# Carbon-Based-Polypyrrole Composite Nanowires for Portable and Remote Trace Sweat Lactate Detection

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**Abstract.** The prompt and remote detection of biomarkers is crucial in personalized medicine and health protection, presenting a significant challenge for current devices. In this context, we introduce a highly sensitive method for remotely analyzing sweat lactate, utilizing carbon nanotube-composite polypyrene with the capability of transmitting data. The sensing mechanism is attributed to the charge transfer of polypyrene during anion doping, enabling the selective detection of lactate anions at specific potentials, while maintaining inertness to neutral and cationic substances found in human sweat. Timed-current studies revealed robust sensing properties for lactate, demonstrating a sensitivity of up to 1.8 mA·mM<sup>-1</sup>cm<sup>-2</sup> and a detection limit of 25  $\mu$ M. Additionally, CNT-polypyrene nanowires exhibited outstanding selectivity for lactate. This breakthrough overcomes the limitations of traditional electrochemical sensors, offering a direction and theoretical foundation for designing wearable sensors to address various stimulus detection needs.

**Keywords:** CNT-PPy; Lactic acid sensor; Electrochemical technology.

# 1. Introduction

In recent decades, biomarker testing has garnered significant attention in healthcare for its potential in early disease diagnosis and personalized health monitoring. It is anticipated to play a pivotal role in the forthcoming era of cloud-based healthcare (CMT). Various studies have highlighted the significance of lactate as a crucial metabolite in clinical cases, serving as an indicator of metabolic disorders under anaerobic conditions[1-3]. The elevation of lactate concentration in tissues is associated with energy demands that exceed what aerobic respiration can meet, leading to anaerobic metabolism. Furthermore, lactate serves as a vital biochemical indicator for a range of diseases and conditions, including sepsis, acute heart disease, and lactic acidosis. Its detection and analysis hold promise in providing valuable insights into the state of health and facilitating early intervention[4-6].

Presently, conventional methods for lactate detection involve gas chromatography/mass spectrometry and ion chromatography[7-9]. Despite their accuracy, these approaches are characterized by being cumbersome, expensive, and time-consuming, lacking the capability for real-time detection. Consequently, there is a pressing need for the development of portable sensors with the capacity to detect lactic acid at low concentrations. Such advancements would address the limitations of current methods, providing a more accessible and efficient means for timely lactate detection[10-13].

Building upon this inspiration, we have developed a highly sensitive and portable sweat lactate sensor. This sensor relies on electrochemical methods to determine lactate concentration in sweat, employing multi-walled carbon nanotube (MWCNT)-polypyrrole nanowires. In this design, we harnessed the redox processes and charge transfer phenomena of the conventional p-type conducting polymer, polypyrrole. By selectively doping only anions, such as lactic acid, at specific potentials, we achieved rapid current responses. Electrochemical doping of acid anions onto the p-type conducting polymer occurred at fixed potentials. The high selectivity of our sensor arises

Advances in Engineering Technology Research ISSN:2790-1688

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from the inertness of neutral and cationic components to the p-type conducting polymers. These inherent properties make p-type conducting polymers ideal for the selective amperometry detection of lactic acid without interference from other sweat metabolites. In summary, we utilized polypyrrole as a representative p-type conducting polymer to amperometrically determine the concentration of lactic acid in human sweat. Furthermore, we incorporated a Bluetooth module for wireless data transmission, enabling real-time monitoring of sweat lactate via tablets and smartphones. This innovation illustrates the potential application of our sensor in health and safety protection, as well as in the context of the Internet of Things.

# 2. Experimental

#### 2.1 Materials and reagents

All chemical reagents used in this study were of analytical grade and not further purified.MWCNTs were purchased from Chengdu Institute of Organic Chemistry. Pyrrole monomer, trisodium citrate, ethylene glycol, Nafion solution, lactic acid, H2O2 (30%), ascorbic acid (AA), dopamine (DA), glucose (GLU), uric acid (UA), and PBS buffer, as well as all other chemical reagents and solvents, were purchased from Shanghai Chemical Reagent Co.

