

Table of contents

1. **Materials and methods.**
2. **Fig. S1:** Theoretical estimation of the relation between the intersheet spacing and the packing density of graphene in a face-to-face arranged assembly.
3. **Fig. S2:** Schematic showing the soft chemistry route to fabrication of the EM-CCG film from the CCG dispersion.
4. **Fig. S3:** Morphology and elemental analysis of CCG/H₂SO₄ films and dried CCG film.
5. **Fig. S4:** XRD patterns of the CCG/electrolyte films and dried CCG film with varied packing densities.
6. **Fig. S5:** Raman spectra of the CCG/H₂SO₄ films.
7. **Fig. S6:** EC performance of CCG/H₂SO₄ films and dried CCG film with H₂SO₄ electrolyte.
8. **Fig. S7:** Volumetric capacitance of the CCG/H₂SO₄ h k n o " * ?) and dried CCG film (=1.49 g/cm³) as a function of areal mass loading.
9. **Fig. S8:** Cycling performance of the CCG/H₂SO₄ h k n o " * ?) in 0.5M H₂SO₄ e o
10. **Fig. S9:** Morphology and properties of CCG/EMIMBF₄ films and dried CCG film.
11. **Fig. S10:** Electrochemical characterization of CCG/EMIMBF₄ films and dried CCG film with EMIMBF₄/AN electrolyte.
12. **Fig. S11:** EC performance of CCG/EMIMBF₄ films and dried CCG film with EMIMBF₄/AN electrolyte.
13. **Fig. S12:** Constant voltage hold tests for an electrochemical capacitor with CCG/EMIMBF₄ h k n o u " * ?) and neat ionic liquid electrolyte EMIMBF₄ (the hold voltage as 3.5 V).
14. **Fig. S13:** Relation of packing density of CCG to corresponding gravimetric or volumetric capacitance.
15. **Table S1:** Estimation of specific surface area of the CCG/H₂SO₄ films with different packing densities.
16. **Table S2:** Results of carbon-based electrode materials used in electrochemical capacitors.
17. **Reference**

1. Materials and methods

Synthesis of EM-CCG films from CCG hydrogel films

Chemically converted graphene (CCG) dispersion was synthesized by following the method described in Ref (23). Briefly, graphene oxide colloid (0.5 mg/ml, 100 ml) made from the o q f k h k g f " J w o o g t u ø " o g v j q f " y c u " o k w a t e r f a n d 0.35 m l j " 2 0 4 " ammonia (28 wt% in water) solution in a glass vial. After being vigorously shaken for a few minutes, the vial was put in a water bath (~100 °C) for 3 hr.

Then CCG hydrogel films were fabricated by following the method we previously reported (24). Briefly, 30 ml as-obtained CCG dispersion was vacuum filtrated through a mixed cellulose ester filter membrane (2 0 2 7 " o). The vacuum was disconnected immediately once no free CCG dispersion was left on the filtrate cake. The CCG hydrogel films were then carefully peeled off from the filter membrane, immediately transferred to a Petri dish and immersed in water overnight to further remove the remaining ammonia and hydrazine. The as-obtained gel films contained ~1.0 mg/cm² of CCG. The structural and electrical characterization results are provided in Figs. 1, S3, S5, S9 and table S1.

The as-prepared CCG hydrogel films were used as a precursor to synthesize all EM-CCG films via a capillary compression procedure. Firstly, CCG hydrogel films were put in a ratio-controlled volatile/non-volatile miscible solution and stirred continuously at a rate of 400 rpm for 12 hr, allowing water in the hydrogel film to be fully exchanged with the mixture solution; afterwards, the films were clipped by two glass slides and moved to a vacuum oven, and the volatile liquid inside the gel film would evaporate and be selectively removed under a high vacuum of 10 Pa for 12 hr. The selective removal of volatile part of the miscible solution exerted capillary compression between CCG layers inside the gel films, leading to shrinkage of film thickness and increase in CCG packing density. As the non-volatile part of the miscible solution in the gel film would remain, the packing density of CCG layers was readily mediated by the ratio of volatile/non-volatile solutions.

Deionized water was used as the volatile liquids and two non-volatile liquids were used in this work, sulfuric acid (H₂SO₄) and an ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate, EMIMBF₄, 99.0 % of purity). For H₂O/H₂SO₄ miscible solutions, four concentration ratios, namely 0.1, 0.5, 1.0 or 5.0 M (H₂SO₄ is the solute in this case) were used to compress CCG/H₂SO₄ films, and finally the CCG were packed in the density of 1.33, 0.76, 0.42 or 0.13 g/cm³, respectively. We accordingly named these films by their packing density values: =1.33 g/cm³, =0.76 g/cm³, =0.42 g/cm³ or =0.13 g/cm³.

Similarly, four concentration ratios of H₂O/EMIMBF₄ solutions (0.065, 0.130, 0.325 or 0.650 M EMIMBF₄) were used to produce CCG/EMIMBF₄ films. The packing density values of CCG in the corresponding films were 1.25, 0.97, 0.65 or 0.39 g/cm³. These samples were thus marked as =1.25 g/cm³, =0.97 g/cm³, =0.65 g/cm³ or =0.39 g/cm³. The temperature for capillary compression of CCG/H₂SO₄ or CCG/EMIMBF₄ films was set at 25 and 50 °C, respectively.

