Utilization of self-powered electrochemical systems: Metallic nanoparticle synthesis and lactate detection

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ABSTRACT

Since the introduction of the first expounded triboelectric nanogenerator (TENG) in 2012, the theoretical and practical aspects of the TENG have been researched as an alternative energy harvesting technology to convert mechanical energy into electricity efficiently. Numerous self-powered sensing systems have adopted the TENG as a power source to further explore its versatile applications toward different targets. In this study, we employed a TENG to replace a traditional power supply for synthesizing different metallic nanoparticles using an electrochemical approach. Carbon fibers were adopted as the conductive substrates to grow the metallic nanoparticles, where the size and density of the nanoparticles on carbon fibers can be controlled by the electric output of the TENG. Additionally, we demonstrated that the as-prepared carbon modified and integrated with the TENG to construct a wearable self-powered sensing system exhibited significant selectivity and sensitivity toward lactate detection. Furthermore, the design of the sensing unit was favorable regarding its adaptability and flexibility to fit human body shapes and postures. As demonstrated in this study, the as-prepared self-powered sensing system could detect the lactate concentration in human perspiration, which can be an ideal wearable device for end users who seek real-time monitoring of their physical condition. This study concludes with a proposal for noninvasive biosensors, which provide boundless potential for future cross-field applications.

1. Introduction

Recent trends in the aging population and the raised awareness of healthcare have given rise to increasing expenses in wearable sensing devices that target daily healthcare management and have further driven research in wearable sensing technology from a biological perspective [4–6]. With all the developments and advances achieved by investigations of wearable biosensor systems for health monitoring, continued attention has been paid by the scientific community and industry to explore the possibilities of biosensors in medical diagnostics [1–3]. To address such a demand, a variety of commercial wearable devices and system prototypes have been introduced, claiming the features of a real-time response and an alert to an individual’s state of health for purposes of fitness management, chronic disorder monitoring, etc [7–9]. As an alternative to traditional invasive treatments, a wearable health monitoring system offers noninvasive approaches to detect vital signs with extensive targets ranging from hyperglycemia [10], hypertension [11], cholesterol control [12], and lactate management [13]. For practical concerns, an ideal wearable device should be compact, lightweight and highly sensitive to meet the demands of both portability and responsiveness, where the self-powered biosensor has unequalled advantages for this application.

A self-powered sensor is able to meet the dual requirements of a compact form factor and a sufficient power supply through the integration of a nanogenerator [14]. Using the concept of a self-powered system, electricity generation and other manners of applications are achieved through the collection of renewable energy based on thermoelectric [15], piezoelectric [16], photovoltaic [17] and triboelectric effects [18]. Among the devices built with an energy harvesting mechanism, a triboelectric nanogenerator (TENG) demonstrates superior output performance with a broad range of alternative and affordable outlay materials, showing its promising potential for versatile applications [19–22]. A TENG can either be designed as a compact and portable power supply device [23–25]; or through surface modification [26–28] to function as a self-powered nanosensor. Furthermore, it has been a common approach to enhance the sensitivity of these self-powered sensing systems through the introduction of nanoparticles [29–31]. Nanoparticles are of great scientific interest as they bridge the gap between bulk materials and atomic or molecular structures [32]. For example, metallic nanoparticles have considerable applications in

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diverse fields such as electronics [33], biotechnology [34], cosmetics [35], coatings [36], and packaging [37]. In previous studies, bimetallic nanoparticles have shown superiority over monometallic nanoparticles in terms of catalytic activity [38–40]. In this study, we managed to directly grow monometallic and bimetallic nanoparticles on weavable, extra lightweight and highly electrically conductive carbon fibers through a TENG-based self-powered electrochemical system.

Breakthroughs in biosensors have contributed to biomedical diagnostics and healthcare management by means of the biochemical interaction between a sensor and an analyte with specificity [41–44]. Lactate, a major metabolite in the anaerobic glycolytic pathway, can function in several biochemical reactions and serve as the critical factor under monitoring circumstances such as surgery, respiratory failure, sepsis and histogenic hypoxia and high concentration accumulation will cause lactic acidosis [45]. Traditional lactate sensing is disadvantageous because it lacks time efficiency and result accuracy and thereby requires the development of a new prototype lactate biosensor [46–48]. In addition, we demonstrated that the TENG-based self-powered electrochemical system introduced a noninvasive lactate biosensor by utilizing the integration of a TENG to provide an instant inspection without an external energy supply. The illustration is shown in Fig. 1. Fig. 1a demonstrates a close-up look at the carbon fibers with metallic nanoparticles and lactate oxidase, and Fig. 1b is the depiction of our TENG. The as-prepared device is shown to possess tremendous commercial potential in providing comfortable wearing experiences as well as accurate monitoring results for end users.

