

Electronic Supplementary Information

In-Situ Polymerization for Catalytic Graphitization of Boronated PAN Using Aluminum and Zirconium Containing Co-Catalysts

Taewoo Kim^{1,2}, Byoung-Suhk Kim², Tae Hoon Ko^{1,2*}, Hak Yong Kim^{1,2*}

¹Department of Nano Convergence Engineering, Jeonbuk National University, Jeonju-561756, Republic of Korea

² Department of Organic Materials and Textile Engineering, Jeonbuk National University, Jeonju-561756, Republic of Korea

***Corresponding author:**

*Tae Hoon Ko.: +82632732351, E-mail: kth1745@jbnu.ac.kr

*Hak Yong Kim, Tel.: +82632732351, E-mail: khy@jbnu.ac.kr

S1. Experimental Section

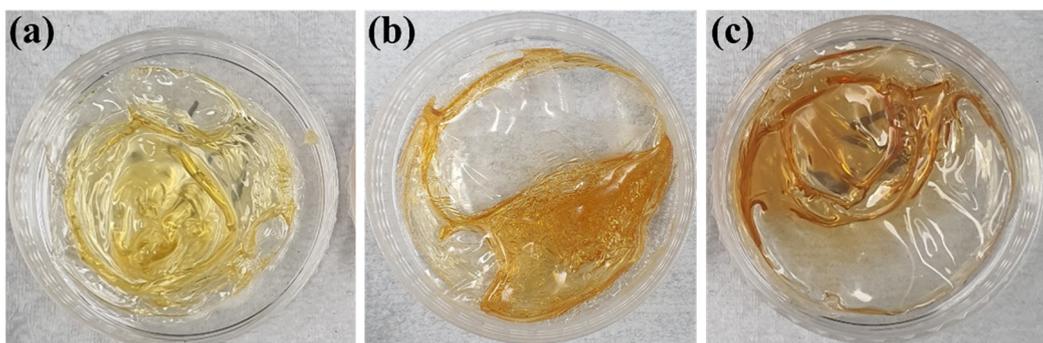
S1.1 Materials

Acrylonitrile ($\geq 99.0\%$), Itaconic acid ($\geq 99.0\%$), 1-Dodecanethiol ($\geq 98.5\%$), 2,2-Azobisisobutyronitrile (KOH, $\geq 98.0\%$), and DMSO ($\geq 99.0\%$) were obtained from Samchun, Republic of Korea. Dibutyl vinylboronate was purchased from the Tokyo chemical industry. aluminum triflate ($\text{Al}(\text{OTf})_3$) is purchased from Alfa Aesar and $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ are purchased from Sigma-Aldrich. All the chemical compounds were analytical grade and used without further purification.

