Achieving high rate and high volumetric pseudocapacitance from compact graphene-polyaniline hydrogel electrodes

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Pseudocapacitors store charge predominantly through reversible faradaic reactions at or near the surface of redox-active materials, and they are a promising approach to obtain higher capacitance values than those of electrical double-layer capacitors (EDLCs). 1-3 Volumetric capacitance is a critical factor to the energy storage efficiency of supercapacitors, particularly for many applications such as portable electronics and mobile devices. 4-6 Recent research has shown that the volumetric capacitance can be significantly improved by increasing the electrode density or by utilizing sub-nanometer pores. 7-11 However, such a highly compact electrode structure is generally expected to hinder ion accessibility to the electrode surface. 12-14 Indeed, it has been widely reported that restricted ion transport, together with limited faradaic charge transfer process in compact electrodes, are major contributors to the reduced capacitance and poor rate capability of pseudocapacitors. 15-20 Accordingly, a combination of micro- and meso-porous structures are commonly proposed as the optimized electrode architecture for pseudocapacitors, 14, 17-19, 21 but their volumetric capacitance is hardly higher than that of compact EDLCs. 10, 11, 22 It remains elusive whether pseudocapacitors could offer a combination of high volumetric capacitance and high power capability.

A great deal of research effort has been directed towards improving pseudocapacitance by synthesizing nanostructured pseudocapacitive materials such as nanofibers, nanofilms, nanorods, nanowires or depositing them onto porous carbon-based substrates to ensure high surface exposure of electrode to electrolyte. 18, 21-24 Upon charging-discharging, these electrodes exhibit redox reactions both at the surface and within the bulk, as well as capacitive contributions from electrical double layers. The kinetics of these charge storage processes differ significantly, particularly between those at the surface and those within the bulk, and
their dynamics is highly dependent on the pore characteristics of the electrodes, especially when the pores come down to sub-nanometer scale in highly compact electrodes. Achieving both high rate and high volumetric pseudocapacitance in compact electrodes requires carefully balancing and optimizing all these factors together, which, however, has so far not been realized.

Polyaniline (PANI), a readily available conducting polymer, has been extensively explored as a model electrode material for pseudocapacitors. Unlike the rigid and intractable morphology of many other pseudocapacitive materials, previous research has shown that PANI can be readily fabricated into a hydrogel form on its own or with hydrated chemically converted graphene (CCG). PANI hydrogels are attractive for energy storage because of the combined properties of high electrical conductivity, mechanical stability and high mass transport ability embedded in a hydrated, porous network. In addition, it has been demonstrated that hydrogels can be easily densified by simple mechanical compression, capillary compression or thermal annealing techniques. In this work, we prepare a series of compact PANI-CCG films by controlled compression of PANI-CCG hydrogels. In contrast to general consideration, we demonstrate that a compact PANI-CCG hydrogel film is indeed able to provide a combination of high rate capability, high volumetric pseudocapacitance (572 F/cm³ at a charge rate of 5 A/g and 548 F/cm³ at 100 A/g) and long cycling life. The high pore connectivity in the compact electrodes, which ensures rapid ion transport and well-maintained nanostructured PANI, is found to be critical to fast kinetics of faradaic charge-storage processes.

PANI-CCG hydrogel films, containing over 85 wt.% of water, were synthesized as the starting materials by in-situ chemical polymerization of aniline in the presence of CCG hydrogel films (Figure 1a), prepared by vacuum filtration of CCG dispersion. Given that the CCG hydrogel films have a relatively large interlayer spacing (ca. 10 nm) and highly open pore structure, the in-situ chemical polymerization method allows controlled deposition of a thin layer of PANI onto individual CCG sheets, leading to the formation of PANI-CCG hydrogel films with a layered structure. The PANI-CCG hydrogel films with PANI content of 50 wt.%, which have an areal mass loading of 0.97 mg/cm² (including CCG and PANI) and exhibit a high gravimetric capacitance, are selected as our model materials in this study.
Fabrication of compact PANI-CCG films. (a) Schematic diagram of the formation of compact PANI-CCG films by capillary compression of PANI-CCG hydrogel films; (b-c) cross-sectional SEM images of compact PANI-CCG films (50 wt.% of PANI) prepared by liquid-mediated method (a ratio of EmImBF₄/water of 0.5 vol.%, 1.25 g/cm³), and (d) density and average void space of compact PANI-CCG films prepared using different methods.

