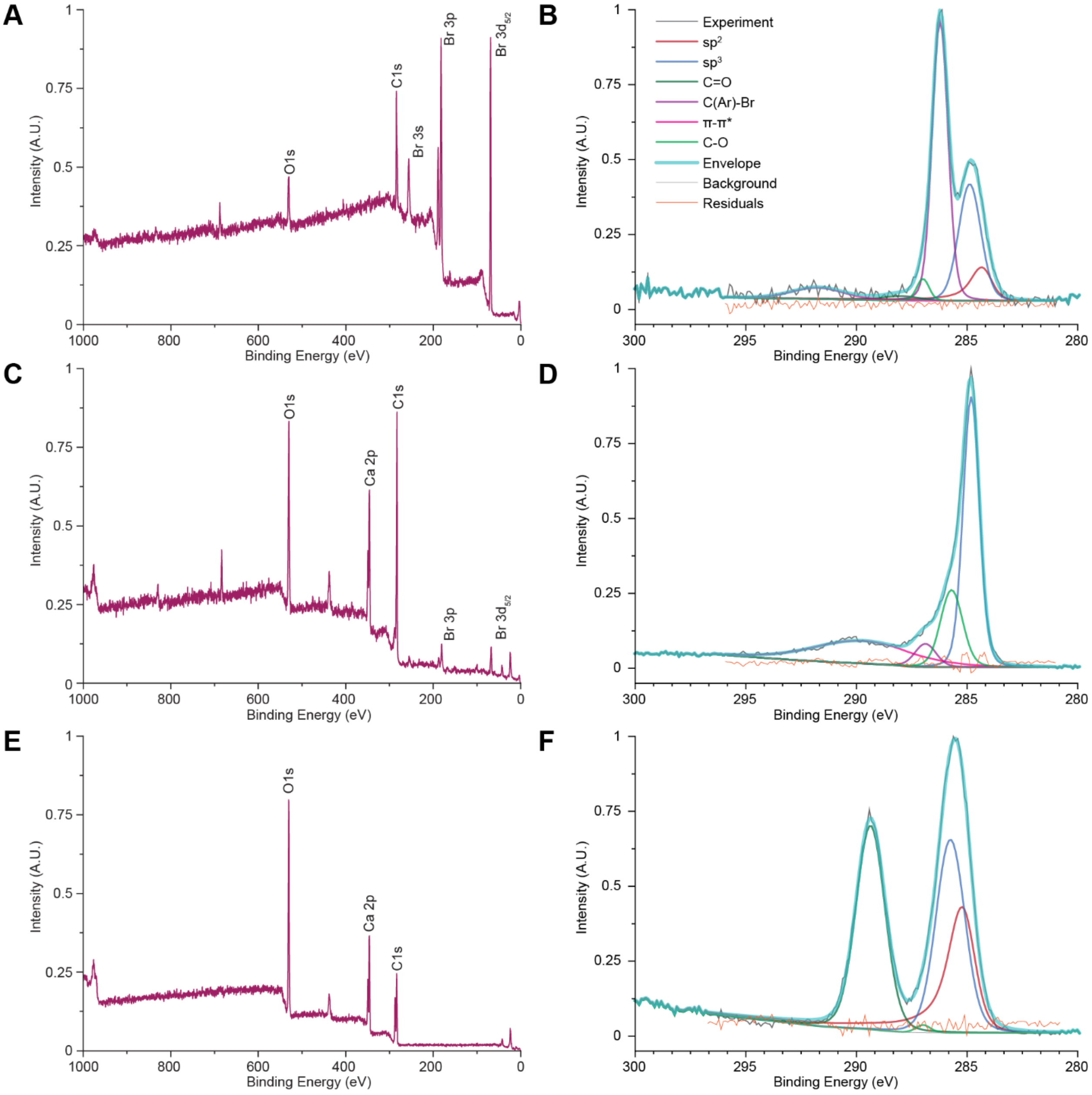

Figure 4. XPS of the products of ball milling. (A), (B): survey and high-resolution C1s spectra of (CaC_2/C_6**Br**$_6$/EtOH)$_{char}$ from *Carbon* [3]; (C), (D): survey and high-resolution C1s spectra of (CaC_2/C_6**Br**$_6$)$_{char}$ from *Small* [5]; and (E), (F): survey and high-resolution C1s spectra of (CaC_2/C_6**H**$_6$/EtOH)$_{char}$ from *J. Mater. Chem. A* [9].

