Constructing 3D bacterial cellulose/graphene/polyaniline nanocomposites by novel layer-by-layer \textit{in situ} culture toward mechanically robust and highly flexible freestanding electrodes for supercapacitors

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\begin{abstract}
Rational structure, mechanical robustness, high conductivity, and favorable flexibility are important requirements for superior electrodes, which should not only possess high capacitance but also have freestanding structure without collector to improve the overall performance of supercapacitors. Herein, we demonstrate the fabrication of three-dimensional (3D) porous graphene-containing nanocomposites with highly dispersed graphene (GE) nanosheets in a 3D matrix of bacterial cellulose (BC) by a novel layer-by-layer \textit{in situ} culture (LBLC) method. The BC/GE nanocomposites are then deposited with polyaniline (PANI), leading to the formation of BC/GE/PANI nanocomposites. Mechanical tests demonstrate excellent robustness and flexibility of the as-prepared BC/GE/PANI nanocomposites, which are used as electrodes directly without any nickel foam or stainless steel wire. The BC/GE/PANI electrode with an optimal GE content has a specific capacitance of 645 F g\textsuperscript{-1} at a current density of 1 A g\textsuperscript{-1}, which is 2.5 times higher than that of BC/PANI and superior to most previously reported PANI-based electrodes. In addition, the symmetric supercapacitor assembled with BC/GE/PANI demonstrates a high energy density of 14.2 Wh kg\textsuperscript{-1} at a power density of 200 W kg\textsuperscript{-1}. The excellent electrochemical performance of this BC/GE/PANI electrode is due to its unique 3D porous structure with the uniform distribution of GE nanosheets in the BC matrix and even PANI on BC nanofibers and GE nanosheets, which makes it very promising for diverse flexible energy storage devices. The methodology presented in this work can be extended to the preparation of other BC-based nanocomposite electrodes.
\end{abstract}
1. Introduction

Supercapacitors are widely considered as a class of very promising energy storage devices because of their rapid charge and discharge rate, moderate energy density, long operating lifetime, and high power density [1,2]. Recently, much research has been devoted to the exploration of flexible and freestanding electrodes with high electrochemical performance and good mechanical properties [3]. Although the combination of nanocarbonaceous materials and metal oxides [4,5] or all-carbon materials [6] can make flexible electrodes, the deposition of active conducting materials (such as nanocarbonaceous materials and conducting polymers) on flexible polymeric substrates shows better flexibility [7,8]. Moreover, increasing attention to environmental issues has driven researchers to focus more on renewable, biodegradable, and environmentally friendly polymer substrates. Among many polymers, cellulose is an attractive emerging renewable material, which has advantages of low cost, wide availability, and biodegradability. Compared to plant-derived cellulose, bacterial cellulose (BC) is superior because it has higher crystallinity and is free of lignin/seemcellulose. Additionally, its production requires no harsh chemical and mechanical treatments, and it can be mass-produced through a microbial fermentation process. With these advantages, BC has gained great interest as the light and flexible electrodes for supercapacitors [9]. In general, BC is combined with various conductive additives. Conductive polymers including polypyrrole (PPy) [10] and polyaniline (PANI) [11] are common additives. Carbon nanotube (CNT) was also combined with BC [12]. Among these additives, graphene (GE) shows great promise in supercapacitors [13] as well as other applications such as conductive switching and bioimaging [14,15]. For example, Xu et al. fabricated the PPy/BC flexible supercapacitor electrodes with a low initial capacitance of 459.5 F g$^{-1}$ at 0.16 A g$^{-1}$ [16]. In another study, PPy/nickel sulfide/BC electrodes were produced and a high initial capacitance of 713 F g$^{-1}$ at 0.8 mA cm$^{-2}$ was achieved [17]. The supercapacitors using PPy/CuO/BC electrodes had a specific capacitance of 601 F g$^{-1}$ which retained at 385 F g$^{-1}$ after 300 cycles [6]. Very recently, Huang et al. reported the nitrogen-doped carbon networks/graphene/BC supercapacitors, which had exceptional cycling stability (~100% retention after 20000 cycles), although the specific capacitance was not attractive (318 F g$^{-1}$) [13]. However, similar to many previous reports [13,18], the compounding of BC with GE nanosheets was realized by mechanical mixing, which may destroy the advantageous intrinsic three-dimen- sional (3D) network nanostructure of BC and could not ensure uniform distribution of GE nanosheets in the BC matrix. The breakage of the 3D continuity not only reduced the electrical conductivity but also greatly degraded the mechanical robustness and stability.

