Efficient synthesis of alkynyl carbon materials derived from CaC_2 through solvent-free mechanochemical strategy for supercapacitors

Yangyang Li³ · Yingjie Li^{1,2} · Xiaojun He² · Jing Gu² · Moxin Yu² · Wenfeng Li¹ · Chunxi Li¹

© Springer Nature Switzerland AG 2019

Abstract

The synthesis of new carbonaceous electrode materials for supercapacitors and the discovery of efficient techniques for the CaC_2 activation are meaningful subjects. In this study, unique alkynyl carbon materials (ACMs) were effectively synthesized through solvent-free mechanochemical reactions of CaC_2 with C_2Cl_6 or C_6Br_6 . Their components and structure were comprehensively characterized, and their supercapacitor performances were examined in detail. The mechanochemistry has proved to be an efficient and targeted technique for the reactive activation of CaC_2 . The *sp*-C dominated ACMs feature interconnected framework with hierarchical pores, tunable structures, and low cost of raw materials. As electrodes for supercapacitors, the ACMs exhibit high specific capacitances in the range of $48.4\text{--}132.4\text{ F g}^{-1}$ with excellent electrical conductivities and outstanding cycling stabilities. This work provides an efficient, green, and cost-effective strategy for the synthesis of ACMs from widely available precursors, and a significant assistance for the renaissance of CaC_2 chemistry.

Graphical abstract

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-0205-1>) contains supplementary material, which is available to authorized users.

✉ Yingjie Li, liyingjie0408@163.com; ✉ Chunxi Li, licx@mail.buct.edu.cn | ¹State Key Laboratory of Chemical Resource Engineering and College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, China. ²Anhui Key Lab of Coal Clean Conversion and Utilization, School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan, Anhui, China. ³Anhui University of Technology, Maanshan, Anhui, China.

SN Applied Sciences (2019) 1:195 | <https://doi.org/10.1007/s42452-019-0205-1>

Received: 25 December 2018 / Accepted: 21 January 2019 / Published online: 31 January 2019

Keywords Alkynyl carbon materials · CaC_2 · Mechanochemistry · Characterization · Supercapacitors

1 Introduction

The fast depletion of fossil energy and the global environmental challenges have greatly inspired the exploration and utilization of sustainable energy storage devices [1, 2]. In the last few decades, supercapacitors, especially for the electric double layer capacitors (EDLCs), have attracted widespread attentions and researches owing to their short charge–discharge time, high power density, and long cycle life. Generally, the electrode materials are the key to the electrochemical performance of EDLCs [3–5]. To meet the requirements of the high-performance electrodes, various carbon materials including activated carbons, carbon fibers, porous carbons, carbon nanotubes, carbon aerogels, graphene, and alkynyl carbons have been widely investigated as electrode materials for EDLCs [5–9]. Among them, alkynyl carbon materials (ACMs) with unique structures of intriguing electronic properties have shown the great potential to become one of the most promising electrode materials [8–11]. However, the types of ACMs that have been developed are rare, and their synthetic methods and appropriate precursors are still scarce [8, 9, 12]. Therefore, it is necessary to exploit the efficient methods and new precursors for the synthesis of ACMs with unique structures that can deliver excellent supercapacitor performance.

Calcium carbide (CaC_2) is a crystalline ionic compound that simply composes of Ca^{2+} and $[\text{C}\equiv\text{C}]^{2-}$, and thus may be served as an ideal precursor for the synthesis of ACMs [13]. However, it is very difficult to realize the CaC_2 -related reactions except its hydrolysis due to the restrictive effect of its lattice structure [9, 13–15]. To date, few researches have been attempted to straightly synthesize the ACMs by CaC_2 . Huang et al. synthesized a series of CMs in autoclave through radical reactions of CaC_2 and chloralkanes [16, 17]. Almost simultaneously, CaC_2 -derived CMs have been synthesized by Wang et al. via etching effect of fresh chlorine for CaC_2 under medium-high temperature, and their supercapacitor performance were investigated [18–20]. These studies demonstrate that the synthesis of ACMs from CaC_2 is very hard to implement through conventional methods. In addition, in consideration of their thermal instability, the alkynyl groups may be destroyed during the synthetic processes of these CMs [21]. Thus, it is very important to find a suitable method for the efficient activation of CaC_2 . Recently, mechanochemistry (MC), as an effective and green technique, has attracted more and more attention owing to its high efficiency, facile operability, and environmental friendliness [22–25]. Significantly, it has demonstrated inestimable potentials in materials synthesis through solid–solid reactions, and especially

