Letter

Controllable fabrication of elastic foam with ordered helical carbon nanofiber arrays

Siren Guo¹, Xialong Cai¹, Rongling Zhang¹, Wei Feng¹, Hanjun Wei², Ying Li^{1,3*}

¹School of Mechanical Engineering, Chengdu University, 2025 Chengluo Avenue, 610106 Chengdu, China
 ²Institute for Advanced Study, Chengdu University, 2025 Chengluo Avenue, 610106 Chengdu, China
 ³Department of Physics, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Received 16 October 2024; accepted in revised form 19 November 2024

Abstract. In this work, a foam composed of helical carbon nanofiber arrays was successfully synthesized via chemical vapor deposition. By controlling synthesis parameters including the synthesising temperature and gas flow rate, carbon nanofibers with straight, kinked, and spring-like morphologies were obtained. Adjusting the precursor feed led to the formation of foams with well-ordered carbon nanofiber structures. The nanofibers exhibit diameters ranging from 98 to 175 nm and lengths extending to the centimetre scale. Experimental results confirm that these fibers are organic carbon nanofibers, attributed to low-temperature catalytic synthesis. Structural characterization reveals that the catalyst assumes a regular polyhedral shape and becomes embedded within the fibers, which symmetrically grow from both faces of the catalyst. Structural analysis indicate that the carbon nanofibers are hollow, multi-walled structures with numerous defects. The resulting foam demonstrates porous, along with excellent elasticity and high mechanical strength.

Keywords: fibrous assemblies, nanofiber, foam, advanced foam applications, helical carbon nanofiber arrays

1. Introduction

Carbon nanofibers (CNFs) have attracted considerable attention as a novel nanomaterial due to their outstanding mechanical properties, electrical conductivity, and thermal stability [1, 2]. CNF synthesis methods include flame synthesis [3], arc discharge [4], and chemical vapor deposition(CVD) [5]. Among these, CVD is widely employed for CNF production due to its simplicity, high material purity, and controllable structure [6]. By adjusting reaction parameters such as temperature, gas flow rate, and catalyst selection, CVD can yield CNFs with diverse morphologies and structures. However, traditional CNFs, often characterized by small aspect ratios, are typically produced as powders that lack self-supporting properties and are difficult to disperse in composite matrices, limiting their practical applications. Macroscopic CNF assemblies with larger aspect ratios and

self-supporting characteristics can be viewed as predispersed composite reinforcements with percolating networks, simplifying processing and enhancing application efficiency. Moreover, CNFs with helical structures offer unique functionalities compared to conventional straight fibers, such as cross-polarization in electromagnetic fields. When arranged in orderly arrays, these periodic structures can further enhance material properties, improving elasticity in mechanical applications and extending functionality in structural electromagnetic interference shielding [7]. In this study, macroscopic carbon nanofiber foam with high aspect ratios were successfully fabricated via the CVD method by precisely adjusting the synthesis parameters. The fibers within these assemblies were arranged in well-ordered arrays, with straight, twisted, and spring-like morphologies also obtained. A comprehensive investigation will be conducted to

express polymer letters

^{*}Corresponding author, e-mail: <u>liying@cdu.edu.cn</u> © BME-PT

analyze their microstructure, surface characteristics, and mechanical properties. This research provides valuable insights into the fabrication of advanced carbon fibers and their multifunctional applications.

2. Experimental

2.1. Materials

The materials includes: copper(II) chloride dihydrate $(CuCl_2 \cdot 2H_2O, AR, Cologne Chemical Co., Ltd, Chengdu, China), Potassium sodium tartrate tetrahydrate (C₄H₄O₆KNa \cdot 4H₂O, AR, Cologne Chemical Co., Ltd, Chengdu, China), ceramic boat (Puxi Optical Components Co., Ltd, Yixing, China), high-purity argon (Ar, Chaohong Industrial Gas Co., Ltd, Chengdu, China) and acetylene gas (C₂H₂, Chaohong Industrial Gas Co., Ltd, Chemical reagents were used as received without further purification.$