In general, the incorporation of GE or CNTs into the inner core of 3D BC network by filtration or post immersion in the solution of GE or CNTs is challenging due to the lack of large pores (> 10 μm) in pristine BC [19]. To tackle this, we previously prepared highly dispersed GE-incorporated BC by the novel in situ biosynthesis method, in which the BC biosynthesis and hybridization of GE into the BC network were simultaneously achieved [20]. Although the in situ biosynthesis by the static culture can maintain the intrinsic 3D porous network structure of BC [20], there were no GE nanosheets in the inner part of BC when the thickness of BC hydrogel is larger than 3 mm. Up to date, there is no effective approach to prepare BC/GE nanocomposites with highly dispersed GE nanosheets in the BC network.

In this work, we report a novel layer-by-layer in situ culture (LBLC) method that can produce BC/GE nanocomposites with highly dispersed GE nanosheets in the BC network. This method is facile, versatile, cost-effective, and ecofriendly. Of particular importance is that GE nanosheets can be uniformly distributed in the 3D interconnected network of BC throughout the samples even when the sample thickness is larger than 3 mm and GE nanosheets are firmly bundled by BC nanofibers, which ensures a close mechanical linking and thus an ultrahigh mechanical strength. Furthermore, when deposited with PANI, one of the most promising supercapacitor materials due to its low cost, simple preparation, and reversible doping/dedoping electrochemistry, the as-obtained BC/GE/PANI nanocomposite electrodes show excellent flexi- bility and capacitive performance. Furthermore, when the BC/GE/ PANI nanocomposite was assembled into the symmetric supercapacitor, a high energy density can be achieved. These properties come from its 3D interconnected porous structure, large surface area, large quantity of mesopores and macropores, highly dispersed GE nanosheets in the BC matrix, and evenly deposited PANI on BC nanofibers and GE na- nosheets.

2. Materials and methods

2.1. Preparation of BC/GE nanocomposites

The bacterial strain used in this work was A. xylinum X-2 and the culture medium was composed of 2.5% (w/v) glucose, 0.75% (w/v) yeast extract, 1% (w/v) tryptone, and 1% (w/v) disodium phosphate (Na2HPO4). The BC pellicles used in this work was prepared by a novel LBLC method. Briefly, the BC base film was prepared by the conventional static culture method reported in our previous work [21-23]. The culture medium was sprayed onto the BC base film using a nebulizer, forming a membrane-medium interface, on which BC was grown until the sprayed medium was completely consumed. The subsequent cycles of spraying-growing continued until a predetermined BC thickness was obtained. The resultant BC was purified by soaking in deionized water at 90 °C for 2 h, boiled in a 0.5 M NaOH solution for 15 min, and then washed several times with deionized water until it became neutral. To prepare BC/GE nanocomposites, a GE-dispersed culture medium was prepared following the process reported in our previous work [24,25]. Thereafter, GE suspension (monolayer, purity ≥ 99.4 wt%, concentra- tion of suspension = 1 mg mL$^{-1}$, Institute of Coal Chemistry, Chinese Academy Sciences, China) was added to the culture medium afore- mentioned at a volume ratio of 1: 5, followed by intense stirring for 60 min. The subsequent preparation procedures for BC/GE nano- composites were the same as those for the preparation of BC. The r- sultant nanocomposite hydrogel was named BC/GE-1. BC/GE-2 and BC/GE-3 were obtained when the volume ratios of the GE suspension to the culture medium were 1: 3 and 1: 1, respectively. The GE content in each BC/GE nanocomposite is presented in Table S1.