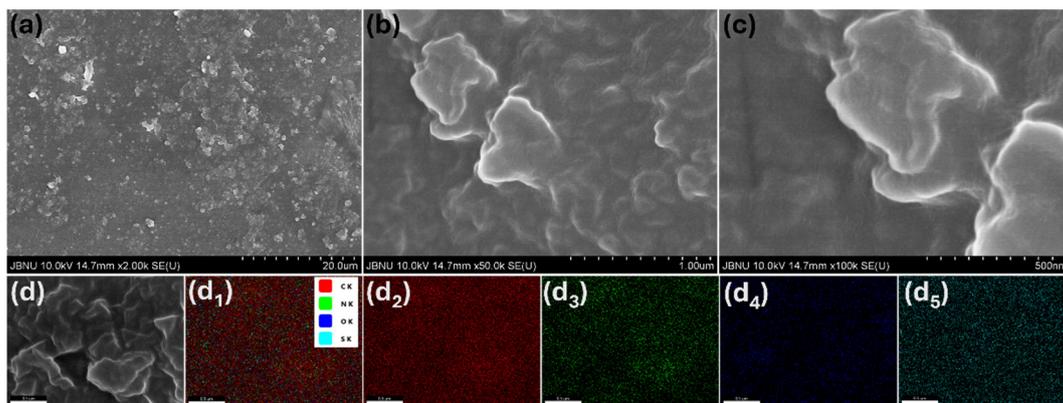
S2. Materials characterizations

The structural features, morphology, and elemental compositions of the synthesized materials were analyzed using advanced characterization techniques. The field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Germany), equipped with energy-dispersive X-ray spectroscopy (EDXS), provided high-resolution images of the surface morphology and elemental analysis of the prepared sample. The phase composition and crystalline structure of all the samples were studied using X-ray diffraction (XRD, Rigaku Corporation, Japan, $\text{CuK}\alpha$ radiation, wavelength $\lambda=0.154$ nm) in the 2θ range from $5-80^\circ$ at a scan rate of 2° min^{-1} . Additionally, Raman spectroscopy was utilized at room temperature with a RAMANtouch spectrometer from Nanophoton and an argon ion laser excitation source at 523 nm to analyze the degree

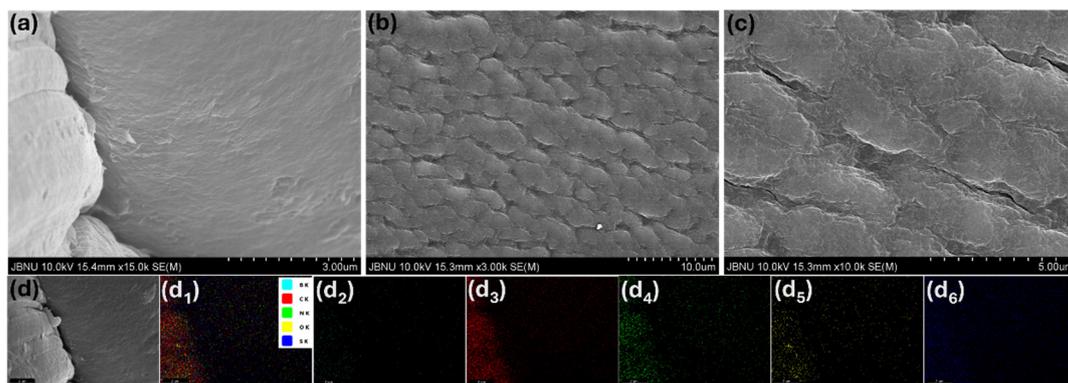
of graphitization, offering insights into the vibrational modes of carbon atoms, particularly through the presence of D (disordered) and G (graphitic) peaks. All characterization techniques, including FE-SEM, EDX, XRD analyses, and Raman, were conducted at the Center for University-wide Research Foundation (CURF) at Jeonbuk National University



FigureS1: Photographic image of (a) solidified B-PAN_{Al}, (b) solidified B-PAN_{Zr}, and (c) solidified B-PAN_{Al+Zr} polymer before graphitization.



FigureS2: (a, b, and c) FE-SEM image of PAN before graphitization, and (d, d₁, d₂, d₃, d₄, and d₅) its elemental mapping.



FigureS3: (a, b, and c) FE-SEM image B-PAN before graphitization, and (d, d₁, d₂, d₃, d₄, d₅, and d₆) its elemental mapping.

