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Highly conductive nanocomposites based on cellulose nanofiber networks via NaOH treatments

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ABSTRACT

Developing functional nanocomposites with the utilization of the sustainable natural resources (e.g. cellulose) is one most importance strategy. In this study, a novel method was developed and used to fabricate flexible conductive nanocomposite. The key innovation of this method is that carbon nanotubes (CNTs) was incorporated into cellulose nanofiber (CNF) gel which processed by alkali treatment. We found that the gelation process caused the shrinking of CNF/CNT gel-film, which result in forming a robust 3D network structure. While the shrinking attributed to constructing high density CNTs electron transport pathways and achieve improved electrical conductivity. Results clearly show that CNFs, a dispersing agent, were used to well-dispersed the CNTs in the nanocomposite. After the alkali treatments, the as-prepared CNF/CNT gel-film had a conductivity of 5.02 S/cm, which is almost 3-fold higher than the CNF/CNT film (without alkai treatment), at 20 wt% CNTs. Conductivity of the CNF/CNT gel-film was further improved to as high as 17.04 S/cm, when adding 50 wt% CNTs. Morphology investigation exhibited that CNFs and CNTs formed into a high density 3D network affording adequate electron transport pathways, and giving the gel-film remarkable electrical conductive properties. Additionally, in lights of its excellent electrical performance, low cost, and environmental friendliness, the CNF/CNT gel-film may have a promising application in the flexible electrodes and conductive papers.

1. Introduction

Cellulose (β-(1,4)-D-glucopyranose polymer), which originate from higher plant, bacteria, and algae, has become attractive from the view of sustainable development, since it is the most abundant bioresource [1,2]. Nano-fibrillated cellulose, in the form of cellulose nanofibers (CNFs), exhibite outstanding mechanical properties, such as high strength (2–6 GPa), high Young's modulus (30–150 GPa) and large aspect ratio [3]. Given these properties, CNFs have potential uses as reinforcement or skeleton agents in the transparent composites, polymer hybrid-gels, and flexible conductive composites [4–9]. Among the functional nano-scale materials, highly conductive nano-carbon materials, such as carbon nanotubes (CNTs), graphene, and CNT/graphene hybrid, have been strongly considered for the application as conductive additives [10–16]. The one-dimensional CNTs afford high conductivity and are beneficial for the construction of a conducting network due to the large diameter ratio. However, limited attention has been paid to prepare high conductive CNT-based nanocomposites, due to the challenges including CNTs agglomeration and low CNT content (when mixing with matrix). Recently, many researchers are devoting to solve these problems by combining the green biomass (cellulose) and conductive CNT to fabricate high-performance conductive nanomaterials [17,18]. The incorporation of CNTs into 3D network structure could bring well dispersion of each nano-elements and lead to multi-functional materials. For example, bacterial cellulose (BC, having an ultrafine network structure) and CNT has been combined to prepare freestanding and flexible conductive paper electrode by immersing swollen gellike BC into CNTs solutions [19,20]. The CNTs content in the hybrid composite depended on the dipping time and conductivity of the obtained BC/CNT, which would up to 0.14 S/cm with approximately 10 wt% CNT [18,19]. One other method to build 3D conductive network was making use of a solution of cellulose with

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CNTs dispersed homogeneously in a dissolution system (e.g. NaOH/urea solution, lithium chloride/N,N-dimethylacetamide and ionic liquids) [21,22]. Then the cellulose/CNT composite are produced through a simple wet-spinning process or directly casting into a film [13,17]. Combining CNFs with functionalized CNTs to prepare hybrid aerogels is another approach to achieve high conductive properties. By freeze-drying or supercritical drying, CNFs and CNTs were co-aggregated with close contact, thus forming a continuous conductive network [10,23]. Additionally, Koga et al. reported that transparent, conductive nanocomposite were prepared by mixing CNTs and TEMPO-oxidant cellulose. The surface-anionic cellulose had reinforcing and nano-dispersing effects on the CNTs, providing a conductivity as high as 10 S/cm [4].

On the basis of these studies, aiming at simultaneously functionalizing, reinforcing cellulose/CNT nanocomposite, a novel gelation process was developed to not only avoid the aggregation of CNTs in the nanocomposites but also increase the electrical conductivity. As a consequence, a CNF/CNT gel with a 3D network structure was fabricated with the shrinking characteristic using 15 wt% NaOH treatments. The morphology feature and electrical conductivity testing were evaluated to demonstrate the proof-of-the-concept of the synergy effects between CNFs and CNTs during the gelation. Therefore, we are reporting a simple method for preparing highly conductive film based on an abundant and sustainable natural (i.e., CNF) and carbon materials that possess highly electrical properties desirable for flexible electrode materials.