2.2. Preparation of BC/GE/PANI nanocomposites

The BC hydrogel (20 × 20 × 1 mm$^3$) was immersed in an HCl (1 M, 50 mL) aqueous solution followed by adding aniline monomer (2.5 mmol) under constant stirring for 24 h at room temperature to allow the impregnation of aniline into the inner area of the BC aerogel. The mixture solution was transferred into an ice-water bath at 5 °C and an ammonium persulfate solution (10 mL, 2.5 mmol) was added dropwise to the above solution under vigorous stirring. The molar ratio of the aniline monomer to the ammonium persulfate solution was 1: 1. After chemical reaction for 6 h, the BC/PANI product was washed with deionized water several times followed by freeze-drying for 24 h, re- sulting in the BC/PANI hydrogel. The hydrogel was freeze dried at −50 °C for 24 h to obtain the BC/PANI aerogel. The preparation of BC/ GE/PANI was identical to that of BC/PANI except that BC/GE hydrogel rather than BC hydrogel was employed. When BC/GE-2 was used as the substrate, the resultant product was BC/GE/PANI-2, and likewise BC/ GE/PANI-1 and BC/GE/PANI-3 were obtained. The compositions of each BC/GE/PANI nanocomposite are presented in Table S1.

2.3. Characterizations

The morphology of BC, BC/PANI, BC/GE, and BC/GE/PANI aerogels was observed by a Nanosem 430 field emission scanning electron mi- croscope (FE-SEM, FEI, USA) and a JEM-2100 F transmission electron

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microscope (TEM). Structural characterization was carried out by a Rigaku D/max 2500 diffractometer operating with Cu Kα radiation (λ = 0.1541 nm) at a scanning rate of 4° min⁻¹ over a 2θ range of 5–40°. Fourier transformed infrared spectroscopy (FTIR) spectra were recorded using a Shimadzu IRPrestige-21 FTIR spectrometer in a spectral range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. Surface chemical nature was determined using a PHI Quantera X-ray photoelectron spectroscope (XPS, ULVAC-Phi, Inc., Japan), and the binding energy was calibrated with C 1s = 284.8 eV. The specific surface area and pore structure were determined by N2 adsorption-desorption isotherm hysteresis using a NOVA 2000 surface area and pore size analyzer operated at 77 K. Thermal properties were determined from the thermogravimetric analysis (TGA), using a thermal analyzer (DTG-60H, Shimadzu) at a heating rate of 5°C min⁻¹ over the temperature range of 25–800°C under flowing nitrogen at the rate of 150 mL min⁻¹. Wettability of BC/PANI and BC/GE/PANI was evaluated by deionized water contact angle measurement using a contact angle meter (Drop Master 300).

2.4. Measurements of electrochemical performance

The electrochemical measurements were carried out using a three-electrode configuration in a 1 M H₂SO₄ electrolyte. Each of the as-prepared electrodes was used directly as the working electrode (10 × 5 × 1 mm³) without binders or other additives. A platinum gauze was used as the counter electrode and a standard calomel electrode acted as the reference electrode. Cyclic voltammetry (CV), galvanostatic charge/discharge, and impedance spectroscopy measurements were carried out using a potentiostat (CHI 660D, Shanghai Chenhua Instrument Co., Ltd, Shanghai, China). CV tests were performed between −0.2 and 0.8 potential window at a scan rate of 25–50 mV s⁻¹. The galvanostatic charge-discharge cycle tests were conducted at a current density range of 0.5–8 A g⁻¹. The electrochemical impedance test was carried out at a frequency range of 0.01–10⁵ Hz. Symmetric supercapacitor was measured in two-electrode sandwich-configuration supercapacitor using two pieces of BC/GE/PANI-2 as electrodes (immersed in 1 M H₂SO₄), which were separated with cellulose acetate membrane (Fig. S1 in the Supporting Information). The potential range for both CV and galvanostatic charge/discharge tests varied from 0 to 0.8 V.

3. Results and discussion

3.1. Morphology, structure, and physical properties

The preparation processes for BC/GE/PANI and BC/PANI are schematically illustrated in Fig. 1a. In this work, the BC/GE was prepared using a novel LBLC method, which produced a 3D BC/GE nanocomposite with highly dispersed GE nanosheets in the 3D porous BC network (Fig. 1b). The close crosslink between BC nanofibers and GE nanosheets (Fig. 1c) forms continuous conductive paths and then favors fast electron transport during the charge/discharge process, thus improving electrochemical performance of the resultant BC/GE/PANI electrodes. After adding aniline monomer molecules into the precursor solution of BC/GE, they migrate into the inner network of BC/GE/PANI and form PANI networks (Fig. 1d).