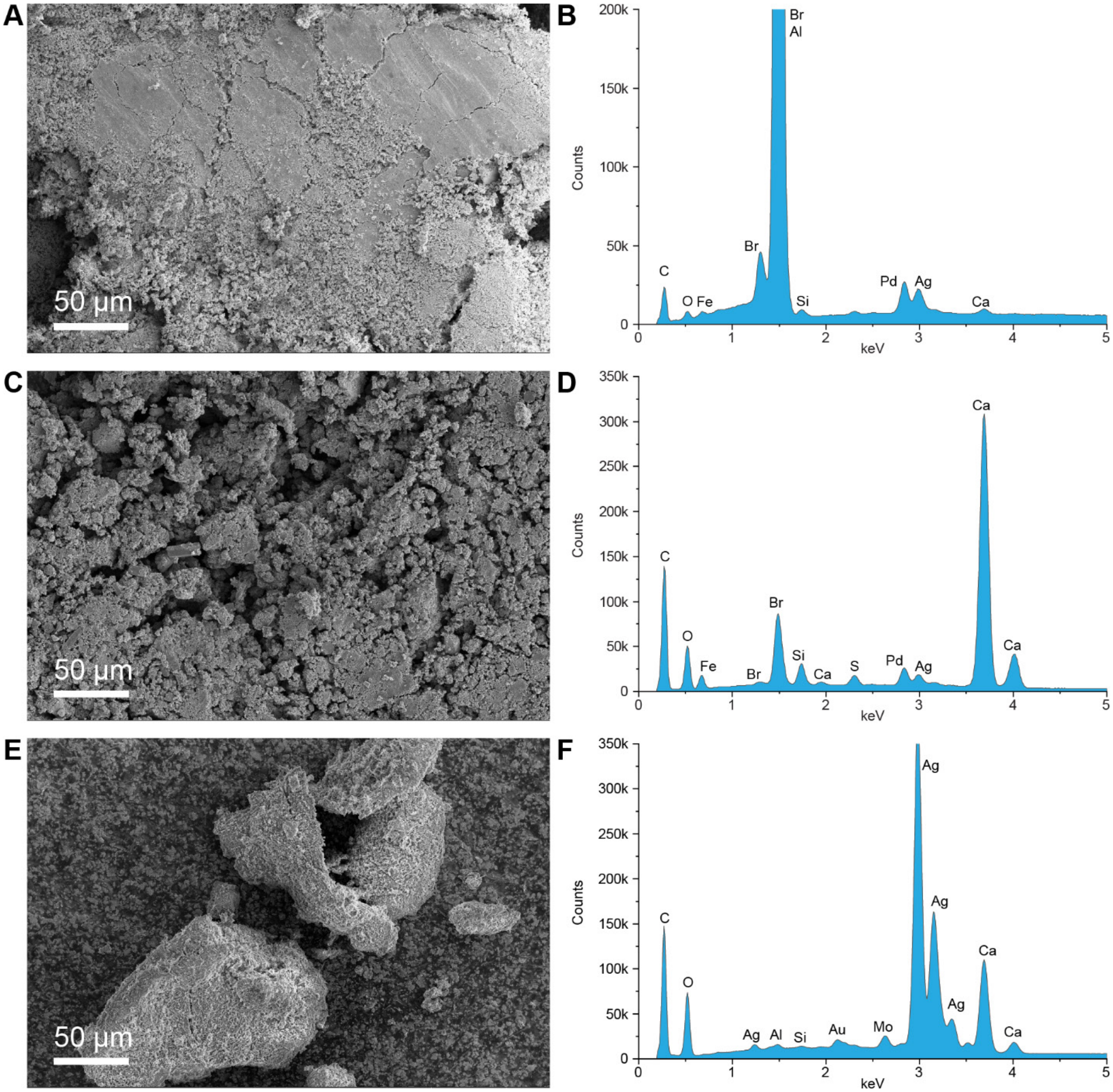

Figure 5. SEM and EDS of the products of ball milling. (A), (B): SEM and EDS of $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ from *Carbon* [3]; (C), (D): SEM and EDS of $(CaC_2/C_6\mathbf{Br}_6)_{char}$ from *Small* [5]; and (E), (F): SEM and EDS of $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ from *J. Mater. Chem. A* [9].

