Synthesis and Characterization of Bacterial Cellulose/Nano-Graphite Nanocomposite Membranes

by Henry Aritonang 4

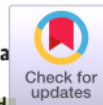# Synthesis and Characterization of Bacterial Cellulose/Nano-Graphite Nanocomposite Membranes

Henry F. Aritonang,* Restu Wulandari, and Audy D. Wuntu

A bacterial cellulose (BC)/nano-graphite nanocomposite membrane has been synthesized by impregnating nano-graphite into the BC membrane. Microscopic measurements show that nano-graphite flakes are evenly distributed in the BC matrix, and the thickness size of a nano-graphite is around 28 nm. In addition, X-ray measurements showed that the best average size of nano-graphite crystallites in the BC matrix is 33.4 nm. Nano-graphite flakes entered the membrane pores and are trapped between the nano fibrils of cellulose. This process is assisted by an ultrasonic process (contact time). For each concentration of nano-graphite or graphite solution, mass of the nanocomposite membrane containing nano-graphite is greater than that containing graphite. The mass is increased with increasing contact time between nano-graphite solutions and BC membranes. The increasing mass indicated the increase in the carbon content which is shown by energy dispersive spectroscopy data. Conductivity of the nanocomposite membrane, in consequence, is significantly increased with the increasing concentration of nanographite solution. For contact time of 24 h, the conductivity is 1.74 S cm^{-1}.

1. Introduction

The development of composite technology is increasingly developing because generally composites have new properties and their functions are far better than when standing alone. Composites are generally composed of binding materials (matrices) and reinforcing materials called fillers.[1] Currently, composite technology is supported by the development of nanomaterial technology. Various studies have shown that composites using nanomaterials produce better properties. Until now, one of the most developed nanocomposite technologies is nanocarbon.[2,3]

Carbon with nanostructures is one of the unique things in the material field due to its interesting physical and chemical properties, including mechanical strength, chemical resistance, good electrical and thermal conductivity, and high surface area. The use of nanocarbons to produce and store energy, storage of hydrogen, nanocomposites, and catalysts.[4,5] One of the nanocarbons is nanographite.

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Nanographite is nano-sized carbon that has 2D and is composed of graphene sheets. The nanographite has been used as a filling material in bacterial cellulose (BC). Kiziltas et al.[6] has synthesized BC/nano-graphite composite membranes, where the BC acts as a matrix so that nano-graphite is perfectly dispersed. The study used the culture medium Hestrin–Scharamm (HS) to produce BC. However, the study did not use surfactants in dispersing the nanographite. Whereas surfactants are used to disperse nanographic solutions so that they are spread evenly before they are dispersed into BC, as has been done by Zhou et al. which uses sodium dodecylbenzensulfonate (NaDDBS) surfactants. However, the study also used HS culture media to produce BC and did not research differences in the characteristics of graphite and nano-graphite that were inserted into BC.[7] Until now, BC composite membranes containing carbon have been used as biosensors, capacitors, and other electronic equipment.[8–10]

Therefore, based on the above research, we wants to synthesize BC/nano-graphite nanocomposite membranes by using coconut water as a source of BC production. Thus, these nanocomposites can be used as useful materials, such as electrodes.[11] This research will also compare it with BC/graphite nanocomposite membranes. To disperse nano-graphite solution, cetyltrimethylammonium bromide (CTAB) surfactant is used. In addition, bacterial cellulose was used in this study because bacterial cellulose has unique properties, such as crystallinity, porosity, and high tensile strength,[12,13] so it is widely used as a matrix to produce nanocomposites.

2. Experimental Section

2.1. Materials

NaOH, urea, glacial acetic acid, ethanol, graphite, CTAB were obtained from Sigma-Aldrich (99.9%). All chemical materials and solvents used in the experiments were analytical grade reagents, and were used without further purification. Meanwhile, white sugar, *Acetobacter xylinum*, and coconut water were obtained from a local traditional markets.

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2.2. Synthesis of BC Gel

BC was obtained in the laboratory from a *Acetobacter xylinum* pellicle incubated for 6 days at 28 C in a static culture containing 10% (w/v) sugar and coconut water adjusting pH with acetic acid to 4 in a glass flask. BC pellicles, grown in the air/liquid interface with an average thickness of 0.6 cm, were boiled in 1 wt% NaOH solution, 1 v/v% CH$_3$COOH solution for 24 h in order to remove non-cellulosic compounds and then thoroughly washed under running water until the pH of BC becomes neutral (pH 7).

