

# **A method for producing conductive graphene biopolymer nanofibrous fabrics by exploitation of an ionic liquid dispersant in electrospinning**

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## **Abstract**

Owing to its high conductivity, graphene has been incorporated into polymeric nanofibers to create advanced materials for flexible electronics, sensors and tissue engineering. Typically, these graphene-based nanofibers are prepared by electrospinning synthetic polymers, whereas electrospun graphene-biopolymer nanofibers have been rarely reported due to the poor compatibility of graphene with biopolymers. Herein, we report a new method for the preparation of graphene-biopolymer nanofibers using the judicious combination of an ionic liquid and electrospinning. Cellulose acetate (CA) has been used as the biopolymer, graphene oxide (GO) nanoparticles as the source of graphene and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) as the ionic liquid (IL) to create CA-[BMIM]Cl-GO nanofibers by electrospinning for the first time. Moreover, we developed a new route to convert CA-[BMIM]Cl-GO nanofibers to reduced GO nanofibers using hydrazine vapor under ambient conditions to enhance the conductivity of the hybrid nanofibers. The graphene sheets were shown to be uniformly

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incorporated in the hybrid nanofibers and only was needed to 0.43 wt% of GO increase the conductivity of the CA-[BMIM]Cl nanofibers by more than four orders of magnitude (from  $2.71 \times 10^{-7}$  S/cm to  $5.30 \times 10^{-3}$  S/cm). This ultra-high enhancement opens up a new route for conductive enhancement of biopolymer nanofibers to be used in smart (bio) electronic devices.

## 1. Introduction

Enormous volumes of synthetic polymers accumulating in the natural environment has become a major threat to the planet due to their poor degradability and high CO<sub>2</sub> footprint. In response to this growing concern, the past decade has seen a considerable interest in the replacement of synthetic polymers with biopolymers owing to their abundance in nature and excellent biocompatibility and biodegradability [1]. In parallel, biopolymeric nanofibrous fabrics can deliver superior performance in terms of functionality and degradability due to their high surface area-to-volume ratio. Electrospinning has been shown to be a versatile method for fabricating nanofibers from a wide range of polymers, allowing the facile incorporation of additives, such as drugs, nanoparticles or nanofillers to produce hybrid nanofibrous materials for a wide range of applications (*e.g.* as therapeutic, protective, electrical or sensing materials) [2-7]. Developing functionalized polymer materials such as conductive nanofibers from abundant and biodegradable biopolymers is more challenging and has attracted an increasing amount of attention for the benefit of energy utilization and the environment [1]. A number of synthetic polymers, such as poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), polyaniline (PANI) and poly(vinyl pyrrolidone) (PVP), have been successfully combined with graphene sheets and carbon nanotubes to produce conductive nanofibers [8, 9]. However, very few contributions have been made to the electrospinning of biopolymers with carbon nanotubes or graphene. Of these contributions, carbon nanotubes are more popular and have been successfully electrospun with biopolymers such as chitosan, cellulose triacetate and biodegradable polylactide [10-12]. Graphene (layered sp<sup>2</sup>-hybridized honeycomb lattice

carbon sheets) has gained particular interest owing to its multifunctional properties such as high specific surface area, electrical and thermal conductivity and superior mechanical strength [13]. Most pertinently, the excellent electrical properties of graphene renders it a promising nanomaterial for novel practical applications such as smart fabrics, nanosensors and flexible electrode materials [14, 15].

Producing graphene/biopolymer nanofibers by electrospinning has three distinct challenges: 1) disrupting the extensive hydrogen bonding within the biopolymer; 2) breaking the aggregation of the graphene sheets into nanoparticles to prepare a uniform mixture for electrospinning; and 3) establishing appropriate interactions in the hybrid material to facilitate electron transport. A dispersing agent is required to break-up the graphene sheets due to its inherent insolubility, atomically smooth surfaces and strong aggregation tendency. Choosing an appropriate dispersing agent therefore becomes the key to formulating spinnable mixtures to fabricate hybrid biopolymer nanofibers. Ionic liquids (ILs) present an interesting class of reagents that can be used as dispersing agents because of their novel dissolution ability and have the potential to play more functional roles such as stabilizers, compatibilizers, modifiers and additives in the fabrication of polymer composites containing carbon nanotubes or graphene sheets [16]. ILs are organic salts which exist in the liquid state below 100°C, preferably at room temperature, and offer chemical and thermal stability, non-flammability and immeasurably low vapor pressure [17, 18].

Imidazolium chloride-based ILs show outstanding dissolving capacity of many biopolymers such as cellulose, cellulose acetate, chitin, wool and chitosan. The high chloride concentration of the IL breaks the extensive hydrogen-bonding network of these biopolymers to enable successful electrospinning [18-25]. In such ILs, graphene oxide sheets can be effectively exfoliated, stabilized and reduced by chemical and thermal treatment methods [26, 27]. Peng

and colleagues fabricated graphene-cellulose nanocomposite films successfully by casting, through the exploitation of imidazolium chloride-based ILs [28]. These cast films showed conductivities up to  $3.2 \times 10^{-2}$  S/cm, thus demonstrating an approach for ionic liquid-biopolymer conductive nanocomposites with graphene. Further, the use of IL, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, 20%), in the production of electrospun hybrid carbon nanotube nanofibers with styrene-acrylonitrile resin showed a significant increase in the conductivity from  $1.08 \times 10^{-6}$  S/cm to  $5.9 \times 10^{-6}$  S/cm for samples containing 3 wt% carbon nanotubes [29]. However, the fabrication of electrospun graphene-biopolymer conductive nanofibers remains a significant challenge.

In the first report of its kind, we present an electrospinning study of cellulose acetate (biopolymer), graphene oxide (source of graphene) and [BMIM]Cl (ionic liquid) to create hybrid nanofibers. A chemical reduction method using hydrazine in an ultrasound humidifier has been developed to reduce graphene oxide to enhance the electrical conductivity of the biopolymer nanofibers. Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Raman, Fourier Transform Infrared (FTIR) and X-ray Photoelectron (XPS) spectroscopies have been used extensively to probe the interactions within our novel hybrid nanofibers.