2. Experimental section

2.1. TENG fabrication

A layered TENG based on a vertical contact-separation operation mode was designed. Two polyethylene terephthalate (PET) sheets with highly transparent and flexible characteristics were cut to specific dimensions and used as the substrates. Conductive aluminum films (thickness of 100 nm) were deposited onto the PET sheets by using an e-beam evaporator. Polydimethylsiloxane (PDMS) and gelatin covered the top of two PET/Al sheets separately, then two copper wires as the electric output leads of the TENG were connected to the aluminum films. To construct the nanostructures on the PDMS and gelatin, a Si wafer with a protruded pyramidal nanostructure surface was ultrasonically cleaned in acetone, isopropyl alcohol, and deionized water (DI), then dried in air. The PDMS mixture with a weight ratio of 10 (base/curing agent), which was prepared in advance, was coated onto the wafer and cured at 60 °C for more than 12 h. The 16 wt% gelatin solution was stirred steadily with glycerol and water, then dispensed onto the peeled-off nanostructured PDMS film and dried in a fume hood overnight. Both surface features of the PDMS and gelatin films were observed by scanning electron microscopy (SEM). The transparency of the PDMS and gelatin films were recorded by UV–vis spectroscopy.

2.2. Growth of metallic nanoparticles on carbon fibers through a TENG-based self-powered system

The metallic nanoparticles were controllably grown on the commercial carbon fibers. The carbon fibers were cleaned with acetone, isopropanol, and deionized water before the growth of the metallic nanoparticles. To grow the monometallic nanoparticles on carbon fibers, a metal salt (K₂PtCl₄, K₂PtCl₆, HAuCl₄, K₂PdCl₄, or AgNO₃) with a concentration of 1 mM and 10 mM sodium dodecyl sulfate (SDS) were dissolved in a glass bottle. In the electrochemical cell setup, the carbon fibers were utilized as the cathodes and were paired with different metal rods as the anodes. Then, the electrochemical reduction of the metal ions was conducted to synthesize the metallic nanoparticles, where the power supply comes from a capacitor charged by the TENG. With the same technique, PdAu bimetallic nanoparticles were prepared by using mixed precursors of 1 mM HAuCl₄ and 1 mM K₂PdCl₄.

2.3. Self-powered lactate sensing with synthesized monometallic and bimetallic nanoparticles

The self-powered lactate sensor mainly contains a TENG, a full-wave diode bridge, a capacitor, a resistor and a self-fabricated bandage as the electrochemical sensing unit. In the sensing unit, carbon fibers with as-synthesized metallic nanoparticles were used as the anodes and carbon fibers with deposited Pt nanostructures as the cathodes. The carbon fibers with as-synthesized metallic nanoparticles were modified with L-lactate oxidase before lactate detection. Only 10 μL of L-lactate oxidase was needed for electrode modification. Finally, a thin chitosan layer was coated on the sensing unit to protect the metallic nanoparticles and carbon fiber electrodes. A 1 wt% chitosan solution was prepared by dissolving chitosan powder in 1 wt% acetic acid. The lactate sensing procedure was conducted in phosphate-buffered saline (PBS) solution.

