



# Simultaneously depositing polyaniline onto bacterial cellulose nanofibers and graphene nanosheets toward electrically conductive nanocomposites

Yizao Wan<sup>a,b</sup>, Jin Li<sup>a</sup>, Zhiwei Yang<sup>b,\*\*</sup>, Haiyong Ao<sup>b</sup>, Lingling Xiong<sup>b</sup>, Honglin Luo<sup>a,b,\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, China

<sup>b</sup> School of Materials Science and Engineering, East China Jiaotong University, Nanchang 330013, China



## ARTICLE INFO

### Keywords:

Bacterial cellulose  
Graphene  
Polyaniline  
Mechanical property  
Electrical conductivity

## ABSTRACT

In this study, we report the construction of a ternary flexible nanocomposite of bacterial cellulose/graphene/polyaniline (BC/GE/PANI) via a facile two-step strategy. Bacterial cellulose/graphene (BC/GE) is first prepared by a novel *in situ* membrane-liquid-interface method, in which the three-dimensional continuous BC nanofibers can be maintained and the introduced GE can improve the mechanical properties mainly due to the uniform dispersion of GE in the BC matrix. To construct the effectively interconnected conductive paths between separated GE nanosheets, polyaniline (PANI) is simultaneously deposited on the surfaces of both BC nanofibers and GE nanosheets to obtain BC/GE/PANI with excellent electrical conductivity. It is found that the as-prepared BC/GE/PANI has an electrical conductivity of  $1.7 \pm 0.1 \text{ S cm}^{-1}$ , which is higher than most of PANI-based composites. It is believed that the BC/GE/PANI nanocomposite possesses great potential for applications in electromagnetic shielding and flexible electrodes.

## 1. Introduction

Bacterial cellulose (BC) is produced by *Acetobacter* species cultivated in a culture medium containing carbon and nitrogen sources. It is pure cellulose which exhibits a sophisticated three-dimensional (3D) porous network structure [1–3]. In recent years, BC has attracted much attention of the scientific community due to its unique characteristics such as high porosity, high water retention capacity, high mechanical strength, low density, biocompatibility, non-toxicity, and biodegradability [4,5]. These features make BC an outstanding material particularly suitable for biomedical applications such as tissue engineering, skin repair treatment, artificial blood vessel and drug delivery [1,6–9]. Over the last few decades, owing to numerous advantages of BC, BC-based nanocomposites have recently emerged from combining BC with different functional components for many other potential applications [10–13]. For instance, it is possible to develop BC-based conductive nanocomposites when BC is combined with conductive components such as carbon nanotube (CNT) [12,14] and graphene (GE) [15]. These conductive composites may have great potential for practical applications in electromagnetic shielding and flexible supercapacitor.

As early as 2006, Yoon et al. employed CNT to improve the electrical conductivity of BC by simply dipping BC into the CNT dispersion

[12]. Unfortunately, unlike the one-dimensional (1D) feature of CNT, the lateral dimension of most GE nanosheets is larger than the diameter of the pores in BC. Thus, this simple method is invalid in the preparation of BC/GE composites. Currently, BC/GE nanocomposite can be manufactured by the following two methods. The first one is called mechanical mixing, which involves the mixing of BC fragment and GE suspension [16]. The drawback of this method is the breakage of the integrated nanofibrous structure of BC, which not only reduces the mechanical robustness but also damages the 3D porous structure of pristine BC. The second method is called *in situ* static biosynthesis [15,17], which can maintain the intrinsic 3D interconnected porous structure of BC. However, GE nanosheets are non-uniformly dispersed in the BC matrix due to the gradual decrease of GE content in the culture medium during the fermentation process, particularly when the nanocomposite becomes thick after long-time culture. In addition, a portion of GE is inevitably wasted because the medium cannot be completely consumed. Thus, there is an urgent need to develop a feasible strategy to overcome these above-mentioned obstacles.