## **2. Experimental**

### *2.1. Materials*

1-Methylimidazolium (99%), ethyl acetate (99%) and 1-chlorobutane (99%) were purchased from Merck. CA powder ( $M_n = 30,000$  Da, acetyl content 39.8 %), acetone, dimethylacetamide (DMAc) and hydrazine solution (35 wt% in H<sub>2</sub>O), all from Sigma Aldrich, were used as received. Graphene oxide powder (15-20 sheets, 4-10% edge-oxidized) was purchased from Garmor Inc. U.S.A. 1-Butyl-3-methylimidazolium chloride [BMIM]Cl was synthesized by the method described elsewhere [30].

## 2.2. Preparation CA and [BMIM]Cl-GO blends

First, a 17 wt% CA solution was prepared in 2:1 (w/w) acetone/DMAc at room temperature under constant stirring until a homogenous, transparent solution was obtained. [BMIM]Cl-GO solutions were prepared by adding a given amount of GO (0.11-0.43% by weight of CA) to [BMIM]Cl (12% by weight of CA) under constant stirring at 60 °C for 24 h. Finally, [BMIM]Cl-GO was added to the CA solution and stirred at room temperature for a further 2 h (experimental details given in the Supporting Information). This solution, denoted as CA-[BMIM]Cl-GO throughout this work, was then ready for electrospinning.

## 2.3. Electrospinning of CA-[BMIM]Cl-GO nanofibers

Solutions for electrospinning were loaded into a 1 mL syringe with a stainless-steel needle (0.6 mm inner diameter). Electrospinning was performed at room temperature in a horizontal geometry with an applied voltage of 20-25 kV (Gamma High Voltage Research power supply, ES 40R-20W/DM/M1127 Ormond Beach FL). The flow rate of the solution was fixed at 1.5 mL/h using a syringe pump (NE-1010 Programmable Single Syringe Pump, New Era Pump Systems, Inc). The distance between the needle tip and the collector was maintained at 8–10 cm. CA-[BMIM]Cl-GO nanofibers were continuously deposited onto an electrically grounded rotatory collector covered with aluminum foil. The CA-[BMIM]Cl-GO hybrid nanofibers were then carefully removed from the aluminum foil and dried at room temperature for 24 hours.

## 2.4. Preparation of CA-[BMIM]Cl-rGO nanofibers

To reduce the oxygen content of the GO to create electrically conductive nanofibers, CA-[BMIM]Cl-GO nanofibrous mats were reduced by a hydrazine solution mist [31, 32]. In short, the hydrazine solution was placed in an ultrasound humidifier (BONECO Ultrasonic U7146,

Switzerland). The fibrous mats were clamped in a universal extension retort clamp in the front of the humidifier at maximum humidity (see supplementary video in the supporting Information) for 15-30 minutes until the mats changed into the typical black graphitic color. Following reduction, the mats were allowed to dry at room temperature for 2 h to give CA-[BMIM]Cl-rGO nanofibers.

## 2.5. Characterization

The surface morphologies of the nanofibers were analyzed by scanning electron microscopy (SEM, Zeiss FEG-SEM Ultra-55) and intermolecular interactions within the nanofibrous mats were analyzed by FTIR (Interspec 200-X) spectroscopy. The thickness of the mats was measured by a Mitutoyo Muchecker M519-402 micrometer and the approximate porosity of the final electrospun nanofibrous mats was calculated by image analysis, as described in the Supporting Information. Chemical states and surface composition were characterized by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD X-ray Photoelectron Spectrometer). Raman spectroscopy (Renishaw inVia Raman spectrometer) was used to probe the surface composition and X-ray diffraction (XRD) patterns were recorded by a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV at 40 mA) using a silicon strip detector D/teX Ultra with the scan range of  $2\theta = 5.0 - 30.0^\circ$ , scan step  $0.02^\circ$ , scan speed  $5^\circ/\text{min}$ . The electrical conductivities of the solutions were analyzed using a conductivity meter (SevenCompactS230 Mettler Toledo, Switzerland) at room temperature while the conductivity of the nanofiber mats was measured using a two-probe method with an AlphaLab, Inc. multimeter by placing the mats between two gold electrodes at a separation of 1 cm. The thermal stability of CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO nanofibers was analyzed using Thermogravimetric Analysis (TGA, Setaram LabsysEvo 1600 thermo analyzer) under argon between  $25^\circ\text{C}$  to  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

