Hierarchical Porous Graphene Carbon-Based Supercapacitors

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ABSTRACT: A high-rate graphene-based supercapacitor is very attractive for the practical application of graphene. Here, we first synthesized the films of the hybrids of biomass cellulose and large literal sheet sizes and weakly defective graphene flakes reaching high thermal conductivity and then converted them into hierarchical porous graphene carbon materials reaching superior supercapacity. The interconnected porous carbon framework, with macroporous walls sandwiched by micro/mesoporous activated carbon covering graphene flakes, was synthesized by template-free low-temperature activation of the cellulose/graphene hybrids at 650 °C. The graphene flakes could probably assist both the decrease in the temperature of the chemical activation of cellulose and the formation of the hierarchical carbon pores without destroying their sp² bonds. The porous graphene carbon-based supercapacitors exhibit a reversible specific capacitance of ~300 F/g and ultrahigh energy storage performance of 67 Wh/kg, 54 Wh/L, and 60 kW/kg over a 45 s discharge time.

INTRODUCTION

High-energy density storage and fast response supercapacitors are needed to serve the people to keep up with the high pace of modern life.1−6 A hierarchical porous carbon framework with micro-, meso-, and macropores can be made into desirable electrodes for high-performance supercapacitors.7−10 The macropores can work as a fast buffering reservoir for electrolytes, minimizing the diffusion distance of the ions and electrolytes from each pore, while the meso- and micropores provide a large accessible surface area for ion transport and charge accommodation.11−12 Recently, porous graphene-based composites have received intense attention because the flat open atomic structure of graphene allows ions and electrolytes fast access to its surface with the result being a fast charging or discharging rate for energy storage.13−17 On the other hand, although the theoretical specific surface area of a single graphene sheet is 2630 m²/g, experimentally accessible surface areas of graphene materials are far below this value because of the strong self-aggregation/stacking tendency of graphene flakes (GFs). To prevent the aggregation, many scientists and engineers are trying to design a three-dimensional (3D) framework, including converting flat flexible two-dimensional (2D) into 3D structure or making a treated carbon and graphene hybrids.18−22 Recently, Zhu and his co-workers23 reported that reduced graphene oxide activated KOH at 800 °C to yield a special 3D activated carbon analogue with a large surface area of >3000 m²/g as the electrode in a two-electrode symmetrical supercapacitor with excellent electrochemical performance. More recently, graphene oxide and polymer were also activated to produce 3D porous carbon with a large surface area and high specific capacity.24,25 However, in most cases, (reduced) graphene oxides were used as a starting material, which remains costly and is not competitive with commercial activated carbon. In addition, (reduced) graphene oxides were covalently converted because they were rich in defects without reflecting the intrinsic capacitance of individual graphene flakes.

Graphene is a two-dimensional material forming hexagonally sp² covalent-bonded carbon atoms.26 The strong and anisotropic bonding and the low mass of the carbon atoms give graphene an extremely high in-plane thermal conductivity (K) of up to 5300 W m⁻¹ K⁻¹ besides unique mechanical properties and chemical stability.27−29 The in-plane thermal conductance of graphene can reach a significant fraction of the theoretical ballistic limit in submicrometer samples, because of the large phonon mean free path (λ ~ 775 nm estimated near room temperature).28−30 However, the thermal conductivity of graphene is dependent on the layer number and crystal size of GFs and also strongly affected by interfacial interactions, atomic defects, and edges.30−33 This size effect is similar to that of graphite, where the large crystal size of highly oriented pyrolytic graphite (HOPG) has an in-plane K of ~2000 W m⁻¹ K⁻¹ at room temperature while small crystal size pitch-derived graphite has a much smaller in-plane K of ~200 W m⁻¹ K⁻¹.34,35 Recently, the thermal conductivity of graphene-based thermal interface materials has significantly increased over that of the matrix because of low Kapitza resistance at the graphene–matrix interface.31,36,37 In addition, reduced gra-
phenoxide-based materials have also been shown to exhibit high thermal conductivity. However, to the best of our knowledge, there is no report about the relationship between the thermal conductivity of graphene and the formation of hierarchical porous carbon materials.