To make BC/GE composites with dispersed GE nanosheets in BC matrix, we have developed a new strategy called membrane-liquid interface culture method. During the preparation process, a thin-layer GE-dispersed culture medium is deposited on the pre-grown BC. The new

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [yzwheb@163.com](mailto:yzwheb@163.com) (Z. Yang), [hlluotju@126.com](mailto:hlluotju@126.com) (H. Luo).

BC grows at the membrane-liquid interface until the complete consumption of the culture medium. The second cycle initiates by depositing GE-dispersed culture medium on newly grown BC/GE layer and subsequent growth of BC. These deposition and growth process repeat until a desired thickness is reached. Obviously, the thickness of BC/GE can be easily and precisely controlled by the cycle numbers. More importantly, the intrinsic continuous 3D structure can be well maintained and the GE nanosheets are uniformly dispersed in the BC matrix and strongly adhered with BC nanofibers.

Despite these, the GE nanosheets cannot interconnect one another, which limits the electrical conductivity of the resultant BC/GE. It is anticipated that depositing polyaniline (PANI), which is one of the most promising conducting polymers due to its tunable electrical conductivity, low cost, facile synthesis, good environmental stability, and non-toxicity [15,18,19] on the surfaces of both BC nanofibers and GE nanosheets, may greatly improve the electrical conductivity of BC. The resultant BC/GE/PANI exhibits excellent electrical conductivity and mechanical properties, showing great potential for application in many fields such as electromagnetic shielding and flexible supercapacitor.

In this study, we report a process of simultaneously depositing PANI onto the surfaces of both BC nanofibers and GE nanosheets such that a ternary composite can be obtained with enhanced electrical conductivity over BC/GE nanocomposite. The dependence of the morphology, electrical conductivity, and mechanical properties of BC/GE/PANI on the processing parameters such as reaction time and temperature was investigated.

## 2. Materials and methods

### 2.1. Materials

Commercially available GE aqueous dispersion with a concentration of  $1 \text{ mg mL}^{-1}$  was purchased from XFNANO (Nanjing, China). Regents for BC production included glucose, yeast extract, tryptone, disodium phosphate and acetic acid, which were supplied by Alfa Aesar (Tianjin, China). Aniline, ammonium persulfate, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Aladdin-Reagent (Shanghai, China). All chemicals were used without any further purification.

### 2.2. Preparation of BC/GE nanocomposite

To prepare the BC/GE nanocomposite, a BC substrate was first synthesized according to our previous work [8,15,20]. A GE dispersed culture medium was subsequently prepared, and the volume ratios of GE suspension to BC medium were 1:10, 1:6 and 1:4, respectively. Typically, 5 mL GE suspension was respectively added to 50 mL culture medium followed by ultrasonic treatment. The medium was uniformly sprayed onto the BC substrate in the form of dispersed droplets through a nebulizer (Ping'an Medical Instrument, Yangzhou, China). The bacteria grew up along the surface of the BC by consuming the medium. In this experiment, the BC/GE hydrogel with a thickness of 1 mm was obtained after atomization 5 times, and each atomization time interval was 12 h. Bare BC hydrogel was prepared by the same procedure except that no GE was added to the culture medium. The harvested BC/GE and BC hydrogels were separated and purified by soaking in deionized water at  $90^\circ\text{C}$  for 2 h and then boiled in a 0.5 M NaOH solution for 2 h. Finally, the hydrogels were repeatedly washed with deionized water until reaching neutral pH, thus obtaining BC/GE-1 and BC. BC/GE-2 and BC/GE-3 were obtained at the volume ratios of 1:6 and 1:4, respectively.

