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Short communication

Wearable temporary tattoo sensor for real-time trace metal monitoring in human sweat

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ABSTRACT

A wearable electrochemical sensor for non-invasive monitoring of trace metals in human perspiration is described. The temporary tattoo-based printable stripping-voltammetric sensor has been applied for real-time monitoring of zinc in sweat using a bismuth/Nafion film electrode during physical activity. The Zn temporary tattoo sensor withstands repeated mechanical stress and displays a well-defined Zn response during on-body testing. Such a non-invasive stripping-voltammetric detection could be readily expanded to epidermal measurements of other relevant heavy metals.

1. Introduction

Wearable sensors can provide significant insights into the health status and performance of individuals [1]. Early efforts in this field have resulted in a variety of physical sensors to monitor activity and vital signs such as heart rate, skin temperature, respiration rate, or bodily motion [2,3]. Recently, our laboratory has extended these studies for non-invasive monitoring of electrolytes and metabolites on epidermis based on flexible temporary tattoo electrodes that adhere to the skin surface [4–8]. Such body-compliant printable electrochemical sensors offer elasticity characteristic of temporary tattoos along with resistance to mechanical stress and compatibility with the non-planarity of the epidermis. Expanding this attractive skin-worn platform towards new classes of analytes, in connection to different electrochemical techniques, should benefit diverse healthcare, fitness, and military applications.

In this article, we describe, for the first time, the fabrication and characterization of a wearable temporary tattoo sensor for the non-invasive monitoring of zinc, and trace elements in general, in sweat directly on the human epidermis (Fig. 1). Zinc is an important trace component of biochemical processes relevant to enzymes, hormones, and transcription-related factors [9]. Changes of the zinc concentration in bio-fluids can be used as indicators for wide ranging physiological states, such as muscular damage due to physical stress and the immune system [10–12]. Cordova et al. [13] observed that human subjects experienced decreased endurance during physical activity associated with variation in zinc metabolism due to increased zinc excretion and stress. Perspiration represents an important pathway for the excretion of zinc, leading to its deficiency in the body [14]. While identifying the loss of zinc during physical activity is extremely important, currently no tools exist for real-time detecting of trace (physiological) levels of metals in sweat.

The stripping-voltammetric determination of Zn in sweat has been reported using collected sweat [15–17]. The use of collected sweat may be subject to inaccuracy due to sample contamination during collection, evaporation of sweat, and treatment steps. Additionally, it cannot yield real-time information on dynamic events. To address these limitations, we have combined in the present study, our expertise in fabricating skin-worn electrochemical temporary tattoo sensors [4–8,18], screen-printed electrodes for trace metal detection [19–21], and bismuth film electrodes for stripping-voltammetric metal measurements [22,23]. On-body electrochemical measurements of trace metals during exercise activity are thus demonstrated by implementing our printable temporary tattoo sensors directly on human skin. The sensor is prepared by modification of a flexible screen-printed electrode on a temporary tattoo-transfer paper with Nafion coating and ex situ plated bismuth film. The sensor response was characterized in buffer and on-body and tested under mechanical deformations associated with common physical activity. The Zn temporary tattoo sensor was applied successfully to several human subjects for direct epidermal metal sensing. Its attractive performance is discussed in the following sections.

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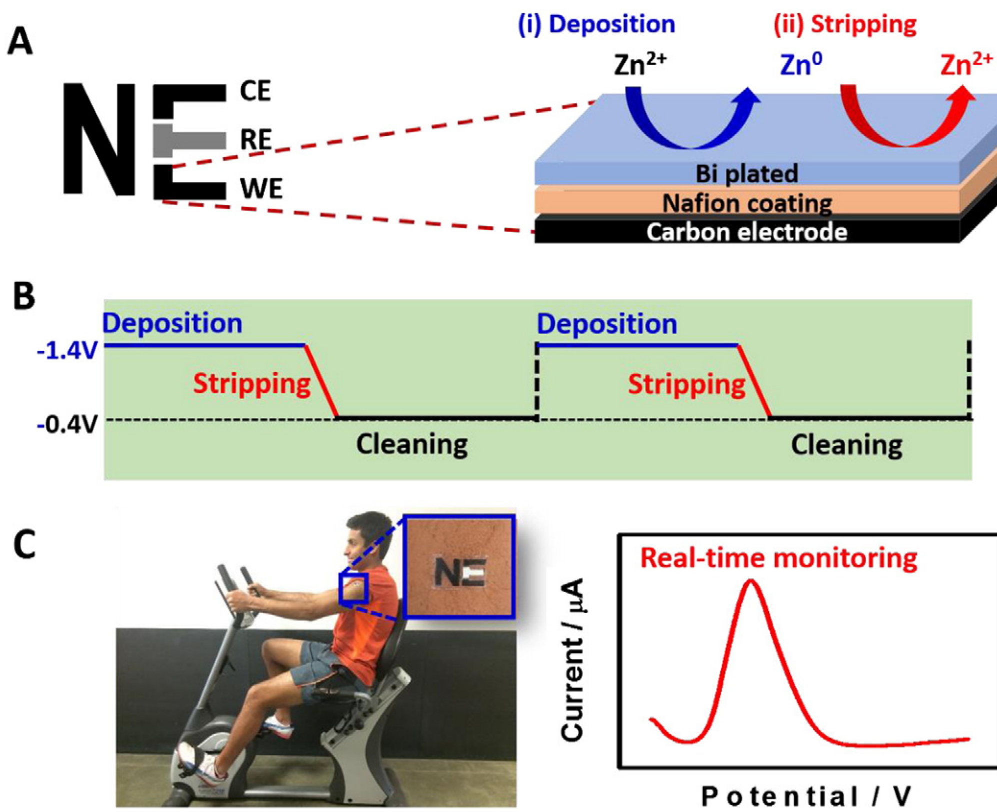