The compact PANI-CCG hydrogel film was obtained by controlled capillary compression of PANI-CCG hydrogel films (Fig. 1a). Typically, the PANI-CCG hydrogel film was first exchanged with a mixture containing a volatile liquid (water) and a non-volatile liquid (1-ethyl-3-methylimidazolium tetrafluoroborate, EmImBF₄), followed by removal of water via vacuum evaporation. Upon removal of water, the thickness of the film was reduced significantly as a result of capillary compression while its plane dimensions remain almost unchanged. The packing density can be adjusted by changing the volumetric ratio of EmImBF₄/water. A ratio of 0.5 vol.% led to a compact film with a packing density of 1.25 g/cm³ (including PANI and CCG). The SEM images reveal that the film is rather dense (Fig. 1b) and the pore size cannot be resolved even by high-resolution SEM (Fig. 1c & S1). No significant change in thickness was observed over time or after rinsing with water, indicating that its structural evolution during preparation is irreversible and their structure is stable. For comparison, the PANI-CCG hydrogel films (50 wt.% of PANI) were also dried by vacuum evaporation or thermal annealing to prepare slightly more compact films, containing 1.27 g/cm³ and 1.36 g/cm³ of PANI and CCG, respectively (Fig. 1d).
Electrochemical characterizations of compact PANI-CCG films (50 wt.% of PANI) prepared using different methods. CV curves at (a) 0.01 V/s and (b) 0.5 V/s; Charge-discharge curves at (c) 5 A/g and (d) 100 A/g; (e) Volumetric and gravimetric capacitance, and (f) Ragone plots of energy density and power density of compact PANI-CCG films (against the volume of the electrode only).

Electrochemical tests were carried out to characterize the charge storage behaviors of compact PANI-CCG films. For all the electrochemical experiments, the compact PANI-CCG films are thoroughly rinsed by water to remove the remaining EmImBF$_4$ before testing, and are then directly used as electrode without the need for binders or additives. The assembled pseudocapacitors are in two-electrode configuration. The cyclic voltammetry (CV) curves of all the PANI-CCG films (Fig. 2a-b) show a rectangular curve superimposed with a pair of
redox peaks at 0.2 – 0.6 V, indicating the presence of PANI which exhibits pseudocapacitance. The compact PANI-CCG hydrogel film (1.25 g/cm³) can largely maintain its CV profiles over a wide range of scan rates from 0.01 V/s to at least 0.5 V/s without significant peak shifts or distortions (Fig. 2a-b), indicative of rapid and reversible redox reactions in the film. In contrast, the films prepared by vacuum evaporation (1.27 g/cm³) and thermal annealing (1.36 g/cm³) show distorted CV curves with increasing scan rate (Fig. 2b). The similar trend is also shown by galvanostatic charge/discharge profiles with current density varied from 5 A/g to 100 A/g (Fig. 2c-d).