exhibited ultra-high activation effect for the crystalline substance [26–30]. Therefore, MC may be used as a viable method for the synthesis of ACMs by using of CaC_2 as alkynyl source.

In this context, two kinds of ACMs were efficiently synthesized via the solvent-free mechanochemical reaction between CaC_2 and C_2Cl_6 or C_6Br_6 under mild conditions. In this study, the synthetic processes under mechanochemistry were investigated, the unique structures of the ACMs were characterized, and the supercapacitor performances of the ACM electrodes were examined. This study can hopefully provide an efficient strategy for the ACM syntheses, as well as a perspective approach toward the reactive activation of CaC_2 .

2 Experimental section

2.1 Synthesis and characterization of ACMs

In this study, a planetary ball mill was used for the mechanochemical synthesis of ACMs. For a typical process, a mixture of CaC_2 and C_2Cl_6 powder ($\text{CaC}_2/\text{C}_2\text{Cl}_6 = 4.5:1$ in molar ratio) was added into a 250 mL stainless steel pot with approximately 250 g milling balls. Then, the planetary ball mill was operated at 550 rpm for 3 h under vacuum conditions and ambient temperature. The resultant mixture was washed by dilute nitric acid and ultrapure water repeatedly to remove the impurities. Finally, the ACM-1 was obtained by filtration and vacuum drying, and the filtrate was analyzed by ICS-900 ion chromatography to measure the ionization of halogen derived from C_2Cl_6 . Similarly, ACM synthesized by C_6Br_6 ($\text{CaC}_2/\text{C}_6\text{Br}_6 = 4.5:1$ in molar ratio) under the same conditions is termed as ACM-2. Furthermore, the as-prepared ACMs were comprehensively characterized by scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), high-resolution transmission electron microscopy (HR-TEM), low-temperature nitrogen adsorption, Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The detailed synthetic processes and characterization conditions are listed in Supplementary Information (SI).

2.2 Electrochemical performance measurements of ACMs

The electrochemical performance of ACMs was investigated using three-electrode cell on a CHI 660E electrochemical workstation at room temperature. Three test methods, including cyclic voltammetry (CV), galvanostatic

charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were employed. Details related to the fabrication of ACM electrodes and the test conditions have been provided in the Experimental Section in SI. Furthermore, the gravimetric specific capacitance (C_m , $F\ g^{-1}$) of the ACM electrodes were calculated using CV and GCD curves. On the basis of the CV curves, the C_m values were calculated as follows:

$$C_m = \frac{\int IdV}{2m\nu\Delta V}$$

where m (g) is the mass of the ACMs, ν ($V\ s^{-1}$) is the potential scan rate, ΔV (V) is the range of potential, I (A) is the response current, and $\int IdV$ is the mathematical integral of the CV curve. On the basis of the GCD curves, the C_m values were calculated as follows:

$$C_m = \frac{I\Delta t}{m\Delta V}$$

where m (g) is the mass of the ACMs, I (A) is the charge/discharge current, ΔV (V) is the potential range of charge/discharge, and Δt (s) is the discharge time.