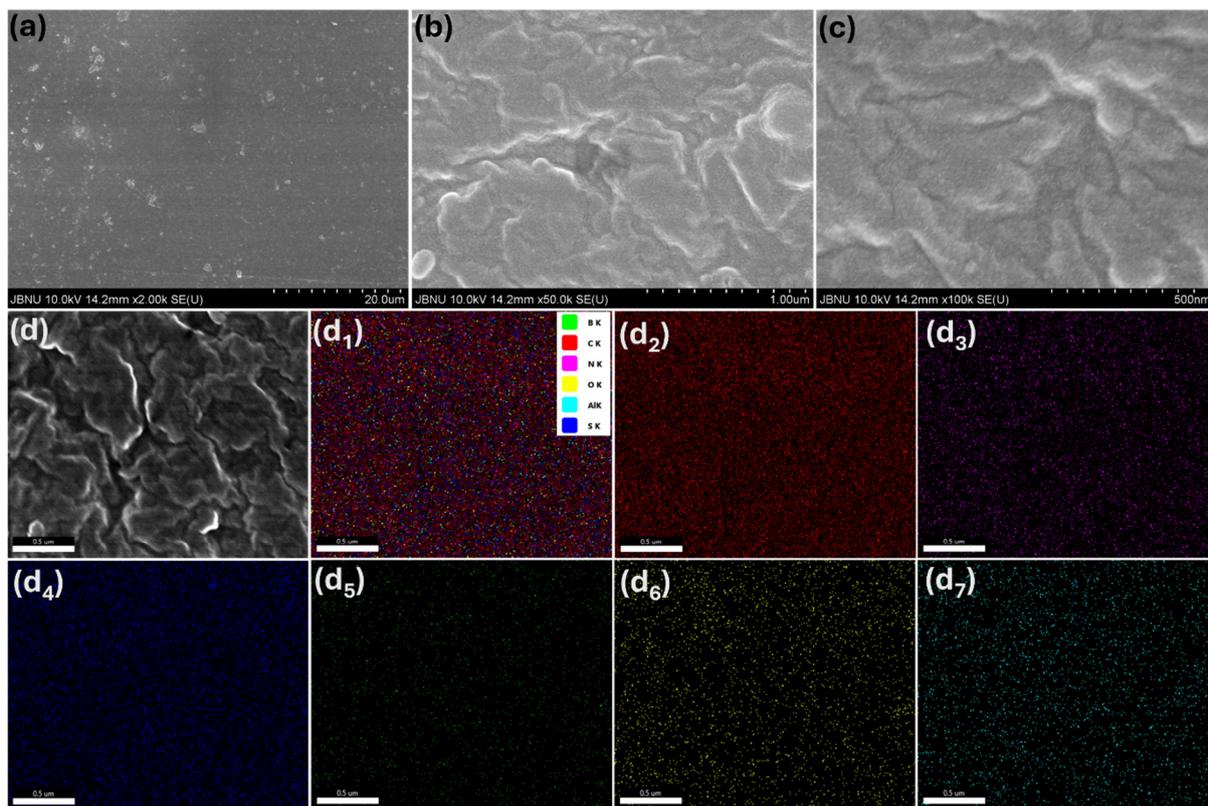


Figure S4: (a, b, and c) FE-SEM image B-PAN_{AI} before graphitization, and (d, d₁, d₂, d₃, d₄, d₅, d₅, and d₅) its elemental mapping.