As a control, the dried CCG film was fabricated directly via vacuum vaporizing the water inside the CCG hydrogel film without exchanging with any volatile/non-volatile miscible solutions.

Characterization methods

The EM-CCG films were placed on a flat sample holder and the X-ray diffraction (XRD) patterns were recorded on a Philips 1130 X-ray diffractometer with a Scintag 5000 goniometer at a scanning rate of 2°/min and a step of 0.02° shown in fig. S4. Raman spectra of the EM-CCG films were recorded using a WiTec Raman system (Alpha 300) with a 100× objective lens and a 532 nm He-Ne laser beam at room temperature.

The morphology and elemental information were analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy (JEOL JSM 7001F SEM and Oxford-Horiba Inca XMax50 EDX) with the accelerating voltage of 5 kV. The thickness of the films was measured with five independent samples and the average values were used to calculate the corresponding packing density.

The volume of the EM-CCG films was calculated through multiplying the thickness by area (usually $\sim 1.0 \text{ cm} \times 1.0 \text{ cm}$). The volume of pre-incorporated electrolyte can be calculated from dividing its net mass (the mass of whole EM-CCG film subtracts the mass of CCG) by the density (1.840 and 1.294 g/cm^3 for sulfuric acid and EMIMBF₄, respectively). The volumetric ratio (Fig. 1B and S9G) of incorporated electrolyte was obtained by dividing the volume of electrolyte by the volume of the corresponding EM-CCG film.

The specific surface area of EM-CCG films was measured using the methylene blue adsorption method. Methylene blue is a common dye probe used to determine the surface area of graphitic materials, with each molecule of adsorbed methylene blue representing 1.35 nm^2 of surface area (18, 30). The surface area was calculated by adding a known mass of CCG into a standard concentration of methylene blue in deionized water. The EM-CCG films were first soaked in deionized water to remove the incorporated electrolytes and then stirred in the methylene blue solution continuously at a rate of 300 rpm for a total of 36 hr to reach maximum adsorption. The mixture was then allowed to settle and further centrifuged to remove any suspended material. The methylene blue concentration was determined by analyzing the supernatant through UV-Vis spectroscopy at a wavelength of 665 nm and compared to the initial standard concentration of methylene blue prior to interacting with CCG.

Electrical conductivity measurement of the CCG/EMIMBF₄ films was carried out on a Jandel 4-point Conductivity Probe using a linear arrayed four-point head.

The average intersheet spacing in multilayered EM-CCG films was estimated using the following formula under the assumption that the CCG sheets were flat and evenly separated:

$$\text{Intersheet spacing} = \frac{\text{areal mass density of graphene}}{\text{mass of CCG}} \times \text{area of CCG}$$

where the areal mass density of graphene (0.77 mg/m^2 , taken from *Scientific Background on the Nobel Prize in Physics 2010*) (31). Note that XRD has been widely used to characterize the intersheet spacing of well-crystallized layered compounds. However, in our case, because CCG sheets are micro-corrugated, the (002) XRD peak only reflects the spacing ($\sim 0.39 \text{ nm}$) of the

micro-regions of CCG sheets in contact, not the real intersheet spacing. See more discussion on this issue in the caption of fig. S4.

Characterization of the electrochemical capacitors

Prototype ECs were assembled in a symmetrical two-electrode configuration using a similar procedure reported in the literature (18, 25, 32). Both the EM-CCG films and dried CCG films were directly used as electrodes without adding any other polymeric binders or conductive additives. The sizes of all electrode films were fixed to $\sim 1.0 \text{ cm} \times 1.0 \text{ cm}$, and unless specifically stated in the figure captions, the areal mass loading of CCG in the electrodes of both EM-CCG films and dried CCG films was 1.0 mg/cm^2 . Note that the EM-CCG films were firstly stirred in the electrolyte solution continuously at a rate of 400 rpm for 3 hr prior to the device assembly. Two Pt foils were used as current collectors. At the end of Pt foils, platinum wires were clipped onto the foils by toothless alligator clips, which were then connected to a VMP2/Z multi-channel potentiostat/galvanostat for electrochemical characterization. A glassy fiber filter paper was sandwiched between two CCG/electrolyte or dried CCG films and then infiltrated with corresponding electrolyte solutions, 1.0 M H_2SO_4 or 1.0 M EMIMBF₄/AN. Finally, the devices were wrapped and tightly sealed by parafilm. The assembly of ECs with the electrolyte of EMIMBF₄/AN was done in a glove box under a nitrogen filled atmosphere.

Thicker electrode films were made through stacking a certain number of CCG/electrolyte or dried CCG films together in a face-to-face manner. The thickest CCG/ H_2SO_4 ($\approx 1.33 \text{ g/cm}^3$) and CCG/EMIMBF₄ ($\approx 1.25 \text{ g/cm}^3$) films tested have an areal mass loading of CCG up to 10 mg/cm^2 , reaching the standard of commercial EC electrodes (8, 32).

