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A flexible self-powered T-ZnO/PVDF/fabric electronic-skin with multi-functions of tactile-perception, atmosphere-detection and self-clean

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ABSTRACT

A flexible self-powered e-skin has been presented with multi-functions of tactile-perception, atmosphere-detection and self-clean. Piezoelectric PVDF and tetrapod ZnO (T-ZnO) nanostructures are hybridizing on the flexible fabric substrate. The piezoelectric, gas sensing and photocatalytic properties of T-ZnO nanostructures are combined together. The piezoelectric effect of T-ZnO/PVDF leads to the motion-powered tactile-perception behavior, e.g. the e-skin can detect elbow bending or finger pressing. The piezoelectric/gas-sensing coupling effect of T-ZnO nanostructures delivers the motion-powered atmosphere-detection performance, and the piezoelectric output of the e-skin is different upon exposure to different atmosphere conditions, acting as the gas-sensing signal. The piezo-photocatalytic activity of T-ZnO nanostructures results in the distinct self-clean characteristics, and the organic-pollutants/bacteria can be degraded/sterilized on the surface of the e-skin. This novel material system and device architecture can promote the development of flexible self-powered multi-functional e-skin.

1. Introduction

With the development of emerging portable/flexible electronics, the flexible electronic devices and systems can be integrated with the human body and skin, such as implantable, stick-on, and wearable electronics [1–9]. These approaches can be applied on illness/health monitoring, sensation enhancing or artificial bionic prostheses, realizing "the body electric" and transforming the healthcare mode [10–16]. There are three key factors in flexible electronic application in human body and skin: multi-functions, flexible construction and embeddable power source. As an emerging application, flexible electronic-skin (e-skin), that mimics the physical properties and multi-modal characteristics of human skin, needs to be designed to function like a real human skin, be conformably covered on the human body, and even be integrated with skin-like battery or self-sustainable power source [17,18]. Many research groups have contributed to the development of e-skin with different functions, e.g. highly-sensitive tactile-perception, heart-beating monitoring or electrolyte-balance detection [19–21]. However, realizing these multi-functions in a single physical/chemical process of the e-skin is a challenge. ZnO nanostructure with piezoelectric, gas sensing, photocatalytic properties can probably deliver the above multi-functions at the same time, making it a promising candidate for the next-generation of e-skin [22–25].

The real human skin is an organ of the integumentary system made up of multiple layers of ectodermal tissues performing multi-functions, which interfaces with the environment and is the first line of defense from external factors. It possesses a large amount of tactile-perception tissues for distinguishing a variety of mechanical stimulations (touching, pressing, vibration, strain, bending, etc.) and outputting bioelectric signals to brain. As an important somatosensory system, the real skin can also jump to the sensation of the environmental atmosphere, such as humidity, chemical/biological stimuli, and air temperature. For guarding the underlying muscles, bones and internal organs, the skin also plays a key role in protecting the body against pathogens using immune system, and realizing self-clean through excluding pollutants by sweat and secreta. Comparing to real human skin, the flexible e-skin needs to be designed for detecting environmental change or feeding back human activity, which can establish the interaction with different external stimulations as a multi-functions sensor-based system, e.g. transforming various physical and chemical stimulations to electric

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signals [26,27].

In application, another key factor of the e-skin is novel power source. For easily fabricating, integrating battery is a conventional design in flexible electric system. However, the presence of batteries greatly limits the e-skin application. Battery-free or self-powered systems become the center of attention as prospective solution for flexible e-skin systems. The flexibility and stretchability of artificial e-skin not only ensure the conformable covering on the arbitrarily-curving/moving surface of the human body, but also provide motion-power source. Many research efforts have been made on developing novel flexible/stretchable power source fully embedded in the e-skin to replace the bulky batteries [28,29]. Moreover, some other research groups have focused on the self-sustainable power source to remove the batteries from the system, negating the periodical maintenance service. A fabric-based organic/inorganic hybrid architecture is very suitable for e-skin with this requirement, because the fabric can exploit arbitrary deformation like stockings or other tights. Nowadays, piezo-electric/triboelectric nanogenerators, solar cells and etc. have been reported [11,15,22]. Basing on this consideration, the organic/inorganic hybrid composed of piezoelectric polymers (such as PVDF) and ZnO nanostructures could have the capability of converting mechanical energy of body motion into electric energy, very suitable for fabricating self-powered e-skin, as the device is constantly under applied mechanical deformation during the operation [30,31].

In this paper, a flexible self-powered ZnO/PVDF/fabric e-skin has been presented with multi-functions of tactile-perception, atmosphere-detection and self-clean. Piezoelectric PVDF and tetrapod ZnO (T-ZnO) nanostructures are hybridizing on the flexible fabric substrate. The piezoelectric, gas sensing and photocatalytic properties of T-ZnO nanostructures are combined together. The piezoelectric effect of T-ZnO/PVDF leads to the motion-powered tactile-perception behavior, e.g. the e-skin can detect elbow bending or finger pressing. The piezoelectric/gas-sensing coupling effect of T-ZnO nanostructures delivers the motion-powered atmosphere-detection performance, and the piezoelectric output of the e-skin is different upon exposure to different atmosphere conditions, acting as the gas-sensing signal. The piezo-photocatalytic activity of T-ZnO nanostructures results in the distinct self-clean characteristics, and the organic-pollutants/bacteria can be degraded/sterilized on the surface of the e-skin. This novel material system and device architecture can promote the development of flexible self-powered multi-functional e-skin.