2.3. Moisture Content Analysis

Determination of BC water content was done using gravimetric methods. First of all, BC was cut into pieces with the size of 4 × 4 cm by six pieces; three pieces were pressed with a weighing stone for 15 min and the other three were not pressed. After that, they were weighed and placed on a petri dish, put in an oven at 105 °C for 3 h, refrigerated in a desiccator for 30 min to room temperature, and then weighed to a constant weight. Calculation of BC water content was done using Equation (1).[14]

$$\text{Moisture content} = \frac{W_o - W_1}{W} \times 100\% \tag{1}$$

where, W_o is the initial weight (sample + cup) before pressing, W_1 is the final weight (sample + cup) after pressing, and W is the sample weight.

2.4. Synthesis of BC/Nano-Graphite Nanocomposite Membranes

The preparation of BC/nano-graphite nanocomposite membranes followed the procedure reported by Zhou et al.[7] modified. First, as much as 5 g graphite was put into a porcelain cup, then graphite was calcined at 1000 °C for 5 min in the furnace. After that, the combustion product (nano-graphite) was dissolved into 100 mL distilled water with a concentration variation of 0.05% and 0.5% (w/w), then CTAB was added as much as 0.3 g (0.2% w/w), then the solution was sonicated for 7 h. BC gel was cut to the size of 4 × 4 cm, weighed, pressed for 15 min using a weighing stone. After that, BC was put into 15 mL of nano-graphite solution that was previously sonicated for 7 h. Furthermore, the solution was sonicated again for 3, 6, 12, and 24 h, then filtered. BC/nano-graphite gel was weighed, then washed using distilled water, pressed again for 15 min and finally dried for 6 days and the resulting nanocomposite membrane was coded, namely BC/NG-0.05 and BC/NG-0.5. The same procedure was also carried out on graphite, but without the combustion process in the furnace and the resulting nanocomposite products were BC/G-0.05 and BC/G-0.5 code. All the nanocomposite membranes were characterized using Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and electrical conductivity.

2.5. Characterization of the Nanocomposite Membranes

XRD patterns were measured with a PW1835 Philips diffractometer using Cu Kα radiation. XRD measurements were performed with a step width of 0.01 and a time per step of 0.25 s. XRD peaks were used to estimate qualitatively, the average size of crystallites from nano-sized materials using the Scherrer formula. Crystallite sizes were determined based on Full Width Half Maximum (FWHM), using the following Equation (2):

$$d = \frac{K.\lambda}{\beta \cos\theta} \tag{2}$$

where λ is the X-ray wavelength in nanometer (nm), β is the peak width of the diffraction peak profile at FWHM resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9. The value of β in 2θ axis of diffraction profile must be in radians. The θ can be in degrees or radians, since the $\cos\theta$ corresponds to the same number.[15]

SEM was employed to study the morphology of the obtained nanocomposite membranes. SEM images were taken with a JEOL-JSM-6510 LA at an acceleration voltage of 15 kV. The obtained nanocomposite membranes were covered with gold using MCIOOO-Hitachi Sputter coater. EDS was used for the elemental analysis of the composite membranes surface. The thickness of the nanographite flakes was analyzed using the ImageJ program. The electrical conductivities of the nanocomposite membranes were measured using a four electrode probe with a current-voltage Fluke. The thickness and diameter of the nanocomposite membranes were precisely measured for calculating the electrical conductivity. For each measurement, three samples were tested three times at different positions on the nanocomposite membranes surface, and then the average was reported.

3. Results and Discussion

3.1. Bacterial Cellulose Membranes

Coconut water fermentation for 6 days and with the help of the *Acetobacter xylinum*, produce white BC gel (**Figure 1**).

BC gel has an average thickness of 3.61 mm (Figure 1a). Meanwhile, BC from the press has an average thickness of 1.58 mm and a dry membrane has an average thickness of 0.03 mm (Figure 1b, it appears that this thin dry membrane was transparent). The average water content of BC, before and after the press was 98.03% and 97.17%, respectively. That is, the water that is reduced after the press process was 0.86%.