3 Results and discussion

3.1 Mechanochemical synthesis processes of ACMs

As shown in Table 1, the mechanochemical reactions between CaC_2 and polyhalogenated hydrocarbons (PHHCs) can reach deep level, as evidenced by the high carbon yield and dehalogenation degrees. Notably, the experimental carbon yields (CY_{exp}) are greater than the theoretical ones ($CY_{theo.}$). This phenomenon can be attributed to the existence of insoluble impurities in CaC_2 , small quantity of halogen residues from PHHCs, and the chemical adsorption of oxygen on ACM surface, as proved from the EDS spectra of the ACMs (Fig. S1). Even if the above impurities are ignored, the carbon yields obtained from the mechanochemical reactions are still very high. Furthermore, the reactivity of CaC_2 can be effectively activated

under mechanochemistry due to the targeted treatment on the CaC_2 lattice structure [9, 31, 32]. As shown in Fig. 1, once the mechanochemical reactions are triggered, they will proceed in a rapid, comprehensive, and deep manner owing to the strong nucleophilicity and electron-withdrawing effect of the alkynyl group [33]. Thus, the mechanochemical synthesis of ACMs can proceed under very mild conditions [32, 34]. In addition, the raw materials used here are cheap and abundant, and no hazardous materials are released into the environment during the ACM synthetic process. Therefore, this mechanochemical process can be considered as a green, efficient, and cost-effective approach for the synthesis of ACMs.

3.2 Characterizations of ACMs

As shown in Fig. 2a–d and Fig. S2, the SEM images display an accumulated roe-like morphology, indicating that the as-prepared ACMs are aggregates of carbon nanoparticles (CNs) with a micro–mesoporous structure. Obviously, the CNs in ACM-2 has bigger size but broader size distribution than that in ACM-1 (Fig. S3). In addition, the pore structure of ACM-2 appears to be more developed than that of ACM-1. These differences may be attributed to the existence of benzene rings in PHHC precursors, and the possible structural rearrangement of ACM-1 during its synthesis. These results indicate that the morphology and pore structure of ACMs can be modulated through selecting different PHHC precursors.

Furthermore, the nitrogen adsorption–desorption isotherms of the ACMs shown in Fig. 2e are typical IVa type with obvious H_4 hysteresis loops at a relative pressure P/P_0 of 0.4–1.0 and pronounced N_2 uptake at low P/P_0 , demonstrating the existence of mesopores and micropores in ACM samples [35]. As can be observed from Fig. 2f, ACMs exhibit micropores centered at 0.7 and 1.2 nm and mesopores ranging from 2 to 10 nm. Notably, there are more micropores in ACM-2 in comparison with ACM-1, which is well consistent with the SEM observation. Table 2 summarizes the pore structure parameters of ACM samples. The S_{BET} of ACM-2 reaches $648.6\ m^2$

Table 1 Mechanochemical synthesis processes and results

Sample	PHHC precursor	CY_{theo} (%)	CY_{exp} (%) ^a	CY_{exp} (%) ^b	Halogen ionization (%)	C content (weight/atom, %) ^c
ACM-1	C_2Cl_6	22.4	33.2	24.6	97.8	76.3/82.9
ACM-2	C_6Br_6	19.38	34.6	26.4	95.1	68.5/82.1

^aThe actual carbon yield from the experiments

^bThe carbon yield excluding insoluble impurities from industrial CaC_2

^cResults obtained from EDS analysis

Fig. 1 Proposed mechano-chemical synthesis pathway of the ACMs

Fig. 2 SEM images of ACM-1 (a, b) and ACM-2 (c, d), N₂ adsorption-desorption isotherms (e), and pore size distribution (f) obtained by the density functional theory

Table 2 The pore structure parameters of ACMs

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{mic} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)
ACM-1	332.8	54.5	0.642	7.71
ACM-2	648.6	114.7	0.866	5.34

g^{-1} , which is around twice that of ACM-1 ($332.8 \text{ m}^2 \text{g}^{-1}$). Meanwhile, the pore size of ACMs decreases from 7.71 nm (ACM-1) to 5.34 nm (ACM-2) when the PHHC precursor changes from C_2Cl_6 to C_6Br_6 . These results illustrate that the rigid brace effect of benzene rings and the placeholder effect of large size halogens facilitate the formation of the developed pore structure, which is beneficial to their application in supercapacitors [36, 37].