Before EC performance was recorded, cyclic voltammetry (CV) scanning with a rate of 50 mV/s was conducted for several cycles to allow the device to stabilize. It was not until the *I-E* loops completely overlapped with the previous ones would the data be recorded. CV tests were carried out at different scan rates from 5 to 500 mV/s. The galvanostatic charge-discharge tests were carried out at different current densities starting from 0.1 to 200 A/g. The operating voltages for the electrolytes of 1.0 M H_2SO_4 aqueous solution and 1.0 M EMIMBF₄/AN were set at 1.0 and 3.5 V, respectively. Electrochemical impedance spectroscopy measurements were performed

under a sinusoidal signal over a frequency range from 100 kHz to 10 mHz with a magnitude of 10 mV.

To investigate the electrochemical stability of the CCG films under a working voltage of 3.5 V, we fabricated an EC with a neat ionic liquid, solvent-free EMIMBF₄, as the electrolyte and tested the stability using the voltage holding method reported in Ref. (33). The constant voltage holding test was recommended to be more demanding than the traditional charging/discharging cycling tests (33). In brief, a voltage of 3.5 V was applied to the EC cell with CCG/EMIMBF₄ films (=1.25 g/cm³) as electrodes and neat EMIMBF₄ electrolyte. Three charging/discharging cycles from 0 to 3.5 V at a constant current of 2.5 A/g were performed every 10 hr to obtain the corresponding retaining capacitance. The results of constant voltage holding test are presented in fig. S12.

Details of calculation formula for the EC data

The specific gravimetric capacitance (C_{wt-C}) and volumetric capacitance (C_{vol}) of CCG/electrolyte and dried CCG films in one electrode were calculated from the galvanostatic charge/discharge curves at different current densities using the formula:

$$C_{wt-C} = \frac{I \cdot t}{m \cdot \Delta V} = \frac{I}{m} \cdot \frac{t}{\Delta V} \quad (1)$$

$$C_{vol} = \frac{I \cdot t}{V \cdot \Delta V} = \frac{I}{V} \cdot \frac{t}{\Delta V} = C_{wt-C} \cdot \rho \quad (2)$$

where I is the constant current applied, I/t is the slope obtained by fitting a straight line to the discharge curve, m is the net mass of CCG in one electrode, I_s is the current density, V is the volume of one electrode and ρ is the packing density of CCG in the electrode.

The volumetric energy density ($E_{vol-stack}$) was normalized by the volume of the whole stack according to the following formula:

$$E_{vol-stack} = E_{vol-electrode} \cdot f_{electrode} = \frac{E_{vol-electrode} \cdot C_{vol} \cdot U}{m} \cdot f_{electrode} \quad (3)$$

where $E_{vol-electrode}$ is volumetric energy density of two electrodes, C_{vol} is the specific volumetric capacitance of one electrode, U is the operating voltage (obtained from the discharge curve subtracted by the U_{drop}), $f_{electrode}$ refers to the volumetric fraction of two electrodes in a device stack.

Following the procedure reported by Kaner and co-workers (18), the volume of the whole device stack, including two electrodes (CCG/electrolyte or CCG film + electrolyte in thickness) was used to calculate the $E_{vol-stack}$. As the value of the energy density of ECs reported in the literature was often calculated against the mass/volume of the active electrodes only, to facilitate the reader to apprehend and compare our results against others, we have also provided data of the volumetric energy density against the two electrodes only, which was denoted as $E_{vol-electrode}$:

$$E_{vol-electrode} = \frac{E_{vol-stack}}{f_{electrode}} \quad (4)$$

The volumetric power density ($P_{vol-stack}$) normalized by the volume of stack was calculated from the galvanostatic curves at different charge/discharge current densities using the following formula:

$$P_{vol-stack} = P_{vol-electrode} \cdot f_{electrode} = \frac{P_{vol-electrode} \cdot C_{vol} \cdot U}{m} \cdot f_{electrode} \quad (5)$$

where $P_{vol-electrode}$ is volumetric power density of two electrodes, U is the operating voltage (obtained from the discharge curve subtracted by U_{drop}) and m is the net mass of CCG on one electrode, ρ is the packing density of CCG, $f_{electrode}$ refers to the volumetric ratio of two electrodes in a device stack. R is the internal resistance of the device which was calculated via dividing the voltage drop at the beginning of the discharge (U_{drop}) by the applied constant current (I) using the formula:

$$R = \frac{C}{m} \quad (6)$$

Generally one-electrode calculations can be done properly if one-electrode capacitance and half-cell voltage values are used properly. However, note that specific gravimetric capacitance of one electrode is fourfold higher than that of two electrodes (32). If one calculates the energy density on the basis of the capacitance value of one electrode, the obtained value of energy density will be fourfold higher than that normalized by two electrodes. Thus, when one compares these gravimetric values reported in the literature, special cautions need to be taken to examine the metrics used and whether one or two electrodes were considered.

It is worth noting that several different metrics were used to calculate the capacitance and energy/power density in the literature. The data reported in the Ragone plots in the literature including our previous publications (25) were often normalized against the mass of active carbon materials only. As pointed out by Gogotsi and Simon recently (8, 10), because the packing density (ρ) and the volume fraction of electrodes ($f_{electrode}$) were not factored in these calculations, the reported values of energy and power density were often overestimated, thus leading to unrealistic claims, especially for some low packing density materials.

As suggested by Gogotsi and Simon, the volumetric energy density is more important than widely used gravimetric ones for evaluating the potential of a porous carbon material for use in ECs (8). Following this suggestion, we focused on our study on the volumetric performance of CCG-based electrodes in this work.