The specific capacitance of compact PANI-CCG films at different charging rates is calculated from the galvanostatic charge/discharge results. Our previous work²⁰ has demonstrated that in the PANI-CCG hybrid films, the CCG sheets are fully covered by PANI thin layers, and thus the total capacitance of PANI-CCG film is predominantly attributed to the pseudocapacitance of PANI (ca. more than 80%). It is found that all the compact PANI-CCG films (50 wt.% of PANI) prepared using different methods yield similar gravimetric capacitance at a current density of 5 A/g (Fig. 2e). This result indicates that the PANI in these samples can all contribute to the capacitance at this current density. Meanwhile, as all the films are rather dense, they present similar volumetric capacitance at low current density (Fig. 2e). For example, the compact PANI-CCG hydrogel film (1.25 g/cm³) exhibits a volumetric capacitance of 572 F/cm³ at 5 A/g, which is higher than that of most PANI-based pseudocapacitors reported in the literature at the similar charging rate.³⁶-³⁹

The capacitance difference among these compact films, however, becomes very pronounced at high current densities. It is clearly shown that the extent of decrease in both gravimetric and volumetric capacitance varies among these compact PANI-CCG films. For the compact PANI-CCG hydrogel film (1.25 g/cm³), its capacitance values are very well retained with the increase of current density, and a retention of 96% is obtained by comparing the capacitance value at 5 A/g against that at 100 A/g. In contrast, the fully dried compact PANI-CCG films (1.27 and 1.36 g/cm³) present rapid reduction in capacitance with the increase of current density (retention of 58% and < 24%, respectively). Such a remarkable property is further reflected from the Ragone plots (Fig. 2f) where the compact PANI-CCG hydrogel film (1.25 g/cm³) exhibits not only a high volumetric energy density of 15.8 Wh/L (against the volume of the electrode) but also greatly improved power density by more than an order of magnitude.
Given that the packing density of these samples are very close (1.25, 1.27 and 1.36 g/cm$^3$ respectively), the above results indicate that the density or average void space of compact PANI-CCG films should not be the dominant factor that influences their faradaic charge storage behavior, but rather it appears to be mainly related to the sample preparation approach employed. As widely documented, drying of the gels is generally accompanied with the development of capillary pressure by the solvent, leading to volume shrinkage and pore collapse of the porous gels upon removal of the solvent. Consequently, full drying of the porous gels will result in significantly reduced pore connectivity. We thus postulate that the pore connectivity of the PANI-CCG film prepared by vacuum evaporation (1.27 g/cm$^3$) is greatly reduced as a drying-induced pore collapse. Further thermal annealing would cause more serious pore collapse, resulting in even less pore connectivity. In the case of compact PANI-CCG hydrogel film (1.25 g/cm$^3$), however, the non-volatile liquid retained during the drying process can greatly prevent the capillary collapse of pores, and therefore help maintain a highly interconnected pore structure.

Figure 3 Charging kinetics analysis of compact PANI-CCG films: (a) EIS spectra; (b) Plot of ESR (derived from charge/discharge curves) and time constant $\tau_0$ (derived from EIS results) versus the density of PANI-CCG films; and (c) Plot of $I\sqrt{\nu}$ versus $\nu^{1/2}$ from CV curves.
The unique role of the residual liquid in maintaining the pore connectivity can also be evidenced by electrochemical impedance spectroscopy (EIS) analysis. As shown in Fig. 3a, the compact PANI-CCG hydrogel film (1.25 g/cm$^3$) display a small semicircle and steep vertical line in its EIS spectrum, indicative of a low intrinsic resistance and good capacitive response as a result of fast ion transport in its porous structure. By comparison, the films prepared by vacuum evaporation (1.27 g/cm$^3$) and thermal annealing (1.36 g/cm$^3$) show a distinct -45° line, revealing much increased intrinsic resistance which is mainly attributed to diffusion-limited redox reactions, as also illustrated from their Bode plots (Fig. S2). Moreover, we have also tested a series of PANI-CCG films and plotted their equivalent series resistance (ESR) value and time constant versus their density. Figure 3b shows that among all the PANI-CCG films (50 wt.% of PANI with different packing densities), those are prepared by the liquid-mediated method display much lower ESR values and smaller time constants than those of fully dried films (1.27 and 1.36 g/cm$^3$). Similar results were also obtained with compact PANI-CCG hydrogel films with different PANI contents (packing density ranges from 1.11 g/cm$^3$ to 1.38 g/cm$^3$) (Fig. S3).

