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Full paper

A flexible transparent one-structure tribo-piezo-pyroelectric hybrid energy generator based on bio-inspired silver nanowires network for biomechanical energy harvesting and physiological monitoring

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ABSTRACT

The rapid development of wearable electronics like e-skins calls for self-powered sensing to harvest diverse bio-energies from human body as well as detect human physiological signals. Here, we report a novel, flexible and biocompatible triboelectric-piezoelectric-pyroelectric hybrid nanogenerator based on a significantly simplified structure with good transparency which mainly due to high-performance transparent electrodes (TEs). Inspired by gradually optimized leaf venation (LV), silver nanowires were arranged into a LV-like network through a green and cost-effective approach. The unique structure led to an ultra-high transmission up to 99% (at 68.2 $\Omega\,sq^{-1}$ sheet resistance) and sheet resistances as low as 1.4 $\Omega\,sq^{-1}$ (with 82% transmission). With 3 effects coupled, the generator can scavenge a maximum open-circuit output voltage of 55 V and 86 V to produce mechanical energy and thermal energy, respectively. In addition, the transparent hybrid nanogenerator can be conformally attached on different parts of body for real-time monitoring of various human vital signs including breath, heartbeat pulse and swallowing. With high transparency, the hybrid nanogenerator can be integrated with a thin liquid crystal film possessing thermochromic properties, potentially as a visualized thermometer for medical diagnostics. The research is a substantial advancement toward the realization of cost-effective self-powered sensing like pressure and temperature and its potential applications in device dimension miniaturization, healthcare monitoring, energy conversation, and wearable electronics.

1. Introduction

In recent years, wearable sensors have attracted ever-increasing attentions as a result of the growing demands of human interactive applications such as health monitoring, artificial e-skins and robotics [1–5]. Correspondingly, renewable, flexible, and sustainable energy source is highly desired to power wearable sensors. Scavenging energy from human activities and surroundings is a feasible choice in self-powered wearable sensing systems. Apart from mechanical energy via piezoelectric or triboelectric mechanism, thermal energy via pyroelectric effect has attracted extensive attentions [6–9]. To improve the overall output, some hybrid nanogenerators incorporating multi-effects have been developed [10,11]. However, previous investigations mainly concentrate on integrating different nanogenerators in series or in parallel rather than in a one-material structure. The few one-structure-based multi-effects hybrid nanogenerators subsequently proposed is usually unable to stretch and flex, limiting its application on soft surfaces as wearable energy sources [12,13]. Therefore, it is highly desired that a flexible and compatible hybrid generator with significantly simplified structure designed for scavenging various forms of energy from human body. Such a generator firmly attached on the human body may realize self-powering with multi-form deformation. It can function as a real-time monitoring sensor through measuring and quantifying electrical signals generated by human activities. In addition, generators with high transparency have aroused great interest for realizing displaying input/output information onboard wearable self-powered sensing system. To achieve this, all the components of the hybrid generator are required to be flexible, stretchable and transparent, including the electrode.

Currently, tin-doped indium oxide (ITO) and fluorine tin oxide (FTO) have been main candidates for transparent electrodes in these technological applications [14]. However, serious drawbacks [15]

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associated with the use of ITO and FTO like ever-growing price, high operating temperatures and brittleness have limited their development in flexible and stretchable electronics. Various alternatives have been pursued to replace traditional TEs to meet the requirements such as graphene and metal grids [8,16,17]. Among these, metal nanowires, especially, silver networks hold great promise because of their high conductivity and optical transmittance. A large number of techniques have been developed for the assembly of silver nanowires like the bubble template [18], the microchannel wetting [19],and Langmuir-Blodgett (LB) trough [20]. These methods, however, remain deficient in many ways, such as expensive equipment, complex operating process and toxic solvents. These limits call for new, improved, and scalable approaches to fabricate high-performance silver nanowire networks. Natural leaf-venation (LV), which has been gradually evolved to achieve a balance between transparency and transportation of substances, was therefore introduced to help array the silver nanowires into network with favorable properties [21].

Herein, we proposed a novel one-structure transparent, flexible and compatible triboelectric-piezoelectric-pyroelectric hybrid generator sharing common electrode by integration of PDMS, PVDF, and silver nanowires, favorable in terms of the massive production and device dimension miniaturization. The high-performance TEs may tune the transparence through both spaces between venations and pores between nanowires, superior to common nanowires film or metal grid reported previously. In addition, the silver nanowires prepared by green galvanic displacement reaction in our previous research [21–23] can reach a maximal length over 200 μm with 50 nm in diameter, bringing a high aspect ratio over 4000. The Ag nanowires assembled into this unique network exhibits a sheet resistance as low as 1.4 $\Omega\,sq^{-1}$ with compatible transmittance about 82% and reaches a peak of transmittance as high as 99% with sheet resistance of 68.2 $\Omega\,sq^{-1}$. Apart from the transparent TE, polyvinylidene fluoride (PVDF) with piezoelectric and pyroelectric properties and microstructured polydimethylsiloxane (PDMS) with protection and friction function were integrated to fabricate the innovative hybrid generator. By virtue of the coupled effect of triboelectric and piezoelectric mechanism, the generator can scavenge mechanical energy from human body. In addition, thermal energy can be scavenged due to pyroelectric effect confronting temperature fluctuations between the human body and the ambient environment. The 3 cm × 3.5 cm hybrid generator produces maximum open circuit voltage up to 55 V and 86 V for the mechanical and thermal part, respectively. The hybrid nanogenerator can be attached on different parts of human body to monitor various human physiological signals including breath, heartbeat pulse and swallowing besides the self-powering function. Furthermore, The integration of transparency characteristics is of significant importance in the development of nanogenerators, especially for its potential applications in displaying flexible electronics, artificial skins with screens. We realized transparent flexible hybrid generator with three effects for the first time and established a smart device through integrating the hybrid nanogenerator with thermochromic thin liquid crystal film (LCD) which changes its colors with the temperature. Instead of complex computer readout, the integrated device is able to function as a visualized thermometer for medical diagnostics conveniently. The research is a substantial advancement toward the realization of cost-effective self-powered sensing like pressure and temperature and its potential applications in healthcare monitoring, energy conversation and wearable electronics.