2.2. Preparation process of arrayed carbon nanofibers

ACNFs were synthesized through acetylene decomposition on a novel precursor derived from precipitation/sol-gel/reduction techniques via CVD [8]. The preparation flowchart is shown in Figure 1. Firstly, 100 mL of 0.1 mol/L copper(II) chloride dihydrate and potassium sodium tartrate solutions were prepared in deionized water, respectively. The copper chloride solution was then gradually added to the potassium sodium tartrate solution using a pipette, with continuous stirring for 30 min. The resulting compound is copper tartrate precursor, with the primary chemical reactions occurring as shown in the Equation (1) [9]:

$$CuCl_2 \cdot 2H_2O + NaKC_4H_4O_6 \cdot 4H_2O \rightarrow$$

$$\rightarrow CuC_4H_4O_6 + NaCl + KCl + 6H_2O$$
(1)

The resulting copper tartrate was subsequently dried in an oven at 80 °C for 6 h. 0.1 mg of the obtained precursor was spread in a ceramic boat and placed in a tubular furnace under an argon atmosphere. The temperature was raised to $280 \degree C/380 \degree C$ with a heating rate of $1 \degree C/min$ and maintained for 30 min. Subsequently, the argon was replaced by acetylene and kept for 2 h to obtain arrayed carbon nanofibers. In this reaction, acetylene gas decomposes, and the resulting carbon atoms are adsorbed by the nanocopper catalyst, which facilitates their polymerization to form carbon nanofibers. This reaction can be expressed by the Equations (2) and (3) [10]:

$$\operatorname{CuC}_{4}\operatorname{H}_{4}\operatorname{O}_{6}^{6} \xrightarrow{\Delta} \operatorname{Cu} + \operatorname{CO}_{2} + \operatorname{H}_{2}\operatorname{O}$$
 (2)

$$Cu + 2C_2H_2 \xrightarrow{\Delta} C_nH_m + Cu_x$$
 (3)

It is important to note that the specific carbon nanostructures formed depend on several factors, including the reaction temperature, gas flow rate, and the particle size of the copper catalyst [11]. For example, Jin et al. [12] reported that variations in temperature can lead to different fiber morphologies, which is consistent with the structure of SCNFs observed by us at 380 °C. Jian et al. [13] suggested that spiral-tapered nanofibers are more easily fabricated at lower heating rates. In this study, a temperature setting of 280 °C resulted in the formation of twisted carbon nanofibers (TCNFs), while a temperature of 380 °C produced spring-shaped carbon nanofibers (SCNFs). For the preparation of CNFs, a heating rate of 5 °C per minute was applied, with a reaction temperature maintained at 280 °C.

2.3. Characterization

The morphology of the prepared samples was examined using a scanning electron microscope (SEM, JEOL JIB-4700F, Japan). To further investigate the internal structure, transmission electron microscopy (TEM, JEOL JEM-F200, Japan) was employed. X-ray diffraction (XRD) was conducted using a Bruker D8 Advance instrument with Cu Ka radiation $(\lambda \sim 1.54 \text{ Å})$ to analyze the crystallinity and phase composition of the ACNFs. Scans were performed over a 2θ range of 5 to 80° with a step size of 0.02° . Raman spectra, excited at a wavelength of 532 nm, were collected using a Renishaw InVia Raman spectrometer (UK) to analyze the structure of the carbon nanofibers. Additionally, the Raman spectra of arrayed carbon nanofibers were recorded with the same Raman spectrometer to provide further structural insights. Fourier Transform Infrared Spectroscopy (FT-IR, Bruker Tensor II, Germany) were conducted with spectral resolution of 2 cm^{-1} .

3. Results and discussion

Figure 2a presents the SEM image of copper nanoparticles formed by decomposing 0.1 mg of copper tartrate at a heating rate of 1 °C/min to 380 °C. The



Figure 1. The synthesising process diagram of CNFs, TCNFs, and SCNFs.