Fig. 1. Schematic diagram of the wearable self-powered lactate sensor. (a) The biocompatible gelatin-based TENG for harvesting biomechanical energy from human walking and running. (b) The nanoparticle-based lactate sensor (NP) with portable, bendable and attachable properties. The PdAu nanoparticles are uniformly dispersed on the carbon fibers with lactate oxidase on top, and the chitosan coating acts as a protection layer. The high sensitivity and selectivity of the self-powered lactate sensor results from the electrocatalytic bimetallic PdAu nanoparticles and L-lactate oxidase.
2.4. Characterization

The high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F) and field-emission scanning electron microscopy (FESEM, Hitachi S-4800) were used to define the size and shape of synthesized metallic nanoparticles. For the HRTEM analysis, the as-synthesized metallic nanoparticles were placed onto 400-mesh C-coated Cu grids and dried at ambient temperature (25 °C). An Oxford Inca energy dispersive X-ray (EDX) system (Oxford, UK) was used to determine the compositions of the as-synthesized metallic nanoparticles. X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCA210 electron spectroscope (West Sussex, UK). Binding energies were corrected using the C 1s peak at 284.6 eV as a standard. The TENG electric output measurement was completed by a programmable electrometer (Keithley Model 6514) and a low-noise current preamplifier (Stanford Research System Model SR570). The response of the as-developed biosensor was detected by an Electrochemical Analyzer (CH Instruments, 624E).

3. Results and discussion

Fig. 1 presents our proposed wearable self-powered lactate sensor that integrates four main functional units: a TENG to harvest mechanical energy and act as the power source, a full-wave diode bridge to rectify the electric output generated from the TENG, a capacitor to store the rectified electricity, and a nanoparticle-based electrochemical sensor for lactate detection.

The TENG is chosen as the power source because it has the characteristics of device flexibility and is an efficient way to convert mechanical energy into electricity. A layered TENG based on a vertical contact-separation mode is designed and can be integrated into shoes to collect the biomechanical energy from human walking and running (Fig. 1a). Polyethylene terephthalate (PET) sheets were chosen as substrates to construct the TENG because they are lightweight with favorable hardness but flexible features. These substrates can produce firm TENGs to accommodate varying conditions and can be attached to the curved human figure. Conductive aluminum films (thickness of 100 nm) were deposited onto the PET sheets by using an e-beam evaporator. Polydimethylsiloxane (PDMS) and gelatin were covered on the top of the two PET/Al sheets separately, then two copper wires as the electric output leads of the TENG were connected to the aluminum films. If the application of a TENG is to harvest biomechanical energy from human motion and thus will be contact with human body, then the biocompatible property of a TENG is highly needed. This is also why we use PDMS and gelatin films as the triboelectric materials in the TENG (Fig. 1a). Fig. 1b shows the self-fabricated electrochemical sensor with portable, bendable and attachable properties. The high sensitivity and selectivity of the electrochemical sensor results from the electrocatalytic bimetallic PdAu nanoparticles and L-lactate oxidase.

To further enhance the electric output of the TENG, nanostructures were constructed on the surface of the contact materials (Fig. 2a). A Si wafer with protruded pyramidal nanostructures was used as the starting template for the fabrication of nanostructures on the PDMS and gelatin films. Before the fabrication process, the Si wafer was ultrasonically cleaned with acetone, isopropyl alcohol, and deionized water. Then, the mixture of a PDMS base and curing agent with a weight ratio of 10 was dropped on the Si wafer surface. After a curing time of 12 h at 60 °C, a PDMS film with hollow nanostructures on the surface was formed (Fig. 2b). The peeled PDMS film was used as the contact material as well as the template for patterned gelatin film formation. The gelatin solution (16 wt%) with glycerol was dispensed on the peeled PDMS film and dried at ambient temperature. Fig. 2c clearly shows the pyramidal nanostructures that were formed on the surface of the gelatin film. In addition, the use of both PDMS and gelatin films maintain the high transparency property of the TENG (Fig. 2d). Both PDMS and gelatin films show a transmittance of ≥ 80% from the visible to near-infrared spectral range (400–900 nm).

The output performance of the TENG was carefully studied by periodic contact and release of the PDMS and gelatin films (Fig. 3). The operation frequency and amplitude of the TENG was controlled by a
linear motor. The maximum output voltage and current density reached 500 V and 14 mA m$^{-2}$, respectively (Fig. 3a and b). To further explore the output power density, the TENG was connected to an external electrical load with different resistances to investigate the change in the output voltage and current density. As shown in Fig. 3c, when the load resistance is below 0.1 MΩ, the output voltage remains close to 0 and the current does not change significantly. When the load resistance is raised from 0.1 MΩ to 0.1 GΩ, the voltage through the load increases, but the current across the load follows a contradictory tendency. Therefore, the power density of the TENG remains small when the load resistance is below 0.1 MΩ and reaches a maximum of 2.5 W m$^{-2}$ with a load resistance of 20 MΩ (Fig. 3d). The AC output of the TENG was transformed to the unidirectional output through the connection of a full-wave rectifying bridge (Fig. 3e). The rectified electric output can then be utilized to charge a 1000-μF capacitor. The time for the TENG to charge a capacitor up to 5 V needs only 30 min under an operation frequency of 1 Hz (Fig. 3f). The electricity discharged from the capacitor will turn into the power of electrochemical system for the synthesis of the metallic nanoparticles and lactate detection.

