Electronic Supplementary Information

The electrochemical performances of CB, CB-9, GCB, and GCB-24 as the anode materials for lithium ion batteries (LIBs) were also measured with a two-electrode system that was described in previous work of our group¹. Lithium sheets were used as the counter electrode, and composite electrode comprising active mass (90 wt%) and poly (vinylidene difluoride) (PVDF, 10 wt%) binder was used as working electrode. 1 M LiPF6 solution in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) from Merck Co. was used as electrolyte. It should be noted that for no other conduction additives were added in our testing systems thus the intrinsic electrochemical properties of the electrode materials could be precisely carried out. The cells were galvanostatically charged and discharged in the voltage range from 0.01 to 2.50 V vs. Li/Li⁺ at the current density of 50 m Ag⁻¹. After 20 cycles, the voltage of the cells were charged to 2.0 V and the electrochemical impedance spectroscopy (EIS) was further taken on an electrochemical workstation (CHI660B) using the frequency response analysis. The impedance spectra were obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz. Fitting of impedance spectra to the proposed equivalent circuit was performed by the code Zview.



Figure S1 (a) Equivalent circuit model for LIB, (b) Eis spectra of CB, GCB, CB-9 and GCB-24, and (c) detail of the marked area in Figure S1 (b).

 R_b is the electrolyte resistance, and R_{sei} and C_{sei} are the resistance and capacitance of the solid-state interface layer formed on the surface of the electrodes, respectively. C_{dl} and R_{ct} are the double-layer capacitance and charge-transfer resistance, respectively. Z_w is the Warburg impedance related to the diffusion of lithium ions into the bulk of the electrode²⁻⁴. The Nyquist complex plane impedance plots of CB, CB-9, GCB, and GCB-24 are given in Figure S1 (b) and (c).

	$R_{b}(\Omega)$	$R_{sei}(\Omega)$	$R_{ct}(\Omega)$
СВ	3.85	5.11	21.21
CB-9	11.96	20.57	48.44
GCB	4.28	6.84	31.87
GCB-24	16.15	24.92	74.45

Table. S1 Kinetic parameters of the electrode materials

The kinetic parameters of the electrodes are summarized in Table. S1. It is clearly observed that with high crystallinity and defect density, all of the resistances of the electrodes are improved. It indicated that the highly crystalline hollow graphitic structures obtained after ball-milling for both CB and GCB are not suitable for both charge transfer and lithium ion diffusion.



Figure S2 Galvanostatic charge-discharge curves of (a) CB and CB-9, and (b) GCB and GCB-24.

Reference:

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