![Fig. 1.](image-url)
absorbed onto the surfaces of BC nanofibers and GE nanosheets, and finally polymerize in situ. These steps lead to uniform PANI coating on BC nanofibers and GE nanosheets (Fig. 1d and e and Fig. S2), which allows for extensive exposure of PANI to electrolytes. Furthermore, due to the highly flexible nature of BC, the freestanding BC/GE/PANI is also very flexible (inset in Fig. 1e). To further determine its flexibility, we compared its electrical conductivity and microstructure before and after 100 bending cycles. The results demonstrate no significant changes in electrical conductivity (Table S2) and microstructure (Fig. S3), suggesting its excellent flexibility.

X-ray diffraction (XRD) analysis was carried out to determine the structure of PANI, BC, BC/PANI, BC/GE, and BC/GE/PANI-2. As shown in Fig. 2a and Fig. S4, three sharp peaks of BC located at 14.5, 16.2, and 22.6° correspond to (110), (1 1 0), and (2 0 0) planes of cellulose I, respectively [20,26]. The XRD pattern of BC/GE shows sharply reduced peak intensity of (110) and (1 1 0) (Fig. S4). The calculated crystallinity indices (C<sub>i</sub>), according to the Segal's method [27,28], are 91, 79, 69, and 62% for BC and BC/GE-1, BC/GE-2, and BC/GE-3, respectively. The reduction of C<sub>i</sub> for BC/GE is related to the disturbance of the bacteria movement as a result of the viscosity change with the GE additive [31,32]. As shown in Fig. 2b, there are seven peaks in the spectrum of PANI, which are located at 3434 (N–H stretching of the benzenoid ring), 1485 (C–C stretching of the quinoniod ring), 1244 (–C–H bending of secondary aromatic amines), 1111 (–C–H bending of the benzenoid ring), and 796 cm<sup>−1</sup> (–C–H bending of secondary benzenoid ring) [35–37]. The BC/PANI and BC/GE/PANI-2 present the peaks of PANI and BC, further confirming the formation of PANI on BC and GE. Interestingly, the intensities of the O–H stretching of BC at 3344 cm<sup>−1</sup> and the N–H stretching vibration of PANI at 3434 cm<sup>−1</sup> decrease sharply in the spectrum of BC/GE/PANI-2. Moreover, the BC peaks at 1164 and 1060 cm<sup>−1</sup> (Fig. S5) red shift to 1154 and 1057 cm<sup>−1</sup>, respectively (Fig. 2b). These results indicate the formation of hydrogen bonds at the BC-PANI interfaces between the -OH groups of BC and the N–H groups of PANI [38], which play an important role in guiding the polymerization process of PANI.

We also conducted Raman analysis to determine the chemical nature of BC/GE, BC/PANI, and BC/GE/PANI-2. As shown in Fig. S6, two typical bands (at 1348 and 1595 cm<sup>−1</sup>) are observed for BC/GE and GE, which can be ascribed to the G and D bands of GE, respectively [39]. Furthermore, there is no difference in the I<sub>D</sub>/I<sub>G</sub> values between GE and BC/GE, which represents the number of structural defects existing in carbon materials [40]. This finding indicates that the structure of GE is not affected by the LBLC process, agreeing with our previous result [20]. As shown in Fig. 2c, BC/GE/PANI-2 and BC/PANI show similar characteristics peaks of PANI (420, 605, 821, 1346, and 1595 cm<sup>−1</sup>), suggesting the complete wrapping of GE nanosheets and BC nanofibers by PANI.

The chemical bonding in BC, BC/GE-2, and BC/GE/PANI-2 was further confirmed by XPS measurements. The XPS survey spectra (Fig. 3a) of BC and BC/GE-2 show the presence of C and O elements while two extra elements (N and Cl) are noted for BC/GE/PANI-2. The presence of N proves the deposition of PANI and the existence of Cl confirms the doping of PANI by HCl [39]. High-resolution XPS spectra are shown in Fig. 3b-f. The C 1s of BC (Fig. 3b) shows three distinct peaks at 284.6 eV (C–C), 286.7 eV (C–O), and 288.5 eV (O–C–O)
In addition to the above three peaks, the C 1s of BC/GE-2 (Fig. 3c) exhibits another peak at 287.7 eV (C–O) [41,42]. The C 1s spectrum of BC/GE/PANI-2 (Fig. 3d) can be deconvoluted into peaks of 284.9 eV (C–C), 286.6 eV (C–N), 287.6 eV (C–O), and 288.6 eV (O–C–O) [39]. The presence of C–N indicates the occurrence of hydrogen bonding between the –OH groups of BC and the N–H groups of aniline [38], in agreement with the FTIR results. The N1s of BC/GE/PANI-2 (Fig. 3e) consists of three peaks at 399.0 eV (Quinoid imine =N–), 399.5 eV (Benzooid amine, –NH–), and 401 eV (positively charged nitrogen, N+) [43,44]. Deconvolution of Cl 2p (Fig. 3f) yields multiple peaks at 197.3 eV (Cl−), 198.8 eV (Cl+), and 200.1 eV (–Cl) [45]. The XPS results, together with the FTIR and Raman results, indicate the formation of PANI in BC/GE/PANI-2.