surface appears relatively rough, with irregularly shaped small particles and noticeable aggregation. In Figure 2b, nanocopper particles are clearly seen to adopt various polyhedral forms, including spherical and cubic shapes. The high-resolution TEM image in Figure 2c further identifies the (111) and (200) crystal planes of the nanocopper. The size and morphology of these Cu particles are critical factors influencing the resulting carbon nanostructure variations in both size and shape [13]. Using acetylene as the carbon source and nanocopper as the catalyst, densely packed and well-arrayed carbon nanofibers (ACNFs) were synthesized within a porcelain boat (Figure 2d). These fibers exhibit surface roughness, likely due to the deposition of nanoscale particles. As shown in Figure 2e, the ACNFs are arranged in an orderly way, forming a distinct array structure, indicating effective control of the growth conditions during synthesis. Additionally, the interior of the sample exhibits a distinct porous structure, resembling foam. Figures 2f–2h display the various morphologies of carbon nanofibers obtained by adjusting



Figure 2. Synthesis of ACNFs. SEM images of a) catalyst nano copper. TEM images of b) and c) catalyst nano copper, d) optical images of ACNFs. SEM images of e) ACNFs. SEM images of f) CNFs, g) TCNFs and h) SCNFs.

experimental parameters. At the microscopic level, the fibers exhibit diverse shapes. For instance, heating 0.1 mg of copper tartrate at a rate of 5 °C/min to 280 °C produced CNFs. As shown in Figure 2f, the CNFs have diameters ranging from 110 to 180 nm. In Figure 2g, TCNF represents the product obtained by heating 0.1 mg of copper tartrate at a rate of 1 °C/min to 280 °C, with tubular diameters ranging from 75 to 98 nm and helical diameters from 110 to 140 nm. By contrast, Figure 2h depicts the SCNF morphology, which is more coiled and was obtained by heating 0.1 mg of copper tartrate at a rate of 1 °C/min to 380 °C. The tube diameters ranging from 360 to 400 nm, helical diameters of 1.3 to 2.5 µm, and pitch lengths varying from 40 nm to 1.3 μ m. The different experimental conditions, such as temperature, reaction time, and heating rate, along with the corresponding key morphological results, such as fiber shape and diameter, are summarized in Table 1. Detailed examination of the local structure of ACNFs (Figure 3a) reveals a smooth surface morphology. Figure 3a1-3a4 shows the ACNFs obtained

 Table 1. Effect of reaction parameters on the structure of arrayed carbon nanofibers.

Fiber type	Reaction temperature [°C]	Heating rate [°C/min]	Reaction time [h]	Fiber diameter [nm]
TCNFs	280	1	2.0	75~98
SCNFs	380	1	2.0	360~400
CNFs	280	3	2.0	110~180

by heating 0.1 mg of copper tartrate at a heating rate of 5 °C/min to 280 °C. The elemental mapping indicates that the ACNFs surface is composed of C, Cu, and O elements. Carbon, as the primary component of the nanofibers, is present in the highest proportion. The detectable Cu arises from nano copper, used as a catalyst during synthesis, which may have either not fully reacted or become encapsulated within the carbon fibers, as indicated by energy dispersive Xray spectroscopy (EDS) analysis. The presence of O is attributed to oxidation upon exposure to air. SCNFs were obtained at a lower heating rate and a higher reaction temperature. Figure 3b presents a



Figure 3. Structure analysis of ACNFs. SEM images of a) ACNFs. a1)–(a4) colour mix and elemental distribution maps of the ACNFs. b) TEM images of catalyst particles located at the node of SCNFs. b1) HRTEM image of a catalyst particle. c), d) TEM images of a single TCNF. d1), d2) HRTEM image of a TCNF. d3) SAED pattern of TCNF.

structural analysis of an individual SCNF through TEM, showing a catalyst with a regular elliptical shape, symmetrically aligned perpendicular to the fiber growth direction. High-resolution TEM (HRTEM) images (Figure 3b1) reveal distinct lattice fringes in the catalyst particles, with an interplanar spacing of 0.22 nm. Figure 3c shows a TEM image of a single TCNF without a catalyst, displaying a hollow tube with an opening diameter of 87.7 nm. The outer surface of the TCNF features a multi-layered carbon structure, while HRTEM images (Figure 3d1) highlight well-ordered, long-range parallel carbon layers on the exterior surface. In contrast, the interior of the TCNF exhibits a more disordered structure, likely due to variations in temperature and reaction atmosphere during synthesis, leading to irregular carbon atom arrangements and complex structural formation. Furthermore, structural defects are visible in the graphite particles of the carbon nanofibers (Figure 3d2), including lattice distortions and short-range ordered lattice fringes [14]. The selected area electron diffraction (SAED) pattern in Figure 3d3 shows diffuse diffraction rings, indicating the presence of defects and disorder within the TCNFs, consistent with the observations from HRTEM images.