Here, we present a scalable template-free energy-efficient approach to activating biomass cellulose and graphene hybrids to synthesize a novel hierarchical porous carbon graphene framework material. We used a large size of 10–40 μm and weakly defective GFs that were synthesized by a modified electrochemical exfoliation of graphite to replace reduced graphene oxide (Figure S1 of the Supporting Information presents the electron microscope images of the graphene flakes and a photograph of free-standing pure graphene films). The films of graphene and cellulose hybrids exhibit improved mechanical strength and thermal conductivity compared to those of cellulose. During the thermal activation of the films soaked by KOH, graphene flakes (GFs) were kept without destroying sp² bonds and covered with micro- and mesoporous activated carbons (Ac) converted from cellulose. At the same time, the hybrid of micro/mesoporous Ac-coated GFs formed as the sandwiched walls of macro pores to yield a hierarchical porous carbon framework that is interconnected. Surprisingly, we found that the temperatures of cellulose activation and gaseous decomposition of cellulose in the presence of KOH could decrease >150 °C compared with that of the control sample without graphene. We proposed that the high in-plane thermal conductivity of large size of GFs significantly contributed to both the significant decrease in the activation temperature of cellulose and the formation of hierarchical pores. These new carbons as supercapacitor electrodes perform significantly contributed to both the significant decrease in the activation temperature of cellulose and the formation of hierarchical pores. These new carbons as supercapacitor electrodes perform

### EXPERIMENTAL SECTION

#### Materials

Graphite (99.95% purity, Qingdao Huarun graphite Co., Ltd.), cellulose (98%, weight percentage, Sinopharm Chemical Reagent Co., Ltd.), potassium hydroxide (KOH, 97%, Wuhan Chujiang Chemical Co., Ltd.), poly(tetrafluoroethylene) (PTFE, solid powder, Dupont), activated carbon (Nanjing XFNANO Materials Tech Co., Ltd.), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄], Novolyte), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMI][BF₄], Novolyte), tetraethylammonium tetrafluoroborate/acetonitrile (TEABF₄/AN, Novolyte), lithium perchlorate (LiClO₄ powder, 98%), propylene carbonate (PC, anhydrous, 99.7%), lithium chloride (LiCl, 99%), ammonium (28%), N,N-dimethylformamide (DMF), and hydrochloric acid (HCl, 37%) were used in this study. The porous membranes were Celgard 3501 membranes. All the chemicals were used without further purification.

#### Preparation of Hierarchical Porous G-ac Materials

The graphene was prepared according to a modified electrochemical method reported in a previous work. The preparation of the hierarchical porous 3D G-ac composite materials with various mass ratios of cellulose to graphene flakes involves the synthesis of the films of cellulose/graphene hybrids followed by a chemical activation step by KOH. Typically, with the control of the weight ratios of cellulose to graphene, a certain volume of a cellulose aqueous solution (0.1 g/mL) and a graphene flake aqueous dispersion (4.8 mg/mL) were homogeneously mixed together and stirred at room temperature overnight. Then, the graphene/cellulose (GC) hybrid films were obtained by filtering and drying in vacuum at 60 °C for 6 h. Next, the hybrid films (1.0 g) were thoroughly mixed with a 7.0 M aqueous KOH solution (4.0 g of KOH) for 24 h. After that, the mixtures were placed in a furnace and heated at 650 °C for 1 h under an Ar flow with the temperature increasing at a rate of 5 °C/min. After being cooled to room temperature, the annealed samples were thoroughly washed with 0.1 M HCl and deionized water at least six times until the pH value reached 7.0. The final products were obtained after drying in vacuum at 100 °C for 20 h. A series of products denoted as G-ac1, G-ac8, G-ac16, G-ac24, and G-ac32 were prepared with various ratios of cellulose to graphene, where the number represents the mass ratio of cellulose to graphene. For example, G-ac24 is the G-ac product made of the precursor with a 24/1 cellulose/graphene mass ratio.