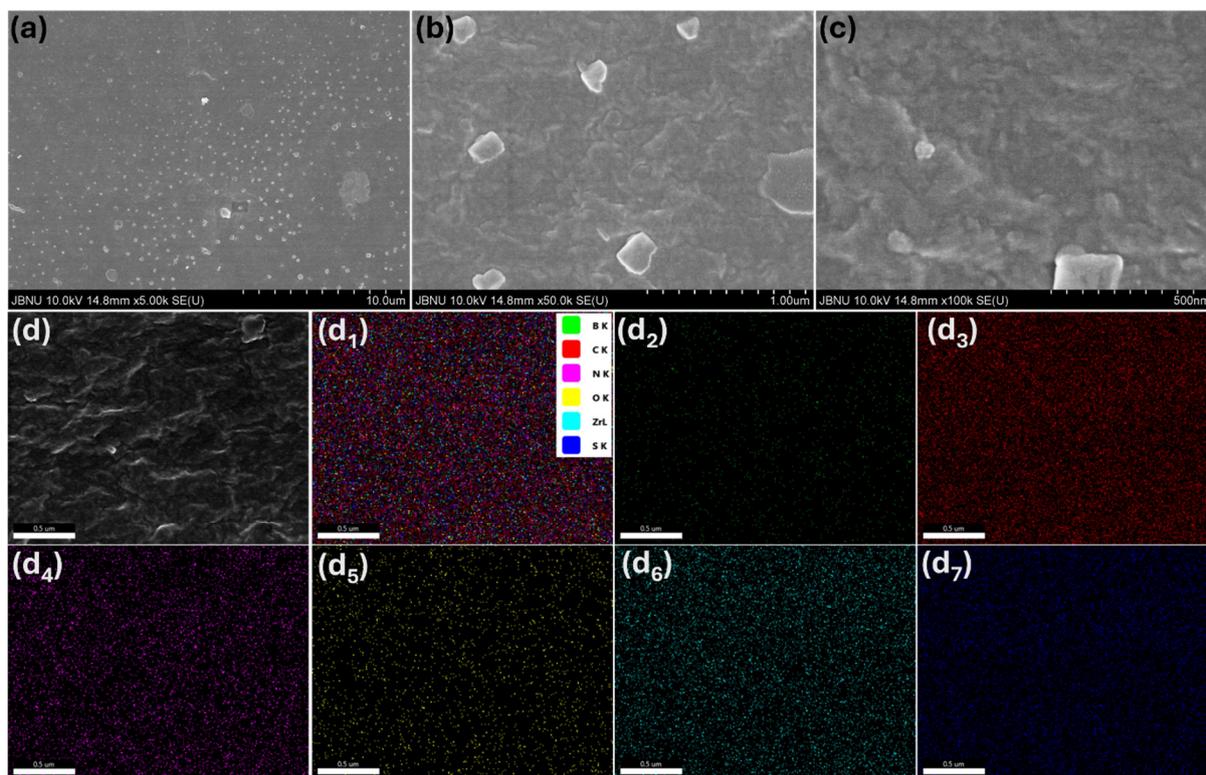
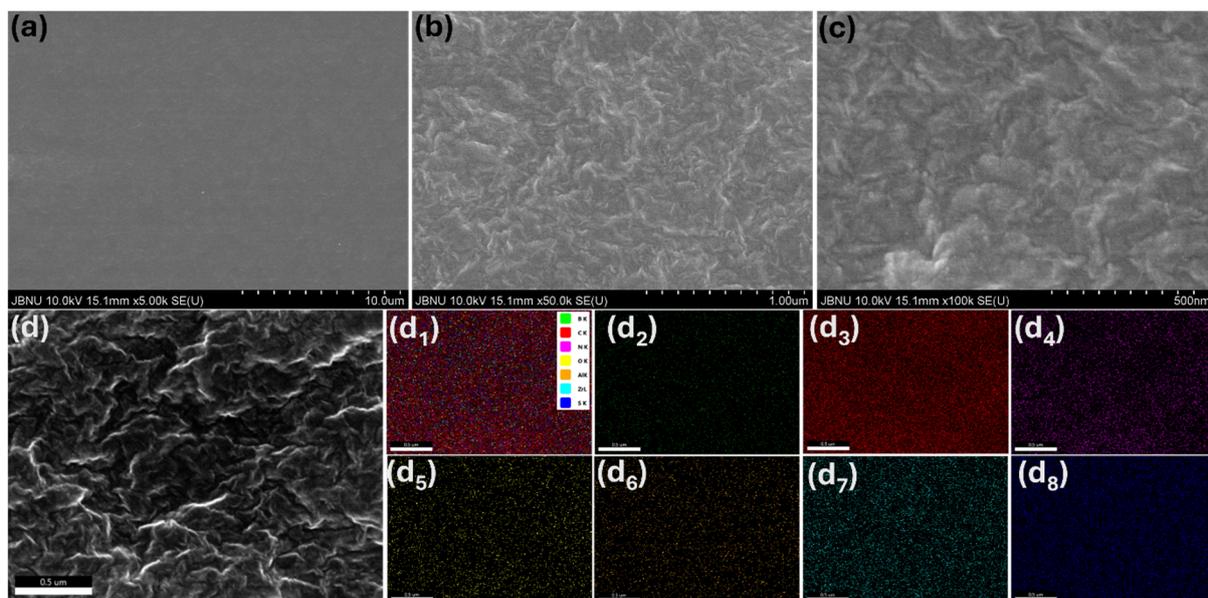
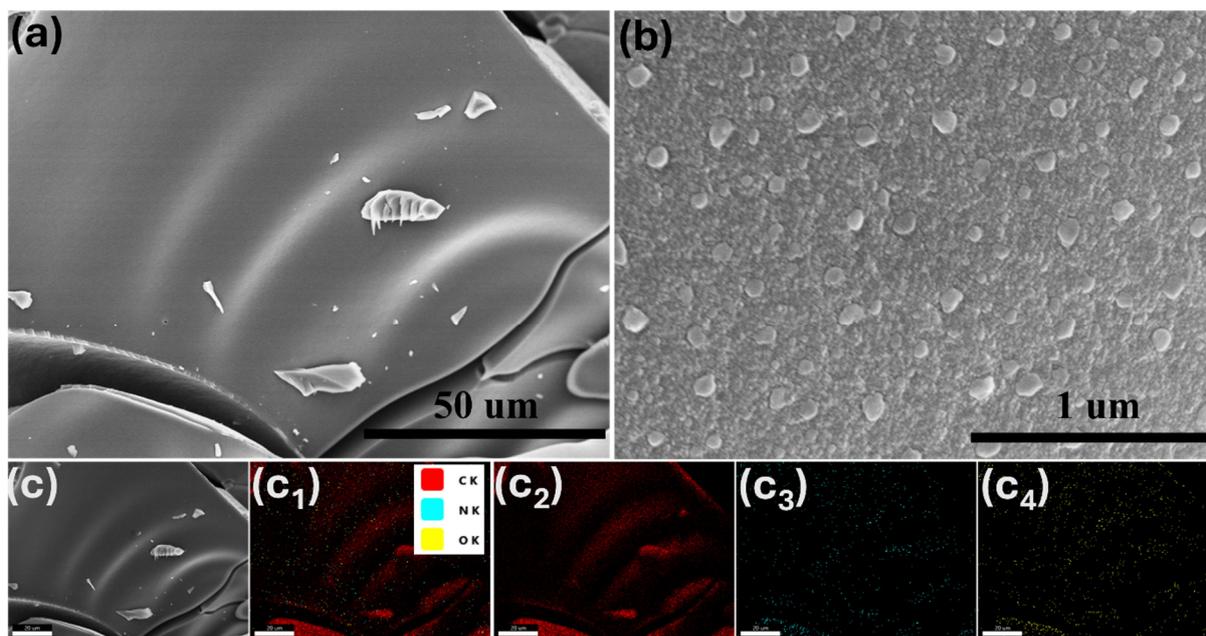