As shown in Fig. 3a, b and Fig. S4, disordered and layered carbon structures are clearly observed in the

HR-TEM images of ACMs, and the two types of carbon are interconnected with each other via carbon-carbon chemical bonds. This stable, cross-linked, porous structure is expected to improve the electron conduction, shorten the ion transport distance, and result in an excellent electrochemical performance for ACMs when they are used as electrode materials in supercapacitors. For ACM-2, the layered carbon is derived from highly conjugated planar structure constructed by sp - and sp^2 -hybridized carbon atoms, while that in ACM-1 may attribute to the structural rearrangement due to the instability of the sp^3 and sp hybridized structure [38]. Especially, lattice fringes were measured to be $3.50 \text{ \AA}$ for ACM-1 and $3.65 \text{ \AA}$ for ACM-2, which are greater than that of grapheme ($3.35 \text{ \AA}$). This phenomenon can be attributed to their high electron density of adjacent layers [38, 39], which is helpful for fast charge transport and excellent supercapacitance.

Fig. 3 HR-TEM images and the corresponding FFTs of **a** ACM-1 and **b** ACM-2, XRD patterns (**c**), and Raman spectra (**d**)

The XRD patterns of ACMs (Fig. 3c) exhibit two strong reflections at around 26° and 44° accompanied by some weak reflections. The former coincides well with the (002) and (10) reflections of graphite (PDF 41-1487), indicating a certain content of well-ordered graphitic carbon in ACMs; while the latter is attributed to the reflections of SiC (PDF 49-1428), $C_{0.14}Fe_{1.86}$ (PDF 44-1289), and FeSi (PDF 38-1397), indicating the chemical insertion of the impurity elements in ACMs. These results are in good agreement with the HR-TEM observation and EDS analysis. Notably, compared with ACM-1, ACM-2 has broader (002) reflections and lower crystallinity (Table S2). This result indicates the structural diversity of ACM-2 owing to the rotation effect of the alkynyl group and irregular cross-linking between monomers when the PHHC precursor changes from C_2Cl_6 to C_6Br_6 [38, 40]. In addition, the Raman spectra of ACMs are presented in Fig. 3d. D-band at 1335 cm^{-1} attributed to the disorder carbonaceous structures and G-band at 1580 cm^{-1} attributed to the typical graphite bond stretching are observed, indicating the existence of defects in the crystalline carbon structure of ACMs [41, 42]. This result is consistent well with those obtained from XRD and HR-TEM above. Furthermore, the intensity ratio between D and G bands (I_D/I_G) of ACM-2 is 1.21 (Table S2), which is smaller than that of ACM-1 (1.38), indicative of a higher graphitization degree. This result reveals that more defects are formed in ACM-1 due to the possible structural rearrangement. The high graphitic structure of ACM-2 is expected to improve its electron conduction and supercapacitor performance [43].

To further investigate the structural features of ACMs, XPS spectra were recorded. As shown in Fig. 4a, C 1s peak at 284.8 eV and O 1s peak at 532.7 eV are observed. The former indicates that carbon is the main element of ACMs, and the latter is attributed to the chemical adsorption of O_2 and slight oxidation of $C\equiv C$ bonds on ACMs surface [9, 11, 44], which can improve the wettability of electrode materials in electrolytes. After fitting with a combination of Lorentzian and Gaussian functions, the high-resolution asymmetric C1s peak is mainly deconvoluted into four sub-peaks at around 284.6, 285.1, 285.5, and 286.5 eV (Fig. 4b), assigned to binding energy of $C=C$ (sp^2), $C\equiv C$ (sp), $C-C$ (sp^3), and $C-O$ bonds, respectively [8, 44]. To further confirm the structure of ACMs, the area ratio of the sub-peaks is calculated. For ACM-1, the area ratio of $sp^2/sp/sp^3$ is 12/3/1, confirming that the structural rearrangement occurs during its synthetic process; while the area ratios of sp^2/sp for ACM-2 is 1/1, confirming that its structure features benzene rings linked through alkynyl linkages. These results provide a powerful demonstration for the inferences about the ACMs structure and synthetic process (Fig. 1).