While we cannot ascertain all the assumptions made by Cui and colleagues, their interpretations of the high resolution XPS data appear to be universally inaccurate. The FWHM of most critical C1s subpeaks is arbitrary and consistently exceeds 2 eV, significantly higher than the commonly accepted range of 1.0-1.6 eV [24-26]. The relatively small contribution of the purported C-O and C=O subpeaks (Fig. S15, SI) appears to be inconsistent with the high oxygen content observed in most of the corresponding survey spectra (Fig.

S14, SI). Moreover, Cui and colleagues consistently omit sp^3 species from the fits of their C1s peaks. The 2018 *Carbon* paper [3] explicitly states that "no... XPS peak was observed for sp^3-hybridized carbon...". Discriminating between sp^1 and sp^3 carbon species in XPS is not possible due to overlapping chemical shifts [27]. However, Cui and colleagues provide no justification for excluding sp^3 species from their fit. We argue that the absence of characteristic sp^1 peaks from all vibrational spectra justifies excluding the *sp^1* species from the C1s fits. We hypothesize that the erroneous C1s fits provided by Cui and colleagues are a product of instrument software operating on default settings; the software will always fit a peak if instructed to do so. Nonetheless, this does not excuse reporting artifactual data fitted to a fundamentally incorrect model.

Scanning electron microscopy (SEM) imaging of our samples unveiled highly disordered morphologies (Fig. 5A, C, E). This observation broadly aligns with findings from the Cui group publications, where all the reported SEM images depict similar materials indicative of amorphous chars. EDS analysis indicated varying but significant amounts of calcium in all three chars, along with bromine in $(CaC_2/C_6\mathbf{Br}_6/EtOH)_{char}$ and $(CaC_2/C_6\mathbf{Br}_6)_{char}$ (Fig. 5B, D, F), in broad agreement with the XPS survey (Fig. 4A, C, E). Moreover, we detected traces of Fe, Mo, and possibly Cr, consistent with the composition of the milling balls. Trace amounts of these elements can be expected to be present and could have been avoided by using an alternative milling ball other than the stainless steel employed by both us and Cui. Elemental mapping of $(CaC_2/C_6\mathbf{H}_6/EtOH)_{char}$ revealed that the larger particles likely correspond to char-coated $CaCO_3$, further corroborating our analysis of the XPS spectra (Fig. 4F and S12C, SI). These results suggest that the decomposition of CaC_2 under the experiment conditions yielded a carbonaceous film impermeable to water and solvents, sequestering trace metal impurities from the dilute HNO_3 wash. We expect that a harsher nitric acid wash would be able to remove these impurities, but the mild washes used in the studies, which vary in the reported protocols (Table 1) from no wash, through 0.05 M, 0.1 M and 1 M nitric acid, are clearly insufficient.

In addition to XPS, EDS, and vibrational spectroscopy, two of the surveyed papers reported solid-state NMR characterization [5, 7]. However, neither publication provided key details of the NMR experiments, such as the magic angle spinning (MAS) rate or the pulse sequence. Assuming the NMR experiments were conducted using the most appropriate technique, direct polarization MAS, the ratio between the purported sp^1 and sp^2 ^{13}C peak intensities is inconsistent with expectations for γ-graphyne in both reported spectra (Fig. S16, SI). Furthermore, both spectra exhibit exceptionally noisy signals and broad, irregularly shaped peaks. Other than these disagreeable features, the correspondence between the two reported NMR spectra is weak at best. Therefore, these results are likely artifactual and do not support the purported structure.

