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Nanozyme - Based Flexible Wearable Devices for the Detection of Human Biomarkers

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ABSTRACT
Wearable sensors have emerged as pivotal tools in health management and disease prevention owing to their portability, noninvasive nature, and capacity for real-time monitoring. In this study, a zirconium-based metal–organic framework (UiO-66) was employed as a carrier, and a Pt/UiO-66 nanocomposite was constructed to enable the specific detection of human glucose levels. Utilizing the mesoporous effect, Pt nanoparticles with an average diameter of approximately 3.8 nm were successfully formed within the UiO-66 channels, endowing the composite with outstanding oxidase- and peroxidase-like activities. Based on these findings, a flexible wearable sensor platform integrating Bluetooth and wireless transmission technologies was further developed, offering a novel solution for personalized medicine and remote health monitoring[1].

KEYWORDS
Nanozyme, Pt/UiO-66; Flexible wearable devices; Noninvasive monitoring; Real-time detection

1 Introduction

In recent years, rapid advances in sensor technology and materials science have spurred the widespread application of flexible wearable devices in health monitoring. Owing to their excellent conformity with the skin, lightweight construction, and durability, such devices are capable of real-time monitoring of physiological indicators and can be seamlessly integrated into various locations such as the wrist or clothing. This provides robust technical support for personalized medicine and remote diagnostics. However, current flexible sensing platforms still exhibit limitations in detection sensitivity, selectivity, and long-term stability, which have, to some extent, impeded their clinical and practical deployment [2-4].

Nanozymes, as nanomaterials endowed with natural enzyme-like catalytic functions, have attracted significant attention in recent years due to their high catalytic efficiency, stability, and the advantage of low-cost mass production [5]. Nanozymes not only catalyze reactions pertinent to biomarkers—thereby generating a signal amplification effect—but can also be rationally designed to achieve highly selective recognition of specific target molecules [6-8]. Moreover, their ability to maintain high stability under extreme conditions renders them suitable for sensor applications in environments characterized by high temperatures, strong acids, or strong alkalis [9]. In this work, our team utilized flexible fabric as a substrate in combination with graphene oxide (GO) and MXene/MOF composites. By employing a self-assembly technique to fabricate a MXene/Pt/UiO-66-GO electrode, and incorporating Bluetooth and wireless transmission technologies, a flexible glucose sensor was successfully constructed. This approach provides a new strategy for achieving real-time, sensitive, and specific biomarker detection through nanozyme technology, thereby advancing personalized medicine and remote health monitoring.

2 Fabrication Methods of Pt/UiO-66-Based Flexible Wearable Sensing Materials

2.1 Fabrication of a Pt/UiO-66-Based Flexible Fabric Sensor

In this study, cotton fabric was selected as the substrate, and a functional film was constructed by depositing UiO-66 on its surface. The specific procedure is as follows:

First, 1.26 g (5.4 mmol) of $ZrCl_4$ was dissolved in 50 mL of DMF at room temperature. After sonication for 10 minutes, 10 mL of concentrated HCl (12 M) was added. A piece of cotton fabric measuring 3 cm × 2.5 cm was then immersed in the solution for 30 minutes to ensure complete interaction with the precursor. Subsequently, 1.26 g (7.58 mmol) of H_2BDC was dissolved in 62 mL of DMF and, following 30 minutes of sonication, was added dropwise to the $ZrCl_4$ mixture. The resulting mixture was transferred to a 200 mL Teflon-lined autoclave and reacted at 120 °C for 24 hours. Upon completion of the reaction, the system was allowed to cool naturally to 25 °C, followed by three washes each with DMF and methanol, and finally vacuum-dried at 70 °C. The obtained sample, denoted as UiO-66@CT, retained approximately 90% of its capacitance after 500 charge-discharge cycles, demonstrating excellent cycling stability and rate performance [10].