First, we validated that the self-powered electrochemical system is an effective approach for the synthesis of monometallic and bimetallic nanoparticles. As shown in Fig. 4a, the self-powered electrochemical system contains the as-developed TENG, a full-wave bridge rectifier, a resistor, a capacitor, a switch and an electrochemical cell. In the electrochemical cell, conductive carbon fibers were utilized as cathodes paired with different metal rods as the anodes. For the growth of monometallic nanoparticles on carbon fibers, a metal salt (AgNO$_3$, HAuCl$_4$, K$_2$PtCl$_4$, K$_2$PtCl$_6$, or K$_2$PdCl$_4$) solution with a final
concentration of 1 mM was used as the precursor. Sodium dodecyl sulfate (SDS) (10 mM) was dissolved in the metal salt solution and functioned as the nanoparticle stabilizer. Then, the electrochemical reduction of the metal ions was conducted to synthesize the metallic nanoparticles, where the electricity comes from the capacitor charged by the TENG. Because the nanoparticle distribution on carbon fibers will predominantly affect their electrocatalytic activity, the synthesis of Au nanoparticles to optimize the electrochemical reduction condition is discussed. Au nanoparticles with unique optical, molecular recognition and biocompatible properties have been widely studied with a variety of diagnostic applications [49]. The SEM images in Fig. S1 indicate that the nanoparticle size and density on carbon fibers can be controlled by the discharging voltage and frequency of the capacitor. A low applied voltage results in a growth-dominated process for nanoparticle formation. Therefore, the average size of Au nanoparticles changed from 510 nm to 60 nm as the discharging voltage of the capacitor decreased from 5 V to 1 V. In addition, a decrease in discharging frequency of the capacitor from five times to one further helps to reduce the size of the synthesized Au nanoparticles from 60 nm to 24 nm. Similar results were observed for the synthesis of Pt nanoparticles when using K2PtCl4 as the precursor (Fig. S2). The discharging voltage and frequency of the capacitor were 5 V and five times, respectively. Compared with the electrocatalytic activity offered by the monometallic Pd nanoparticles, the PdAu nanoparticles have improved electrocatalytic activity because of the synergistic effect that exists at the Pd and Au interface [50]. For example, the incorporation of Au into Pd catalysts improved the electrocatalytic performance toward ethanol oxidation as well as the resistance to poisoning. The inset of Fig. 5a shows an HRTEM image of a single representative PdAu nanoparticle. The d spacings of 0.238 and 0.205 nm correspond to the (111) and (200) planes of face-centered cubic (fcc) Au and Pt, respectively. The elemental mapping of Au and Pd obtained by high-angle annular dark-field scanning TEM energy dispersive X-ray spectroscopy (HAADF-STEM-EDX) reveals that the Au and Pd atoms were uniformly dispersed on the PdAu nanoparticles (Fig. 5b). This result suggests that there are many active interfaces between Pd and Au. The XPS spectra show significant shifts of the Pd 3d peaks toward lower binding energies and Au 4f peaks toward higher binding energies, indicating the modification of the electronic structures of the metals (Fig. 5c and d).

Next, we demonstrate that the self-powered electrochemical system can also function as a wearable lactate sensor. Intrusive methods used for lactate detection have been time consuming and uncomfortable to users. To accomplish lactate detection without causing harm to the body, secretion such as sweat is used favorably. Lactate will accumulate in sweat while the length of time spent exercising increases, which makes sweat a simple, convenient and easily available sample for lactate detection [51, 52]. In the self-powered lactate sensor, we designed a bandage-based electrochemical sensing unit, which has attachable, portable and bendable properties. The as-prepared carbon fibers with metallic nanoparticles were modified with lactate oxidase and served as the anode in the electrochemical sensing unit, while the carbon fibers
with deposited Pt nanostructures were used as the cathodes. A thin chitosan layer was coated on the sensing unit to protect the metallic nanoparticles and carbon fiber electrodes. The lactate detection was carried out in a phosphate-buffered saline (PBS) solution. For lactate detection, we optimized the capacitor discharging voltage of 0.1 V to drive the electrochemical sensing process (Fig. 6a). To charge the capacitor voltage to 0.1 V, the TENG only needs to operate for 30 s.