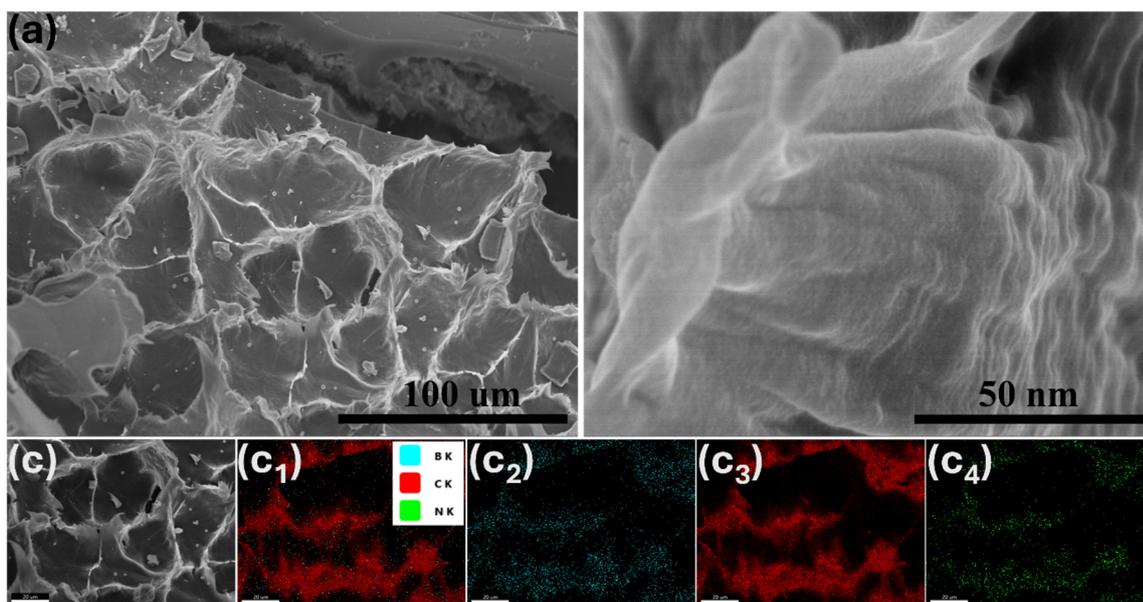
Figure S5: (a, b, and c) FE-SEM image B-PAN_{Zr} before graphitization, and (d, d₁, d₂, d₃, d₄, d₅, d₆, and d₇) its elemental mapping.