Fig. 4 XPS spectra of ACMs: **a** survey scans, **b** narrow scans of carbon fitted with the combination of Lorentzian and Gaussian function

3.3 Electrochemical performance of ACM electrodes

Figure 5a and Fig. S5a-b show the CV curves of ACMs at different scan rates. The typical rectangular shapes without obvious redox peaks indicate their representative capacitive behavior and low contact resistance [45, 46]. Even at high scan rate of 30 mV s^{-1} , their CV curves still retain quasi-rectangular shape without obvious distortion, demonstrating the excellent rate capabilities due to the perfect electrical double layers with high reversible systems. Notably, the ACM-2 electrode has much higher C_m value than ACM-1 electrode (Table S3) due to its structural advantage.

Furthermore, the GCD curves of the ACMs (Fig. 5b and Fig. S5c-d) exhibit symmetrical triangular shapes, indicating a typical double-layer capacitive behavior due to the reversible adsorption and desorption of the electrolyte ions [47, 48]. The C_m values of ACM-1 and ACM-2 electrodes calculated from the GCD curves at 0.1 A g^{-1} reach

Fig. 5 Electrochemical performance of ACM electrodes: **a** CV curves, **b** GCD curves, **c** long cycling performance, and **d** Nyquist plots obtained from EIS measurements

48.4 and 132.4 F g⁻¹, respectively, and the ACM electrodes show good C_m retentions with increasing current density (Table S3). These results demonstrate that the reasonable selection of PHHC precursors can effectively regulate the pore structures of ACMs and further improve their capacitance performance [49]. In addition, Fig. 5c presents the long cycling performance of ACM electrodes. The capacitance retention at 1 A g⁻¹ is 97.9% and 93.9% for ACM-1 and ACM-2, respectively, after 1000 charge–discharge cycles, which is indicative of their excellent reversibility and good electrochemical stability.

The Nyquist plots obtained from EIS measurements for ACM electrodes are presented in Fig. 5d. The straight lines with high slope values at low frequency regions reveal that the ACM electrodes show near-ideal electric-double-layer capacitor behavior with excellent pore accessibility for the electrolyte ions [50, 51]. The semicircles with small diameters at the high-frequency regions indicate their low charge–discharge resistances. More importantly, the equivalent series resistance (ESR) value is 0.42 Ω for ACM-1 and 0.39 Ω for ACM-2, respectively, as obtained from the x-intercepts of the Nyquist plots. The low ESR values reveal

the high charge–discharge rates and excellent electrical conductivities of the ACM electrodes.

Table 3 compares the performance of ACMs with other carbonaceous electrode materials. Considering their relative low specific surface area, the ACMs exhibit superior electrochemical performance with C_m values range of 48–132 F g⁻¹ as compared with other CM electrodes reported previously [7, 8, 52–56]. The relative high capacitance, good rate performance, and excellent electrical conductivity of ACM electrodes can be attributed to their structural advantages, including optimized pore structure, high electron density, and excellent interconnected framework. Furthermore, the structure of ACMs can be adjusted in accordance with the relevant requirements of the electrode materials used in supercapacitors. Meanwhile, the synthetic process is cost-effective and environmentally friendly, resulting in viable massive production of ACMs. Therefore, the as-prepared ACMs have the great potential to be a new candidate for electrode materials with excellent supercapacitor performance.