The porosity of BC, BC/PANI, BC/GE-2, and BC/GE/PANI-2 was analyzed by N2 adsorption-desorption measurement. Fig. 4 reveals that all materials exhibit a characteristic type IV isotherm, suggesting the presence of many mesopores. Brunauer-Emmett-Teller (BET) analysis (Table 1) indicates that the specific surface areas of BC, BC/PANI, BC/GE-2, and BC/GE/PANI-2 are 80.4, 23.2, 105.5, and 79.3 m² g⁻¹, respectively. The pore size distribution (insets in Fig. 4) is calculated from the adsorption branches of the isotherm. The result reveals the formation of the pores with an average pore size of about 4.7, 4.2, 5.3, and 4.6 nm for BC, BC/PANI, BC/GE-2, and BC/GE/PANI-2, respectively. The smaller pore size and specific surface area of BC/PANI than BC are simply due to the blockage of PANI coating on BC nanofibers. Likewise, similar blockage leads to smaller pore size and specific surface area of BC/GE/PANI-2 than BC/GE-2. The larger pore size and specific surface area of BC/GE-2 over bare BC can be ascribed to the facts that GE nanosheets have large specific surface area and they acts as support to reduce shrinkage of BC aerogel during freeze-drying.

The wettability of BC, BC/PANI, BC/GE-2, and BC/GE/PANI-2 was measured (Fig. S7). BC, BC/PANI, BC/GE, and BC/GE/PANI-2 show contact angles of 39.2, 39.0, 43.5, and 42.8°, respectively. This indicates that the incorporation of GE reduces the wettability of BC while PANI has no obvious effect on the wettability of BC/GE-2. Overall, each material exhibits favorable wettability due to the –OH groups from BC and the mesoporous structure [46]. The good wettability is beneficial to the fast transport and diffusion of electrolytes.

Fig. S8 presents the TG profiles of GE, BC, BC/GE, and BC/GE/PANI-2. GE shows a total weight loss of around 15.8% due to the removal of...
adsorbed water and –OH groups. Three weight loss stages can be observed for pure BC while it only shows a typical single drastic weight loss step at 280–420 °C, which is similar to that observed in our previous study [47,48]. This is attributed to the thermal degradation of BC fibers including depolymerization, dehydration and decomposition of glucosyl units followed by formation of a charred residue [49]. The slight weight losses from ambient to 280 °C and from 420 to 800 °C are due to the dehydration of BC and the decarboxylation and decarbonylation reactions, respectively. The TG curves of BC/GE show obvious similarity to pure BC. The only difference is their residual percentages, which are 10.6, 13.2, 15.9, and 19.3%, for BC and BC/GE-1, BC/GE-2, and BC/GE-3, respectively. Notably, the TG profile of BC/GE/PANI-2 shows three distinct stages. It exhibits a slight weight loss of about 8.3% before 120 °C due to the loss of adsorbed water. The weight loss (~14.9%) between 210 and 320 °C is due to the decomposition of cellulose into D-glucopyranose and free radical [6] and the removal of dopants from PANI [50,51]. The highest rate of weight loss is observed after 320 °C due to the decomposition of BC/GE/PANI-2.