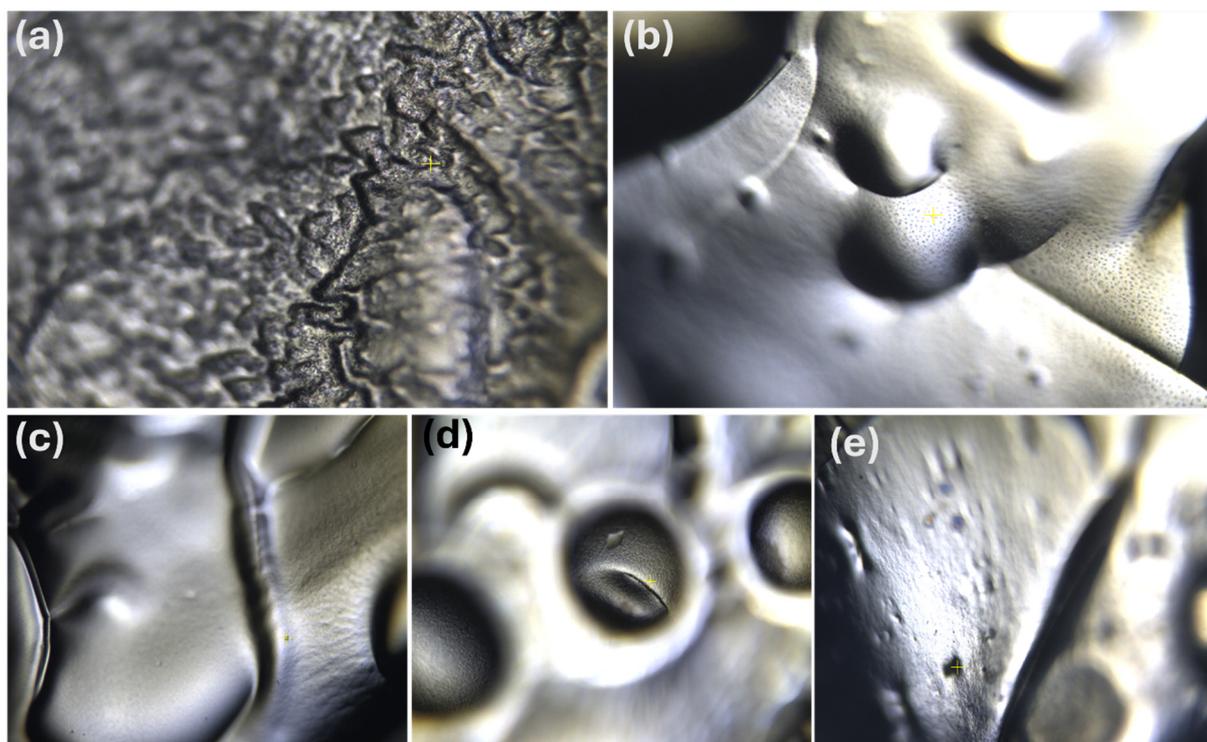
FigureS6: (a, b, and c) FE-SEM image B-PAN_{Al+Zr} before graphitization, and (d, d₁, d₂, d₃, d₄, d₅, d₆, d₇, and d₈) its elemental mapping.