Table 3 Comparison of various carbon electrode materials for supercapacitors [7, 8, 52–56]

Carbon materials	Specific surface area (m ² g ⁻¹)	Capacitance in aqueous electrolyte		Cost
		C_m (F g ⁻¹)	C_v (F cm ⁻³)	
Carbon nanotubes	120–500	50–100	< 60	High
Graphene	2630	100–205	–	High
Commercial activated carbon	1000–3500	< 200	< 80	Low
Templated porous carbon	500–3500	120–350	< 200	High
Functionalized porous carbon	300–2200	150–500	< 180	Medium
Activated carbon fibers	1000–3000	120–370	< 150	Medium
Carbon aerogels	400–1000	100–125	< 80	Low
Graphdiyne	600–1300	< 80	–	High
This study	330–650	48–132	75–153	Low

4 Conclusion

In summary, two kinds of ACMs have been synthesized from CaC₂ and PHHCs (C₂Cl₆ or C₆Br₆) through mechanochemical reaction under mild conditions. The reactivity of CaC₂ can be effectively activated under mechanochemistry, and the ACMs are obtained via successive nucleophilic substitution of halogens in PHHCs with the activated alkynyl groups. The as-prepared ACMs feature unique structures of hierarchical pores, atomic layer structures, interconnected frameworks, and specific alkynyl presences. Meanwhile, the structure of ACMs can be adjusted by selecting the appropriate PHHC precursors. Benefiting from these structural merits, the ACM electrodes exhibit superior electrochemical performance, including high specific capacitances of 48.4–132.4 F g⁻¹, excellent electrical conductivities with 0.39–0.42 Ω of ESR, and outstanding cycling stabilities with 93.9–97.9% of capacitance retention after 1000 cycles at 1 A g⁻¹. This novel strategy may provide a perspective approach for efficient synthesis of unique ACMs for supercapacitors, as well as a significant insight into the reactive activation of CaC₂.

5 Supporting information

Experimental section, material preparation details, electrode fabrication, and supplementary results and discussion.

Funding This study was funded by the National Natural Science Foundation of China (Nos. 21776015 and 21503108), and the Natural Science Research Project of Anhui Province (No. KJ2018A0065).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Shao Y, El-Kady MF, Sun J et al (2018) Design and mechanisms of asymmetric supercapacitors. *Chem Rev* 118:9233
- Chu S, Majumdar A (2012) Opportunities and challenges for a sustainable energy future. *Nature* 488:294
- Wang G, Zhang L, Zhang J (2012) A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev* 41:797
- González A, Goikolea E, Barrena JA, Mysyk R (2016) Review on supercapacitors: technologies and materials. *Renew Sustain Energy Rev* 58:1189
- Zhang Y, Yu S, Lou G et al (2017) Review of macroporous materials as electrochemical supercapacitor electrodes. *J Mater Sci* 52:11201
- Borenstein A, Hanna O, Ran A, Luski S, Brousse T, Aurbach D (2017) Carbon-based composite materials for supercapacitor electrodes: a review. *J Mater Chem A* 5:12653
- Wang Q, Yan J, Fan Z (2016) Carbon materials for high volumetric performance supercapacitors: design, progress, challenges and opportunities. *Energy Environ Sci* 9:729
- Huang C, Li Y, Wang N et al (2018) Progress in research into 2D graphdiyne-based materials. *Chem Rev* 118:7744
- Li Y, Liu Q, Li W, Meng H, Lu YZ, Li C (2017) Synthesis and supercapacitor application of alkynyl carbon materials derived from CaC₂ and polyhalogenated hydrocarbons by interfacial mechanochemical reactions. *ACS Appl Mater Interfaces* 9:3895
- Krishnamoorthy K, Thangavel S, Veetil JC, Raju N, Venugopal G, Sang JK (2016) Graphdiyne nanostructures as a new electrode material for electrochemical supercapacitors. *Int J Hydrog Energy* 41:1672
- Shang H, Zuo Z, Zheng H et al (2018) N-doped graphdiyne for high-performance electrochemical electrodes. *Nano Energy* 44:144
- Matsuoka R, Toyoda R, Shiotsuki R et al (2018) Expansion of the graphdiyne family: a triphenylene-cored analogue. *ACS Appl Mater Interfaces*. <https://doi.org/10.1021/acsami.8b00743>