#### Fabrication of G-ac Working Electrodes and Supercapacitor Devices

Briefly, 95 wt % G-ac product and 5 wt % PTFE were homogeneously mixed in an ethanol solution to form a slurry state. Then the slurry was rolled into a uniform film onto a nickel foil. The weight of active material was calculated from the weight difference between the dried electrode of G-ac on nickel foil and pure nickel foil of the same size. For carbon materials and electrolytes, the G-ac powder was hot-pressed onto the current collector nickel foil and dried at 180 °C for 6 h under vacuum. Then, the electrode was punched into disks with a diameter of 1.2 cm (active area of 1.13 cm²). The supercapacitor devices were assembled in a glovebox filled with Ar by constructing two current collectors with active material and a porous film (Celgard3501) separator sandwiched. The electrolytes are [EMIM][BF₄], [BMI][BF₄], and TEABF₄/AN (1.0 M). The commercial activated carbon (Ac) with a BET specific surface area of 2007 m²/g and an average pore diameter of 1.9 nm and synthesized graphene flakes were used for comparison.

#### Electrochemical Measurement of Supercapacitor Performance

All the electrochemical tests were conducted at room temperature. Galvanostatic charge/discharge cycle tests, cyclic voltammetry (CV), and electrical impedance spectroscopy (EIS) studies were performed using CHI660E. The gravimetric capacitance (C) was calculated from galvanostatic discharge by using the formula C = (4ΔI)/ΔmV for the two-electrode cells, where I is the constant current, m is the total mass for both carbon electrodes, Δt is the discharge time, and ΔV is the voltage change during the discharge process. The energy density (1 Wh/kg = 3.2 kJ/kg) was estimated by using the formula E = CV²/8. The effective series resistance (ESR) was estimated using the voltage drop at the beginning of the discharge, \( V_{\text{drop}} \) at a certain constant current, I, with the formula \( \text{ESR} = V_{\text{drop}}/2I \). The resistance of two-electrode cell. The maximal power density calculated from RESR and normalized with the weight of the cell (two electrodes) is given by \( P_{\text{max}} = V^2/(4\text{RESR} \times m) \).

#### Thermal Conductivity Measurements

All the thermal conductivity tests were conducted at room temperature. The thickness (d) of CG films was recorded by an HK-210C instrument, and thermal diffusivity (a) and specific heat capacity (Cₜ) tests were conducted using an LFA447 instrument (NETSCH). The thermal conductivity (λ) was calculated with the formula \( \lambda = a \cdot C \). The density of the film was calculated with the equation \( \rho = m/V = SD, \) where \( m \) is the mass, \( V \) the volume, and \( S \) the area.

#### Material Characterizations

Scanning electron microscopy (SEM) images were recorded on a JSM-7001F field emission scanning electron microscope. Transmission electron microscopy (TEM) images were recorded with a JEM-2100F microscope at an acceleration voltage of 200 kV. The samples were supported on ultrathin carbon film-supported Cu TEM grids. X-ray powder diffraction (XRD) was recorded at a scan rate of 0.02°/s using the Cu Kα (1.540600 Å) line. XPS measurements were performed using a Thermo ESCALAB 250 spectrometer, employing an Al-Kα X-ray source with a 500 mm electron beam spot. Raman data were measured in a Jobin-Yvon HR-800 Raman system with the 488 nm line of an Ar laser as the excitation source. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a VERTEX70 (Bruker) spectrometer with the KBr source. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a VERTEX70 (Bruker) spectrometer with the KBr source. The thermal conductivity of large size of GFs significantly contributed to both the significant decrease in the activation temperature of cellulose and the formation of hierarchical pores.
The synthesis procedure of the G-aC framework includes the steps of the preparation of cellulose/graphene hybrid (CG) films and the chemical activation of the films by KOH at low temperature, as illustrated in Scheme 1. First, with the control of mass ratios of cellulose and graphene, a certain volume of a cellulose aqueous solution (0.1 g/mL) and a GF aqueous dispersion (4.8 mg/mL) (Figure S1 of the Supporting Information) were mixed and stirred at room temperature overnight to produce a homogeneous colloidal solution. Then, a film (Figure 1a) was obtained after the mixture had been filtered and dried. At this stage, a robust CG film with 4.0 wt % graphene has a mechanical strength of ~17 MPa (Figure 1b), which is more than 5-fold greater than that of the reported pure cellulose film (2.8 MPa). We think that the increase in mechanical strength can be attributed to the large size of robust GFs that were synthesized by the electrochemical process. They can serve as a platform for the self-assembly of cellulose microfibers and for the dehydroxidation and interconnection by the reaction of the oxygen group onto the edges and defects of GFs with the hydroxide group of cellulose, as shown in Scheme 1 (1). This interconnected structure could assist in the formation of the 3D porous carbon framework in the latter activation step.