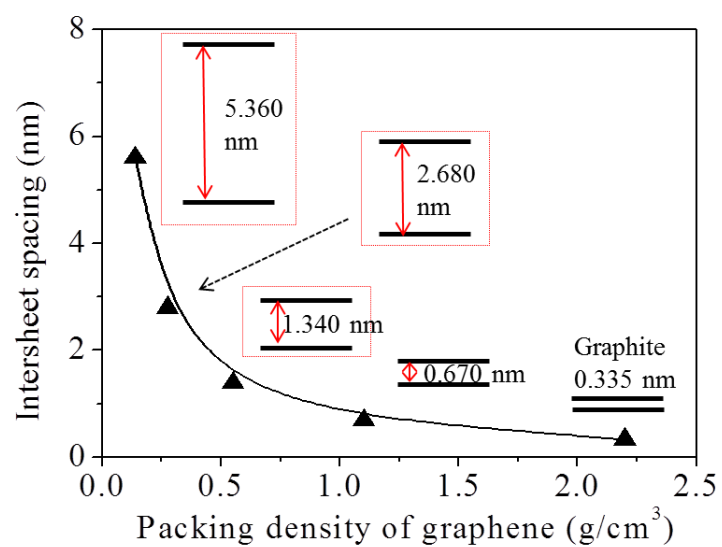


Fig. S1. Theoretical estimation of the relation between the intersheet spacing and the packing density of graphene in a face-to-face arranged assembly.

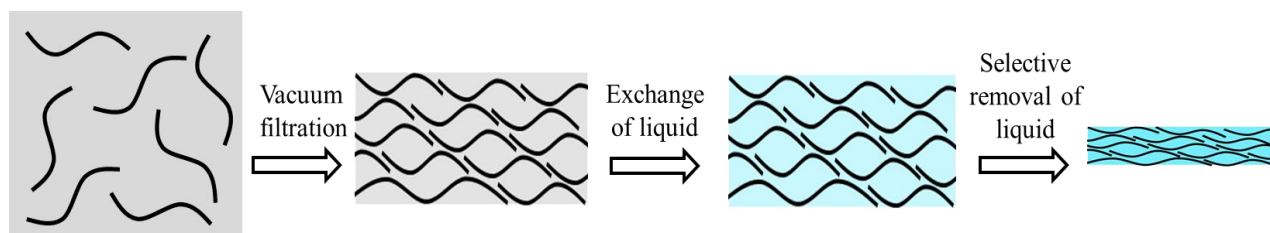


Fig. S2. Schematic showing the soft chemistry route to fabrication of the EM-CCG film from the CCG dispersion: preparing CCG hydrogel film from CCG dispersion by vacuum filtration (24); exchanging the trapped water inside CCG hydrogel films with volatile/non-volatile miscible liquids and finally selectively removing the volatile liquid to obtain EM-CCG films.

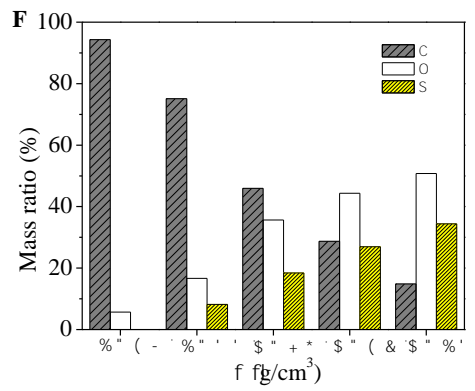
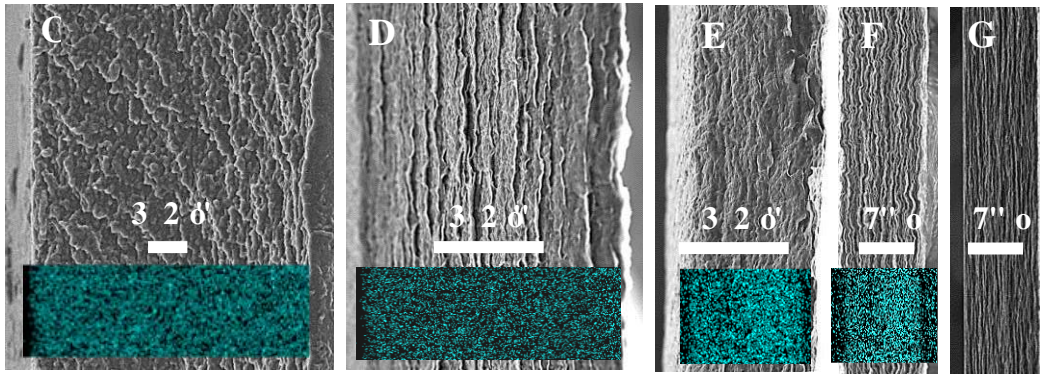


Fig. S3. Morphology and g n g e p p v n'q{6CG lu U Q'h k ñcopuf " E E ñhgfnCFO+ " UGO " k öccpifg"ue q t t g Z'b e p r f k pwin"hgñt ""q 6CGpl uUgQ" h"kuñ*ð 2 0 3 5 . " 2 0 6 4 . " 2 0 9 8 ⁵+c"Q+f" E3E0K5n5 "" ð* D 6 ñ+c pi H+e"bO cuu " t c v k q u " q h " l Q z { i g p " u w Q h wkt p " F Uj+g" " e q t t'g d v a l p f g Z " e p h d d b G E