2. Results and discussion

Inspired by unique structure of LV, we replicated LV morphologies in silver nanowires arrangement as naturally organized conductive network with high transparency. A schematic flow chart is shown in Fig. 1. A piece of ramified leaf, as shown in Fig. 1**(a)**, was used as the mold for fabrication of naturally patterned TEs. Here, we choose the plant Osmanthus fragrans (common name sweet olive tree) with leaves about 11 cm in length of lanceolate shape and prominent secondary veins paired oppositely. The leaf was then immersed in the KOH solution at about 90 °C for 1 h to etch away the *meso*phyll cells and obtain the LV skeleton as shown in Fig. 1**(b)**. Subsequently, the LV skeleton was pressed with moderate strength to make its rough surface smooth and then tailored to a square shape as shown in Fig. 1**(c)**. With the as-prepared LV skeleton as mold, we set out to fit silver nanowires of high aspect ratio. As is shown in the inset of Fig. 1**(d)**, silver nanowires were synthesized in a small sample bottle (20 mL in volume) through galvanic displacement method without adding external capping agent at room temperature. The morphology of silver nanowires prepared was characterized by SEM as seen in Fig. 1**(d)**, showing uniform diameter with significant high yield. As depicted in Fig. 1**(e)**, a measured amount of a silver nanowire was well-dispersed in absolute ethanol and further diluted down to 0.018 mg/mL with deionized water. After magnetic stirring for 20 min, the suspension of silver nanowires was vacuum filtered on a commercially available cellulose acetate membrane with a pore size of 0.2 μm. The silver nanowires are trapped on the surface of the filter as the solvent falls through the pores, forming an interconnected network. The density of this network can be controlled by the number of silver nanowires filtered through the membrane which is simply determined by the volume of dilute suspension (same concentration). Dried at room temperature, a uniform Ag NWs film was then obtained on the membrane, as shown in Fig. 1**(f)**. To obtain the LV-like silver nanowires network, a modified dry transfer printing technique was adopted and is schematically illustrated in Fig. 1**(g)**. The as-prepared LV skeleton was brought into contact with the back of cellulose acetate membrane while the front membrane with nanowires on it was against the receiving substrate like PET or PDMS. The whole structure was then under a moderate pressure for a few minutes. The cellulose acetate membrane with LV on it was peeled off slowly from the substrate resulting in transfer of the patterned silver nanowires to the substrate. In the end, a moderate mechanical pressure of 10 MPa was needed to enhance the junction between AgNWs as well as to reduce surface roughness and adhesion of films [23–25]. A photograph of silver nanowires assembled LV-like network on PDMS is shown in Fig. 1**(h)**. (In order to ensure the leaf-venation-like network assembled by silver nanowires could be observed through naked eye, we took a higher volume of prepared silver nanowires solution of 6 mL to fabricate the transparent electrodes.) In regard to mimicking the advanced structure of leaf venation to fabricate high-performance transparent electrodes, we did not metallize leaf venation directly with leaf venation remained. Although such a method may bring high transparency and conductivity, the large-scale veins of metallic leaf venation is clearly visible, making this network not suitable for display applications. Our innovative method can obtain a leaf-venation-like electrode composed of nanowires successfully without the presence of leaf venation itself, imposing no limitation in displaying applications. Notably, leaves are abundant on the earth and our experiment only needs several pieces of leaves. A leaf venation skeleton can be reused for many times, which further lowers the cost. The process of pattern fabrication and transfer is cost-effective, facile, environment-friendly as well as superior to either widely employed conventional photolithography or nanoimprint method.

The morphology of the as-prepared TE is further characterized by SEM. As shown in Fig. 2**(a)** and **(b)** in different scales, the silver nanowires were assembled into LV-like network on PDMS mimicking some regions of the LV skeleton. The spaces between veins led to the existence of space areas between LV-like silver nanowires network for light passing through, which was marked with white dash lines in Fig. 2**(a)**. Obviously, the conductive network is composed of interconnected "veins". Each "vein" of the LV-like network consists of a certain amount of silver nanowires as shown in Fig. 2**(b)**. Fig. 2**(c)** illustrates mechanisms of three different structures of TEs in terms of transparency. As is shown in the first picture of Fig. 2**(c)**, matching our TE, the transmittance of the structure can be tuned by both spaces