3.2. Morphology

The pressed BC gel was dried in the open air for 6 days, then analyzed using SEM to observe surface morphology, as shown in **Figure 2**.

It appears that BC consists of nano-sized fibers that are intertwined to overlap and form pores/cavities. The average pore size and fiber diameter were 60.7 and 74.0 nm, respectively. Therefore, this BC can be used as a matrix[16] to adsorb nano-graphite and graphite.
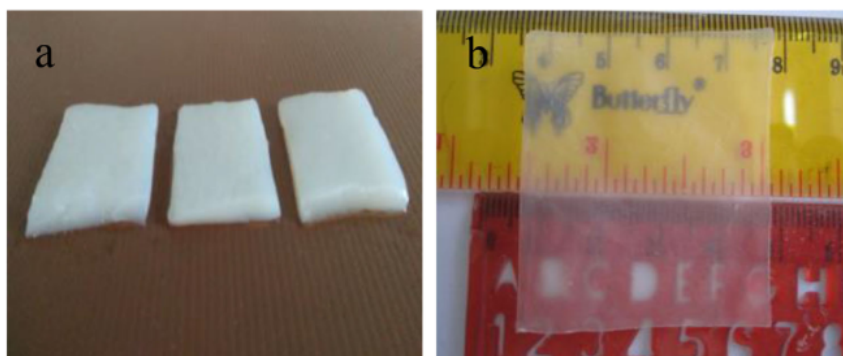
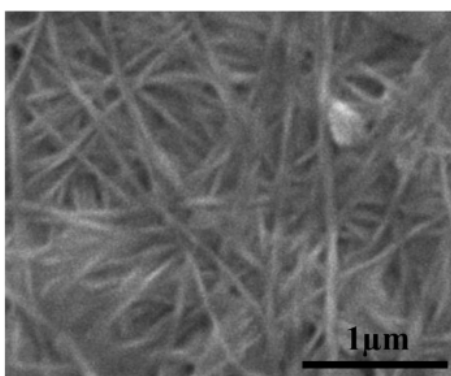**Figure 1.** Photograph of BC; a) before pressing, b) after drying.
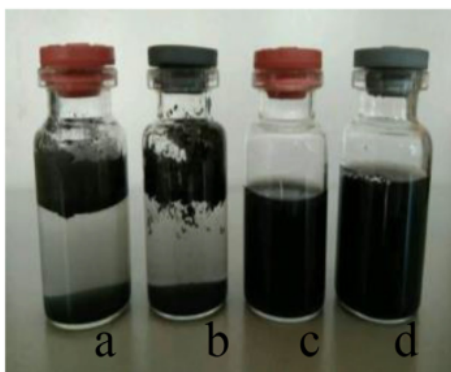

Figure 2. SEM images of BC membrane.

Table 1. Composition of elements contained in nanocomposite membranes.

The nanocomposite membrane	Carbon [% mass]	Oxygen [% mass]
BC/G-0.05	84.71	15.29
BC/G-0.5%	96.03	3.97
BC/NG-0.05%	88.07	11.93
BC/NG-0.5%	96.72	3.28
BC	49.94	53.06

compounds, while the tail group was interacted with nonpolar compounds from graphite or nano-graphite, so that graphite and nanographite were fully dispersed in the solution.[17]

Nano-graphite morphology appears to form pieces that have been separated from the graphite chunks due to being heated to 1000 °C. These pieces are referred to as graphite nanoplatelets with a thickness of 10–100 nm.[6,18] The results show that the thickness of nano-graphite products was an average of 28 nm so that they are included in graphite nanoplatelets. Different characters are shown by graphite. Graphite morphology was chunks of graphite with thick diameters, averaging about 883 nm (0.883 μm), as shown in **Figure 4**.

Furthermore, when BC was immersed in each of the graphite and nano-graphite solutions with variations in contact time, the mass of the composite membrane increased (**Figure 5**). The highest average mass of nanocomposite membranes occurs at 24 h contact time. The increase in mass of the nanocomposite membrane is due to the increasing amount of nano-graphite which is inserted into BC fibers. This shows that more nano-graphite particles are absorbed into the cellulose fibers.

