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Conductive bacterial cellulose/multiwall carbon nanotubes nanocomposite aerogel as a potentially flexible lightweight strain sensor

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ABSTRACT

In this work, in-situ biosynthesized bacterial cellulose (BC) /multiwall carbon nanotubes (MWCNTs) nanocomposite hydrogels converted to the conductive nanocomposite aerogels via the supercritical CO_2 method. A low percolation threshold value of 0.0041 (volume concentration) predicted for BC/MWCNTs nanocomposite aerogels by the proposed modified model. The piezoresistive behavior of the nanocomposite aerogel at percolation threshold, evaluated in tension mode. The strain sensing outcomes revealed a linear trend during loading until a critical strain, afterward began to decline with further increasing of strain. Moreover, by applying loading unloading cyclic tension for 10 times at two different strain amplitudes (2% and 8%), the variation of relative resistance was different. This attributed to the rearrangement of MWCNTs at high strain condition. The gauge factor of 21 and response time of 390 ms obtained for flexible lightweight strain sensor. The fabricated strain sensor utilized to monitor human detection motion.

1. Introduction

Cellulose aerogels as a third generation of aerogels have attracted a great deal of attention in energy storage devices (Zhang, Zhang, Zhao, & Yang, 2015), water purification (Wan & Li, 2015) and smart magnetic materials (Olsson et al., 2010), due to their high porosity (> 80%), low density (0.004–0.5 g/cm^3), flexibility, high specific surface area and three-dimensional interconnected fibrous structure (Demilecamps, Beauger, Hildenbrand, Rigacci, & Budtova, 2015).

Generally, resistance-type strain sensors, which convert the external stimuli (stress or strain) to electrical resistance signal, have been extensively used in the electronic skin (Minjeong et al., 2015) and wearable devices (Liu, Cao, Ma, & Wan, 2017). Nevertheless, pivotal requirements for the strain sensing material are including highly flexible matrix and efficient conductive nanofiller network. Recently, the utilization of cellulose, as one of the most abundant biopolymers on earth, reported in the field of strain sensing devices. For example, Huang, Liu, Wu, Li, and Wang (2017) fabricated composite aerogels based on graphene/carboxymethylcellulose for compressive strain sensing evaluation and a gauge factor (GF) value of 1.58 obtained (Huang et al., 2017). Yao et al. (2017) reported flexible Ag/cellulose nanofiber aerogel, gained from bamboo, with a maximum GF of 1 up to 20% strain (Yao et al., 2017). Zhuo et al. (2018) introduced a carbon aerogel via carbonization of cellulose nanocrystalline/graphene oxide in compression strain and pressure detection with a GF of 5.81 (Zhuo et al., 2018).

It explains that the presence of cellulose plays a critical influence on the viscoelastic properties of the resultant strain sensor. Moreover, the homogeneous dispersion of carbon-based nanofiller within the polymer matrix is vital to improve the performance of sensory materials.

BC possesses high purity, crystallinity, and higher flexibility than plant cellulose or other derivatives of cellulose (Ul-Islam, Khan, & Park, 2012). A variety of conductive nanofillers such as carbon nanotube (CNT) and graphene introduced into BC aerogels. Accordingly, the in-situ method suggested as a proper strategy for achieving conductive BC based nanocomposite due to adjusting the shape, structure, and properties of resultant BC along with excellent dispersion of nanofillers during cultivation and biosynthesis process (Erbas Kiziltas, Kiziltas, Blumentritt, & Gardner, 2015). A few works have been reported about the incorporation of MWCNTs into the BC culture medium and characterize resultant composites (Park, Kim, Kwon, Hong, & Jin, 2009; Yan, Chen, Wang, Wang, Wang et al., 2008; Yan, Chen, Wang, Wang, & Jiang, 2008), or evaluate bone regeneration (Park et al., 2015) and enzymatic biofuel cell (Lv et al., 2016). No one investigated the electrical conductivity and strain sensing behavior of composites.

The literature survey clearly illustrates lack of experimental and theoretical works on the electrical conductivity and strain sensing behavior of in-situ biosynthesized BC/MWCNTs nanocomposite aerogels.

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Furthermore, the designing along with the development of flexible, lightweight, and conductive nanocomposite aerogels as well as prediction of their overall electrical conductivity is immensely challenging. It has been expressed that the variations of resistance for strain sensors around the percolation threshold are significantly sensitive to tensile strain (Hu et al., 2017). Hence, the calculation of percolation threshold is the crucial step for evaluating the strain sensing behavior. In our previous work (Hosseini, Kokabi, & Mousavi, 2018), a model modified by the implementation of porosity as a third term and proposed for predicting the percolation threshold and electrical conductivity of BC/rGO nanocomposite aerogels. The effective medium approach that pointed out by Wang, Weng, Meguid, and Hamouda (2014) utilized as a basic model, owing to its computational simplicity, determination of percolation threshold, dealing with the electron tunneling along with interface effect, and also compatibility with our physical case. Herein, the proposed model applied for predicting the percolation threshold and overall electrical conductivity of BC/MWCNTs nanocomposite aerogel.

In this study, based on predicted percolation threshold value, various contents of MWCNTs, around predicted value, incorporated into the culture medium solution. Subsequently, *G. xylinus* bacteria inoculated into culture media, and the nanocomposite hydrogels harvested at the end of the culture period. The obtained nanocomposite hydrogels then converted to nanocomposite aerogels via $ScCO_2$ drying method to obtain electrical conductive nanocomposite aerogels. The products characterized and compared with neat BC aerogel using FTIR, N_2 adsorption-desorption methods, and FESEM analysis. Finally, the strain sensing behavior of conductive nanocomposite aerogel evaluated in the tension mode.