More remarkably, the thermal conductivity of the CG films could be significantly improved over that of pure cellulose. The "laser flash point" method was used to measure the thermal conductivity of the films. The values of thermal diffusivity, specific heat, and density of the CG films with various mass percentages of GFs were measured. As presented in Table S1 of the Supporting Information and Figure 1c, the thermal diffusivity and thermal conductivity increase with an increase in the mass ratio of GFs. When the graphene content increases from 4.0 to 20 wt %, the thermal diffusivity increases from 2.15 to 16.3 mm²/s and the calculated thermal conductivity increases from 6.36 to 30.8 W m⁻¹ K⁻¹. The values are much higher than that of cellulose (0.46 W m⁻¹ K⁻¹).  

To activate cellulose, the film (1.0 g) was immersed (soaked) with a 7.0 M KOH (4.0 g) aqueous solution. After that, the sample was transferred into a furnace for chemical activation. The annealing condition was to heat the sample at 650 °C for 1 h with the temperature increasing at a rate of 5 °C/min under a flow of Ar gas. After being completely washed by HCl and deionized water and dried in vacuum at 100 °C for 20 h, product G-aC was obtained. As shown in Scheme 1 (2), the pore size distribution of G-aC is hierarchical in that GFs covered by micro- and mesoporous activated carbon form the sandwiched walls of macropores.

The pore size distribution and Brunauer-Emmett-Teller (BET) measurement data that were obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System. STA409PC) at a heating rate of 5 °C min⁻¹ from 20 to 1200 °C in Ar. Thermal conductivity measurement was done at LFA447 (NETSCH). The pore size distribution and Brunauer-Emmett-Teller (BET) specific surface area were deduced from the N₂ physical adsorption measurement data that were obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System.

### RESULTS AND DISCUSSION

The synthesis procedure of the G-aC framework includes the steps of the preparation of cellulose/graphene hybrid (CG) films and the chemical activation of the films by KOH at low temperature, as illustrated in Scheme 1. First, with the control of mass ratios of cellulose and graphene, a certain volume of a cellulose aqueous solution (0.1 g/mL) and a GF aqueous dispersion (4.8 mg/mL) (Figure S1 of the Supporting Information) were mixed and stirred at room temperature overnight to produce a homogeneous colloidal solution. Then, a film (Figure 1a) was obtained after the mixture had been filtered and dried. At this stage, a robust CG film with 4.0 wt % graphene has a mechanical strength of ~17 MPa (Figure 1b), which is more than 5-fold greater than that of the reported pure cellulose film (2.8 MPa). We think that the increase in mechanical strength can be attributed to the large size of robust GFs that were synthesized by the electrochemical process. They can serve as a platform for the self-assembly of cellulose microfibers and for the dehydroxidation and interconnection by the reaction of the oxygen group onto the edges and defects of GFs with the hydroxide group of cellulose, as shown in Scheme 1 (1). This interconnected structure could assist in the formation of the 3D porous carbon framework in the latter activation step.

