## **Electronic Supplementary Information**

## Vertically-oriented graphene nanosheet as nano-bridge for pseudocapacitive electrode with ultrahigh electrochemical stability

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*Experimental details:* Flexible asymmetric supercapacitors were assembled by sandwiching the NCHN/GN/CC (positive electrode), the GN/CC (negative electrode), and KOH/PVA (as both electrolyte and separator) together. First, the KOH/PVA gel electrolyte was prepared by mixing 3 g KOH with deionized water (60 mL), and then adding 6 g PVA powder. The mixture was heated steadily from room temperature to approx. 85 °C under vigorous stirring until the solution became clear and thoroughly mixed. Then, a piece of NCHN/GN/CC electrode and a piece of GN/CC electrode were immersed in the hot dilute polymer electrolyte solution. The dilute solution soaked and penetrated the porous electrodes well and formed a coating layer on the surface of the electrodes. The electrodes with the electrolyte solution coating on were placed in a fume hood at room temperature to evaporate the excess water. After the KOH/PVA became solidified, the two electrodes were tightly pressed together into one integrated unit. Subsequent, the asymmetric supercapacitors were sealed in a plastic bag for the following electrochemical measurements.

*Calculations:* The capacitance of the electrodes/devices is calculated from charge/discharge curves based on:

$$C_M = (I \times \Delta t) / (\Delta V \times M) \tag{1}$$

where  $C_M$  can represent capacitance normalized by area (F cm<sup>-2</sup>); I (A) is the applied current;  $\Delta t$  (s) is the discharge time;  $\Delta V$  (V) is the discharge potential range; M can be geometric area of the electrodes/devices in cm<sup>2</sup>, respectively.

The surface morphology of GN grown on CC is shown in Fig. S1. Uniform, large-scale coverage of GN on carbon fibers is shown in Fig. S1a. The high-magnification SEM image in Fig. S1b indicates that sharp and thin edges of GN can be clearly distinguished, and GN possesses a typical width of a single, unwrinkled 2D petal ranging from 100 nm to 400 nm.



**Fig. S1.** (a) Uniform and large-scale coverage of GN on carbon fibers within CC; (b) high-magnification SEM image of GN with sharp edges.

The nitrogen (N<sub>2</sub>) adsorption-desorption isotherms and the corresponding Barret-Joyner-Halenda (BJH) pore size distribution curves of NCHN/GN/CC electrode have been provided in Fig. S2. As shown in Fig. S2a, the BET surface area of NCHN/GN/CC is  $60.2 \text{ m}^2 \text{ g}^{-1}$ . Based on the BJH pore size distribution curves (see Fig. S2b), the NCHN/GN/CC electrode predominantly contains pores with size ranging from 10 nm to 50 nm (mainly mesopores). As reported in previous work, a hierarchical porosity composed of mesopores connected with macropores facilitates fast mass transport, resulting in improved electrode performance. The NCHN/GN/CC electrode presents mesoporous structure, which facilitates the fast mass transport and further improves the electrochemical stability at low scan rates.<sup>1</sup>



Fig. S2. (a) N<sub>2</sub> adsorption and desorption curves; (b) BJH pore size distribution curves.

XPS spectra of NCHN/GN/CC hybrid electrode have been provided in Fig S3. As shown in Fig. S3a, the C 1s emission spectrum was fitted three peaks C1, C2 and C3. Specifically, C1 at 284.6 eV indicates carbon atoms of C–C nonfunctional graphitic structures. C2 at 285.8 eV and C3 at 288.3 eV are attributed to C-O functional groups.<sup>2</sup> In the O 1s spectrum (see Fig. S3b), three peaks O1, O2 and O3 have been fitted. The O1 at 531.6 eV and O3 at 533.2 eV are associated with C-O functional groups.<sup>2</sup> After NCHN deposited on GN, some covalent bonds form between C and O, suggesting that a robust bonding exists at the interface between the NCHN and GN. This covalent bonding forms a strong basis for high charge transfer efficiency at the interface. As shown in Fig. S3c, the Ni 2p emission spectrum was also fitted to two spin-orbit doublets (see Fig. S3d), corresponding to Co<sup>3+</sup>, and two shakeup satellite (defined as "Sat.").<sup>3</sup> The XPS results indicate NCHN/GN/CC possess a composition of Ni<sup>2+</sup>, Ni<sup>3+</sup> and Co<sup>3+</sup> on the surface.