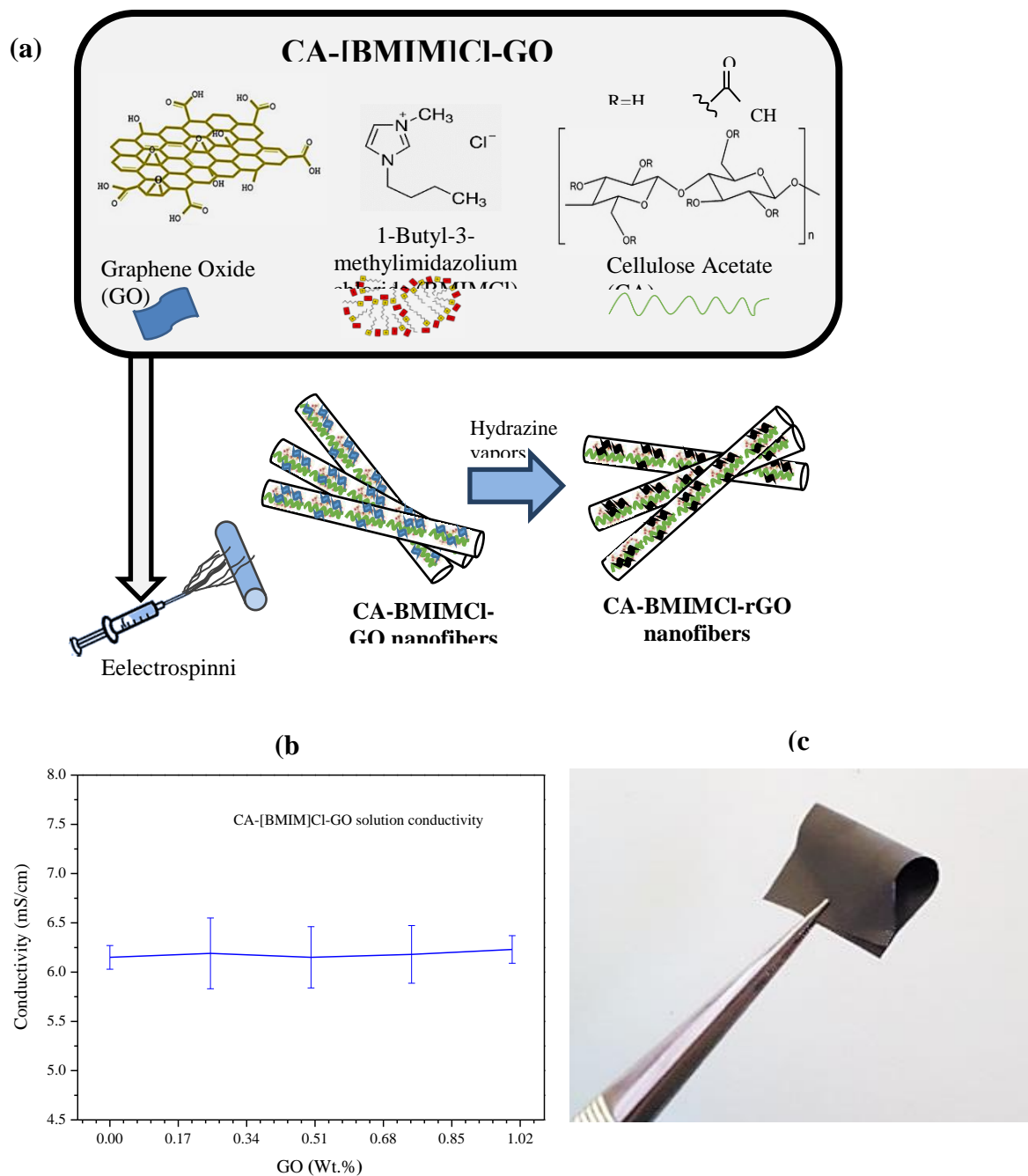
### 3. Results and discussion

#### 3.1 The morphology and the conductivity of the hybrid nanofibers

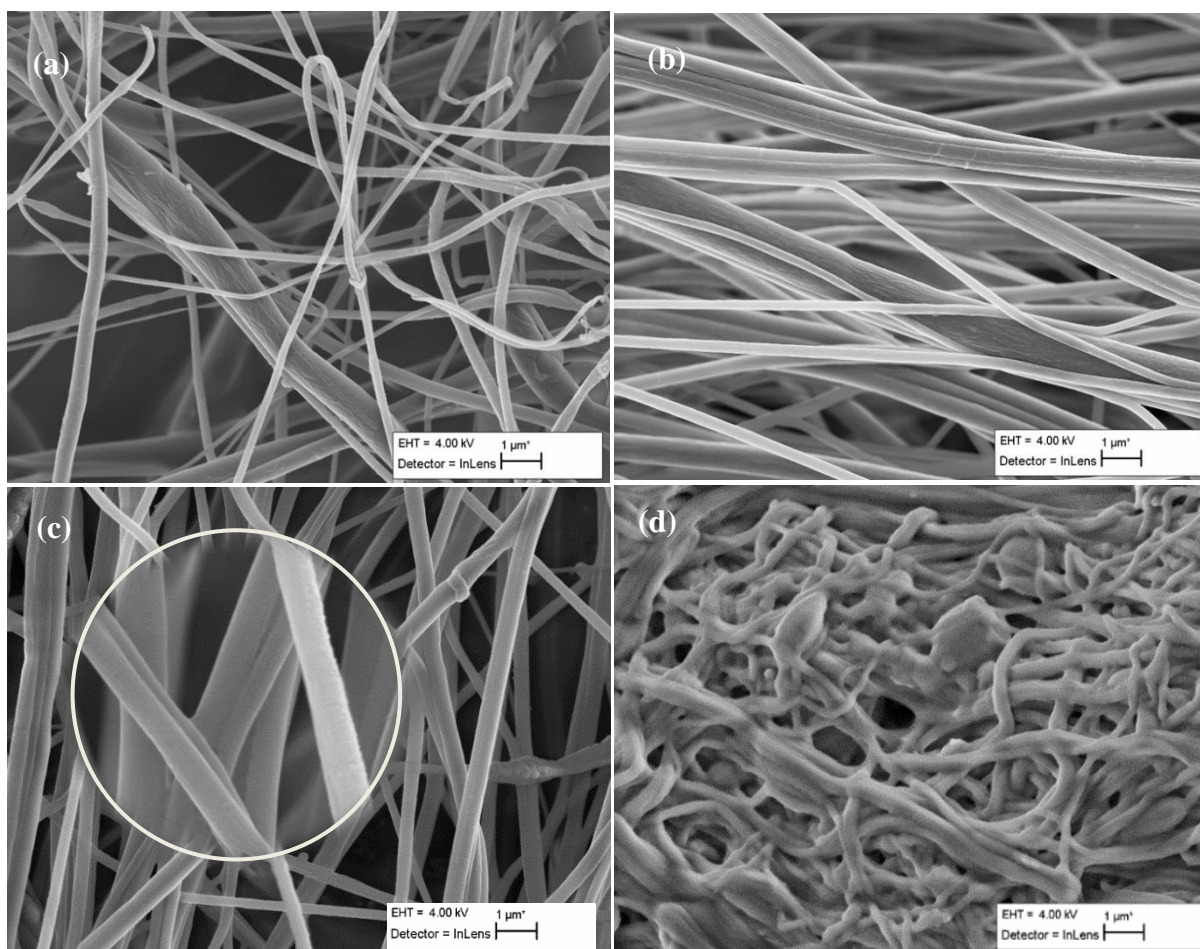
A schematic of the preparation method of CA-[BMIM]Cl-rGO nanofibers is presented in Figure 1a, where GO was first dispersed in [BMIM]Cl and then mechanically mixed in a solution of CA. Dispersing GO into [BMIM]Cl was carried out by magnetic stirring at approximately 60 °C to ensure that the ionic liquid had fully melted. As the melt has a viscosity larger than 150 mPa·s [33], mixing was performed for 24 hours to ensure dispersion of the GO nanoparticles in [BMIM]Cl, which is a critical step for successful electrospinning. The CA-[BMIM]Cl-GO solution was electrospun prior to reduction by hydrazine mist using an ultrasound humidifier. Compared to other chemical reduction methods [31, 32], our ultrasound reduction method by hydrazine mist significantly reduces GO at a lower temperature (room temperature) than previously reported in the literature [31, 32, 34]. This provides a new method to easily control the reduction process for highly conductive graphene-based nanofibers. The conductivity of the CA-[BMIM]Cl solution (prior to the incorporation of GO) was measured at 6.23 mS/cm and remained almost constant (Figure 1b) as the amount of GO increased from 0.11 to 0.43 wt%. This is due to the presence of oxygenated groups on the surface of GO which disrupts the  $sp^2$  hybridization in graphene. Produced nanofibers with controlled amounts of GO in the range of 0 - 0.43 wt% are shown in Table 1. Pure CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO nanofibers were then examined by SEM. Surface morphologies of CA, CA-[BMIM]Cl and CA-[BMIM]Cl-GO (see Figure 2a and b) were smooth and bead-free, while CA-[BMIM]Cl-rGO nanofibers have rough regions where GO appears to have aggregated (as shown in Figure 2d). Higher concentrations of GO hindered the jet flow due to excess GO, which was not fully dispersed in the solution, clogging the needle and therefore electrospinning was unsuccessful. During chemical reduction, the CA-[BMIM]Cl-GO