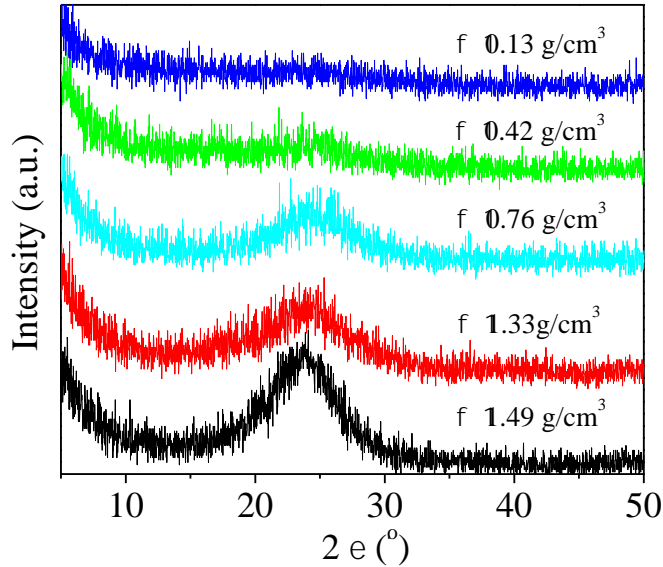
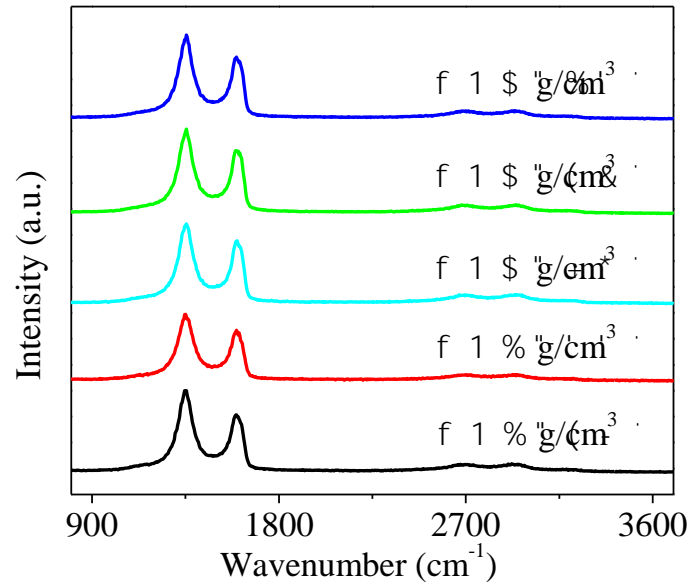


Figure 6. XRD patterns of the EM-CCG films and dried CCG film with varied packing densities. X-ray diffraction (XRD) analysis showed that the as-compressed CCG films displayed a nearly amorphous structure. Only a small and broad peak at around 23° , corresponding to a d_{002} spacing of 0.39 nm, was detected when $>0.76 \text{ g/cm}^3$ but the peak was much smaller than that of the dried CCG film. This result indicates that the majority of CCG sheets, despite being substantially compressed, did not restack back to graphite. No well-defined diffraction peaks were observed at the low angle region, further suggesting that CCG sheets are microscopically corrugated in the films. The alternate situation would be that if stacking were of the perfectly flat face-to-face type, detectable, sharp XRD peaks would be observable which reflect a change in intersheet spacing. The XRD data appear to suggest that only the contacting points of corrugated CCG sheets have an intersheet spacing of $\sim 0.39 \text{ nm}$. The intersheet contacting area increases with the packing density, giving rise to a slightly pronounced XRD peak. The cross-linking of EM-CCG films in the gel state once re-immersed in common solvents as it is known that very few solvents are able to exfoliate graphite unless a high disruptive energy input such as sonication is applied (34).



H k i70 'c U c p " u r g e v J 4 U Q h k n u o j j i g ' k p E I " E E I " k p " c n n " v j g " h k r
 e j g o k e c n " u v t w e v w t g 0