13. Rodygin KS, Werner G, Kucherov FA, Ananikov VP (2016) Calcium carbide: a unique reagent for organic synthesis and nanotechnology. *Chem Asian J* 11:965
14. Hosseini A, Seidel D, Miska A, Schreiner PR (2015) Fluoride-assisted activation of calcium carbide: a simple method for the ethynylation of aldehydes and ketones. *Org Lett* 17:2808
15. Li A, Song H, Xu X, Meng H, Lu Y, Li C (2018) Greener production process of acetylene and calcium diglyceroxide via mechanochemical reaction of CaC_2 and glycerol. *ACS Sustain Chem Eng* 6:9560
16. Xie Y, Huang Q, Huang B (2010) Chemical reactions between calcium carbide and chlorohydrocarbon used for the synthesis of carbon spheres containing well-ordered graphite. *Carbon* 48:2023
17. Yin C, Huang Q, Liu B et al (2007) Synthesis and TEM observation of fluffy hollow carbon spheres by FeCl_3 catalyzed solvent-thermal reaction. *Mater Lett* 61:4015
18. Dai C, Wang X, Wang Y, Li N, Wei J (2008) Synthesis of nanostructured carbon by chlorination of calcium carbide at moderate temperatures and its performance evaluation. *Mater Chem Phys* 112:461
19. Wu H, Wang X, Jiang L et al (2013) The effects of electrolyte on the supercapacitive performance of activated calcium carbide-derived carbon. *J Power Sources* 226:202
20. Zheng L, Wang Y, Wang X, Wang X, An H, Yi L (2010) The effects of surface modification on the supercapacitive behaviors of carbon derived from calcium carbide. *J Mater Sci* 45:6030
21. Kim K, Lee T, Kwon Y et al (2016) Lanthanum-catalysed synthesis of microporous 3D graphene-like carbons in a zeolite template. *Nature* 535:131
22. James SL, Friščić T (2013) Mechanochemistry. *Chem Soc Rev* 42:7494
23. Baláž P, Achimovičová M, Baláž M et al (2013) Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem Soc Rev* 42:7571
24. Ribas-Arino J, Marx D (2012) Covalent mechanochemistry: theoretical concepts and computational tools with applications to molecular nanomechanics. *Chem Rev* 112:5412
25. Takacs L (2018) Two important periods in the history of mechanochemistry. *J Mater Sci* 53:13324
26. Li Q, Li Y, Chen Y, Wu L, Yang C, Cui X (2018) Synthesis of γ -graphyne by mechanochemistry and its electronic structure. *Carbon* 136:248
27. Mahmoud AED, Stolle A, Stelter M (2018) Sustainable synthesis of high-surface-area graphite oxide via dry ball milling. *ACS Sustain Chem Eng* 6:6358
28. Baláž P, Baláž M, Achimovičová M, Bujňáková Z, Dutková E (2017) Chalcogenide mechanochemistry in materials science: insight into synthesis and applications (a review). *J Mater Sci* 52:11851
29. Dreizin EL, Schoenitz M (2017) Mechanochemically prepared reactive and energetic materials: a review. *J Mater Sci* 52:11789
30. Blázquez JS, Ipus JJ, Moreno-Ramírez LM et al (2017) Ball milling as a way to produce magnetic and magnetocaloric materials: a review. *J Mater Sci* 52:11834
31. Li Y, Meng H, Lu Y, Li C (2016) Efficient catalysis of calcium carbide for the synthesis of isophorone from acetone. *Ind Eng Chem Res* 55:5257
32. Li Y, Liu Q, Li W, Lu Y, Meng H, Li C (2017) Efficient destruction of hexachlorobenzene by calcium carbide through mechanochemical reaction in a planetary ball mill. *Chemosphere* 166:275
33. Battistini C, Crotti P, Macchia F (1981) Effect of an alkynyl group on the regio- and stereochemistry of the ring opening of 1, 2-epoxides. Ring-opening reactions of 1-ethynyl-1, 2-epoxycyclohexane. *J Org Chem* 46:434