A theoretical approach for prediction of percolation threshold and overall electrical conductivity presented as the Supplementary Information.

2. Material and methods

2.1. In-situ biosynthesis of BC/MWCNT hydrogels and fabrication of nanocomposite aerogels

BC/MWCNTs nanocomposite hydrogels prepared using the in-situ biosynthesis method similar to our previously reported work for BC/rGO (Hosseini et al., 2018). According to the theoretical prediction of percolation threshold value, 0.5, 0.7, 0.9, 1.1 wt% (based on culture medium solid content) of acid-treated MWCNTs (purchased from Research Institute of Petroleum Industry of Iran) considered and added to the culture medium solutions and autoclaved. Each culture medium solution contained (2% (w/v) glucose, 0.5% (w/v) yeast, 0.5% (w/v) peptone, 0.115% (w/v) citric acid, and 0.27% (w/v) $Na_2HPO_4{\cdot}12H_2O$) and adjusted on a pH of 6.5. All the culture medium materials acquired from Merck, Germany. Seed culture broth with *Gluconacetobacter xylinus* (PTCC 1734, purchased from the Iranian Research Organization for Science and Technology (IROST)) inoculated to the latter culture mediums and transferred to a rotary shaker incubator operating at a rotational speed of 100 rpm at 28 °C for 6 days to prevent the settling of MWCNTs during incubation process. Finally, the biosynthesized nanocomposite hydrogels washed with 1% (w/v) sodium hydroxide (NaOH) solution for 1 h at 85 °C to remove bacterial cell debris and then purified and cleansed using distilled water several times to reach a neutralize pH. The harvested products converted to the aerogels by the $ScCO_2$ drying method at a temperature and pressure of 40 °C and 100 bar, respectively. The details described in Supplementary Information.

2.2. Products characterizations

Evaluating the morphology and microstructure of the fabricated aerogels a TESCAN MIRA 3-XMU (Republic of Czech) field-emission scanning electron microscopy (FE-SEM) employed. Before observation, the samples mounted on a metal stub and sputter coated using a gold sputtering machine with a layer of gold approximately 100 Å thick to reduce charge interruptions.

The DC electrical conductivities of nanocomposite aerogels investigated using a broadband dielectric spectrometer, GW Instek, LCR-8101 G LCR meter-Taiwan. Before testing, a silver paint rubbed over the two surfaces of each specimen to diminish the contact resistance between sample and probes.

The strain sensing capability of BC/MWCNTs nanocomposite aerogel, at the percolation threshold, examined by subjecting to a tensile test via Gotech universal testing machine (GT-TCS 2000, Taiwan). Simultaneously, the variation of resistivity recorded by a digital multimeter (Agilent 34401A). A constant crosshead speed of 1 mm/min applied for loading unloading. The reproducibility of strain sensor evaluated at two different strain amplitudes (2% and 8%) upon 10 cycles. Thrice replicates carried out for each experiment and representative findings recorded. The experiment setup for a strain sensor testing presented in Fig. S1. The flexibility of fabricated strain sensor evaluated over 100 cycles of loading unloading in twisting mode. Accordingly, the variation of resistance recorded using a digital multimeter (Agilent 34401A) upon 100 and 1000 continuous cycles in twisting and bending modes, respectively. These experiments carried out thrice for each of three samples and reprehensive results rendered.

3. Results and discussion

3.1. Morphology and microstructure of aerogels

Fig. 1(A) and (B) represent the FESEM micrographs of BC aerogel. The BC aerogel architecture consists of an interconnected highly porous network with randomly distributed nanofibers. All nanofibers have disorder assembly. The mean diameter of BC nanofiber estimated at 40 nm. The noticeable feature evident in the FESEM micrograph of as-received MWCNTs indicates the presence of partially U-shaped nanotubes that entangle to each other and randomly orient as a bundle, Fig. 1(C). This attributes to the flexibility of MWCNTs, resulting in a U-shaped morphology that remarkably enhances the chance of elastic interlocking of MWCNTs (Sadeghi, Arjmand, Otero Navas, Zehtab Yazdi, & Sundararaj, 2017). The BC growth rout in the presence of MWCNTs presented in Fig. S2.

Fig. 1(D–F) depict the FESEM micrographs of the in-situ biosynthesized BC/MWCNTs nanocomposite aerogel at the percolation threshold. The BC porous and fibrous structure associated with the 3D interconnected network preserves in BC/MWCNTs nanocomposite aerogels.

After incorporation of MWCNTs into the BC culture media and in-situ biosynthesis process, the BC nanofibers and MWCNTs intertwine together and MWCNTs partially cover by BC nanofibers. It reported by Park et al. (2015). In addition, MWCNTs adhere strongly on the surface of BC nanofibers. This attributes to the interaction between the BC functional groups with the oxygen-containing groups of the carboxylic of MWCNTs. Moreover, a bright dots regions are clear in the FESEM images of BC/MWCNTs nanocomposite aerogel due to the high conductivity of MWCNTs, as they distribute uniformly in the BC structure without aggregation (Yoon, Jin, Kook, & Pyun, 2006). Thus, according to FESEM micrographs, the dispersion state of nanotubes is adequate in the 3D framework of BC.

3.2. Electrical conductivity measurements

The modeling and experimental results of the overall electrical conductivity as a function of the MWCNTs volume concentration for nanocomposite aerogels have presented in Fig. 2. The electrical conductivity data depicts a dramatic increase as the MWCNTs contents rise to a critical value, i.e. percolation threshold, suggesting the formation of MWCNTs continuous pathways in the aerogel nanocomposites.