Conductive paper of reduced graphene oxide and nanofibrillated cellulose

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Abstract. The conductive paper has been of great interest due to its flexibility and superior properties. In this work, the facile procedure with scalable possibility was used to prepare conductive paper with graphene oxide (GO) and reduced graphene oxide (rGO). GO synthesized by the modified Hummers’ method was successfully transformed to rGO using ascorbic acid. These GO and rGO were used as a conductive source to improve conductive properties of the as-prepared paper. GO and rGO (0–25 wt\%) were mixed with nanofibrillated cellulose (NFC) to form conductive paper. Results showed that the reduction of the electrical resistance was found from both GO/NFC and rGO/NFC paper sheets with increasing a content of GO or rGO. Furthermore, the paper with rGO exhibited more outstanding electrical conductive than the GO/NFC paper. Also, the water uptake of the conductive paper was affected by the addition of GO or rGO. The significant reduction of water uptake was found to be more pronounced with the introduction of rGO in comparison with the presence of GO. The conductive paper prepared in this study would be useful for applications such as flexible electrode.

1. Introduction
Flexible electronic devices have been of great interest due to a wide range of applications such as portable electronics, energy storage, photovoltaic cells and smart clothing [1, 2]. Due to environmental awareness, bio-based materials with advantages of light weight, biodegradability and superior mechanical properties have attracted much attention [1, 2]. Nanofibrillated cellulose (NFC), a web structure of nanofibers and microfibers entangled, has been named by Herrick \textit{et al.} [3] and Turbak \textit{et al.} [4]. Later, cellulose fibers with diameters in the range of 10–100 nm were finally obtained using several approaches, such as grinding [5], high speed blending [6] or the combination of high speed homogenization and sonication [7-9]. NFC could be used as an alternative raw material to traditional conductive rigid and fragile films like ITO [2].

To improve conductive properties of cellulose, a conductive material is required. In comparison with other conductive materials such as carbon nanotube, conductive polymer and metallic nanowire, two-dimensional-structured graphene has been proved to have greater potential due to its high surface area,
superior mechanical properties and biocompatibility [1, 10]. Recently, the manufacture of graphene in a large production could be feasible via graphene oxides (GO) with the introduction of the reducing agent to remove functional groups such as hydroxyl, carboxyl and carbonyl [1, 11].

In this research, flexible conductive NFC paper with GO and rGO was prepared. Water uptake and electrical resistance of the prepared conductive paper were investigated.

2. Materials and methods

2.1. Materials and chemicals
Nanofibrillated cellulose (NFC, CELISH KY100S) was supplied by Daicel Finechem Co., Ltd. Graphite powder, sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), sulfuric acid (H₂SO₄), hydrochloric acid (HCl) and ascorbic acid were purchased from Sigma-Aldrich Co., LLC.

2.2. Preparation of graphene oxide
Graphene oxide (GO) was synthesized by the modified Hummers’ method as described elsewhere [12]. Briefly, graphite flakes (10 g) and NaNO₃ (5 g) were slowly added into a concentrated H₂SO₄ solution at 0 °C. Then, 30 g of KMnO₄ was used to oxidize the suspension at the temperature below 20 °C. The suspension was further stirred for 120 min at 0 °C, and continue kept stirring at 35 °C for 30 min. After that, 360 ml of distilled water was slowly added to the suspension. At this state, the temperature of the suspension was rapidly increased to ~100 °C due to an exothermic reaction. The suspension was further maintained at 80 °C for 15 min, and was subsequently diluted with 1,140 ml of distilled water, and 10 ml of H₂O₂. Finally, the GO suspension was filtered, and washed with HCl, and distilled water. The obtained GO cake was dried at 70 °C for 48 h. A GO dispersion (5 mg ml⁻¹) was prepared with the aid of ultrasonic bath (50 Hz) for 3 h, and followed by centrifugation at 3,000 rpm for 15 min to remove the un-exfoliated GO. The reduction of GO to rGO was carried out before the conductive paper preparation. 1 g of GO was soaked in the ascorbic acid solution (4 wt%) under stirring for 24 h.

2.3. Preparation of conductive paper of graphene oxide and nanofibrillated cellulose
0.5 wt% NFC suspension was prepared using a high speed homogenizer (Ultra Turrax IKA-T25) for 30 min. Then, a GO or rGO suspension with a concentration of 0 - 25 wt% was slowly added into the NFC suspension. This suspension was stirred for 60 min. The NFC paper with GO or rGO was formed by a filtration method to obtain a wet cake. Subsequently, the wet cake was oven-dried at 40 °C for 48 h under a mass of 4 kg, and was further dried using a compression molding with the pressure of 100 bar at 110 °C for 30 min. The appearance of the NFC/GO paper is illustrated in Figure 1.

2.4. Characterizations

2.4.1. Fourier transform infrared spectrometry (FTIR). Chemical functional groups of GO and rGO sheets were investigated using a Fourier transform infrared spectrometer (Thermo Nicolet 6700) equipped with an attenuated total reflectance (ATR) mode in a range of 4000 – 500 cm⁻¹. Sample spectra were recorded with a resolution of 4 cm⁻¹ and a repetitious scan of 64 times. The background was collected before each test.