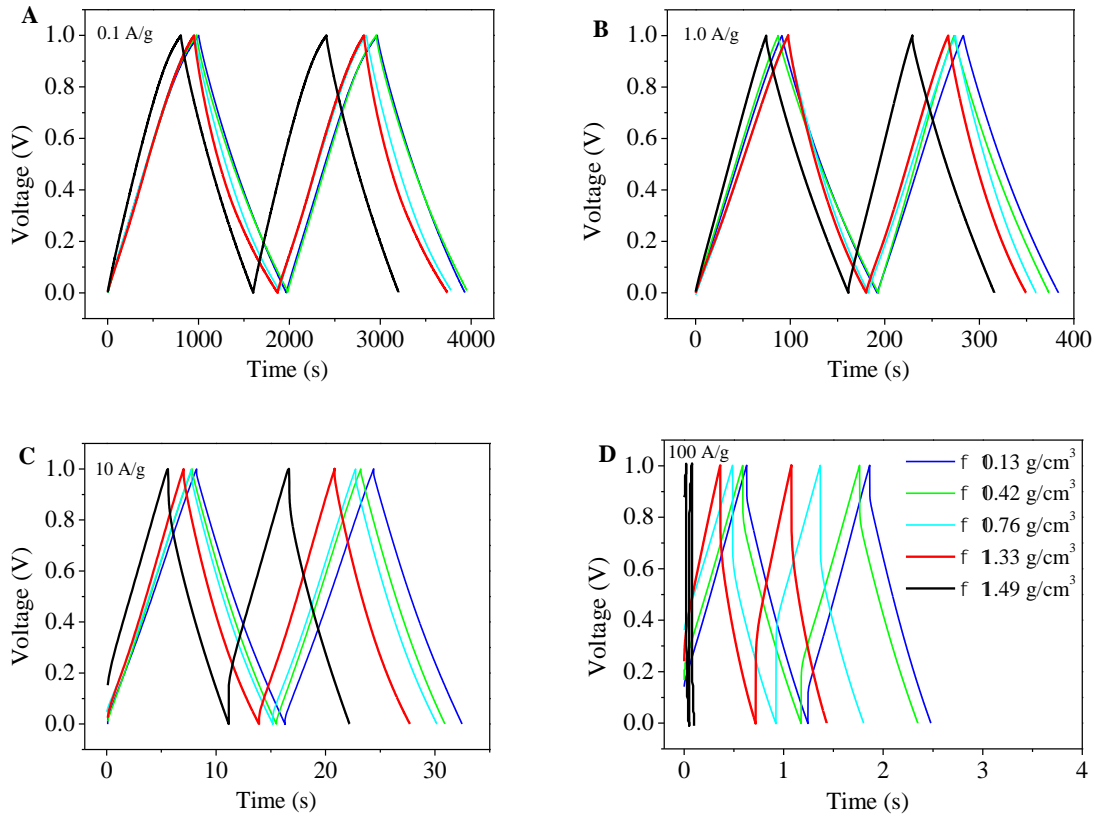


Figure 10. Cyclic voltammetry performance of CCG/J₄U Q films (0.2035, 0.2064, 0.2100 and 0.2130 g/cm³) with H₂SO₄ electrolyte. Charge-discharge curves at (A) 0.1, (B) 1.0, (C) 10.0 and (D) 100.0 A/g.

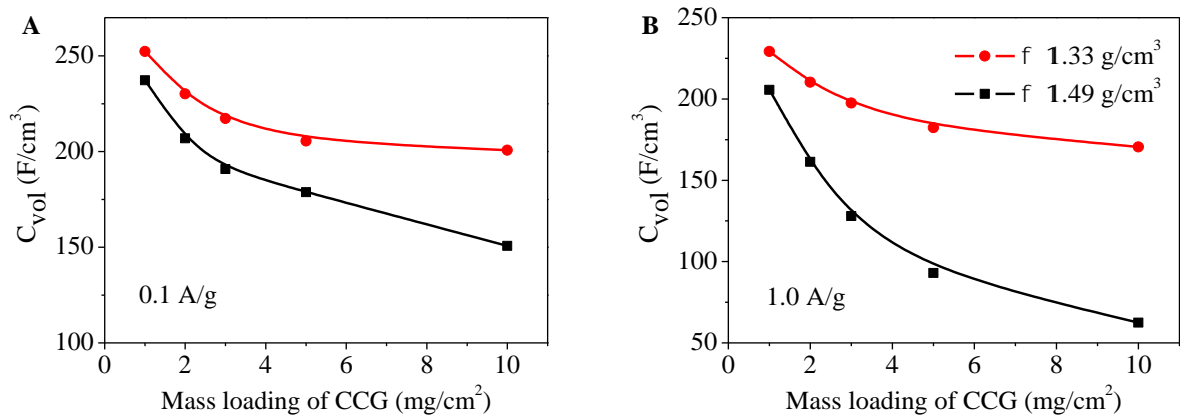


Fig. S7 Volumetric capacitance of the CCG/H₂SO₄ film ($\rho = 1.33 \text{ g/cm}^3$) and the dried CCG film ($\rho = 1.49 \text{ g/cm}^3$) as a function of areal mass loading. The tests were carried out in 1.0 M H₂SO₄ at the current densities of (A) 0.1 and (B) 1.0 A/g.