34. Casco ME, Badaczewski F, Grätz S et al (2018) Mechanochemical synthesis of porous carbon at room temperature with a highly ordered sp^2 microstructure. *Carbon* 139:325
35. Thommes M, Kaneko K, Neimark AV et al (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). *Pure Appl Chem* 87:1051
36. Moyseowicz A, Śliwak A, Gryglewicz G (2016) Influence of structural and textural parameters of carbon nanofibers on their capacitive behavior. *J Mater Sci* 51:3431
37. Tang Z, Jiang S, Shen S, Yang J (2018) The preparation of porous carbon spheres with hierarchical pore structure and the application for high-performance supercapacitors. *J Mater Sci* 53:13987
38. Wang J-T, Chen C, Li H-D, Mizuseki H, Kawazoe Y (2016) Three-dimensional carbon allotropes comprising phenyl rings and acetylenic chains in $sp + sp^2$ hybrid networks. *Sci Rep* 6:24665
39. Baughman R, Eckhardt H, Kertesz M (1987) Structure-property predictions for new planar forms of carbon: layered phases containing sp^2 and sp atoms. *J Chem Phys* 87:6687
40. Zou L, Huang B, Huang Y, Huang Q, Wang Ca (2003) An investigation of heterogeneity of the degree of graphitization in carbon-carbon composites. *Mater Chem Phys* 82:654
41. Dresselhaus MS, Jorio A, Hofmann M, Dresselhaus G, Saito R (2010) Perspectives on carbon nanotubes and graphene Raman spectroscopy. *Nano Lett* 10:751
42. Xu W, Mao N, Zhang J (2013) Graphene: a platform for surface-enhanced Raman spectroscopy. *Small* 9:1206
43. Jiang L, Yan J, Xue R et al (2014) Hierarchically porous carbons with partially graphitized structures for high rate supercapacitors. *J Mater Sci* 49:363
44. Du H, Yang H, Huang C, He J, Liu H, Li Y (2016) Graphdiyne applied for lithium-ion capacitors displaying high power and energy densities. *Nano Energy* 22:615
45. Hu J, Kang Z, Li F, Huang X (2014) Graphene with three-dimensional architecture for high performance supercapacitor. *Carbon* 67:221
46. Wang Q, Yan J, Wang Y et al (2014) Three-dimensional flower-like and hierarchical porous carbon materials as high-rate performance electrodes for supercapacitors. *Carbon* 67:119
47. Wang Q, Yan J, Wei T et al (2013) Two-dimensional mesoporous carbon sheet-like framework material for high-rate supercapacitors. *Carbon* 60:481
48. Wang Y, Shi Z, Huang Y et al (2009) Supercapacitor devices based on graphene materials. *J Phys Chem C* 113:13103
49. Zhang L, Yang X, Zhang F et al (2013) Controlling the effective surface area and pore size distribution of sp^2 carbon materials and their impact on the capacitance performance of these materials. *J Am Chem Soc* 135:5921
50. Chang B-Y, Park S-M (2010) Electrochemical impedance spectroscopy. *Annu Rev Anal Chem* 3:207
51. Orazem ME, Tribollet B (2011) Electrochemical impedance spectroscopy, vol 48. Wiley, Hoboken
52. Zhang LL, Zhou R, Zhao X (2010) Graphene-based materials as supercapacitor electrodes. *J Mater Chem* 20:5983
53. Inagaki M, Konno H, Tanaike O (2010) Carbon materials for electrochemical capacitors. *J Power Sources* 195:7880
54. Zhang LL, Zhao XS (2009) Carbon-based materials as supercapacitor electrodes. *Chem Soc Rev* 38:2520
55. Yu Z, Tetard L, Zhai L, Thomas J (2015) Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy Environ Sci* 8:702
56. Wang Y, Song Y, Xia Y (2016) Electrochemical capacitors: mechanism, materials, systems, characterization and applications. *Chem Soc Rev* 45:5925

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.