Fig. S3. XPS of NCHN/GN/CC electrode: (a) C 1s; (b) O 1s; (c) Ni 2p; (d) Co 2p.

Morphologies of NCHN/CC electrode before and after electrochemical treatments are shown in Fig. S4. Fig. S4a presents a typical carbon fiber with uniform and large-scale coverage of NCHN. From the Fig. S4b, NCHN with sharp edges is clearly distinguished. However, after 300 cycle-low scan rate treatment, a large number of NCHN peeled off carbon fiber surface (see Fig. S4c). Moreover, the remained NCHN aggregated seriously on carbon fiber surface, indicating the collapse of such hybrid structure (see Fig. S4d).



**Fig. S4.** Morphologies of NCHN/CC electrode before electrochemical treatment (a) Uniform and large-scale coverage of NCHN on a typical carbon fiber; (b) high-magnification SEM image of NCHN on carbon fibers; After 300 cycle-low scan rate treatment (c) NCHN peeling off carbon fiber surface; (d) Aggregated and collapsed NCHN on a carbon fiber surface.

CV curves of NCHN/GN/CC electrodes after cyclic charge/discharge treatments are provided in Fig. S5. The high repeatability of CV curves of such hybrid electrodes further confirms the high electrochemical-stability of NCHN/GN/CC hybrid electrodes during cyclic charge/discharge process.



**Fig.S5.** CV curves of NCHN/GN/CC electrodes treated at a scan rate of 5 mV s<sup>-1</sup> over: (a) 100 cycles. (b) 300 cycles. (c) 500 cycles. (d) 1000 cycles.

Galvanostatic charge/discharge profiles of NCHN/GN/CC electrodes after cyclic treatments at a current density of 10 mA cm<sup>-2</sup> are shown in Fig. S6a. The highly overlapped charge/discharge curves indicate the electrochemical performance of such hybrid electrodes is not affected by the low rate scanning or scanning cycles during charge/discharge process. In sharp contrast, NCHN/CC electrodes present great changes in charge/discharge curves after cyclic treatments. Specifically, after 100-cycle treatment, time required for charge/discharge of electrodes decreases slightly (see Fig. S6b), while with increasing cycles of treatments, the charge/discharge time of electrodes decreases significantly, and the voltage plateau becomes mild as well, indicating the capacitance of NCHN/CC electrodes deceases with the increase of the treatment cycle during charge/discharge process.



**Fig.S6.** Galvanostatic charge/discharge curves at 10 mA cm<sup>-2</sup> of: (a) treated NCHN/GN/CC electrodes and (b) treated NCHN/CC electrodes.

Comparative EIS data of NCHN/GN/CC and NCHN/CC has been provided, Fig. S7. EIS measurements of NCHN/GN/CC and NCHN/CC electrodes were executed with AC perturbation amplitude of 5 mV in the frequency range from 0.1 Hz to 1 MHz. As shown in Fig. S7, the  $R_e$  values of NCHN/GN/CC and NCHN/CC electrodes are 2.2 and 2.5  $\Omega$ , respectively, which indicate the NCHN/GN/CC electrode exhibits a lower equivalent-series-resistance. Moreover, Nyquist plot of the NCHN/GN/CC electrode shows a negligible semicircle feature at high frequencies, indicating low charge transfer resistance, while the  $R_{ct}$  value (measured from the semicircle) of NCHN/CC electrode is approx. 0.5  $\Omega$ . From the comparative EIS data, NCHN/GN/CC electrode exhibits low equivalent-series-resistance and high charge transfer efficiency.



Fig. S7. EIS of NCHN/GN/CC and NCHN/CC electrodes (the inset shows the spectra at high frequency).