#### 2.2 Synthesis of CNT-PPy

The procedure involved a mass ratio of 1:3 for pyrrole and ferric chloride, with 20  $\mu$ L of pyrrole utilized. Deionized water (10 mL) was added to the beaker, and carbon nanotubes were subjected to 20 minutes of sonication in an ultrasonic machine to ensure the uniform dispersion of pyrrole in the water. Subsequently, 0.3 g of ferric chloride was weighed on an electronic balance and mixed with 5.95 g of water to create a 4.8 wt% ferric chloride solution. Carbon nanotubes were introduced into the pyrrole solution beaker, and the entire setup was placed in a larger beaker with an ice-water mixture, maintaining a temperature of 0  $^{\circ}$ C. Using a syringe, 5 mL of the ferric chloride solution was slowly injected into the carbon nanotube and pyrrole mixture. The reaction occurred in a freezer at 4  $^{\circ}$ C for 30 minutes. This process was repeated several times, and residual ferric chloride solution was removed using a dropper with deionized water. To finalize the synthesis, the resulting carbon nanotubes based on polypyrrole (PPY) were dried in a 65  $^{\circ}$ C electric thermostatic drying oven for 12 hours. The overall pyrrole content was 20%, and five different PPY-based carbon nanotubes were prepared with varying polymerization times of 10 min, 20 min, 30 min, 40 min, and 60 min, respectively [14].

#### **2.3 Preparation of the CNT-PPy modied electrode and electrochemical measurements**

The Glassy Carbon Electrodes (GCE) underwent successive polishing using 0.05  $\mu$ m Alumina powder on a polishing cloth and were subsequently cleaned in Deionized water. To fabricate the CNT-PPy/GCE, 5 mg of CNT-PPy was added to 0.5 mL Nafion solution and sonicated for 2 hours. Using a micropipette, 5  $\mu$ L of the CNT-PPy/Nafion mixed solution was drawn and dropped onto the GCE, forming a 3 mm diameter coating. All Cyclic Voltammetry (CV) and Amperometric (i-t) experiments were conducted using a CHI 660B work station. The electrochemical studies followed a three-electrode system and were performed under N2 saturated Phosphate Buffered Saline (PBS). Specifically, in the CNT-PPy modified electrode test system, the GCE (surface area = 0.071 cm2) served as the supporting substrate for the Working Electrode (WE), a square platinum sheet (1 cm2) acted as the Counter Electrode (CE), and a standard Ag/AgCl electrode was employed as the Reference Electrode (RE). [15].

# 3. Results and Discussion

### **3.1 Characterization of CNT-PPy**

The preparation of CNT-PPy composite nanomaterials by low temperature polymerization is shown in Fig. 1a.

The functional groups of the acidified CNT substrate and CNT-PPy powder were characterized by FTIR (Fig. 2). In the spectrum of CNT substrate there is -CO- absorption peak at 1678 cm-1 and obvious -OH absorption peak at 3405 cm-1[16-17]. This indicates that p-MWCNT carries a large number of oxygen-containing functional groups after mixed acid treatment.



Fig. 1 Schematic of low-temperature polymerization of polypyrrole on carbon nanotubes (right panel shows the change in the amount of polypyrrole at different polymerization times).

In the CNT-PPy powder spectra, the newly appeared 1168 cm-1 corresponds to the C-N stretching vibration in the pyrrole ring, 1040 cm-1 is caused by the =C-H bending (deformation) vibration in the pyrrole ring, and 965 cm-1 corresponds to the C-H vibration outside the pyrrole ring(Fig. 2) [18-19]. The other characteristic peaks are consistent with the PPy powder. The other characteristic peaks (Fig. 2) are consistent with the CNT, but with some redshift. This pattern indicates that Py was successfully polymerized into PPy on the surface of CNT substrate.



Fig. 2 Characterization of CNT-PPy compositional components. (a) CNT-PPy FTIR spectra with different polymerization times. (b) CNT-Ppy XPS spectra with different polymerization times.

The surface morphology of CNT substrates and CNT-PPy with various polymerization times was examined using SEM (Fig. 3). It is evident that the initially smooth CNT surface becomes coated with a layer of rough spherical particles following the in-situ polymerization of Py (Fig. 3). By comparing this observation with ATR-FTIR results, it is confirmed that these spherical particles are indeed PPy. The polymerization time notably influences the quantity and coverage of these PPy spherical particles, as illustrated in the SEM image. Importantly, the SEM image provides visual confirmation that PPy completely covers the CNT substrate.



Advances in Engineering Technology Research	EMMAPR 2024
ISSN:2790-1688	Volume-10-(2024)
Fig. 3 SEM images of CNT-PPy with different polymeriz	zation times (scale bar is 100 nm).