We tested the mechanical properties of BC, BC/GE-2, BC/PANI, and BC/GE/PANI-2 in hydrogel state. As shown in Fig. 5a and Table S3, the incorporation of GE into BC leads to significant improvements in tensile strength (62.5%) and tensile modulus (172.3%) of BC/GE-2 as compared to bare BC. The surface deposition of PANI also improves the tensile strength and modulus of BC/PANI. As seen in Fig. 5a and Table S2, a similar conclusion can be drawn for BC/GE/PANI-2. Namely, the deposition of PANI on BC/GE-2 also greatly enhances the mechanical strength and modulus of BC/GE/PANI-2. Again, the BC/GE/PANI-2 still presents excellent flexibility (inset in Fig. 1e) despite its reduction of strain at break as compared to BC/GE-2. This is attributable to the excellent flexibility of BC substrate.

Furthermore, we tested the electrical conductivity of BC/PANI and

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**Table 1**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$·g$^{-1}$)</th>
<th>Pore volume (cm$^3$·g$^{-1}$)</th>
<th>Pore size (nm)</th>
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<tr>
<td>BC</td>
<td>80.4</td>
<td>0.27</td>
<td>4.7</td>
</tr>
<tr>
<td>BC/PANI</td>
<td>23.2</td>
<td>0.08</td>
<td>4.2</td>
</tr>
<tr>
<td>BC/GE-2</td>
<td>105.5</td>
<td>0.29</td>
<td>5.3</td>
</tr>
<tr>
<td>BC/GE/PANI-2</td>
<td>79.3</td>
<td>0.29</td>
<td>4.6</td>
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Fig. 4. $N_2$ adsorption-desorption isotherms and pore size distribution of BC (a), BC/PANI (b), BC/GE-2 (c) and BC/GE/PANI-2 (d).

Fig. 5. (a) The tensile stress-strain curves of BC, BC/GE-2, BC/PANI, and BC/GE/PANI-2 nanocomposites; (b) Electrical conductivity of BC/PANI and BC/GE/PANI-2.
BC/GE/PANI-2 by a four-probe method (Fig. 5b). Interestingly, the electrical conductivity of BC/GE/PANI-2 (1.66 ± 0.05 S cm$^{-1}$) is twice that of BC/PANI (0.82 ± 0.03 S cm$^{-1}$), and comparable to previously reported fabric/GE/PPy (1.2 S cm$^{-1}$) [52] and cellulose/GE/PPy (2.3 S cm$^{-1}$) [53].

3.2. Electrochemical performance

The electrochemical performance of BC/PANI and BC/GE/PANI electrodes was determined by a three-electrode system in a 1 M H$_2$SO$_4$ solution. Fig. 6a-d presents the CV curves of BC/PANI and BC/GE/PANI electrodes at varying scan rates from 2 to 50 mV s$^{-1}$. Obviously, the increase of scan rates leads to a positive shift of oxidation peaks and a negative shift of reduction peaks, which can be ascribed to the increased internal resistance [2,39]. Additionally, the redox peaks weaken as the scan rate increases, mainly due to inadequate time for the ionic diffusion [2,54]. Fig. 6e compares the CV curves of BC/PANI and BC/GE/PANI electrodes measured at 2 mV s$^{-1}$. Compared to BC/PANI, the CV curves of BC/GE/PANI electrodes show a larger capacitive area and more distinct redox peaks, indicating that the incorporation of GE improves the electrochemical performance of BC/GE/PANI electrode. Furthermore, two pairs of well-defined redox peaks (A$_1$/C$_1$ and A$_2$/C$_2$) are noted in the CV curves of various BC/GE/PANI electrodes, which are attributable to the transition of two different PANI forms, namely the leucoemeraldine form and polaronic emeraldine form [55,56], and thus reveal the strong pseudocapacitive behavior of PANI [18]. The enhanced performance of BC/GE/PANI electrodes over BC/PANI electrode can be due to the incorporation of GE with improved electrical conductivity (Fig. 5b) and increased surface area (Fig. 4).