Fig. 1. (A) Schematic illustration of a temporary tattoo sensor and stripping-voltammetric analysis using an ex situ plated bismuth/Nafion working electrode. (B) Electrochemical procedure (time-potential cycle) of the stripping detection of Zn. (C) Real-time monitoring of Zn during cycling exercise with a temporary tattoo sensor transferred on a subject's deltoid.

2. Experimental

2.1. Reagents and instrumentation

All reagents were used as received. Acetate buffer, zinc, bismuth, lead, cadmium, and copper standard AAS solutions (1000 mg/L in nitric acid), sodium chloride, and Nafion® (5wt %) were purchased from Sigma-Aldrich (St. Louis, MO). Electrochemical measurements were performed using a μAutolab type II (Eco Chemie, The Netherlands).

2.2. Fabrication of temporary tattoo sensors

The NE temporary tattoo sensor design (Fig. 1A) is an abbreviation of the name of the department, "NanoEngineering". The fabrication process of the screen-printed sensor on temporary transfer tattoo inkjet paper (HPS LLC, Rhome, TX) is similar to our previous work [8]. The patterned "E" portion of the temporary tattoo sensor design consisted of a pseudo-reference (Ag/AgCl), counter, and working electrodes (carbon ink). A transparent insulator was screen printed on the surface of the electrode pattern to confine the electrode and contact areas. Subsequently, the carbon working electrode was modified by drop-casting 2 μl of Nafion®. After drying for 3 h, bismuth was electroplated at −0.8 V for 4 min using a 50 μg/ml of bismuth solution (in 0.1 M acetate buffer) .

2.3. Characterization of temporary tattoo sensors in buffer medium

Square wave anodic stripping voltammetry (SWASV) was employed to characterize the electrochemical stripping trace metal detection of the temporary tattoo sensor. In order to evaluate performance in buffer medium, sensors were transferred onto a plastic substrate for calibration and stability tests and onto a flexible GORE-TEX textile for mechanical strain tests. The operated SWASV is briefly depicted in Fig. 1B. A deposition potential of −1.4 V (vs. Ag/AgCl) was applied for 120 s, followed by a SWASV scan to a final potential of −0.4 V with a frequency of 25Hz, an amplitude of 25 mV, and a potential step of 4 mV in acetate buffer (pH 4.6) containing 0.1 M NaCl. A cleaning step followed every stripping step, a potential of −0.4 V was applied for 2 min to remove any remaining trace metals from the electrode surface. Sensors were calibrated using Zn solutions of 0.1-2.0 μg/ml concentrations. Mechanical strain properties were tested by repeated 90° bending and stretching of the sensors up to 10% for 5 s on a GORE-TEX textile. This was done to mimic the viscoelastic properties of the skin. The sensors were subsequently relaxed for another 5 s and the procedure was repeated 5 times after which the SWASV response for 1 μg/ml of Zn was measured.

2.4. On-body test of Zn temporary tattoo sensor

Epidermal studies were performed as described in our previous work [8], in strict compliance with the protocol that was approved by the institutional review board (IRB) at the University of California, San Diego. A total of 7 healthy volunteers (2 females and 5 males) were recruited. The temporary tattoo Zn sensor was transferred to a subject's arm in order to monitor the Zn concentration during exercise (Fig. 1C). Subjects were asked to ride a stationary cycle. They began cycling with a steady, comfortable cadence and continued with an intense cycling bout. During the exercise, SWASV on-body data were recorded with the μAutolab system. After the exercise, sweat was collected by using a pipette and the level of Zn was estimated by SWASV through standard addition of Zn solution.

3. Results and discussion

The Zn concentration in human perspiration depends on nutritional and health status of individuals. Lack of Zn causes subjects to feel