The ACNFs prepared by heating at a rate of 1 °C/min to 380 °C were subsequently characterized for their structure. Figure 4a displays the infrared spectrum of ACNFs, revealing key chemical structures. Distinct absorption peaks appear at approximately 3450, 2920, and 1620 cm⁻¹ in the FTIR spectrum, corresponding to the stretching vibrations of hydroxyl (O–H), hydrocarbon (C–H), and the bending vibrations of conjugated double bonds (C=C), respectively. The O–H group at 3400 cm^{-1} is likely attributed to moisture adsorption. Additionally, the peaks at 2920 and 1620 cm⁻¹ suggest the presence of organic components within the carbon nanofibers [15]. Raman spectroscopy (Figure 4b) further elucidates structural information, with characteristic graphite peaks (D and G bands) located at 1340 and 1622 cm⁻¹, respectively. The $I_{\rm D}/I_{\rm G}$ ratio of 1.96 indicates a high degree of defects and amorphous carbon in the ACNFs [16]. The XRD pattern (Figure 4c) provides insight into the phase structure, where the prominent peak near 24° corresponds to the (002) plane, indicative of good graphitization. Peaks at 36 and 43° are associated with CuO and Cu₂O phases, resulting from the oxidation of the Cu phase by O₂ [17]. ACNF exhibits the elastic characteristics of foam, as shown in Figures 4d-4f. After compression



Figure 4. Structure analysis of ACNFs. a) FT-IR spectrum, b) Raman spectra and c) XRD of ACNFs. d)–f) The elastic properties of ACNFs.

(*e.g.*, by finger pressure), it quickly recovers its original shape, demonstrating the excellent elasticity of the ACNF foam.

4. Conclusions

In conclusion, we successfully synthesized carbon nanofiber (CNF) arrays via the chemical vapor deposition (CVD) method. By fine-tuning the reaction parameters, we obtained helical-structured SCNFs and TCNFs, both of which exhibited the characteristic multilayered hollow structure. The extended length of these fibers contributes to the material's porosity and self-supporting nature, resulting in a product with a highly elastic foam-like architecture. Furthermore, the arrayed arrangement of fibers in the final product imparts exceptional mechanical strength and elasticity to the arrays, making them highly promising for applications in flexible electronics, wearable devices, and other technologies requiring high-elasticity materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 52202083), Sichuan Science and Technology Program (No. 2024YFHZ0265), the Open Project of High-end Equipment Advanced Materials and Manufacturing Technology Laboratory (No. 2023KFKT0005).

References

[1] Afonnikova S. D., Gilin D. A., Veselov G. B., Trenikhin M. V., Shubin Y. V., Ayupov A. B., Mishakov I. V., Vedyagin A. A.: Hydrogen as the key factor controlling the efficiency of carbon nanofibers synthesis from ethylene. Fuel, **375**, 132542 (2024). https://doi.org/10.1016/j.fuel.2024.132542

[2] Santos P., Silva A. P., Reis P. N. B.: The effect of carbon

- nanofibers on the mechanical performance of epoxybased composites: A review. Polymers, **16**, 2152 (2024). https://doi.org/10.3390/polym16152152
- [3] Hsu H-L., Lin T-H., Huang C-M., Chiu W-C., Huang W-C., Hou S-S.: *In situ* flame-synthesis of nanostructured carbon materials *via* facile alcohol bunsen burner. Arabian Journal of Chemistry, **17**, 105654 (2024). https://doi.org/10.1016/j.arabjc.2024.105654
- [4] Madhurima V. P., Kumari K., Jain P. K.: Synthesis and study of carbon nanomaterials through arc discharge technique for efficient adsorption of organic dyes. Diamond and Related Materials, 141, 110538 (2024). https://doi.org/10.1016/j.diamond.2023.110538