The high mass of BC/NG nanocomposite membranes has been proven based on EDS data (**Table 1**), which is indicated by the high carbon element (C). The content of element C in BC/NG membranes is relatively higher than BC/G membranes, both at 0.05% and 0.5% concentrations, as shown in Table 1. High element C content, derived from 0.5% graphite concentrations, and applies to both types of nanocomposite membranes.

Based on SEM images (**Figure 6**c,d), it appears that single pieces of nano-graphite, while in graphite (Figure 6a,b), the pieces were still in chunks/stack of graphite. Because of the high
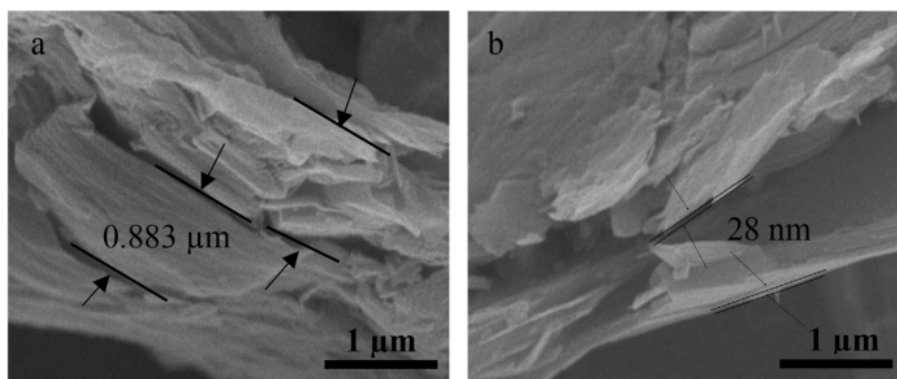

Figure 3. Photographs of a,c) graphite solution and b,d) nano-graphite solution: a,b) solution without CTAB and c,d) solution with CTAB.

Before the BC gel is immersed in a nano-graphite solution, the solution is first prepared. It appears that the solution is completely dispersed when dissolved in CTAB, as shown in **Figure 3**.

CTAB is a cationic surfactant, in which the head part is a hydrophilic ammonium (N^+) group and the tail part is a hydrocarbon chain composed of hydrophobic cetyl groups. The head group from CTAB was interacted with water polar
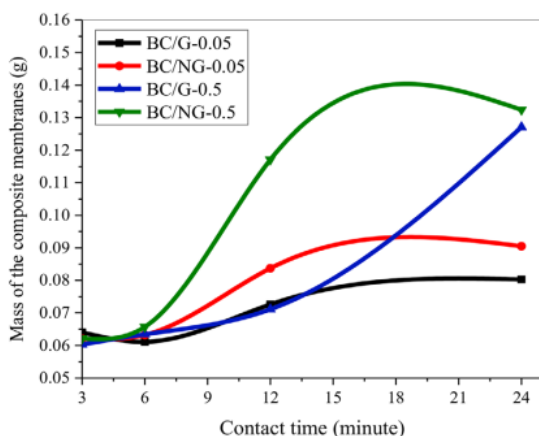
Figure 4. SEM images of a) graphite and b) nano-graphite.

Figure 5. Graph of the relationship between contact time with the mass of the nanocomposite membranes.

Table 2. Nano-graphite and graphite crystallite sizes inside and outside of the BC membrane.

Sample	Crystallite sizes
Graphite	72.0
Graphite in the BC/G-0.05 membranes	36.7
Graphite in the BC/G-0.5 membranes	34.6
Nano-graphite	67.3
Nano-graphite in the BC/NG-0.05 membranes	36.1
Nano-graphite in the BC/NG-0.5 membranes	33.4
BC	55.1

concentration (0.5%), nano-graphite fragments and graphite appear denser than at a concentration of 0.05%. However, it can be said that BC is capable of dispersing nano-graphite and graphite particles.