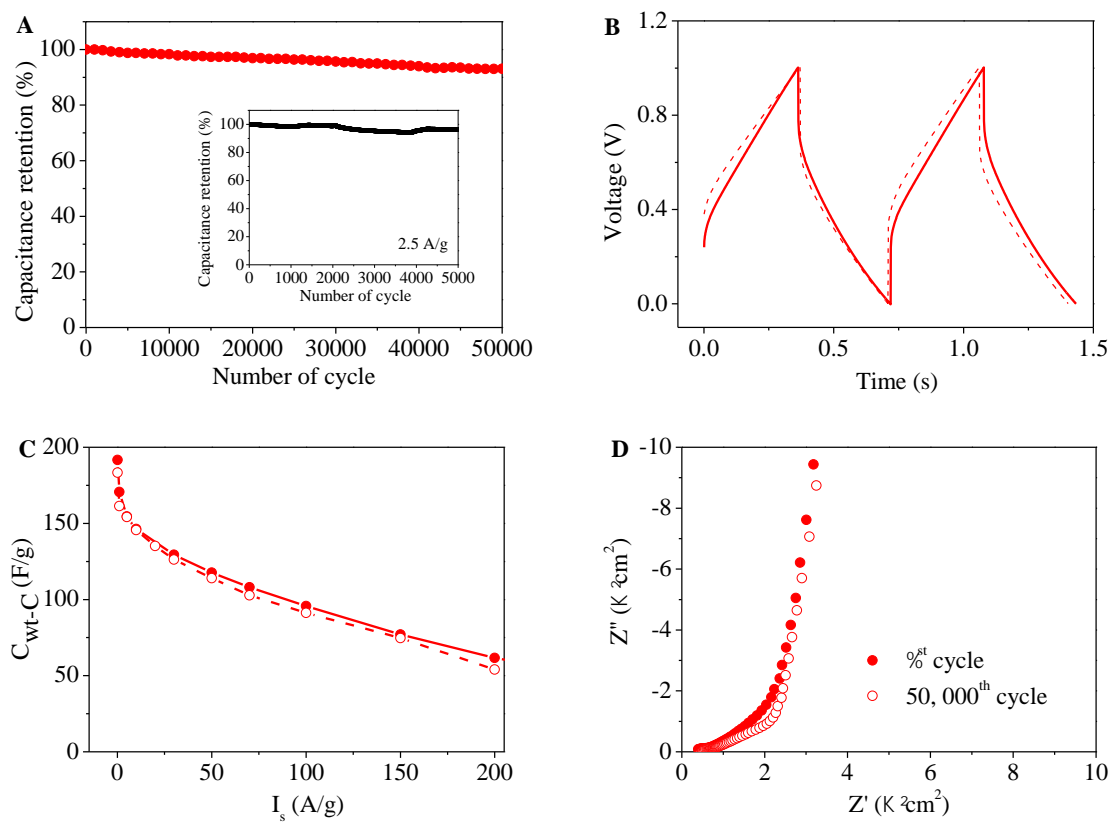
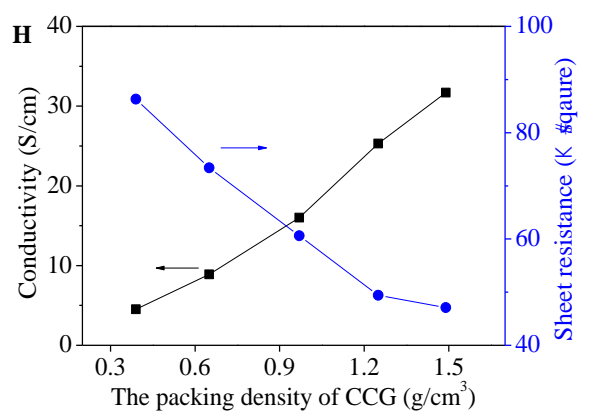
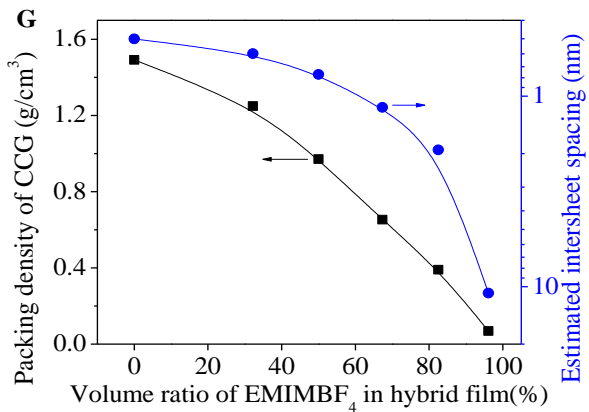
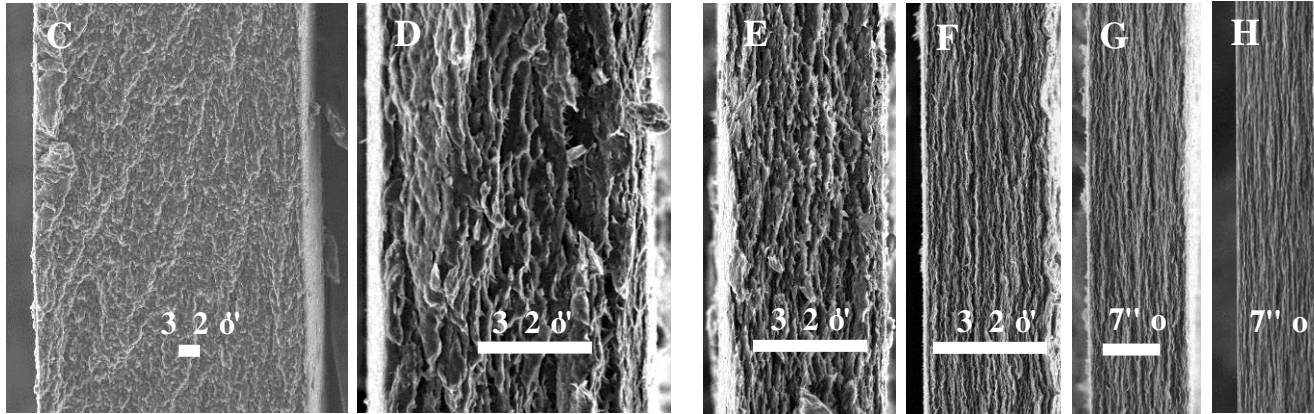


Fig. S8 Cycling performance of the CCG/ J₄UQ film (? 3 0 5 5⁵) in 110 mM H₂SO₄ over 50,000 cycles of charge/discharge at a current density of 100 A/g. **(A)** Capacitance retention (the inset shows the cycling performance at 2.5 A/g); **(B)** Charge-discharge curve at 100 A/g; **(C)** Gravimetric capacitance and **(D)** Nyquist plots before and after cycling test.