### 2.3. Preparation of BC/GE/PANI nanocomposite

The BC/GE/PANI nanocomposite was prepared as follows: firstly, BC/GE hydrogel ( $20 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm}$ ) was fully immersed in

50 mL of HCl aqueous solution (1 M) containing 2.5 mmol of aniline. The solution was vigorously agitated for 24 h to promote the aniline to self-assemble onto the surface of BC nanofibers and graphene nanosheets. Then the reaction system was kept at  $5^\circ\text{C}$ , and 10 mL of aqueous solution containing 2.5 mmol of ammonium persulfate was added into the suspension dropwise with vigorous stirring. The reaction was conducted for 2, 6 and 10 h, respectively, and then samples were freeze-dried or air-dried for further characterizations. For comparison, the reaction was also conducted at 15 and  $25^\circ\text{C}$  using similar procedures. As control, BC/PANI was prepared following the same procedures.

### 2.4. Characterizations

The morphology and structure were characterized by a field-emission scanning electron microscope (SEM, S-4800, Hitachi) and transmission electron microscope (TEM, JEM-2100F, JEOL). The crystalline structure was studied by a Rigaku D/max 2500 x-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ). FTIR spectra were recorded on a Nicolet Magna-560 spectrometer. The specimens were recorded in a spectral range of  $4000\text{--}400 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ . The tensile testing was conducted on a micro electromagnetic fatigue testing machine (IBTC-300, Tianjin Care Measure & Control Co. Ltd., China) at room temperature and humidity of 65%RH with a cross-head rate of  $5 \text{ mm min}^{-1}$ . The samples were tested in original hydrogel state. The in-plane electrical conductivity of the air-dried samples was measured using a Keithley 2635 sourcemeter unit.

## 3. Results and discussion

### 3.1. Morphology and structure of BC/GE/PANI nanocomposite

Fig. 1 shows SEM images of BC/GE nanocomposites. As expected, the amount of GE nanosheets in BC/GE gradually increases with increasing GE concentration in the culture medium (Fig. 1a–c). More importantly, the prepared BC/GE nanocomposites can retain the intrinsic 3D fibrous structure of BC and GE nanosheets are evenly distributed in the BC matrix without serious aggregation for BC/GE-1 and BC/GE-2. In addition, GE nanosheets appear to be enwound by BC nanofibers in a spider web-like manner, as illustrated in Fig. 1d. This unique structure is obviously favorable for weakening the  $\pi\text{--}\pi$  bond interaction among GE nanosheets, thus alleviating the re-stacking of GE nanosheets, which helps to promote the uniform dispersion of GE nanosheets in the BC matrix.

Fig. 2 shows the TEM and HRTEM images of BC and BC/GE-2 nanocomposite (inset showing the corresponding SAED pattern). As can be seen from Fig. 2a, BC has a superfine 3D porous network structure, consistent with SEM observation. Fig. 2b shows a single BC nanofiber with a fiber diameter of about 30 nm. TEM image of BC/GE-2 reveals the close connection of GE nanosheets with BC nanofibers, forming an integrated network (Fig. 2c). HRTEM reveals that GE nanosheet is fully integrated with BC nanofibers, further confirming the merged nanostructure between GE and BC (Fig. 2d). Such sophisticated nanostructure is beneficial to the improvement of mechanical properties.

The effect of reaction (polymerization) temperature and time on PANI deposition on BC nanofibers was investigated using SEM. Fig. 3a demonstrates that at a temperature of  $25^\circ\text{C}$  and a reaction time of 6 h (abbreviated at  $25^\circ\text{C}/6 \text{ h}$  hereinafter), PANI nanoparticles with serious aggregation are observed throughout the surface of BC nanofibers and the curvature of BC nanofibers becomes unclear. A rough fibrous feature is observed at  $15^\circ\text{C}/6 \text{ h}$  (Fig. 3b). When the reaction temperature decreases to  $5^\circ\text{C}$  (still at 6 h), an obvious fibrous morphology is noted and many PANI particles are uniformly distributed on individual BC fibers (Fig. 3c). In other words, the 3D interconnected porous structure of BC is maintained. These results suggest that the reaction temperature significantly affects the deposition (distribution and morphology) of

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