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Thermogravimetric analysis (TGA) of the cellulose/KOH without a graphene precursor and graphene/cellulose/KOH with graphene (4.0 wt %) in Ar is shown in Figure 1d. An approximately 10 wt % loss between 220 and 280 °C could be assigned to the removal of oxygen-containing functional groups from cellulose and graphene. Remarkably, the gaseous decomposition temperature of cellulose in the presence of...
KOH jumped 200 °C from 920 to 720 °C in the presence of 4.0 wt % GFs. The low-temperature activation of cellulose and the formation of macropores and mesopores of G-aC product both could probably be assigned to the presence of large and highly thermally conductive GFs. This was confirmed by our control experiment that showed much less product than we expected was collected when we annealed the cellulose/KOH/graphene samples at 800 °C. According to various measurements, including the TGA–DSC analysis, we selected 650 °C as the optimal chemical activation temperature for CG and estimated that there was ~15 wt % GFs in the resulting G-aC product for a starting precursor of 4.0 wt % graphene of CG film (G-aC24). The highly porous and interconnected three-dimensional (3D) microstructure of G-aC was observed by electron microscopies (SEM and TEM). The walls of the macropores are GFs coated with activated carbon (Ac) (Figure 2a,b), which indicates that a substantial amount of micro- and mesopores is homogeneously distributed throughout the highly porous structure. Notably, the electron diffraction pattern for a graphene sheet covered by Ac shows the hexagonal dots overlaid with light rings (Figure 2c,d). This gives evidence that the single-crystalline-like graphene flake was kept intact without destroying the sp² bonds and grown with nearly amorphous activated carbon. Raman spectra (Figure S4a of the Supporting Information) confirmed the existence of graphene in Ac-G products. The high-resolution transmission electron microscopy (HR-TEM) images (Figure 2e and Figures S2 and S3 of the Supporting Information) further showed the existence of the dense 0.5−2 nm micropores surrounded with ≥2 nm mesopores. X-ray diffraction (XRD) patterns (Figure S4b of the Supporting Information) show that there is little (002) peak of graphite in G-aC or graphene, which demonstrates the homogeneous distribution of GFs and activated carbon to prevent the return of graphene into graphite during the annealing. X-ray photoelectron spectroscopy (XPS) and FTIR analysis further indicated the complete removal of most of the organic functional groups of cellulose except for the surface functional group of the pores at the relatively low activation temperature of 650 °C (Figure S4c,d of the Supporting Information).47

The nitrogen (N₂) adsorption−desorption isotherms of various G-aC samples were determined for the size distribution of the pores. As shown in Figure 3 (G-aC24 sample), the strong nitrogen adsorption below the relative pressure (P/P₀) of 0.1 is a feature of micropore filling.23,48 The continuous rise of the isotherms at the relative pressure of >0.1 implied the presence of an appreciable amount of mesopores.¹¹,49 The pore size calculated by the nonlocal density functional theory (NLDF) method assuming a slit geometry for micropores and a cylindrical pore geometry for the mesopores indicates the existence of well-defined micro- and mesopores. As shown in Figure S5 of the Supporting Information, the content of >2 nm mesopores increases with an increase in the graphene ratio while that of the micropores increases with an increase in the level of cellulose precursor (as activated carbon in G-aC). It shows that <2 nm micropores are dominant and >5 nm mesopores are fewer in number in the activated carbon synthesized using cellulose in the absence of graphene under the same condition. This suggested that the presence of GFs during the chemical activation is probably crucial for the formation of meso- and macropores and hierarchical pores for G-aC. There seems to be multiple relationships in pore sizes in G-aC (Figure 3b) (0.9−1.3, 2.0−2.5, 4−5.0, 8−10, 20, 40, and 60 nm), which may indicate that the walls of micropores were penetrated to form mesopores through quick heating by fast heat dissipation onto GFs. Brunauer−Emmett−Teller (BET) analysis showed that the specific surface area of G-aC was up to 1533 m² g⁻¹ for G-aC24, which is much larger than that of GFs (Table S2 of the Supporting Information). We have to point out the specific surface area was underestimated because <0.9 nm is out of range of our machine (N₂ gas). High-resolution transmission electron microscopy (HR-TEM) (Figure 2e and

