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Bacterial Nano-Cellulose Triboelectric Nanogenerator

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ABSTRACT

Motivated by a desire to resolve the needs of sustainable energy resources, remote sensing electronics, wireless autonomous devices, mobile internet of things (IoT) and portable self-power generators, triboelectric nanogenerators have recently been suggested. However, more specialized target applications to biomedical and wearable devices will require biocompatible and eco-friendly triboelectric materials in power generators. Herein, we report for the first time a bio-triboelectric nanogenerator based on an eco-friendly and naturally abundant biomaterial, bacterial nanocellulose. Initially, bacterial cellulose pellicles were produced in a gel state by *Acetobacter xylinum* KJ1 in the Glu-Fruc medium and then a bacterial nanocellulose film having transparent and flexible functionalities was regenerated on a current collector *via* a solubilization process. The bacterial nanocellulose triboelectric nanogenerator was investigated with various input conditions and structural aspects. The working mechanism was also considered by measuring the contact angle and the surface potential of the friction materials. We believe that this study provides new insights to advancing the biocompatible and eco-friendly triboelectric power generator and optimization strategies to achieve high performance of triboelectric nanogenerators.

1. Introduction

With advances in electronics technology, as the size of electronic equipment is becoming much smaller, the amount of energy needed to operate electronic devices is getting smaller and smaller. As a result, interest in small-sized energy sources has been growing over the past two decades [1,2]. Internet of things (IoT) and ubiquitous technologies, stemming from a convergence of information technology, environmental technology, and biotechnology based on nanotechnology are emerging at the present time [3]. However, the continuous miniaturization of electronics accomplished by depending entirely on general battery technology can cause specific problems when the energy supply is bulky in size [4]. To resolve the power problems of miniaturized electronics, energy harvesting, which is the process of capturing ambient energy from one or more naturally-occurring energy sources such as light, heat, and mechanical movement, accumulating electricity, and storing that electricity for small and mid-sized devices, has been developed [4,5]. Especially as nanotechnology advances, a minute amount of energy that would otherwise easily get lost can be captured. Recently, Zhong Lin Wang's group developed the triboelectric nanogenerator (TENG), which is a new type of energy harvester based on a conjunction of triboelectrification and electrostatic induction [2]. Also, they have intensively investigated various materials for the friction part, verification mechanism, and diverse generation mode, and have proposed the possibility of triboelectric nanogenerator applications [1,2,6–8]. Even though advances in technology have made living more convenient, there are still some remaining problems that need to be resolved. Especially, waste from electronic devices has become one of the main causes of environmental pollution in many countries [9,10]. Research on biomaterials using environment-friendly, clean, sustainable natural materials is an important area, and related research and development (R & D) has been performed with much attention paid to the importance of new material development to cope with environmental pollution and global warming [11]. To replace organic materials, based on petroleum resources that are being depleted, research trends are particularly focusing on the development of new materials made of abundant natural materials [12]. As a natural polymer, cellulose is an organic compound that is very abundant in nature; indeed, among organic fuels it is second only to coal [13]. Most importantly, the discovery of cellulose produced by bacteria, specifi-

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cally from the *Acetobacter xylinum*, was attributed to Brown as early as 1886 [14]. After that, much research has been done on bacterial cellulose, its characteristics, and its production for practical use [15,16]. In the view of environmental preservation, bacterial cellulose is well known as an appropriate polymer because it can be fully decomposed by soil microorganisms in a month due to its great biodegradability [17]. Although bacterial cellulose has excellent intrinsic properties such as high elastic modulus, good degree of polymerization, and biocompatibility [15–17], there has so far been no report on the use of bacterial cellulose in a triboelectric nanogenerator until now.

Herein, in this paper, we report for the first time the bacterial nanocellulose bio-triboelectric nanogenerator (BNC Bio-TENG). As a promising eco-friendly green material, the regenerated bacterial nanocellulose film, which was prepared *via* a solubilization process and has unique functionalities such as transparency, flexibility and biocompatibility, was used as the friction part in the triboelectric nanogenerator. Also, by measuring the contact angle and the surface potential of the friction materials, the working mechanism of the BNC Bio-TENG has been considered. We demonstrate that the fabricated BNC Bio-TENG can generate electrical energy according to surface treatments and has close relationship between electrical output signals and structural aspects such as curvature and friction size.