3.3. XRD

The nano-graphite and graphite diffraction patterns contained in the composite membrane were analyzed by XRD and presented in **Figure 7**. In the picture it appears that nano-graphite and graphite have the same diffraction pattern, namely the appearance of characteristic C peaks in the region $2\theta = 26.67°$. This peak was also similar to nano-graphite and graphite, although in BC fibers. The figure also shows that both nano-graphite and graphite are crystalline because they produce a sharp peak.[19]

The size of nano-graphite crystallites is relatively smaller than graphite, at 67.3 nm and 72.0 nm, respectively (**Table 2**). The size of this nano-graphite and graphite crystallite was relatively smaller after entering and being absorbed in BC fibers and

applies to both solution concentrations. Nano-graphite crystalline size, relatively smaller. Therefore BC was capable of dispersing nano-graphite and graphite particles so that the size of nano-graphite and graphite crystallites was relatively smaller than outside the BC matrix. This trait has also been reported by Ostad-hossein et al.[20]

However, when the concentration is 0.5%, the size of the nano-graphite is relatively smaller than at a concentration of 0.05%. This was because at high concentrations, the composite membrane has been dominated by nano-graphite so when analyzed by XRD, the size of the crystallite was considered to be dominated by nano-graphite. Whereas at low concentrations (ten times lower than 0.5% concentration), the size of the crystallites was influenced by bacterial cellulose, so the crystallite size becomes larger. This was evidenced from the morphology of the nanocomposite membrane between concentrations of 0.05% and 0.5% for both types of nanocomposites, as presented in **Figure 8**.

3.4. Electrical Conductivity

Table 3 shows the electrical conductivity value of nanocomposite membranes.

It appears that the table only gives data for a 0.5% solution. Electrical conductivity at a concentration of 0.05% is not measurable. This shows that the resistance (R) of the sample is so large
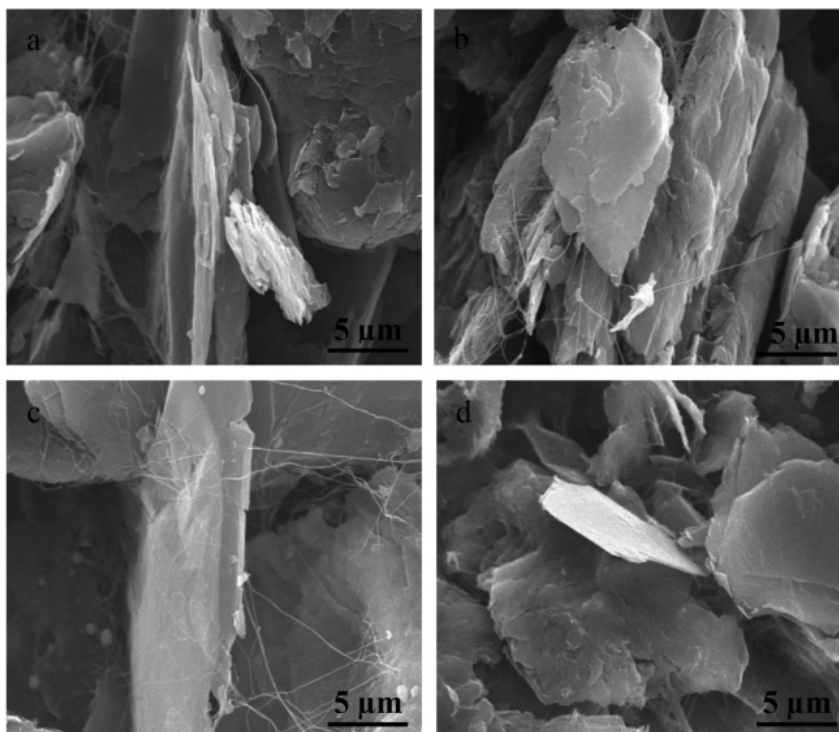
Figure 6. SEM image of a nanocomposite membrane: a) BC/G-0.05%, b) BC/G-0.5%, c) BC/NG-0.05%, and d) BC/NG-0.5%.
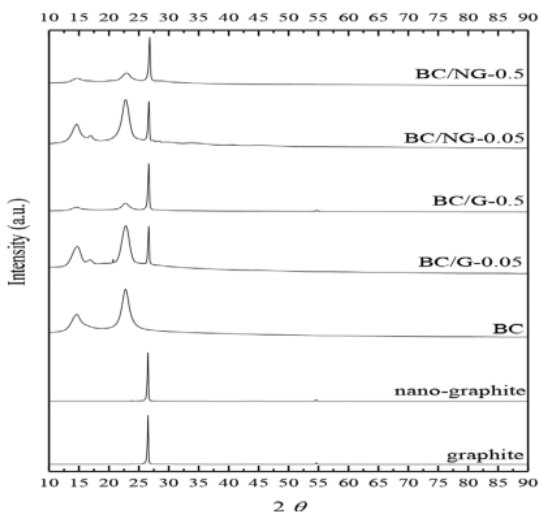

Figure 7. X-ray diffraction patterns of nanocomposite membranes.

that it cannot conduct an electric current. This is due to the fact that nano-graphite and graphite were not evenly distributed (Figure 8a,c) because the concentration is still so low that the particles are not connected/in contact with each other.