To further shed light on the influence of pore collapse on the charge storage behavior, we analyze the CV results in a wide range of charging rates by plotting the relationship between $I/v^{1/2}$ and $v^{1/2}$, where $I$ is the peak current density and $v$ is the scan rate. It has been documented in the literature$^{21, 41, 42}$ that the current response to an applied scan rate varies depending on the kinetics of the charge storage process. For a typical capacitive behavior, the current increases directly with the scan rate, while a diffusion-limited charge storage process leads to a current response with $v^{1/2}$. The plot of the relationship between current and applied scan rate, therefore, has been proposed to evaluate the kinetics of the faradaic charge storage processes in other nanostructured pseudocapacitive materials.$^{21, 41, 42}$ As shown in Fig. 3c, all the plots can be divided into two zones with a clear transition region. At low scan rates (Zone I), the $I/v^{1/2}$ and $v^{1/2}$ plots are linear with an intercept near zero, revealing typical capacitive behavior of all the films. Given pseudocapacitance as the predominant contributor, this result illustrates that at low scan rates, the electrolyte ions can readily access to the surface of electrodes, and all the active sites at or near the surface of PANI layer can participate in reversible faradaic reactions and contribute to charge storage. Nevertheless, after the scan rate is increased into Zone II, the slope of the plots starts to reduce with an associated increase in the intercept. This means that the faradaic charge storage process becomes limited by redox
reactions of PANI. This phenomenon is less obvious for liquid-mediated film, showing that it still behave in a capacitive manner even at high scan rates. This can be attributed to its high pore connectivity which allows fast ion transport as well as much improved diffusion-limited faradaic reactions (see the schematic in Fig. S4a). However, the fully dried PANI-CCG films (1.27 and 1.36 g/cm$^3$) clearly show a critical transition region in scan rates of 0.02 – 0.05 V/s and 0.01-0.02 V/s, respectively (Fig. 3c). This is due to a partially collapsed PANI-CCG layered structure developed during drying (see the schematic in Fig. S4b-c), which hinders the ion transport by blocking its diffusion pathways but also leads to the formation of thick PANI layers. Under such circumstances, many of the reaction sites become less accessible, significantly increasing the intrinsic resistance and making the charge storage process slow. As a result, with the increase of scan rates, the faradaic reactions of PANI become more and more diffusion-limited, restricting the overall charge storage process with the appearance of a critical transition scan rate region (Fig. 3c) as well as reduced rate capability (Fig. 2e).

It is worth pointing out that it has been traditionally suggested that a compact pseudocapacitive electrode would result in restricted ion transport in nano-confinement and it has been considered difficult to achieve high rate performance for compact pseudocapacitive materials. Indeed, despite that compact pseudocapacitive electrodes have been recently developed, most of the reported high redox-pseudocapacitance values are limited to low charging current (e.g. 0.1A/g – 5A/g) with significantly sacrificed power density.$^{43-46}$ In the present work, the average void space or pore size in these highly compact PANI-CCG films is estimated to be less than 1 nm, predominantly in micro-pore range (see Supporting Information). Our results indicate that the key limiting factor for the rate performance of compact pseudocapacitors is not the pore size, but the pore connectivity. Our further experiments have shown that preserving high pore connectivity of PANI-CCG films by keeping the films wetted upon drying also enables fast faradaic charge storage in electrodes with different PANI loadings (Fig. S3) and packing densities (Fig. S5). Such an electrode architecture with high pore connectivity also allows the fabrication of thicker electrodes without significantly sacrificing their capacitance (Fig. S6), as well as exhibiting a long cycling life (Fig. S7).