#### **3.2 Electrocatalytic activity of the CNT-PPy towards lactic acid**

First, CV scans were performed to compare the sensitivity and conductivity of different materials to H2O2. As shown in Fig. 4a, the peak currents varied linearly during the CV cycles with different scanning speeds, which implies that the catalytic process is controlled by diffusion. The electrochemical impedance spectroscopy (EIS) impedance spectra in the low-frequency region revealed a notable impact of the polymerization time on the slope change(Fig. 4c). Remarkably, the CNT-PPy-40mins electrode material exhibited the highest slope, indicating optimal Warburg diffusion impedance [20].

Further, we used amperometry to estimate the electrochemical performance of the CNT-PPy-40mins modified electrode in N2 saturated PBS (pH = 7.4) containing different concentrations of lactic acid (from 0.02 to 12 mM) at 0.45 V voltage. The response currents and fitted response curves recorded during 320 s per experimental cycle are shown in Fig. 4d. We derived the limit of detection (LOD) from the equation "LOD =  $3 \times \text{RSD/slope}$ ", where RSD is the standard deviation. Thus, the sensitivity was approximately 1.8 mA·mM-1cm-2 (correlation coefficient R2 = 0.997). In addition, the resulting LOD was about 0.18 µM with a linear range of 0.001 to 8 mM, respectively.

To assess the selectivity of our prepared sensing materials, we conducted measurements and comparisons with various biochemical interferents such as AA, DA, GLU, and UA in sweat. At a concentration of 0.1 mM, the current exhibited slight fluctuations in the initial seconds after introducing the interferents, potentially attributable to solution instability. However, the current quickly recovered within a few seconds (Fig. 4f). This behavior can be attributed to the fact that neutral or cationic components cannot be effectively doped into p-type conducting polymers, rendering polypyrrole inert to most interferents found in sweat. This inertness enhances the selectivity of the sensor for lactate detection amidst various interferents.



Fig. 4 Characterization of electrochemical sensing. (a) CV data for different sweep speeds and (b) fitting results. (c) CNT-PPy EIS impedance spectra for different polymerization times. (d) Calibration curves and (e) fitting results for lactate detection. (f) Selectivity analysis.

#### 3.3 Electrocatalytic activity of the CNT-PPy towards lactic acid

To assess the applicability of CNT-polypyrrole core-shell nanowires for non-enzymatic amperometric sensing of lactic acid in human sweat, these nanowires were integrated into a commercially available flexible printed electrode (Fig. 5a). The sensing chip exhibited a compact overall size (0.8 cm \* 1.8 cm) and remarkable bending ability, making it easily adaptable to areas with sweat, such as the human wrist or forehead (Fig. 5a).Prior to testing, the electrodes were slightly moistened with electrolyte to facilitate the effective absorption of sweat. Upon contact with the forearm of a volunteer after exercise, the current response was readily observable through the iPad, as illustrated in Fig. 5d. Moreover, the stability and reproducibility of the electrodes were assessed through successive additions of 1 mM lactic acid using a smartphone (Fig. 5e).These unique properties of CNT-polypyrrole core-shell nanowires position them as a promising material

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for selective amperometric biosensors, facilitating the monitoring of lactic acid concentration in human sweat. The compact size, flexibility, and ease of integration onto various areas of the body make this sensing technology practical for real-world applications.



Fig. 5 (a) Schematic diagram of a Bluetooth sensing device. (b) Schematic of portable device and sensing. (c) Circuit design schematic. Real-time data monitoring via ipad (d) and smartphone (e).

#### 4. Summary

ISSN:2790-1688

In conclusion, we introduce a method for the non-enzymatic electrochemical detection of lactic acid in human sweat utilizing MWCNT-PPy nanowires. Through surface modification and low-temperature polymerization, we achieved the construction of uniformly coated CNT-PPy nanomaterials. Cyclic voltammetry (CV) results demonstrated the doping of lactate ions into polypyrrole at approximately 0.45 V. The nanowires exhibited excellent response properties to lactic acid and demonstrated selectivity for lactate over interfering substances coexisting in sweat, such as sodium chloride, potassium chloride, glucose, urea, and riboflavin. Furthermore, we successfully applied the compact-sized, flexible sensing chip designed in this study to a commercially available flexible printed electrode, creating a non-enzymatic amperometric sensor for the selective detection of lactate in human sweat. The versatility of form factors and the use of state-of-the-art low-cost fabrication techniques in our electrode design pave the way for future developments, moving us closer to the commercialization of wearable biosensors. Our experimental results signify a significant advancement in achieving highly selective and sensitive non-enzymatic amperometric detection of lactate using CNT-PPy nanowires.

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