2. Experimental

2.1. Materials

Wood powder from the softwood Hinoki cypress (Chamaecyparis obtusa) through a 60 mesh was used as the raw material. The process of purification of the wood powder chemical as follows: the lignin was firstly removed using an acidified sodiumchlorite solution at 80 °C for 1 h. Next, the hemi-cellulose were removed using 6 wt% potassium hydroxide. After each chemical treatment, the sample was filtered and rinsed with distilled water until the residues were neutralized. Finally, the purified sample was kept in a water-swollen state without drying with the concentration around 1 wt%. The MWCNTs paste (15–20 nm diameter, 5–15 μm length, 97.5 wt% purity) were purchased from Shenzhen Nano-Port Co., Ltd. Sodium hydroxide, sodiumchlorite and potassium hydroxide were all of laboratory grade and used as received.

2.2. Preparation of cellulose nanofibers

1 wt% purified cellulose slurry was passed through a grinder (MKCA6-2; Masuko Corp., Japan) twice at 1500 rpm. The grinding treatment was performed with a clearance gauge of −2.5 (corresponding to a 0.25 mm shift) from the zero position, which was determined as the point of slight contact between the two grinding stones. This treatment allowed us to obtain an aqueous suspension of cellulose nanofibers [24,25].

2.3. Preparation of CNF/MWCNT gel-film

A certain amount of MWCNTs was first mixed under different weight shares of CNF/CNT solution (CNF/CNT: 50%/50%, 60%/40%, 70%/30%, 80%/20% in mass ratio) and then ultra-sonicated in an ultrasonic wave cell crusher (XO-1200, Xianou Biological Technology Co. Ltd., China) for 30 min to give a mixture without visible agglomerates. The mixture was vacuum-filtered and dewatered into a wet CNF/MWCNT film using a polytetrafluoroethylene membrane (PTFE, 0.2 μm) filter. Next, the wet CNF/MWCNT film was immersed into 15 wt% NaOH and kept at 40 °C for 12 h followed by completely neutralized with distilled water. Finally, the CNF/MWCNT gel-film was prepared after freeze-drying overnight. Here, the obtained samples with and without NaOH treatments were denoted as CNF/MWCNT gel-film and CNF/MWCNT film, respectively.

2.4. Characterization

Field emission scanning electron microscope (FE-SEM) observations were to investigate the morphological features. The samples were slowly dehydrated using ethanol (three times, 1 h each) followed by acetone (twice, 1 h each) and then replaced by *t*-butyl alcohol (twice, 1 h each). After freeze-drying, film samples were coated with platinum by an ion sputter coater and then observed with an FE-SEM (JSM-7800F; JEOL Ltd., Tokyo, Japan) operating at 1.5 kV. The X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer (Smartlab-3kw; Rigaku Corp., Tokyo) using Cu-Kα radiation (40 kV and 40 mA), with the scanning speed of 5 deg/min. The tensile mechanical properties of the film samples (after freeze-drying) were investigated by using a universal material-testing machine (SANS, Shenzhen Co. Ltd., China) at room temperature. The sample was cut into 30 mm long, 5 mm wide, and a crosshead speed of 1 mm/min was used for the tests. The average value of the tensile stress was calculated for five specimens. The electrical conductivity of the samples was measured at room temperature using the four-point probe method (RTS-8, China). Shrinkage rate was determined based on the diameter of the CNF/MWCNT film before and after NaOH treatments.

3. Results and discussion

Previously, we reported that cellulose nanofiber/chitin nanofiber can form into tough gel via the alkali treatment followed by neutralization [24,26–28]. In particular, the cellulose nanofiber-based gel with cellulose II demonstrated high strength due to the mercerization process in the crystal conversion from cellulose I to cellulose II. The mercerization process caused the formation of a robust CNF network through interdigitation. In this study, such CNF gel (with three-dimensional network) were used as a nano-network skeleton to support and disperse the conductive CNTs to prepare a CNF/CNT gel-film with high conductivity. As shown in Fig. 1a, the CNF/CNT suspension (mixed using sonication) can keep stable with a uniform black color at least after two weeks,

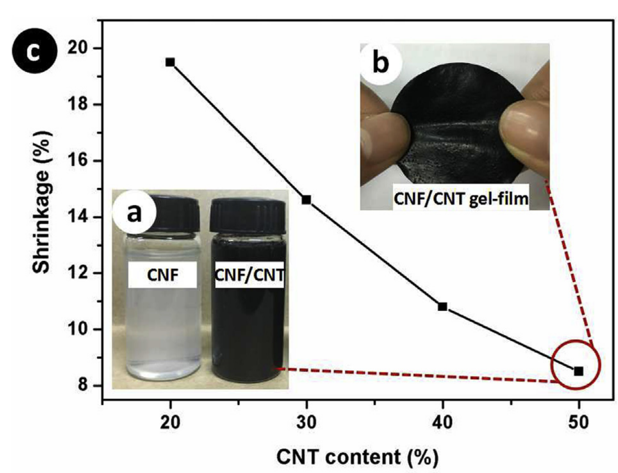

Fig. 1. (a) the image of CNF and CNF/CNT suspensions after sonication process (with 50 wt% CNT); (b) the CNF/CNT gel-film with 50 wt% CNT (in wet state); (c) Shrinkage curves of the CNF/CNT gel-film in different CNT content.