Fig. 6b shows the current response curves of the self-powered lactate sensor when detecting the PBS solution with various concentration of lactate (from 10 µM to 20 mM). The results clearly indicate that the measured current of the self-powered lactate sensor increases linearly with a higher lactate concentration and there is no current response for the pure PBS solution. When the lactate concentrations in the PBS solution were 10 µM, 100 µM, 1 mM, 10 mM and 20 mM, the measured current responses of the self-powered lactate sensor were approximately 0.8, 3.4, 5.5, 6.8 and 10.2 µA, respectively. We then tested the stability of the self-powered lactate sensor by bending the carbon fiber-based electrochemical sensor during detection (Fig. S5). We found that the bending of the carbon fiber-based electrochemical sensor did not cause a different current response compared with the unbending condition. This result demonstrates that the self-powered lactate sensor has the capability to become a wearable device and can provide confident data when people are exercising.

Fig. 6c shows the performance of the self-powered lactate sensor by using the as-prepared carbon fibers with PdAu, Pd and Au nanoparticles as anodes. Apparently, the carbon fibers with bimetallic PdAu nanoparticles resulted in superior electrocatalytic activity compared with the carbon fibers with monometallic Pd and Au nanoparticles. These results indicate that the presence of highly electroactive metallic nanoparticles is important and helpful for the development of the self-powered electrochemical sensor. Common organic compounds contained in human sweat other than lactate, including uric acid, creatinine, ascorbic acid, and glucose were chosen to evaluate the selectivity of the self-powered lactate sensor (Fig. 6d). An obvious measured current difference was revealed between lactate and other organic compounds. Additionally, we also validated the practicality of the self-powered lactate sensor through its use in the determination of lactate in a sweat sample by a standard addition method (Fig. S6). The sweat sample was first diluted with PBS solution and then spiked with the standard lactate solution. The lactate concentration in the sweat sample is calculated to be 11.75 mM, which falls within the healthy human range. The wearable self-powered lactate sensor was also successfully built in this study and presented compact, lightweight and in situ sensing characteristics (Fig. 6e). The “NP” symbol refers to the
proposed nanoparticle-based electrochemical biosensor.

4. Conclusions

TENG-based self-powered electrochemical systems have been successfully demonstrated for the synthesis of metallic nanoparticles and lactate detection. Using discharged electricity from a capacitor to drive the electrochemical reduction of metal ions, size-controlled monometallic Ag, Au, Pt, Pd and bimetallic PdAu nanoparticles on carbon fibers have been synthesized and their electrocatalytic activity has been studied. By using the carbon fibers with metallic nanoparticles as electrodes, the bandage-shaped electrochemical sensing unit provides portable, bendable, lightweight and attachable properties. With the operation of the TENG for less than one minute, the generated electricity was sufficient for the real-time inspection of the lactate concentration accumulated in body sweat. Furthermore, the results also reveal that the wearable self-powered lactate sensor shows detection capability with high selectivity and sensitivity. Ultimately, by utilizing the TENG to power the electrochemical sensing unit, the proposed self-powered sensing system will bring advantages of device size mini-mization, long-term operation, and an avoidance of the use of environmentally unfriendly materials.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2017.10.064.

Fig. 6. Charging and discharging curves of a 1000 μF capacitor by the TENG. (b) Current response curves of the PBS solution containing lactate analyte with different concentrations. (c) Current response of the self-powered lactate sensor when using carbon fibers with PdAu, Pd and Au nanoparticles as the anodes in the electrochemical sensing unit. (d) Selectivity test of the self-powered lactate sensor. The concentrations of lactate, creatinine, ascorbic acid, glucose and uric acid are 10, 100, 10, 200, and 60 μM, respectively. (e) Photograph of the built-up self-powered and wearable lactate sensor.

References