1 nanofibers became more fused (Figure 2d) to form a CA-[BMIM]Cl-rGO nanofibrous mat. The  
2 conductivity of CA-[BMIM]Cl nanofibers was measured at  $2.71 \times 10^{-7}$  S/cm, which was  
3 significantly lower than the conductivity of pure [BMIM]Cl *i.e.*  $4.60 \times 10^{-4}$  S/cm [35].  
4 Incorporation of GO resulted in an increase in the conductivity of the nanofibers, before and  
5 after the reduction. For non-reduced nanofibers, the presence of GO (0.11 wt%) increased the  
6 conductivity (to  $4.33 \times 10^{-5}$  S/cm) and reaching an approximate plateau at  $1.41 \times 10^{-4}$  S/cm at  
7 0.43 % GO. The conductivity of the nanofibers is presented in Table 1 and Figure 3.  
8 Comparing to GO/CA nanocomposites reported in the literature, [34] 0.43 wt% GO is a  
9 relatively low loading for such a significant conductivity enhancement.





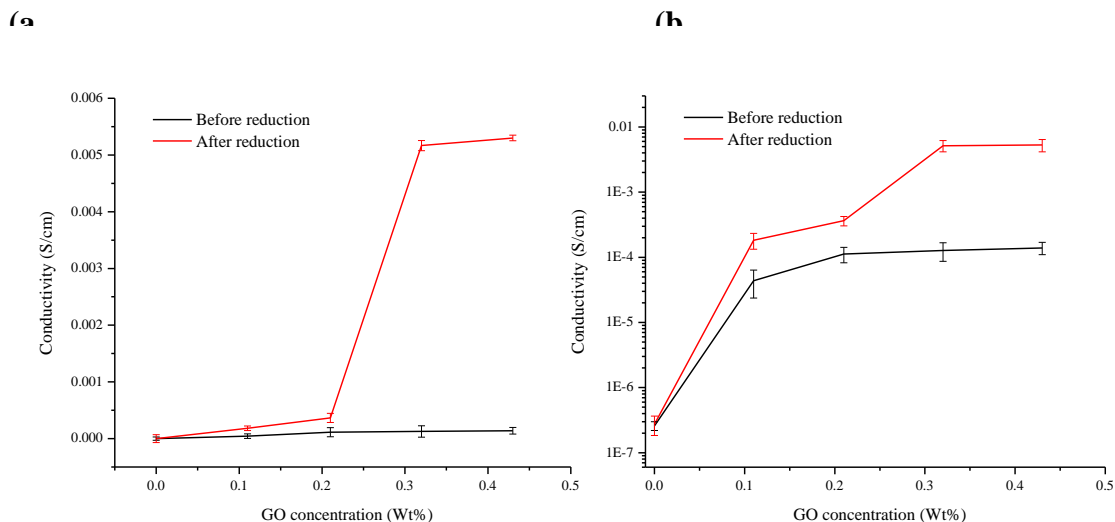
**Figure 1** (a) Schematic of the preparation of CA-[BMIM]Cl-rGO nanofibers, (b) Influence of GO concentration on the conductivity of the CA-[BMIM]Cl solution and (c) a photographic image to demonstrate the flexibility and durability of the final hybrid nanofibrous material.



**Figure 2** SEM images of (a) pure CA; (b) CA-[BMIM]Cl; (c) CA-[BMIM]Cl-GO and (d) CA-[BMIM]Cl-rGO(GO conc. 0.43 wt%) nanofibers.

**Table 1** Conductivity of the hybrid CA-[BMIM]Cl-rGO nanofibers.

Content, wt%			Conductivity (S/cm)	
GO	[BMIM]Cl	CA	before reduction	after reduction
0.00	46.60	53.40	$2.71 \times 10^{-7}$	$2.71 \times 10^{-7}$
0.11	46.50	53.39	$4.33 \times 10^{-5}$	$1.82 \times 10^{-4}$
0.21	46.41	53.38	$1.11 \times 10^{-4}$	$3.65 \times 10^{-4}$
0.32	46.31	53.37	$1.29 \times 10^{-4}$	$5.10 \times 10^{-3}$
0.43	46.21	53.36	$1.41 \times 10^{-4}$	$5.30 \times 10^{-3}$



**Figure 3** The effect of GO concentration in the hybrid CA-[BMIM]Cl-GO nanofibers on conductivity [(a) linear and (b) log scales] before and after reduction.