2. Experimental section

2.1. Synthesis of T-ZnO nanostructures

T-ZnO nanostructures were synthesized in mass production by a simple thermal evaporation method without any catalysts. Pure zinc powder was placed in a quartz boat, and then positioned at the center of a quartz horizontal tube furnace which was heated to 900 °C. The white fog in the tube was blown out by a constant flow of air. After 3 min, the quartz boat was slowly pulled out of the tube furnace, and a large amount of white fluffy products in the boat were collected. This synthesis process was very simple and the production amount was very large, as shown in Fig. S1. This synthesis method can be easily expanded to industrial production.

2.2. Fabrication of the flexible self-powered multi-functional e-skin

T-ZnO nanostructures were firmly anchored on the fabric using PVDF binder by a simple wet-chemical method. Firstly, the fabric (PET fabric screen) was cleaned with deionized water and ethanol for several times to remove surface impurities, and dried at 60 °C in air. Secondly, 2 g PVDF powder was dissolved in 30 mL acetone-DMF solvent with the volume ratio of 6:4 at 60 °C. 2 g T-ZnO nanostructures were then added into the PVDF gel. The T-ZnO/PVDF suspension solution was stirred for 1 h and treated in an ultrasonic bath for 1 h to form uniform paste. Thirdly, T-ZnO/PVDF paste was painted on the pre-cleaned fabric. The fabric was dried at 60 °C in the air. In this step, about 200 mg T-ZnO and 200 mg PVDF were coated on the fabric with the area of 20×7 cm by weighing the fabric before and after coating. It should be pointed that T-ZnO nanostructures with a unique feature of 3D geometries can form a nanoarray structure on the fabric. Finally, for polarizing the PVDF layer, an electric field of 20 kV/mm was conducted on the T-ZnO/PVDF/fabric for 30 min in silicone oil at 80 °C (the silicone oil was removed with ether).

2.3. Characterization

The crystal phase of T-ZnO nanostructures was characterized by X-ray diffraction (XRD, D/max 2550 V, CuK_{α} Radiation). The morphology and microstructure of T-ZnO/PVDF/fabric were investigated by a scanning electron microscope (SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEOLJEM-2010).

2.4. Tactile-perception measurement of the e-skin

Two copper leads were glued on the fabric with PVDF binder as the two electrodes (concentric circles) for piezoelectric measurement. The external force was applied on the edge of the e-skin by a programed stepper motor, generating bending deformation on the device. The bending angle of the e-skin can be controlled by adjusting the operation distance of the stepper motor, as well as the bending frequency. The outputting piezoelectric voltage of the e-skin was monitored using a low-noise preamplifier (Model SR560, Stanford Research Systems).

2.5. Atmosphere-detection measurement of the e-skin

The experiment was conducted in a sealed gas-flow chamber at room temperature. The atmosphere (O_2 concentration or relative humidity) can be controlled by the gas-flow system. Under externally applied bending deformation, the e-skin can output piezoelectric voltage and the piezo-voltage was different under different atmosphere, acting as the gas-sensing signal.

2.6. Self-clean measurements of the e-skin

The degradation of organic dye by the piezo-photocatalytic activity of the e-skin was achieved in an aqueous solution under UV and ultrasonic irradiation (or low-frequency mechanical vibration). The UV irradiation source was provided by a high pressure mercury lamp (100 W) with main emission wavelength of 313 nm. The ultrasonic irradiation was provides by an ultrasonic probe (0–300 W). The low-frequency mechanical vibration was provided by a programed stepper motor. A piece of e-skin containing 200 mg T-ZnO nanostructures was immersed in 100 mL organic dye aqueous solution (5 mg/L). During the experiment, the solution was slightly stirred for keeping homogeneous and any temperature rise was avoided by ventilation with an electric fan. 3 mL of sample solution was taken out periodically and analyzed by a UV–vis spectrometer (Hitachi U-3010). The degradation rate was defined as C/C_0 (C is test concentration, C_0 is initial concentration). The self-clean behavior of the e-skin was performed by exposing a MB-polluted e-skin under UV or solar irradiation for several hours. The antibacterium characteristic of the e-skin was investigated by examining the growth color of bacterial cells (Staphylococcus aureus, S. Aureus) in liquid medium amended with e-skin. Briefly, 100 mL nutrient broth was inoculated with fresh colonies of bacteria growing in a disk. The culture broth was incubated with several pieces of e-skin in an incubator at 37 °C for 24 h. The control experiments were also conducted. The growth of bacteria was determined by measuring the color of the disk.