![Figure 2](image-url)  
Figure 2. Electron microscopy analysis of a hierarchical porous activated carbon graphene framework (G-aC). (a and b) SEM images. They show macropores and up to several-micrometer pores formed by the walls of activated carbon covering GFs. TEM images of (c) pure GFs [inset, selected area electron diffraction pattern (SAED) for comparison] and (d) a sheet of G-aC. In the inset of panel d, SAED has the same shining hexagonal dots as a graphene sheet but with additional light rings of activated carbon. (e) High-resolution TEM image of the edge of panel d, showing the hierarchical micro- and mesopores of activated carbon onto a single graphene sheet.
Figure S3 of the Supporting Information) revealed that G-aC had a highly porous carbon structure with a large fraction of ~0.5 nm micropores. This kind of hierarchical 3D porous material of activated carbon grown onto GFs has several advantages. First, mechanically robust GFs can resist the stability of macroporous frameworks and good electrical contact and ion/electrolyte diffusion pathways. Second, activated carbon with micropores and mesopores counters the stacking behavior of GFs and provides a stable large surface area. Third, the thermal and chemical stability of carbon materials can withstand harsh conditions for long periods of time. Fourth, a rich renewable biomass cellulose precursor and low-temperature activation are able to decrease the cost of synthesis of the porous carbon materials.

These uncommon features allow G-aC to serve as a key component in a high-performance electrochemical energy storage supercapacitor. To test this idea, we used G-aC as an active electrode material to construct two-electrode symmetrical supercapacitor cells of G-aC onto two nickel foams sandwiched by an ion porous separator (Celgard 3501, 25 μm thickness). The electrolytes are a KOH aqueous solution, organic [tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN)] electrolytes, and ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]). For the sake of comparison, commercial activated carbon (Ac, 2007 m² g⁻¹) and pure graphene flakes were used as control samples.