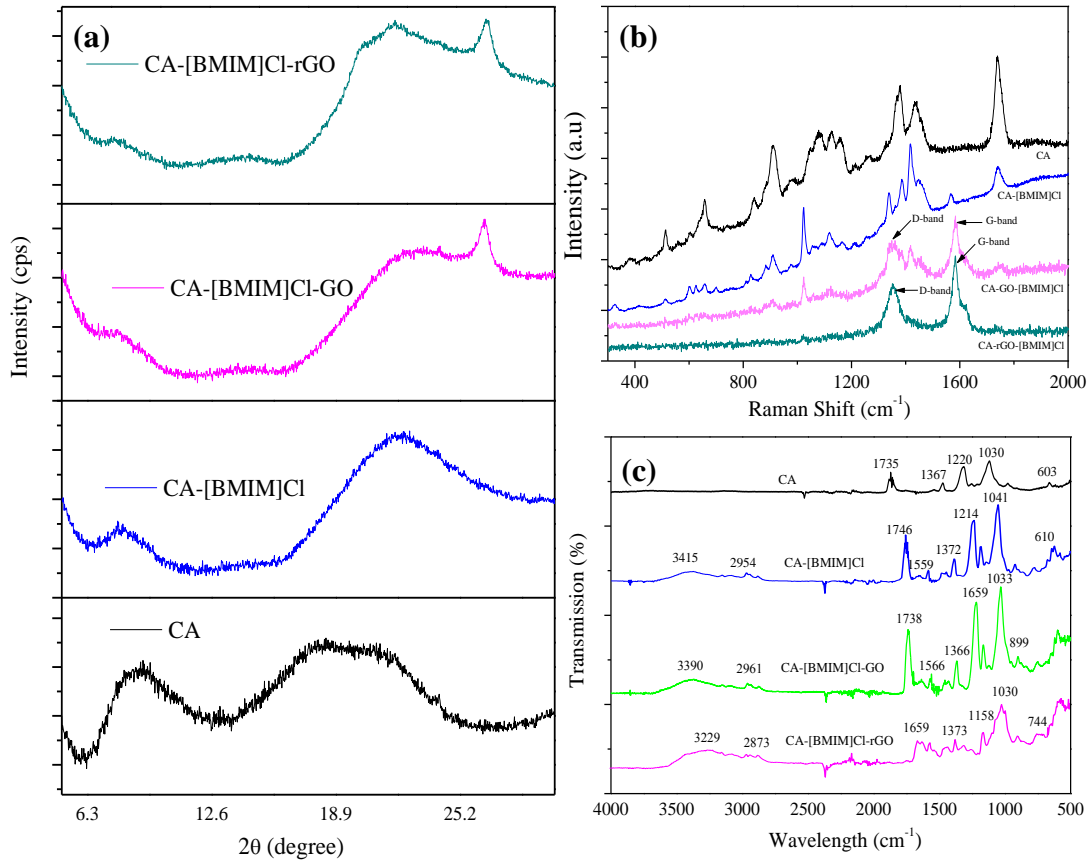
Interestingly, reduction of the hybrid nanofibers using hydrazine boosted the conductivity significantly, surpassing the conductivity of pure [BMIM]Cl when GO loading reached 0.32 wt% ( $4.60 \times 10^{-4}$  S/cm). The highest conductivity attained was  $5.30 \times 10^{-3}$  S/cm with 0.43 wt% GO, which is  $\sim 20,000$  times higher than that of the nanofibers without GO and over an order of magnitude higher than that of pure [BMIM]Cl.

### 3.2. Structure of graphene oxide in the nanofibers

X-ray diffraction (XRD) was used to examine the crystal structure of CA and GO following the electrospinning and reduction processes. The XRD patterns of the CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO nanofibers are shown in Figure 4a. Pure CA nanofibers exhibited three broad diffraction peaks at  $9.0^\circ$ ,  $17.9^\circ$  and  $21.8^\circ$  [36]. The peak at  $21.8^\circ$  is attributed to short-range spacing between neighboring cellulosic repeat units within the individual macromolecules and the peak at  $9.0^\circ$  shows the longer range interactions between cellulose acetate chains [37]. More specifically, the distance between the adjacent cellulosic chains is normally characterized by a d-spacing of  $\sim 9 - 10$  Å, and the neighboring

1 anhydroglucose units in the cellulose chains have a d-spacing of  $\sim 4 - 5.5 \text{ \AA}$ . The peak at  $17.9^\circ$   
2 could arise from the diffraction of the (021) plane. After addition of [BMIM]Cl, the peak at  
3  $9.0^\circ$  became significantly weaker and shifted to  $8.0^\circ$ . This peak weakening and shifting to a  
4 lower angle reflects the decrease in CA concentration in the nanofibers from 100% to 53.4%  
5 and the cellulose packing disrupted by [BMIM]Cl. The presence of [BMIM]Cl breaks up the  
6 H-bonding between the cellulosic chains and enlarges their d-spacing from  $9.8 \text{ \AA}$  to  $11.0 \text{ \AA}$ . A  
7 small shift of the  $21.8^\circ$  peak is also observed, illustrating that the addition of [BMIM]Cl did  
8 not significantly alter the anhydroglucose units in the cellulose acetate chain. The peak at  $17.9^\circ$   
9 almost completely disappeared from the nanofiber samples electrospun in the presence of  
10 [BMIM]Cl, showing less short range order in the amorphous cellulose acetate. The addition  
11 of 0.11 wt% GO resulted in the appearance of a sharper peak at  $\sim 26.5^\circ$ , which is the (002) peak  
12 of graphite. The (002) peak shows that the interlayer spacing of the graphite sheets was  
13 approximately 0.33 nm ( $3.3 \text{ \AA}$ ).

14 This suggests that the graphene sheets are not fully exfoliated and remained in a graphitic-like  
15 state [38]. The oxygen-containing functional groups on the GO are mainly on the external  
16 surface of the nanoparticles. This result is in line with the specification of GO nanoparticles  
17 purchased that have 15-20 sheets and 4-10% edge-oxidized. After chemical reduction, this peak  
18 remained in the CA-[BMIM]Cl-rGO nanofibers, as expected.