Several of the surveyed papers also include powder X-ray (PXRD) (Fig. S17, SI) and selected area electron diffraction (SAED) data (Fig. S18, SI). The PXRD pattern from the *Carbon* paper [3] (Fig. S17A, SI) cannot be matched to any conceivable stacking of γ-graphyne sheets. The relatively low intensity of the purported interlayer peak (2θ = 25.4° using Cu Kα radiation) is inconsistent with a layered van der Waals material. Furthermore, this PXRD pattern is entirely different from that reported by Cui in the subsequent *Small* publication [5] (Fig. S17D). That pattern appears amorphous, with the purported interlayer peak indexed to a broad hump at 2θ = 23.96°. Neither of these PXRD patterns correspond to any of the spacings in the corresponding SAED patterns. The PXRD patterns of the purported mixtures of γ-graphyne with TiO_2 or ZrO_2 (Fig. S17B, C, SI) do not feature any graphyne-specific peaks, and do not match the patterns from either the 2018 *Carbon* [3] or 2019 *Small* [5] papers.

We have substantial concerns regarding the SAED data and its interpretation. In most cases, the Cui group acquired their SAED patterns without a beam stop. This can potentially damage the recording medium and cause significant oversaturation in the transmitted beam region. Tellingly, some of the observed reflections were bright enough to be comparable to the oversaturated central region (Fig. S18, SI). The excessive brightness of the patterns strongly indicates non-parallel illumination of the specimen and potential misfocusing [28]. In the absence of an internal standard, it is unclear how or if the TEM camera length was calibrated for these very specific and poorly defined imaging conditions [29]. Therefore, the accuracy of the provided reciprocal space scale bars is highly questionable.

A closer examination of these scale bars and reflection indexing provided by Cui and colleagues reinforces those concerns. The indexing of the reflections is demonstrably incorrect. Due to the orientation of the samples, diffraction involving spacing in the Z dimension is forbidden, as the Bragg angle for TEM is so small that only diffraction of planes whose poles lie ~90° to the incident beam can be observed. Thus, in the *c* orientation, only reflections corresponding to (hk0) are observable. For this reason, we cannot be looking at a “422” reflection in the case of the pattern in Fig. 2h of the 2019 *J. Mater. Chem. A* paper [9] (Fig. S18B, SI). For the pattern in Fig. 3a of the *Carbon* paper [3], the spacings of the purported “110” and “220” reflections are inconsistent with the structure of γ-graphyne (Fig. S18A, SI).

Based on the included legends, the SAED patterns in *Carbon* and *J. Mater. Chem. A* papers were obtained using the same instrument (Tecnai G2 F20 S-Twin FE-TEM), at the same acceleration voltage (200 kV), and identical camera distance of 490 mm. While both diffractograms present similar hexagonal symmetry, the observed pixel distances are drastically different (compare Fig. S18A and S18B, SI). Furthermore, the *J. Mater. Chem. A* diffractogram matches perfectly with the diffraction pattern for few-layer graphene (Fig. S19, SI). The claimed “422” reflections are almost certainly first-order reflections of the graphene lattice. This indicates that the scale bar in the *Carbon* pattern is not accurate.

For the reasons above, we can confidently conclude that no γ-graphyne or related material is formed under the conditions reported by Cui and colleagues. The claim that these reaction conditions provide high purity γ-graphyne is extraordinary and needs extraordinary evidence to support it. Unfortunately, neither the data provided by Cui and colleagues nor the data from our replication study show any evidence of γ-graphyne. The products of these reactions are amorphous carbon chars with varying levels of contamination. Our findings are unsurprising and align with the extensive literature on nucleophilic aromatic substitutions and the reactivity of CaC_2.

The proposed reactivity employed to make these products bears some discussion as it would be extremely exciting from an organic reactivity perspective. The uncatalyzed, direct, multi-site reaction of CaC_2 with an aryl bromide, as claimed in the 2018 *Carbon* and 2019 *Small* papers, is without credible precedent. Br is one of the poorest leaving groups in nucleophilic aromatic substitutions [30, 31]. Nucleophilic attack at the halogen atom itself ($S_N2@Br$), rather than at the sp^2 carbon, is well established to be kinetically favored in the reactions of $(sp^2)C\text{-}Br$ with carbon nucleophiles [32]. A quantitative reversal of the normal mode of this S_NAr chemistry, as is proposed by Cui and colleagues, would be highly unlikely.