The charge/discharge profiles of BC/PANI and BC/GE/PANI electrodes at current densities of 0.5–5 A g$^{-1}$ are shown in Fig. 7a-d. The charge/discharge duration of each electrode decreases as the current density decreases, which is common for most supercapacitors [57,58] and primarily due to the insufficient employment of active components during the short time. With limited time, the ions are incapable of penetrating further into the electrodes, resulting in limited electrochemical reactions occurring only at surfaces [54]. The charge/discharge curves of BC/GE/PANI electrodes at various current densities...
show better charge/discharge symmetry than BC/PANI electrode, suggesting their superior electrochemical reversibility. However, the charge/discharge curves of BC/GE/PANI electrodes do not show ideal linear profiles, suggesting the coexistence of electric double-layer capacitance and pseudocapacitance [59,60]. The electrical double layer capacitors store the energy in a purely electrostatic way as a consequence of the formation of an Helmholtz electrical double layer at the electrode–electrolyte interface, while the pseudocapacitors store the energy by means of fast and reversible redox reactions that take place on the surface of the electrode [61]. The discharging curves exhibit two voltage stages from 0.8 to 0.45 V and from 0.45 to −0.2 V. The first stage (0.8–0.45 V) has very short discharging duration, which is ascribed to pure electric double layer capacitance while the second stage (0.45–−0.2 V) possesses a much longer discharging duration, which is due to the combination of pure electric double layer capacitance of GE and pseudocapacitance of PANI [39,62]. Moreover, the voltage drop (called IR drop) in the discharge curves (Fig. 7a-d), which is attributed to the internal resistance of electrodes [63], increases as the current...
density increases. Fig. 7e reveals that the discharge curves are not ideal straight lines, similar to that of the BC/CNT/PANI electrode [12], which is an indication of a faradic reaction process [59]. Additionally, the voltage drop of BC/GE/PANI electrodes is much smaller than that of BC/PANI electrode, implying that BC/GE/PANI electrodes have lower internal resistance than BC/PANI electrode, and the lowest voltage drop is observed in BC/GE/PANI-2 electrode. Therefore, the GE incorporation into BC/PANI can effectively reduce its internal electrical resistance. However, as indicated in Fig. 7e, too much GE loading leads to increased internal resistance, which is likely due to GE aggregation. This result agrees well with the CV results.

The specific capacitances of these electrodes can be calculated from the discharge curves according to the following equation [64]:

$$C = \frac{I_m \Delta t}{\Delta V}$$

(1)

where $I_m$ represents current density (A·g$^{-1}$), $\Delta t$ is discharging time (s), $\Delta V$ means potential window (V). As shown in Fig. 7f, the maximum specific capacitance (645 F·g$^{-1}$ at 1 A·g$^{-1}$) is observed in BC/GE/PANI-2 electrode, which is around 3.3 times of the BC/PANI electrode (191 F·g$^{-1}$). When the current density is increased from 0.5 to 8 A·g$^{-1}$, the BC/GE/PANI-2 electrode still maintains a high value of 418 F·g$^{-1}$, showing a retention of 55% of its initial capacitance. The specific capacitance of the BC/GE/PANI-2 electrode is much better than those of most previously reported PANI-based electrodes (Table S4) comparable to that of BC/CNT/PANI (656 F·g$^{-1}$ at 1 A·g$^{-1}$) [12].

The cycling stability of BC/PANI and BC/GE/PANI-2 electrodes was tested at 5 mV·s$^{-1}$ for up to 1000 cycles (Fig. 7g). The capacitance retention, $C_{ret}$, was calculated according to the equation:

$$C_{ret} = \frac{C_m - C_1}{C_1} \times 100$$

(2)

where $C_1$ is the initial capacitance and $C_m$ is the remaining capacitance after $m$ cycles. The $C_{ret}$ of BC/PANI electrode is only 58.3% after 1000 cycles while BC/GE/PANI-2 electrode exhibits a capacitance retention of 82.2% after 1000 cycles, indicating a better cycling performance. The enhanced cycling stability can be attributed to the highly dispersed GE nanosheets in the BC matrix, which strengthen the BC matrix to resist the mechanical deformation in the redox process of PANI. The capacitance retention of BC/GE/PANI-2 electrode is comparable to those reported by Wang et al. who observed a retention of 87% for the GE/PANI electrodes [39] and Yang et al. who declared a retention of 82% after 3000 cycles for the cellulose/CNT/PANI electrode [65].