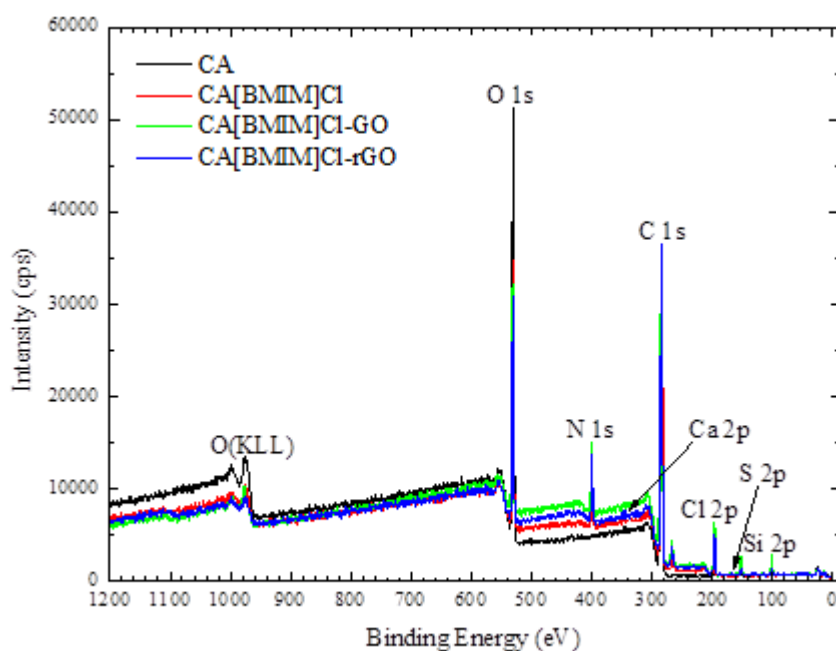
**Figure 4** (a) XRD patterns; (b) Raman spectra and (c) FTIR spectra of CA nanofibers, hybrid CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO nanofibers (GO conc. 0.43 wt% for the latter two samples).

To examine the influence of chemical reduction on the chemical structure of GO in more detail, the samples were studied by Raman spectroscopy, as shown in Figure 4b. The Raman spectra of CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO both showed two bands at  $1350 \text{ cm}^{-1}$  and  $1585 \text{ cm}^{-1}$ . These can be assigned to the D and G bands of the carbon materials, respectively [39, 40]. The G band represents  $\text{sp}^2$ -hybridized C-C bonds in a 2D hexagonal lattice, while the D band corresponds to the defects and disorder on the two-dimensional amorphization of the carbon network [41, 42]. These two peaks reveal that the graphene sheets of the GO have a

significant proportion of carbon disordered away from a perfect 2D hexagonal lattice. More specifically, comparison of the CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO spectra shows that the D and G bands of CA-[BMIM]Cl-rGO nanofibers are more pronounced after chemical reduction, where the spectrum shows less signals from surface functional groups. The relative intensity of the G and D bands does not change significantly, supporting the evidence provided by XRD that graphene sheets in the GO particles were not fully exfoliated showing  $sp^2$ -hybridized C-C bonds in a 2D hexagonal lattice and having sheet spacing close to the 0.33 nm of graphite. Importantly, the chemical reduction did not significantly alter the stacking of the graphene sheets, but modified the surface functional groups through deoxygenation [43-46].

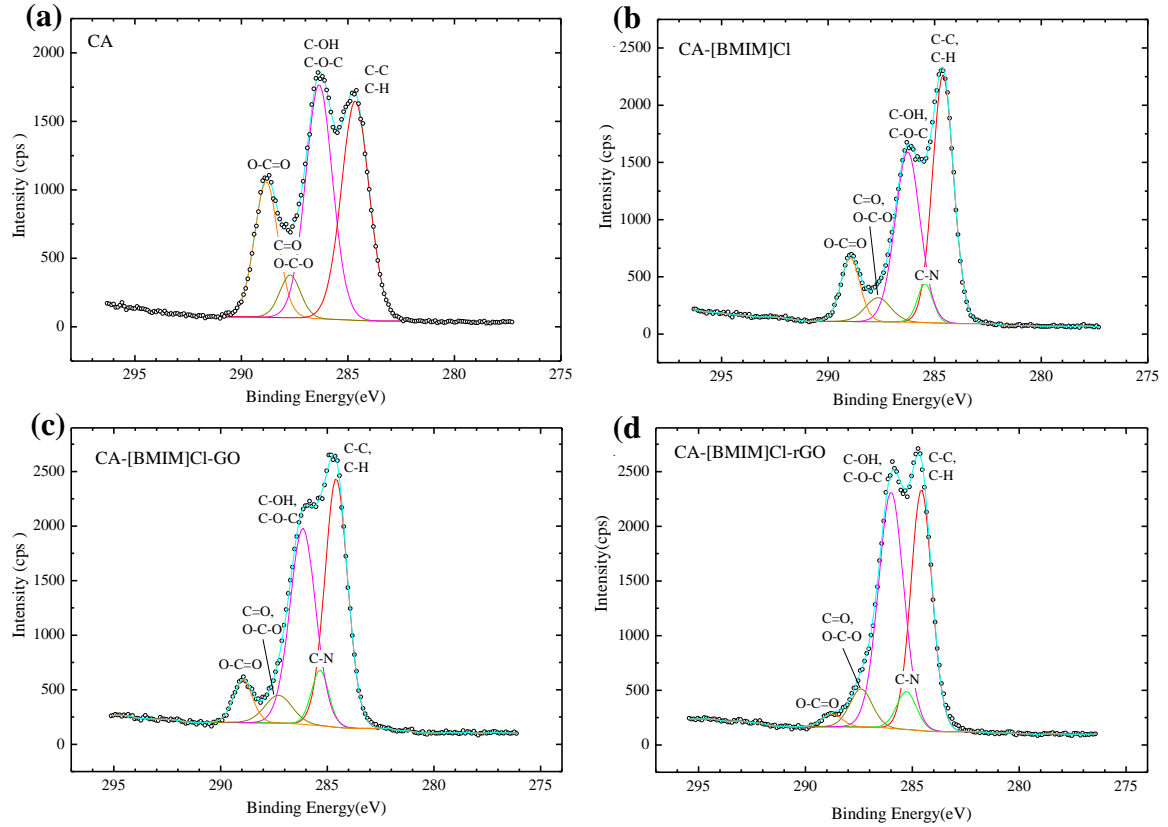
### *3.3 Chemical bonds and their interactions within the hybrid nanofibers*