H k'U;O q t r j q n q i { " & p CCG 1 r G t O q K r Q d H v i k o g u f " E E l h g k f n C G U G O "
 k o c i CCG 1 G I O K Q D H u r * 2 0 2 8 ; . " 2 0 5 p f " 3 0 5 4 c 7 p H 1 * o f E E " g f "
 h k n b 3 ' 0 * 6 ; 4 (G) The relation between volumetric fraction of intercalated EMIMBF₄ and
 packing density of CCG (left axis) or estimated intersheet spacing (right axis); the volume of
 EMIMBF₄ can be calculated from its net mass normalized by the density. * J + " E q p f w e v k x k v {
 u j g g v " t q g CCG l u G O K r Q d H u o

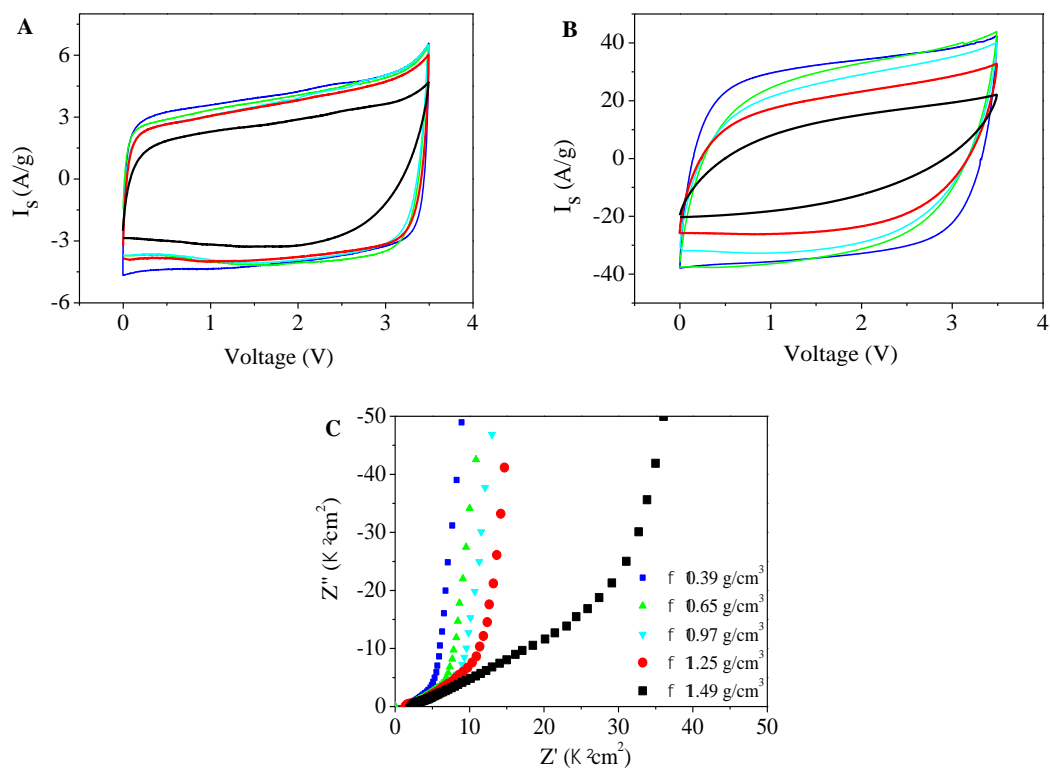


Fig. S10 Electrochemical characterization of CCG/G O K O DHk ricopuf " E E K hg k O C V curves at a scan rate of (A) 50 and (B) 500 mV/s; (C) Nyquist plots. The tests were carried out in 1.0 M EMIMBF₄/AN.

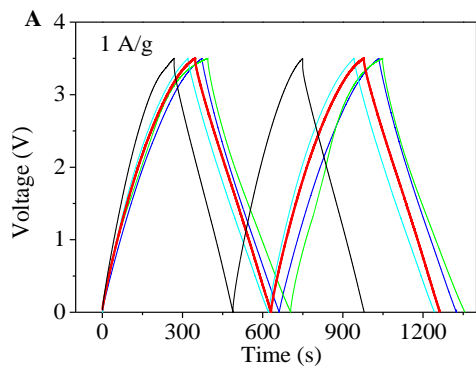


Fig. S11 EC performance of CCG/EMIMBF₄ films and dried CCG film with EMIMBF₄/AN electrolyte. (A-C) Charge/discharge curves measured at current density of 1, 10 and 100 A/g, respectively; (D and E) gravimetric and volumetric capacitance densities against various current densities; (F) capacitance retention of the CCG/EMIMBF₄ film (=1.25 g/cm³) over 5, 000 cycles of charge/discharge at a current density of 10 A/g (the inset shows its cycling performance at 2.5 A/g).