[5] Wang Y., Wen Y., Su W., Fu W., Wang C-H.: Carbon deposition behavior on biochar during chemical vapor deposition process. Chemical Engineering Journal, 485, 149726 (2024).

https://doi.org/10.1016/j.cej.2024.149726

- [6] Zhang L., Jing H., Gao Y., Yu Z., Liu Y.: Enhancement of the tensile properties of cement mortar composites with nanoadditives produced by chemical vapor deposition. Case Studies in Construction Materials, 21, e03469 (2024). https://doi.org/10.1016/j.cscm.2024.e03469
- [7] Vahdani M., Mirjalali S., Razbin M., Moshizi S. A., Payne D., Kim J., Huang S., Asadnia M., Peng S., Wu S.: Bio-disintegrable elastic polymers for stretchable piezoresistive strain sensors. Advanced Sustainable Systems, 8, 2300482 (2024). https://doi.org/10.1002/adsu.202300482
- [8] Meng F., Wang Y., Wang Q., Xu X., Jiang M., Zhou X., He P., Zhou Z.: High-purity helical carbon nanotubes by trace-water-assisted chemical vapor deposition: Large-scale synthesis and growth mechanism. Nano Research, **11**, 3327–3339 (2018). https://doi.org/10.1007/s12274-017-1897-4
- [9] Qin Y., Zhang Z., Cui Z.: Helical carbon nanofibers prepared by pyrolysis of acetylene with a catalyst derived from the decomposition of copper tartrate. Carbon, 41, 3072–3074 (2003).

https://doi.org/10.1016/s0008-6223(03)00435-4

[10] Que L., Han R., Dai M., Su J., Guo Y., Xu X., Jian X., Zhou Z.: Powder-metallurgical construction of graphenelike nanosheet network reinforced Cu composites towards balanced high-performance. Carbon, 225, 119121 (2024).

https://doi.org/10.1016/j.carbon.2024.119121

- [11] Lu W., He T., Xu B., He X., Adidharma H., Radosz M., Gasem K., Fan M.: Progress in catalytic synthesis of advanced carbon nanofibers. Journal of Materials Chemistry A, 5, 13863–13881 (2017). https://doi.org/10.1039/c7ta02007d
- [12] Jin Y., Chen J., Fu Q., Li B., Zhang H., Gong Y.: Lowtemperature synthesis and characterization of helical carbon fibers by one-step chemical vapour deposition. Applied Surface Science, **324**, 438–442 (2015). https://doi.org/10.1016/j.apsusc.2014.10.107
- [13] Jian X., Jiang M., Zhou Z., Yang M., Lu J., Hu S., Wang Y., Hui D.: Preparation of high purity helical carbon nanofibers by the catalytic decomposition of acetylene and their growth mechanism. Carbon, 48, 4535–4541 (2010).

https://doi.org/10.1016/j.carbon.2010.08.035

[14] Zuo X., Zhang Y., Tian J., Sun C., Wen N., Zhang H., Li C., Fan Z., Pan L.: Fabrication of micro mesopores on spiral carbon nanocoils and simultaneous doping with oxygen to expand microwave absorption bandwidth. Advanced Functional Materials, in press, 2410224 (2024).

https://doi.org/10.1002/adfm.202410224

[15] Tseng T-R., Yang C-H., Lu H-C., Liu C-P., Cheng B-M.: Analysis of carbon materials with infrared photoacoustic spectroscopy. Analytical Chemistry, 96, 10732– 10737 (2024).

https://doi.org/10.1021/acs.analchem.4c01797

[16] Shi Y., Li X., Liu Q., Zhang C., Guo W., Tian K., Elias R., Wang H.: High-yield carbon derived from commercial phenol–formaldehyde resin for broadband microwave absorption by balancing conductivity and polarization loss. Journal of Materials Science, 58, 7048– 7059 (2023).

https://doi.org/10.1007/s10853-023-08465-9

[17] Tang N. J., Zhong W., Au C. T., Gedanken A., Yang Y., Du Y. W.: Large scale synthesis, annealing, purification, and magnetic properties of crystalline helical carbon nanotubes with symmetrical structures. Advanced Functional Materials, 17, 1542–1550 (2007). https://doi.org/10.1002/adfm.200600767