Likewise, no precedent exists for direct C-H activation of benzene with CaC_2 or any other carbon nucleophile. The authors do not provide any plausible theory for the direct $(sp^2)C\text{-}H$ activation by CaC_2 beyond stating that the reactions are performed in a ball mill. While mechanochemistry can be a powerful and general approach to chemical synthesis, a ball mill does not obviate the need for a mechanistic pathway from reactants to products or change the underlying thermodynamics of a process. The most common reason for unconventional reactivity under mechanical milling is not direct transduction of mechanical energy, as erroneously implied by Cui, but rather the effects arising from the absence of solvent [33, 34]. Most of Cui's described syntheses, however, were not solvent-free and were performed in ethanol. Consequently, they would not benefit from this effect.

Moreover, the presence or absence of solvent, or the concentration of reactants, does not appear to have a significant effect on the claimed results, which is highly unusual for a true mechanochemical synthesis. Liquid-assisted grinding (LAG) is a process where a mechanochemical transformation, typically hindered by the presence of solvent, can still occur with trace or catalytic amounts of liquid [35]. LAG processes are typically characterized by a liquid-to-reactant mass ratio of 0-2 μL/mg. Slurries, which use more solvent to help suspend solid particles, have ratios between 3-6 μL/mg. The amount of liquid used can significantly affect the reaction outcome [36]. To put this into perspective, the 2018 *Carbon* protocol used a ratio of 12 μL/mg, while the 2019 *J. Mater. Chem. A* protocol used 3 μL/mg. Any extra liquid (>10 μL/mg) can diminish the mechanical impact energy and ionic interactions, effectively turning the solid-state mechanochemical system into a solution reaction agitated by being conducted in a ball mill rather than mechanical or magnetic stirring [37].

A thermodynamic calculation is included in the Supporting Information of *J. Mater. Chem. A* paper [9] to demonstrate that the claimed direct C-H activation chemistry is feasible. This calculation cannot be directly reasoned against, as it can only be characterized as *not even wrong* [38]. Specifically, the authors utilize the Boltzmann-Planck equation and the permutation formula for thermodynamic probability to directly calculate the entropy term. This approach is not directly applicable to any condensed phase. Incorrect and/or cherry-picked values for bond energies are employed, and there is a sign error when bond enthalpies are added up. Finally, the thermodynamics of the C/CaC_2/CaH_2 system has been studied experimentally and is well understood. Hydrogenation of CaC_2 to CaH_2 is unfavorable at ambient pressure [39]. Conversely, CaH_2 directly and cleanly reacts with carbon to yield CaC_2 [40].

To understand the origin of the chars, it is important to note that most of the described syntheses were performed under primarily ambient conditions, with no efforts to exclude moisture. When heated in the presence of trace water, CaC_2 is known to yield graphitic carbon chars [41]. A variety of disordered structures can be accessed by varying the conditions [42, 43]. Furthermore, CaC_2 is capable of directly reacting with ethanol upon heating, yielding a mixture C4-C9 alcohols, ethyl vinyl ether, and char [44]. This is the chemistry that we observed, and which Cui likely conducted. The difference between the composition of the various chars may be due to different moisture content of the starting materials, relative ambient humidity, variation in reaction temperature, the presence of ethanol, and/or the introduction of additional impurities.

We urge extreme caution in interpreting the surveyed articles (Table 1). The key experiments are demonstrably irreproducible, and the reported characterization is either misinterpreted or artifactual. Therefore, the claimed syntheses of γ-graphyne and the corresponding unprecedented chemistry are not supported by the evidence. There is no credible proof that γ-graphyne has been synthesized in any of these studies, and any discussions regarding the applications of this material are unrealistic.

We are not suggesting that γ-graphyne is unattainable or that mechanochemistry couldn't play a role in its synthesis — it certainly could. However, the methods reported in these papers, by this group of authors, did not achieve the synthesis of γ-graphyne. We hope this contribution highlights some of the pitfalls in the characterization of carbon materials and prompts a reexamination or retraction of some, if not all, of the surveyed papers.

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Competing Interests

The authors declare no competing interests.

Author Contributions

Conceptualization: VOR, WBM, JFT

Methodology: VOR, ERK, VGD, GLP, SN, JFT

Investigation: ERK, VGD, GLP, SN, WBM

Visualization: VOR, ERK, VGD, SN

Writing – original draft: VOR, WBM

Writing – review & editing: VOR, JFT, ERK, SN, VGD

Supervision: VOR, JFT

Supporting Information

Full experimental details and additional figures from the replication experiments are available in the online supporting information.

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