The structure and interactions of each component in the hybrid nanofibers were revealed by Raman, FTIR and XPS giving insights into the reason for the enhancement in conductivity. As aforementioned, the Raman spectra of CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO are shown in Figure 4b, whereas the FTIR and XPS spectra are presented in Figures 4c and 5, respectively. The Raman spectra of CA and CA-[BMIM]Cl showed the asymmetric stretching vibration of the C-O-C glycosidic bond at  $1121\text{ cm}^{-1}$  and the pyranose ring at  $1080\text{ cm}^{-1}$  with the presence of C-OH at  $1265\text{ cm}^{-1}$ . The bands at 1736, 1435, and  $1382\text{ cm}^{-1}$  are attributed to the carbonyl group (C=O) and symmetric and asymmetric vibrations of C-H, respectively, in the acetyl group [47-49]. More interestingly, the [BMIM]Cl cation is observed in the CA-[BMIM]Cl sample with bands at 601 and  $627\text{ cm}^{-1}$ . The intensities show the co-existence of gauche and trans conformations of the IL [50, 51]. It is worth noting that the inclusion of GO has resulted in the disappearance of most of the vibrational bands from the Raman spectra of the corresponding hybrid nanofibers.



**Figure 5** XPS survey spectra of CA (black), CA-[BMIM]Cl (red), CA-[BMIM]Cl-GO (green), CA-[BMIM]Cl-rGO (GO conc. 0.43 wt%, blue).

The FTIR spectra of pure CA, CA-[BMIM]Cl and CA-[BMIM]Cl-rGO nanofibers in Figure 4c show that pure CA nanofibers exhibited characteristic bands at  $1735\text{ cm}^{-1}$  and  $1367\text{ cm}^{-1}$  corresponding to C=O and C-H stretching from  $-\text{OCOCH}_3$ , respectively. Bands at  $1220\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  reveal the C-C and C-O stretching vibrations in the pyranoid ring and C-O-C (ether linkage) from the glycosidic units. In the CA-[BMIM]Cl spectrum, characteristic bands at  $1746\text{ cm}^{-1}$  (C=C stretching),  $1214\text{ cm}^{-1}$  (C=N stretching) and  $1041\text{ cm}^{-1}$  (C-O stretching) indicate that the  $\text{BMIM}^+$  and  $\text{Cl}^-$  ions of [BMIM]Cl formed hydrogen bonds with CA, as expected. The FTIR spectrum of CA-[BMIM]Cl-GO is similar to that of CA-[BMIM]Cl while the spectrum of [BMIM]Cl-rGO shows two new bands at  $1659\text{ cm}^{-1}$  and  $3229\text{ cm}^{-1}$  suggesting strong interactions (hydrogen bonding) between the carboxylic ( $-\text{COOH}$ ) groups of graphene and carbonyl (C=O) groups of CA.

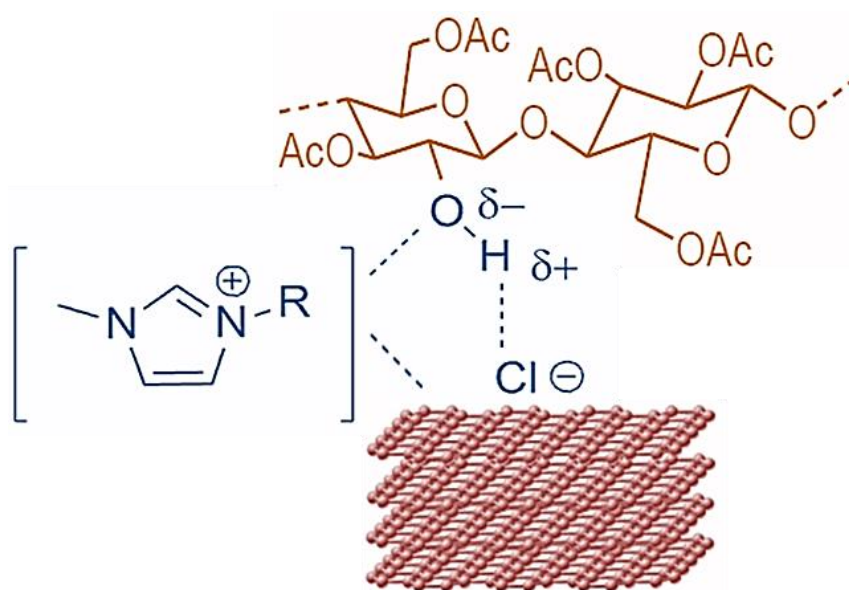


**Figure 6** The C1s XPS spectra of (a) pristine CA nanofibers, (b) CA-[BMIM]Cl, (c) CA-[BMIM]Cl-GO, and (d) CA-[BMIM]Cl-rGO (GO conc. 0.43 wt%).

XPS was used to further examine the differences in chemical functionality in the hybrid nanofibers (Figure 5). The survey spectrum of pure CA nanofibers exhibits only two distinct peaks: C 1s at ~285 eV and O 1s at ~532 eV (Figure 5), while Cl 2p and N 1s peaks are present in all other spectra, confirming the presence of [BMIM]Cl. High resolution C 1s spectra were analyzed by monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). Each spectrum has been deconvoluted into five distinct peaks, as shown in Figure 6a-d for the nanofibers of pure CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO, respectively. The sharp peak centered at 284.6 eV corresponds to C-C bonding and the relatively broad peak around 286.1 eV is attributed to three different functional groups: hydroxyl (C-O); carbonyl (C=O) and imine (C-N). More specifically, the peaks in this region at 285.5, 285.7, 286.6 and 287.8 eV are attributed to carbon atoms in C-N, C=N, C-O, C=O, respectively. In the CA-[BMIM]Cl-



rGO nanofibers, the peak centered at 288.9 eV comes from the carboxyl group [C(O)O]. Comparing the C 1s XPS spectra (Figure 6a and b), it can be seen that the addition of [BMIM]Cl significantly lowers the relative peak intensity of the oxygen-containing functional groups from CA, and introduces a new peak attributed to C-N from [BMIM]Cl. The introduction of GO results in some small changes in the relative peak intensities (comparing Figure 6b and c). After the reduction of the CA-[BMIM]Cl-GO nanofibers, the C 1s spectrum of the CA-[BMIM]Cl-rGO (Figure 6d) shows a dramatic decrease of the carboxyl peak. These changes suggest that the hydrazine vapor step has indeed reduced the carboxyl groups in GO, but may have also partially reduced CA, while the peak intensity of the other oxygen-containing functional groups slightly increased. It is noteworthy to state that it has been shown elsewhere that it is not yet possible to reduce GO completely by chemical reduction [44].