In conclusion, taking advantage of the adaptive nature of hydrogels, we have prepared a series of compact PANI-CCG films by controlled capillary compression, and investigated their pseudocapacitive performance in compact electrode structures. Our results show that the
density or the pore size of PANI-CCG electrodes may not be the dominant factor to pseudocapacitance utilization; but rather the high pore connectivity, which allows fast ion transport and well-retained nanostructured PANI, is the key to ensure fast kinetics of faradaic charge storage in compact electrodes. Challenging the traditional view, we show that a compact pseudocapacitive electrode can be engineered through a simple soft approach to offer a combination of high gravimetric and volumetric capacitance, excellent rate capability and long cycling life.

**Experimental Section**

*Fabrication of PANI-CCG hydrogel films.*

CCG hydrogel films were prepared by vacuum filtration of chemically converted graphene suspension following the procedure reported previously. The CCG hydrogel film was cut into round pieces with area of 0.97 cm², followed by immersion in mixture containing HCl (5 ml, 1.0 M) and aniline monomer (0.15 ml) and stored at 0 °C for 2 hours. Another mixture containing HCl (5 ml, 1.0 M) and ammonium peroxydisulfate (0.09 g), pre-cooled at 0 °C, was then poured into the above mixture to enable chemical polymerization reactions at 0 °C for another 1 hour. The resultant hybrid hydrogel film was subsequently and thoroughly rinsed by HCl aqueous solution, ethanol, ammonia and milli-Q water. The weight percentage of PANI in the hydrogel film was determined by drying a piece of CCG hydrogel film of the same size, as the control sample, in an oven at 50 °C overnight, followed by weight measurement. Note this measurement has been repeated for several times with different sizes of samples. The PANI content is calculated to be 50 wt.% following the above conditions, and it can be tuned from 27 wt.% to 64 wt.% simply by changing the polymerization time.

The liquid-mediated PANI-CCG films were prepared by immersing PANI-CCG hydrogel films in 1-ethyl-3-methylimidazolium tetrafluoroborate (EmImBF₄) aqueous solutions (0.5 vol%, 1 vol% and 2 vol%, respectively) for 12 hours, followed by vacuum evaporation. Note that the ionic liquid was thoroughly washed before weight measurement and electrochemical tests of the compact PANI-CCG films, and the purpose is to remove any effects caused by the residual liquids. For comparison, another two compact PANI-CCG films were prepared by vacuum evaporation (in the absence of non-volatile liquid) and thermal annealing (50 °C for 2 hours), leading to the density of 1.27 g/cm³ and 1.36 g/cm³, respectively. SEM images of the compact PANI-CCG films were obtained using a JEOL JSM 7001F scanning electron microscope, and the thicknesses of the compact PANI-CCG films measured from the SEM
images were used for the calculation of the density of the films. FT-IR spectra of PANI-CCG films were collected by PerkinElmer Spectrum 100 (Universal ATR Sampling Accessory).

**Electrochemical testing**

Pseudocapacitors using compact PANI-CCG films as the electrodes were assembled in a symmetrical two-electrode configuration. Typically, two pieces of compact PANI-CCG films with the same size were attached to platinum foils, and a filter paper containing 1.0 M H2SO4 as electrolyte was sandwiched between them. The resultant device was tightly wrapped by parafilm and clamped. The electrochemical testing was conducted by using a Versastat-4 potentiostat. The CV tests were carried out at scan rates ranging from 1 mV/s to 0.5 V/s with potentials between 0 V and 0.9 V, and the galvanostatic charge/discharge tests were carried out with the same potential range at current densities ranging from 5 A/g to 100 A/g. The gravimetric capacitance \( C_s \) and volumetric capacitance \( C_{vol} \) of the compact PANI-CCG electrode were calculated as follows:

\[
C_s = \frac{2I}{\Delta U \cdot m} = \frac{2It}{U \cdot m}
\]

\[
C_{vol} = C_s \cdot \rho = \frac{2It}{U \cdot m} \cdot \rho
\]