2.4.2. Water uptake. Prior to the measurement, all samples were dried in an oven at 60 °C for 48 h to obtain the constant weight. The samples were subsequently soaked in distilled water for specific times (2, 4, 6 and 8 h) at room temperature. After that, the sample was taken out, wiped out water with filter paper, and immediately weighted. The water uptake of the samples (W) was calculated using the equation.

W(%) = ((W_i - W_f)/W_i) × 100

(1)
where \( W_t \) and \( W_i \) are the weight of the sample at various soaking times and the initial dried weight of the sample, respectively.

2.4.3. Electrical resistance. The electrical resistance of the samples were measured using an ohmmeter. The standard positive and negative probes were attached on samples, and a value was recorded.

3. Results and discussion

Figure 2 presents FTIR spectra obtained from GO and rGO materials. The FTIR spectrum of the GO was more characteristic than that of rGO. The outstanding peak located at 3340 cm\(^{-1}\), attributed to OH stretching vibration could be easily observed from GO [13, 14]. The peaks at 1720 cm\(^{-1}\) could be assigned to C=O stretching of carboxylic and/or carbonyl moiety functional groups. The presence of the 1049 cm\(^{-1}\) peaks indicated the stretching vibration of the C-O-C groups. It would be noted that some of these peaks could not be detected from the rGO material, and the intensity of the remaining peaks was significantly lower in comparison with the GO spectrum. This was an indication of the less hydroxyl groups remained on the rGO sheets after the reduction with the ascorbic acid.

Figure 1. Appearance of the GO/NFC paper

Figure 2. FTIR spectra obtained from rGO and GO.

Figure 3 presents the water uptake of the conductive paper with GO and rGO. Water uptake of the NFC paper without the addition of GO and rGO presented a water uptake of 45.0 %. No significant change of the water uptake for the GO/NFC paper was found when the GO content was higher to even 25 wt%. This might be due to the oxygen functional groups on GO sheets interacted with water. On the other hand, with introduction of the rGO in the NFC paper, the decreased water uptake was monitored. The water uptake of the paper with 5 wt% rGO decreased to 32.2 % after soaking in distilled water for 8 h. When the percentage of rGO in the paper was higher, the water uptake decreased slightly. At 25 wt% of rGO in the paper, its water uptake was 24.5 %. This reduction was due to the hydrophobic rGO (less functional groups interacted with water) and a lower amount of cellulose [14]. With a higher content of rGO, the more hydrophobic paper was formed. This was well agreement with the study of Mianehrow et al. [1] reporting that the hydrophobicity of the composites increased with increasing a quantity of rGO.

The electrical resistance of the paper as a function of the GO or rGO content is presented in Figure 4. In this study, the highest electrical resistance could be obtained from the paper without the presence of GO and rGO. With 4 wt% of GO, the electrical resistance was 771 kΩ, and this was significantly reduced to 19.5 kΩ when the GO content increased to 10 wt%. After 10 wt% of GO, the electrical resistance of the paper decreased slightly. The electrical resistance of 2.6 kΩ was obtained from the paper with 25 wt% of GO. On the other hand, the reduction of GO to rGO could increase the conductivity [1]. A value of 0.78 kΩ could be measured from the paper with 5 wt% rGO. With increasing a content of rGO, the electrical resistance decreased considerably. At 25 wt% of rGO, the paper showed the electrical resistance of 0.038 kΩ. This high conductivity indicated that the less-contaminated and damage rGO sheets were well-dispersed in the NFC paper, allowing electrical
charges to be efficiently transferred. The similar reduction of the electrical resistance has been reported for the recycled pulp mixed with rGO [1].

4. Conclusions
Flexible conductive paper sheets of NFC with two different types of graphene sources (GO and rGO) were successfully prepared. With the introduction of ascorbic acid, GO was reduced to rGO. Due to the 2D-honeycomb structure of graphene sheets with less oxygen functional groups on the surface of rGO, the conductive paper with rGO showed higher electrical conductivity and lower water absorption compared to the GO/NFC paper. With increasing a GO quantity, no significant change of water uptake could be observed from the paper, and the electrical resistivity of the paper decreased considerably with the addition of GO. The NFC paper with 5 wt% GO showed the electrical resistivity of 771 kΩ while the electrical resistivity value of 19.5 kΩ was measured from the NFC paper with 10 wt% of GO. On the other hand, water uptake of the NFC paper with rGO decreased greatly when the rGO content was higher. With 5 wt% of rGO, the electrical resistivity of the NFC paper was plummeted to 0.78 kΩ, and the electrical resistivity decreased to 0.038 kΩ when the rGO content was 25 wt%. We believed the prepared conductive paper of rGO and NFC could be potentially used for low cost and environmental friendly flexible electronic devices.

5. References
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