Electronic Supplementary Information

Space-confined assembly of all-carbon hybrid fibers for capacitive energy storage: Realizing built-to-order concept for micro-supercapacitors

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Figure S1. A typical AFM image of GO sheets used in this work. Height profiles on the right side were obtained along the marked straight lines in different colors on the AFM image. Scale bar in the AFM image is $10 \,\mu$ m.



Figure S2. (a) Photograph of rGO fibers synthesized using space confinement fillers containing cylindrical channels of 0.5 mm in diameter. (b) SEM images of the dried rGO fiber with its fracture end area shown in the inserted image. (c) An enlarged view of fracture end area of the rGO fiber.



Figure S3. Stress-strain profiles of rGO fiber and rGO/MWCNT hybrid fibers in five different diameters.



Figure S4. (a-e) SEM images of rGO/MWCNT hybrid fibers in different diameters with their EDX element (C, O and N) mappings in inserted images: (a) fiber-1, (b) fiber-2, (c) fiber-3, (d) fiber-4, and (e) fiber-5.



Figure S5. (a) XPS spectra of rGO/MWCNT hybrid fibers in different diameters. (b) C_{1s} spectrum and (c) N_{1s} spectrum of fiber-2.



Figure S6. Electrochemical performances of fiber-2 and the rGO fiber measured using a three-electrode cell in 1 M H_2SO_4 electrolyte. (a) CV curve measured at the scan rate of 5 mV s⁻¹. GC curves of the (b) rGO fiber and (c) fiber-2 at different current densities. (d) Specific volumetric capacitance of fiber-2 and the rGO fiber as a function of charge/discharge current density calculated from their GC curves.

Fiber	Fiber	Density of	Volume of a	Total volume of a
	diameter	fiber (g cm ⁻³)	single fiber [*]	two-fiber symmetric
	(µm)		(cm^{3}/cm)	micro-SC [#] (cm ³ /cm)
rGO	42	0.68	1.39×10 ⁻⁵	3.8×10 ⁻⁵
fiber-1 [§]	30	1.06	7.07×10 ⁻⁶	1.9×10 ⁻⁵
fiber-2	48	0.98	1.81×10 ⁻⁵	4.1×10 ⁻⁵
fiber-3	121	0.95	1.15×10^{-4}	2.7×10^{-4}
fiber-4	188	0.87	2.78×10^{-4}	6.3×10 ⁻⁴
fiber-5 [§]	236	0.83	4.37×10 ⁻⁴	9.2×10 ⁻⁴

Table S1 Geometric dimension of fibers and fiber-based micro-SCs

^{*}The volume of a single fiber was calculated by considering the fiber as a cylinder with a length of 1 cm.

[#]The total volume a two-fiber symmetric micro-SC includes the volume of two fibers (1 cm in length) and the surrounding PVA/H_3PO_4 gel electrolyte.

[§] For fiber-1 and fiber-5, fibers in other lengths of 0.5, 2.5, and 5 cm were also used.



Figure S7. CV curves of fiber-based solid-state micro-SCs assembled using rGO fiber and rGO/MWCNT hybrid fibers in different diameters. The CV curves were measured at the scan rates from 2 to 50 mV/s.



Figure S8. CV curve of fiber-based solid-state micro-SCs assembled using rGO fiber and fiber-2 at 5 mV s⁻¹.



Figure S9. GC curves of the fiber-based solid-state micro-SCs assembled using the rGO fiber and rGO/MWCNT hybrid fibers in different diameters. The GV curves were measured at different charge/discharge current densities specified in the individual figures.



Figure S10. Specific volumetric capacitances of hybrid carbon fibers calculated from their GC curves as a function of the volumetric charge/discharge current density.



Figure S11. (a) Nyquist plot of hybrid carbon fibers in different diameters with frequency from 10 kHz to 0.01 Hz. (b) Nyquist plot normalized based on the volume of each fiber. The inset shows the enlarged normalized curves of fiber-1 and fiber-2.



Figure S12. GC curves the fiber-based micro-SCs assembled using the rGO/MWCNT hybrid (a) fiber-1 and (b) fiber-5 in different lengths of 0.5, 1, 2.5, and 5 cm. All measurements were carried out under the same volumetric current density of about 85 mA cm⁻³. The actual currents used were adjusted according to the total volume of each micro-SC (Table S1).