2.2 Fabrication of a Pt/UiO-66-Based Flexible Sensor via the MXene/MOF Strategy

To further enhance the sensor's performance, this study adopted a MXene/MOF composite as a conventional strategy for constructing flexible sensors. The fabrication process is as follows:

Initially, single-layer MXene nanosheets were obtained by reacting the MAX phase (Ti_3AlC) with hydrochloric acid and lithium fluoride, followed by centrifugation and vacuum drying. Next, PVDF-HFP was dissolved in a mixed solvent of DMF and acetone, and the pre-prepared UiO-66-NO_2 along with MXene were added. After ultrasonic dispersion and thorough stirring, a uniform nanofiber membrane was fabricated via electrospinning. Finally, this composite nanofiber membrane was employed as the core layer of the sensor, with PDMS (polydimethylsiloxane) coated on both sides for encapsulation. After thermal curing, a complete flexible sensor device was obtained. Experimental results demonstrated that the device exhibited high sensitivity (20.99 V/N), rapid response time (20 ms), and recovery time (10.8 ms), as well as excellent stability over 1000 cycles [11].

3 Factors Affecting the Performance of Pt/UiO-66 Composites

3.1 Intrinsic Factors

3.1.1 The Impact of Protonation on Pt/UiO-66 Composites

During the crystal growth of UiO-66, the degree of ligand deprotonation plays a decisive role in sustaining crystal growth. Research by Bohan Shan and colleagues has demonstrated that partially deprotonated ligands can impede further crystal growth; the accumulation of protons in the reaction solution leads to incomplete ligand deprotonation, ultimately terminating crystal growth and adversely affecting the overall sensor functionality. To mitigate this, deprotonating agents such as triethylamine (TEA) were employed. By controlling the diffusion of TEA in the reaction system via a biphasic solvothermal method, excess protons were effectively consumed, thereby ensuring complete deprotonation of the ligands. This promoted continuous crystal growth and interconnection to form a dense crystalline film, ultimately enhancing sensor performance [12].

3.1.2 Effects of the Fabrication Process on the Composite Material

The catalytic activity of UiO-66 is closely related to the number of exposed basic sites, which play a crucial role in the biomarker-catalyzed reactions and directly influence the sensor's selectivity and sensitivity. Moreover, the size of the nanoparticles is a critical parameter in determining the nanozyme activity. When the particle size is too large, the diffusion of reactants within the MOF channels is significantly hindered, thereby reducing the reaction rate. In contrast, controlling the particle size within 10 nm helps mitigate diffusion barriers, allowing the reaction to proceed under kinetic control. Additionally, an appropriate number of defects can increase the number of active sites, although excessive defects may result in structural instability or partial coverage of active sites. Therefore, optimizing the reaction conditions and precisely controlling both the particle size and defect distribution are essential measures to balance catalytic activity and structural stability [13].

3.2 Extrinsic Factors

In sensor design, the oxidation degree and the amount of graphene oxide (GO) exert significant influence on both the growth of UiO-66 crystals and the thermal conductivity. Experimental results indicate that with an increase in the oxidation degree of GO, the average crystal size of UiO-66 gradually decreases; similarly, increasing the GO content also results in smaller crystal sizes. When the mass fraction of oxygen in GO exceeds a certain threshold, the normal growth of UiO-66 is inhibited, primarily because the abundant oxygen-containing functional groups on the GO surface provide excessive nucleation sites that limit crystal expansion. Based on these findings, rational control of the oxidation degree, dosage, and the proportion of oxygen-containing functional groups in GO during sensor electrode fabrication is critical for optimizing sensor performance, as well as improving thermal conductivity and crystal growth conditions [14].

4 Conclusion

Nanozyme-based flexible wearable sensors exhibit unique advantages in biomarker monitoring, smart health management, and disease diagnosis. Although challenges remain in balancing catalytic activity with selectivity, ensuring long-term stability in complex environments, achieving biocompatibility while mitigating potential toxicity, controlling signal amplification versus background noise, and scaling up production with cost efficiency, these issues are expected to be effectively addressed through the fine-tuning of material synthesis and device fabrication strategies. Future interdisciplinary collaborations and further breakthroughs in materials science, biology, and engineering will provide a more solid foundation for the development of flexible sensors, thereby promoting the widespread application of personalized medicine and remote health monitoring technologies.

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