Figure 4 shows the electrochemical performance of the supercapacitor with G-aC as electrodes immersed in 6 M aqueous KOH. Cyclic voltammetry (CV) testing (Figure 4a) shows nearly rectangular curves of G-aC compared with those of the graphene precursor and commercial Ac. The specific capacitance of G-aC is around 300 F/g at a slow scan rate of 5.0 mV/s, which is much higher than that of commercial Ac (100 F/g) or the graphene precursor (50 F/g). The galvanostatic charge/discharge curves at three current densities are shown in Figure 4b. The specific capacitances were calculated on the basis of the discharge curves with values of 280 and 203 F/g obtained at current densities of 1.0 and 8.0 A/g, respectively. The voltage drop at the initiation of the discharge is 0.04 V (for a current density of 1.0 A/g), suggesting a very low equivalent series resistance (ESR) in the test cell. Electrochemical impedance spectroscopy (EIS) confirmed the high quality of G-aC and the fast ion transport within the graphene electrodes. Frequency response analysis of the frequency range from 100 kHz to 1 mHz yields the Nyquist plot shown in Figure 4c. The near ~90° phase angle at low frequencies indicates capacitive behavior, and 90° phase angles at high frequencies indicate inductive behavior. The apparent areal specific capacitance at 0.01 Hz is high as 0.46 F/cm² (active area of 1.0 cm²) and remains 0.12 F/cm² at 10 Hz. The 1.2 Ω semicircle may result from electrode contact between the metal current collector and active graphene layer (Figure 4d, inset). There is nearly no fading after scanning for 5000 cycles (Figure 4d), which indicates the chemical stability of synthesized G-aC. High levels of performance of the organic electrolyte and ionic liquids are also obtained. Figure 5a presents the CV curve in the voltage range of 0–3.5 V with specific capacitances of 196, 187, and 160 F/g in ionic liquid of [EMIM][BF₄] at current densities of 1.0, 2.0, and 6.0 A/g, respectively (Figure S7 of the Supporting Information), which is comparable to the product by the chemical activation of reduced graphene oxide. The corresponding volumetric capacitances are 157, 150, and 128 F/cm³, respectively (the density of compressed G-aC is ~0.8 g/cm³). The energy density for G-aC calculated can reach 83.1 Wh/kg (66.4 and 53.6 Wh/L, respectively) at current densities of 1.0 and 6.0 A/g (charging or discharging time of 45
Moreover, the supercapacitor device could have a practical energy density of >20 Wh/kg (the active carbon material is around one-fourth of the device in weight), which is several times higher than that of commercial supercapacitors (~5 Wh/kg). For organic TEABF₄/AN, the voltage is the range of 0−2.7 V. The specific capacitances were calculated from the discharge charge curves with values of 171, 128, and 105 F/g obtained at current densities of 2.0, 5.0, and 10 A/g, respectively (Figure S6 of the Supporting Information). Moreover, 97−99% of the capacitances for G-aC-based supercapacitors were retained after 5000 constant current charge−discharge cycles at a current density of 1.0 A/g in various electrolytes (Figure 5c). The specific capacitances with different electrolytes tend to increase with a decrease in the molecular size of the electrolyte of TEABF₄/AN, [BMIM]BF₄, [EMIM]BF₄, and KOH. This may be related to the easier accessibility of the smaller size of charged electrolyte molecules (cations and anions) to small micropores of G-aC. A number of ~0.5 nm micropores (as shown in Figure 2e) can be accessible for the small sizes of K⁺ (0.27 nm) and OH⁻ (0.26 nm) but not for the sizes of solvated ions (~1.3 nm for Et₃N⁺·AN and ~1.1 nm for BF₄⁻·9AN) of the organic TEABF₄/AN system. Besides ion size, the electrical conductivity and viscosity of the electrolytes could also affect the specific capacitances (Table S3 of the Supporting Information). Further, the specific capacity of the G-aC-based supercapacitor was affected by the synthesis conditions, including the ratios of the precursors and activation temperature of theirs, as shown in Figure S8 of the Supporting Information. Many comparative data proved that the synthesis conditions have important effects on the pore size distribution and surface area of G-aC products and, subsequently, the supercapacitor performance with the G-aC as the active electrode layers.

**CONCLUSION**

In summary, hierarchical porous carbon graphene interconnected framework material was synthesized by a scalable template-free approach to activate biomass cellulose with KOH in the presence of graphene flakes (GFs) at 650 °C. The large size, weakly defective, and highly thermally conductive GFs that were synthesized by a modified electrochemical exfoliation of graphite could improve the mechanical strength and thermal conductivity of cellulose/graphene hybrids. In addition, GFs probably assisted the low-temperature activation and formation of hierarchical carbon pores. The synthesized carbon material exhibits the features of graphene flakes coated with micro- and mesoporous activated carbon forming the sandwiched walls of macropores. The supercapacitors with the new carbons as electrodes performed at a level of ~300 F/g in aqueous KOH and both high gravimetric (180−200 F/g) and high volumetric (145−160 F/cm³) specific capacitances in organic/ionic liquid electrolytes. The energy density and power density calculated for the supercapacitor with [EMIM]BF₄ ionic liquid reached a stable gravimetric value of 67.0 Wh/kg and a volumetric value of 54 Wh/L at a high current density of 6.0 A/g within 45 s. The new porous carbon material of activated carbon grown on graphene allowed us to combine each advantage of graphene and activated carbon and to overcome the disadvantage of graphene stacking; this combination could show great potential for commercialization.

**ASSOCIATED CONTENT**

### Supporting Information

Additional SEM and TEM images of graphene flakes and G-aC samples, thermal conductivity of cellulose/graphene hybrid films, spectroscopic characterization and nitrogen gas adsorption/desorption isotherms, and electrochemical performance of G-aC-based supercapacitors in organic electrolytes or ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**