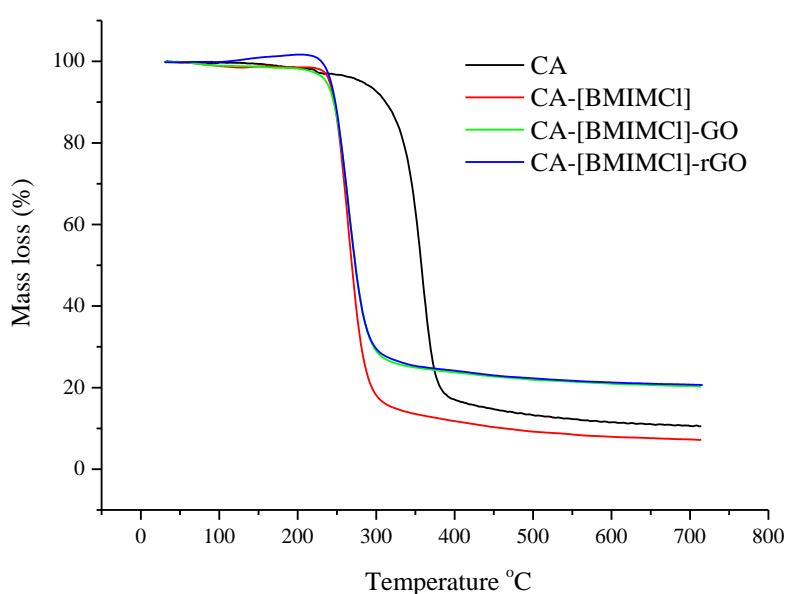
**Figure 7** Schematic illustration of the suggested interaction of graphene with CA and [BMIM]Cl.

The proposed interactions of stacked graphene sheets with CA and [BMIM]Cl are schematically shown in Figure 7. Removal of carboxyl groups and formation of more hydroxyl

groups may promote the formation of hydrogen-bonds with dissociated BMIM<sup>+</sup> and Cl<sup>-</sup> ions through unsubstituted hydroxyl functional groups in both GO and CA [52, 53]. The  $\pi$ -electrons in the imidazole ring of BMIM<sup>+</sup> may interact with the rich  $\pi$ -electron clouds of the graphene rings resulting in some delocalization and enhanced electrical conductivity.

### 3.4 Thermal analysis of the hybrid nanofibers

TGA has been carried out under argon to further examine the thermal stability and chemical bonding differences in CA, CA-[BMIM]Cl, CA-[BMIM]Cl-GO and CA-[BMIM]Cl-rGO nanofibers. These weight loss profiles (Figure 8) show that pure CA is more stable than the composites. Pure CA decomposes in the range of 330 - 375°C with a corresponding weight loss of approximately 82 wt%. In contrast, the addition of [BMIM]Cl lowers the decomposition temperature range to 240 - 290°C with a corresponding weight loss of 85%.



**Figure 8** TGA profiles of pure CA (black), CA-[BMIM]Cl nanofibers (red), CA-[BMIM]Cl-GO nanofibers (green) and CA-[BMIM]Cl-rGO nanofibers (blue).

The addition of 0.43% GO did not cause significant change in the decomposition temperature but does decrease the weight loss to ~75%. Reduction using hydrazine does not cause any identifiable changes in thermal decomposition nor char formation. These findings confirm that the ionic liquid has fully separated CA molecular chains with no CA H-bonding following mechanical mixing. This separation lowers the thermal stability of the CA by approximately 90°C. The addition of 0.43% GO does not affect the thermal stability of the CA, but introduced an effective mass transfer barrier and char formation nucleus, resulting in an increased amount of char formed. Such an enhancement could suggest that the graphene pallets were well aligned during extrusion and spinning. The morphology, crystal structure, chemical bonding and thermal analysis of the CA-[BMIM]Cl-GO nanofibers show that graphene stacks have been successfully incorporated into CA nanofibers by dispersing GO in a [BMIM]Cl ionic liquid. Polar functional groups, such as  $\text{-C=O}$ ,  $\text{-COOH}$  and  $\text{-OH}$  on GO have not only assisted its dispersion in the ionic liquid, but also facilitate strong and uniform interactions with CA in the hybrid nanofibers. The well-dispersed and strongly bonded system allowed the graphene stacks to form a continuous conductive network, achieving a drastic enhancement in electrical conductivity after reduction using hydrazine, similar to the polystyrene-GO system reported by Wu *et al.* [54]. These insights demonstrate that this new graphene-based hybrid nanocomposite is a promising candidate for smart and flexible electronic and bio-electronic applications, particularly in those systems which require high electrical conductivity.

#### **4. Conclusions**

In summary, a new method of exploiting a [BMIM]Cl ionic liquid for the fabrication of graphene-based, bio-inspired (cellulose acetate) conductive CA-[BMIM]Cl-GO nanofibers through electrospinning has been introduced. Combining the advantages of both GO and [BMIM]Cl materials allowed a homogeneous dispersion of GO and better solubility of CA to

be achieved. The modest incorporation of 0.43% graphene oxide into the hybrid material greatly enhanced the conductivity of the nanofiber mats by more than four orders of magnitude to  $5.30 \times 10^{-3}$  S/cm. The uniform nanostructure of graphite oxide and BMIM in CA nanofibers forms the conductive paths, which has been enhanced by chemical reduction of hydrazine via an ultrasonic process. Such a facile strategy for the fabrication of bio-based, ultrathin, lightweight, flexible nanofibers could open a new avenue towards sustainable material development in the quest for high-performance next-generation smart electronic devices.

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