Table 3. The electrical conductivity of nanocomposite membranes at 0.5% solution concentration.

Sample	Contact time [min]	Conductivity [S cm^{-1}]
Graphite	–	0.0143
Nano-graphite	–	0.0203
BC/G nanocomposite membranes	3	1.1198
	6	1.5540
	12	1.6191
	24	1.7197
BC/NG nanocomposite membranes	3	1.1506
	6	1.5654
	12	1.6425
	24	1.7361

Meanwhile, at a concentration of 0.5%, all composite membranes have electrical conductivity and their values increase with increasing contact time (Figure 8b,d). The value of electrical conductivity is still higher than that of nano-graphite and graphite outside the BC matrix. The electrical conductivity of BC/NG nanocomposite membrane was relatively higher compared to BC/G nanocomposite membrane for each same contact time.
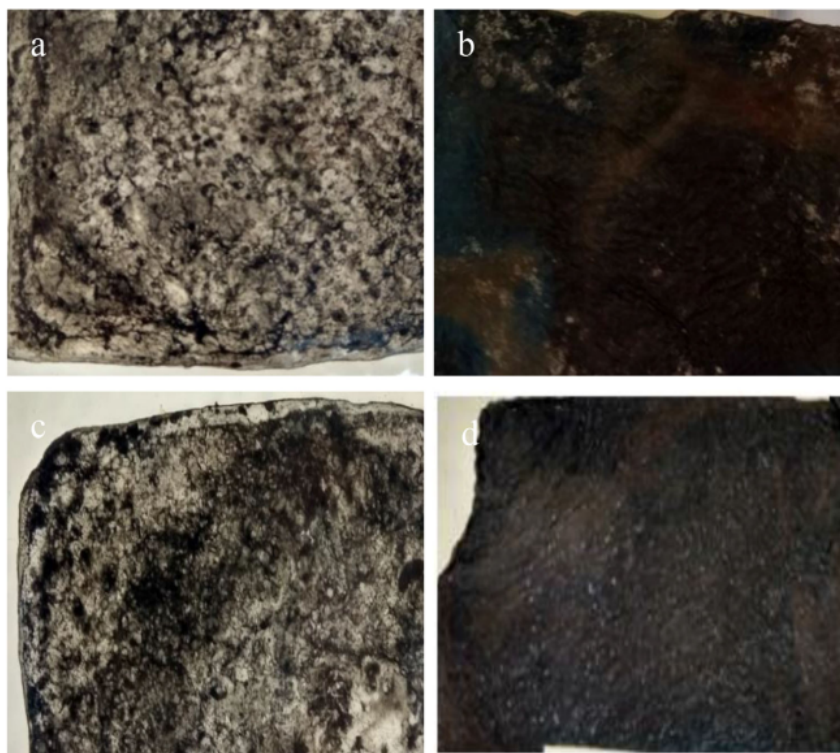
Figure 8. Photograph of composite membranes: a) BC/G-0.05, b) BC/G-0.5, c) BC/NG-0.05, and d) BC/NG-0.5.

4. Conclusions

Nano-graphite can be spread evenly on all parts of the BC fibers, which shows that the BC matrix can disperse nanographites, especially at a solution concentration of 0.5% w/w. Therefore, the mass of nanocomposite membranes containing nano-graphite was relatively heavier than those containing graphite, which was indicated by the high content of element C. In addition, the size of nano-graphite crystallites contained in nanocomposite membranes was relatively smaller than graphite, and even with nanographites outside nanocomposite membranes. As a result, the electrical conductivity of BC/NG nanocomposite membranes was relatively higher than BC/G for each solution concentration and contact time.

Conflict of Interest

The authors declare no conflict of interest.

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