where \( I \) is the applied constant current, \( m \) is the mass of single electrode, \( t \) is the discharging time, \( U \) is the operating voltage upon discharge (excluding the \( iR \) drop), and \( \rho \) is the density of the compact PANI-CCG film. The volumetric energy density \( E_{vol} \) and volumetric power density \( P_{vol} \) against the compact PANI-CCG electrode only were calculated as follows:

\[
E_{vol} = \frac{C_{vol} \cdot U^2}{8}
\]

\[
P_{vol} = \frac{U^2 \cdot \rho}{8Rm}
\]

where \( R \) is the internal resistance calculated by dividing \( iR \) drop by the current change between charge and discharge. Note that these values are obtained against the volume of the electrode only.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**High rate and high volumetric pseudocapacitance** is generally considered very challenging to achieve. This work reports that a compact polyaniline-graphene hydrogel film can provide a combination of high volumetric pseudocapacitance, excellent rate capability and long cycle life. The presence of a continuous ion transport network and well-maintained nanostructured polyaniline in the electrode are the critical factors.

Keyword: pseudocapacitance, graphene, polyaniline, hydrogel

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Supporting Information

**Achieving high rate and high volumetric pseudocapacitance from compact graphene-polyaniline hydrogel electrodes**

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**Supplementary methods:**
- Estimation of PANI coating thickness
- Determination of average void space in compact PANI-CCG films

**Supplementary figures:**
- **Figure S1** SEM images of compact PANI-CCG film (50 wt.% of PANI) prepared by vacuum evaporation (1.27 g/cm$^3$) and CCG film.
- **Figure S2** Bode plots of compact PANI-CCG films (50 wt.% of PANI) prepared using different methods.
- **Figure S3** Electrochemical characterization of compact PANI-CCG films with PANI content ranging from 27 wt.% to 64 wt.% prepared by the liquid-mediated method.
- **Figure S4** Proposed schematic diagram of the nanostructures of compact PANI-CCG films.
- **Figure S5** Gravimetric and volumetric capacitance of compact PANI-CCG films (50 wt.% of PANI) with different densities prepared by liquid-mediated method, and plots of capacitance value versus density of the films.
- **Figure S6** Effect of thickness on the volumetric capacitance of compact PANI-CCG film (1.25 g/cm$^3$) prepared by liquid-mediation method.
- **Figure S7** Capacitance retention of compact PANI-CCG film (50 wt.% of PANI; 1.25 g/cm$^3$) at a current density of 10 A/g for 5000 cycles.
- **Figure S8** Structural characterization of PANI-CCG films (50 wt.% of PANI) and CCG film.
Supplementary methods

Unlike the hard texture of traditional electrode materials, the compact PANI-CCG films have a dynamic structure and may contain residual liquids, and their porous structure may collapse irreversibly upon removal of liquid or by thermal treatment. Additionally, the deposited PANI coatings are in an amorphous state (Fig. 1b-c and S1). Therefore, it is impossible to characterize the exact pore size and pore size distribution of the compact PANI-CCG films using traditional characterization techniques such as Brunauer–Emmett–Teller (BET). Indeed, our trials with the XRD (Fig. S8) and Brunauer–Emmett–Teller (BET) measurements did not provide any conclusive results on their pore sizes. Rather, as shown in our previous study, both CCG and PANI-CCG hydrogel films have a layered structured, and such a layered structure can be maintained with a wide range of interlayer spacing (ca. from less than 1 nm to 10 nm). Therefore, we proposed the following method to estimate the average void space of the PANI-CCG films.