Capacitance retentions of NCHN/GN/CC electrodes after different cyclic-treatments at a low scan rate are plotted as a function of current density in Fig. S8. As the current density increases from 5 to 100 mA cm<sup>-2</sup>, all the capacitances of NCHN/GN/CC electrodes undergo a slight decrease, with a capacitance retention of over 88%, which is independent on the treatment cycles.



**Fig.S8.** Capacitance retentions of NCHN/GN/CC electrodes before and after treatments as a function of current density.

The cycle life of NCHN/CC electrodes before and after treatments (100-cycle and 500-cycle samples were chosen as typical examples) provided in Fig. S9 is evaluated over 5000 galvanostatic charge/discharge cycles at a current density of 50 mA cm<sup>-2</sup>. For the original NCHN/CC electrode, the capacitance exhibits a slight increase during the first 1000 cycles and then undergoes a gradual attenuation through the 5000th cycle, with overall capacitance retention of approx. 81% compared to the first cycle. After cyclic treatment at low scan rates over 100 and 500 cycles, the hybrid electrodes exhibit a remarkable decrease in capacitance, with capacitance retentions of 80% during 5000 cycles.



Fig. S9. Cyclic stability tests of NCHN/ CC electrodes before and after treatments measured at a current density of 50 mA cm<sup>-2</sup> over 10000 cycles.

Before supercapacitor applications, GN/CC electrode was electrochemically oxidized to functionalize the GP surface with oxygen-containing functional groups, significantly improving the wettability of the GN/CC electrode and thus increasing charge storage.<sup>4</sup> The CV curves of GN/CC electrode were measured using 2 M KOH as electrolyte. GN/CC served directly as the working electrode. Pt mesh and standard calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The related results have been provided in Fig. S10 displays CV curves of the GN/CC electrode at scan rates of 5, 10, 20, 50, 80 and 100 mV s<sup>-1</sup> with the voltage range between 0 to 1 V. CV curves at all scan rates exhibit two mild redox peaks, which can be attributed to the oxidation/reduction of the oxygen-containing functional groups in the acidic electrolyte.<sup>5</sup>



Fig. S10. CV curves of CN/CC electrode in a three-electrode configuration with 2 M KOH aqueous solution at scan rates from 5 to 100 mV s<sup>-1</sup>.

The Ragone plots showing specific energy density and power density of the present asymmetric device compared with contemporary supercapacitors have been provided in ESI, Fig. S11. The energy density of the present asymmetric device reaches up to 40.5 Wh kg<sup>-1</sup> (based on the active material mass), and the device also deliver a power density up to 15.6 kW kg<sup>-1</sup>, which are significantly higher than those of contemporary supercapacitors.<sup>6-9</sup>



Fig. S11. Comparative Ragone plot (based on active material mass) of contemporary supercapacitor devices and the present asymmetric supercapacitor device.

For practical applications, leakage current and self-discharge should be minimal, and these characteristics of the asymmetric supercapacitors are provided in Fig. S12. The leakage current was measured by keeping the supercapacitor at a constant voltage of 1.5 V for 24 h. The obtained data (see Fig. S12a) indicates that leakage current drops quickly at an initial stage and gradually stabilizes, reaching 0.0015 mA after maintaining a constant voltage for 24 h. Such a low leakage current indicates good capacitor performance, which could be attributed to few shuttle reactions caused by the impurities in electrode materials<sup>10, 11</sup>. Fig. S12b displays the self-discharge profile of the asymmetric supercapacitor under such an open-circuit voltage condition. The asymmetric supercapacitor maintains approx. 52% of the initial potential after 24 h of self-discharge. These leakage current and self-discharge characteristics of the asymmetric supercapacitors approxes are promising for use in future energy storage systems.



**Fig.S12.** (a) Leakage current of the asymmetric supercapacitor charged to a potential of 1.5 V and kept at the voltage for 24 h. (b) Self-discharge curve of the asymmetric supercapacitor under an open-circuit condition for 24 h after being charged at 1.5 V.

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