FigureS7: (a, and b) FE-SEM image of PAN-GC after graphitization, and (c, c₁, c₂, c₃, and c₄) its elemental mapping.



FigureS8: (a, and b) FE-SEM image B-PAN after graphitization, and (c, c₁, c₂, c₃, and c₄) its elemental mapping.



FigureS9: Raman analysis image of: (a) PAN-GC, (b) B-PAN-GC, (b) B-PAN_{Al}-GC, (c) B-PAN_{Zr}-GC, (d) B-PAN_{Al+Zr}-GC.

Table S1: A comparison table including terms of temperature, and graphitization degree in catalytic graphitization of carbon-based materials.

S.N.	Material Name	Method	Temperature of graphitization (°C)	I _D /I _G	Reference
1.	PAN-based CFs	Conventional (High-temperature carbonization)	3000	0.8	[1]
2.	PAN/CNT	Conventional (High-temperature carbonization)	1700	1.5	[2]
3.	PAN-based CNF HTT 1000	Conventional (carbonization)	1000	1.39	[3]
4.	C/C composite	Conventional (High-temperature carbonization)	3000	1.5	[4]
5.	CNFs from PAN/lignin (E7 carbonized)	Conventional (carbonization)	1000	2.56	[5]
6.	B-PAN_{Al+Zr}-GC	In-situ polymerization with Al+Zr Co-catalysts	1250	0.889	This work

References:

1. Samoilov, V.M.; Verbets, D.B.; Bubnenkov, I.A.; Stepanyova, N.N.; Nikolaeva, A.V.; Danilov, E.A.; Ponomareva, D.V.; Timoshchuk, E.I. Influence of Graphitization Conditions at 3000°C on Structural and Mechanical Properties of High-Modulus Polyacrylonitrile-Based Carbon Fibers. *Inorganic Materials: Applied Research* **2018**, *9*, 890-899, doi:10.1134/S2075113318050258.

2. Ali, A.B.; Slawig, D.; Schlosser, A.; Koch, J.; Bigall, N.C.; Renz, F.; Tegenkamp, C.; Sindelar, R. Polyacrylonitrile (PAN) Based Electrospun Carbon Nanofibers (ECNFs): Probing the Synergistic Effects of Creep Assisted Stabilization and CNTs Addition on Graphitization and Low Dimensional Electrical Transport. *Carbon N. Y.* **2021**, *172*, 283.
3. Kim, C.; Park, S.-H.; Cho, J.-I.; Lee, D.-Y.; Park, T.-J.; Lee, W.-J.; Yang, K.-S. Raman spectroscopic evaluation of polyacrylonitrile-based carbon nanofibers prepared by electrospinning. *Journal of Raman Spectroscopy* **2004**, *35*, 928-933, doi:<https://doi.org/10.1002/jrs.1233>.
4. Feng, J.; Hu, P.; Cheng, Y.; Wang, Y.; Qu, N.; Zheng, L.; Xun, L.; Zhang, C.; Zhao, G.; Zhang, X. Polyarylacetylene as a novel graphitizable precursor for fabricating high-density C/C composite via ultra-high pressure impregnation and carbonization. *Journal of Materials Science & Technology* **2024**, *182*, 198-209, doi:<https://doi.org/10.1016/j.jmst.2023.09.044>.
5. Cintra, I.L.R.; Baldan, M.R.; Anjos, E.G.R.; Silva, T.F.; Guerrini, L.M.; Rezende, M.C.; Botelho, E.C. Processing and characterization of carbon nanofibers obtained from PAN/lignin blends processed by electrospinning. *Polymer Engineering & Science* **2023**, *63*, 1246-1262, doi:<https://doi.org/10.1002/pen.26279>.