2. Experimental methods

2.1. Preparation of regenerated bacterial nanocellulose (BNC)

Bacterial cellulose (BC) was basically produced by *Acetobacter xylinum* KJ1 as BC producer in the Glu-Fruc medium as producer with reference to previous studies [15,18]. After incubating at 30 ℃ for 36 h, one of the BC pellicles was then statically cultured at 30 ℃ for 10 days; it was adjusted to pH 5.25. The purified BC was finally obtained from the above BC pellicle after treatment with 0.1 M sodium hydroxide solution at 80 ℃ for 20 min to lyse the bacteria on the BC pellicle, which was then thoroughly washed several times with distilled water until its color changed to white. The purified BC was slowly and fully dried in a vacuum oven at 50 ℃; finally, it was weighed. To make a uniform BNC film, the purified BC should be dissolved at a specific concentration and then dried. Based on the nitration method proposed by Alexander and Mitchell [19], the dried BC was dissolved in ethyl acetate at a concentration of 0.5 w/v% under magnetic stirring for 100 rpm at room temperature. Subsequently, to make a uniform BNC film, ultra-sonication was employed to remove bubbles in homogenous solution; then, the regenerated bacterial nanocellulose (BNC) film was prepared by casting on petri dish in an oven at 40 ℃ as shown in Fig. 1**a**. For a friction material, the BNC solution was cast on copper foil. (See also Fig. S1 and Fig. S5 in Supporting information).

2.2. Fabrication of triboelectric nanogenerator (TENG)

For the friction parts, the BNC cast on a copper foil and the other copper foil were cut into square pieces with dimensions of 5 cm by 5 cm. The copper foil on the side of BNC was used as the top electrode and was covered with flexible polypropylene (PP) film. The other copper foil, which was covered with a flat polyoxymethylene (POM) plate, played dual roles of bottom electrode and friction part. To fabricate and control the curvature of the arch-shaped nanogenerator, the sides of the PP were prepared so as to be longer than that of the POM; then, the sides of the two covers were taped to each other. For measurement, these two copper foils were connected to each wire.

2.3. Characterization

The morphologies of the bacterial cellulose films were investigated using a field emission scanning electron microscope (Nova230, FEI Company) at a beam landing energy of 3 keV. The changes in the surface chemical bonding of the bacterial cellulose films were characterized by Fourier-transform infrared spectroscopy (FT-IR 4100, Jasco). X-ray diffraction (XRD) patterns of the bacterial cellulose were measured using a high resolution thin-film X-ray diffractometer (D/MAX-2500, RIGAKU). The bacterial cellulose films were scanned at 2 θ from 5° to 35°. The contact angles of water droplets on the material surfaces were measured using a contact angle system (Phoenix300, Surface Electro Optics) at room temperature. 10 μL of the deionized water droplets generated by the automatic dispenser of the contact angle system were placed on each friction material. Kelvin probe force microscopy (KPFM) measurements were carried out using an atomic force microscope (Agilent 5500, Agilent Technologies) with a conductive non-contact cantilever coated with Pt/Ir and a nominal resonance frequency of 75 kHz. In order to evaluate the surface potential of the tip, the contact potential difference (CPD) value on a gold plate can be used as the reference value. All TENG measurements were performed under ambient conditions (temperature=20~24 ℃ and relative humidity=25~40%). For electrical measurements, an oscilloscope (DPO 2002B, Tektronix) with a passive probe (TPP0100, Tektronix) and a data acquisition system (PXI-1042Q and LabVIEW, National Instrument) were used. A repeated press and release process was performed using a function generator (AFG 3022, Tektronix), a power amplifier (BAA 120, TIRA GmbH), and a vibration exciter (S51075, TIRA GmbH). UV–vis spectrometer (V-570, Jasco) was employed to record the optical transmittance of BC before solubilization and BNC after solubilization over the wavelength of 200–800 nm, as shown in Fig. S4.

3. Results and discussion

Initially, the BC pellicle produced by bacteria is in a gel-state, with the remaining BC producer and production medium; its size depends mainly on the shape of the incubator [20]. So, in order to fabricate a uniform BNC film with no other components, the BC pellicle should be treated by solubilization at a specific concentration [21]. As can be seen in Fig. 1a, the solubilization step should be proceeded to make the BNC film not only uniform but also flexible and transparent, which gives it much more potential for future transparent devices. The structure and working mechanism of the BNC Bio-TENG are schematically shown in Fig. 1b. BNC and Cu foil were used as friction parts on the upper and lower layers. The layer of Cu foil on the upper side is just a current collector, whereas the layer on the lower side plays dual roles of current collector and friction part. To prevent electrical shorting and to protect the TENG from the external environment, cover layers were attached on the outside of each of the current collectors. The length of the upper cover was slightly longer than that of the lower cover; this curvature of the upper sides was fabricated intentionally. As a result, after two friction films are brought into contact and rub together by compressive force, the TENG will be able to return to its initial shape due to the presence of an elastic and flexible film (see also Fig. S2, Supporting information) [7,22]. It is generally known that the working principle of a TENG is based on coupling effects including triboelectrification and electrostatic induction [23,24]. Under a pressing force, the two friction surfaces can come into physical contact with each other, resulting in oppositely charged surfaces that can compensate for the difference of the physical properties, such as the surface energy, between the surfaces [25,26]. When the two friction surfaces are subsequently separated upon release, an electric potential difference is created between the two electrodes [27]. Then, there is electron flow through the external circuit until the accumulated charges reach an equilibrium state. Subsequently, when the TENG is pressed again to come into contact with the two friction surfaces, an electric potential difference is created with reversed polarity [23,27], resulting in electron flow in a reverse direction.