To understand the electrochemical behaviors of the above electrodes, electrochemical impedance spectroscopy (EIS) analysis was carried out in the frequency range of 0.01 Hz–100 kHz. Fig. 7h shows the Nyquist plots of BC/PANI and BC/GE/PANI electrodes. The Nyquist plots have a semicircle in high frequency region (the diameter of the semicircular indicates charge-transfer resistance, $R_{ct}$) and a straight line at low frequency region (indicator of the capacitive behavior). Obviously, the BC/GE/PANI-2 electrode shows the lowest $R_{ct}$ value among four electrodes, suggesting that the GE incorporation at an optimal content can reduce the electrical resistance and improve the electron transfer and ion transport. Furthermore, the first intercept at $Z'$ axis represents the intrinsic ohmic resistance, which is 6.1, 4.8, 3.3, and 4.1 Ω for BC/PANI, BC/GE/PANI-1, BC/GE/PANI-2, and BC/GE/PANI-3 electrodes, respectively. Therefore, the BC/GE/PANI-2 electrode shows the lowest charge transfer resistance and intrinsic ohmic resistance (3.3 Ω), which is also much lower than that of the BC/CNT/PANI electrode (19.5 Ω) [12]. These results agree with the conductivity testing.

To further explore the practical application of the as-prepared BC/GE/PANI-2 composite for supercapacitors, a two-electrode symmetric supercapacitor was fabricated with BC/GE/PANI-2 in 1 M H$_2$SO$_4$ aqueous electrolyte. Fig. 8a shows the CV curves of the symmetric supercapacitor measured at different scan rates. Note that the near rectangular shape of these CV curves can be well kept without any obvious distortion, which suggests good charge propagation through the electrical double layer at the electrode/electrolyte, similar to the reported sulfonated PANI/graphene supercapacitor [66]. Fig. 8b shows the galvanostatic charge/discharge curves of the symmetric supercapacitor at
different current densities in the range of 0.5–8 A g⁻¹. It is clearly seen that all of the charge/discharge curves show slight deviations from the ideal triangular shape, indicating the significant pseudocapacitance contribution of PANI [67]. The specific capacitance of the electrode obtained at different current densities was presented in Fig. 8c. At a low current density of 0.5 A g⁻¹, the specific capacitance of the electrode is as high as 643 F g⁻¹. Even at a high current density of 8 A g⁻¹, the specific capacitance of the electrode remains at 413 F g⁻¹. Fig. 8d gives the Ragone plots of the symmetric supercapacitor in 1 M H₂SO₄ aqueous electrolyte. It can be found that the as-fabricated symmetric supercapacitor exhibits the maximum energy density of 14.2 Wh kg⁻¹ at a power density of 200 W kg⁻¹ and retains at a value of 9.2 Wh kg⁻¹ at a higher power density of 3900 W kg⁻¹. Although the maximum energy density is lower than some PANI-based supercapacitors (such as PANI/boron-doped graphene [68] and PANI/multiwalled CNT [69]), it is higher than most other PANI-based supercapacitors, such as graphene-mesoporous PANI hybrid [70], PANI-graphene nanoribbons [71], PANI/CNT [72], PANI/cellulose nanoporous microspheres [73], and porous carbon/PANI [74].

Based on these results, it can be concluded that BC/GE/PANI-2 electrode is very promising considering its excellent electrochemical performance as well as integrated structure, mechanical robustness, and scalable fabrication process. We propose the following mechanisms that govern the electrochemical performance of the BC/GE/PANI electrodes. Firstly, the use of GE nanosheets greatly facilitates electron transport during the charge–discharge process. Secondly, the BC nanofibers and GE nanosheets enable the high mass loading of PANI. Thirdly, the porous nanofibrous network structure shortens the ions diffusion distance. Lastly, the enlarged specific surface area maximizes the exposed active sites to electrolytes.

4. Conclusions

In summary, mechanically strong and highly flexible freestanding bacterial cellulose/graphene/polyaniline (BC/GE/PANI) nanocomposites with 3D porous structure have been prepared by a novel LBLC method followed by in situ chemical polymerization. Through this synthesis route, GE nanosheets are well distributed in the highly porous 3D BC network and PANI is uniformly deposited on the surfaces of both BC nanofibers and GE nanosheets. Excellent gravimetric capacitance (645 F g⁻¹ at 1 A g⁻¹) and cycling stability (with capacitance retention of 82.2% after 1000 cycles) are achieved due to the presence of numerous mesopores and a large specific surface area. Moreover, the symmetric supercapacitor made of BC/GE/PANI-2 electrodes exhibits a high maximum energy density of 14.2 Wh kg⁻¹ at a power density of 200 W. We believe that the strategy presented here provides a versatile, facile, and scalable method for fabricating mechanically robust and binder-free electrodes for potential applications in flexible electronic products.

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Appendix A. Supplementary data

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