Estimation of PANI coating thickness

This work makes use of graphene hydrogel film as the substrate followed by deposition of PANI using in-situ chemical polymerization. The benefit of this method is that PANI can be uniformly coated on the surface of CCG sheets (Fig. S1) and its coating thickness is readily controllable. Given the compact PANI-CCG films may remain solvated and the PANI is in amorphous state, it is very difficult to characterize the nano-texture of the compact PANI-CCG films. We therefore proposed the following method to estimate the coating thickness of PANI. Since the CCG hydrogel film has a layered structure and a thin layer of PANI was deposited on each CCG sheets, the thickness of PANI coating can be determined by dividing the total loading amount of PANI by the number of layers. The number of layers is derived by dividing the areal mass density of CCG hydrogel film (ca. 5050 mg/m²) by that of graphene (0.77 mg/m², taken from Scientific Background on the Nobel Prize in Physics 2010). With the known loading amount of PANI, the coating thickness of PANI in the PANI-CCG films with 27 wt.%, 36 wt.%, 50 wt.%, 60 wt.% and 64 wt.% of PANI is estimated to be 0.19 nm, 0.3 nm, 0.55 nm, 0.82 nm and 0.97 nm, respectively.

Determination of average void space in compact PANI-CCG films

The average void space of the compact PANI-CCG films is estimated by substracting the coating thickness of PANI from the interlayer spacing of the CCG sheets. The interlayer spacing of CCG sheets is derived by dividing the areal mass density of graphene (0.77 mg/m²)
by the density of CCG in the hybrid film. With the coating thickness of PANI derived from above, the average void space in compact PANI-CCG films with PANI content of 27 wt.%, 36 wt.%, 50 wt.%, 60 wt.% and 64 wt.% is determined to be 0.74 nm, 0.72 nm, 0.65 nm, 0.58 nm, and 0.54 nm, respectively. For comparison, the compact PANI-CCG film prepared by vacuum evaporation and thermal annealing obtain an average void space of 0.63 nm and 0.55 nm, respectively.
**Figure S1** SEM images of CCG film and compact PANI-CCG film (50 wt.% of PANI) prepared by vacuum evaporation. (a-b) the cross section view and (c) the top view of CCG film; and (d-e) the cross section view and (f) the top view of PANI-CCG film (50 wt.% of PANI) prepared by vacuum evaporation (1.27 g/cm³);

![SEM images](image1)

**Figure S2** Bode plots of compact PANI-CCG films (50 wt.% of PANI) prepared using different methods

![Bode plots](image2)
Figure S3 Electrochemical characterization of compact PANI-CCG films with PANI content ranging from 27 wt.% to 64 wt.% prepared by the liquid-mediated method: charge/discharge curves at (a) 5 A/g and (b) 100 A/g; (c) EIS spectra; (d) frequency response; (e) gravimetric and (f) volumetric capacitance; and plot of (g) ESR and (h) time constant $\tau_0$ versus the density of the PANI-CCG films.
Figure S4 Proposed schematic diagram of the nanostructures of compact PANI-CCG films: Compact PANI-CCG films (PANI content from 27 wt.% to 64 wt.%) prepared by (a) liquid-mediated method, (b) vacuum evaporation and (c) thermal annealing, and proposed ion transport and charge transfer behavior within the various nanostructures.
Figure S5 (a) Gravimetric and (b) volumetric capacitance of compact PANI-CCG films (50 wt.% of PANI) with different densities prepared by the liquid-mediated method; and (c) plots of capacitance value versus density of the films. Note that the density of these films was controlled through tuning their average void space, which is achieved by using different amount of non-volatile liquid as the ‘spacer’ during capillary compression.
Figure S6 Effect of thickness on the volumetric capacitance of compact PANI-CCG film (1.25 g/cm$^3$) prepared by liquid-mediation method (charge/discharge current density: 5 A/g).

Figure S7 Capacitance retention of compact PANI-CCG film (50 wt.% of PANI; 1.25 g/cm$^3$) at a current density of 10 A/g for 5000 cycles.
Figure S8 Structural characterization of PANI-CCG films (50 wt.% of PANI) and CCG film: (a) Raman; and (b) XRD spectrum.
References

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