NON-ENZYMATIC GLUCOSE SENSORS BASED ON 1D METAL OXIDE NANOSTRUCTURES MODIFIED BY THE ELECTROCATALYTIC COATING

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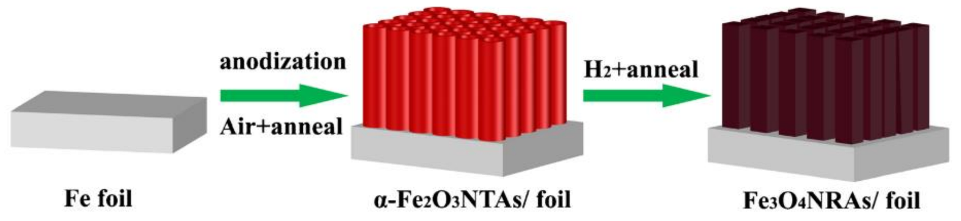
INTRODUCTION

There is a growing demand for sensitive, selective, reliable, and low-cost sensors for regular blood glucose measurements. Over the past few decades, enzyme-based electrode sensors have been the first choice of biosensor systems due to their high sensitivity, short response time and low cost. However, because enzyme-based electrodes often suffer from shortcomings such as complex manufacturing processes and low chemical and thermal stability, researchers are now working to develop enzyme-free electrochemical biosensors. On the other hand, one of the most challenging analytical factors in biosensors is their ability to eliminate interfering responses produced by other species in the blood that have a similar reaction power to the target analysis, including Ascorbic acid, Dopamine and Uric acid. The necessity and importance of this study are to focus on the glucose biosensors without functional enzyme, very sensitive, low cost, and also with selective glucose sensing capability.

Application of nanomaterials in non-enzymatic electrochemical glucose sensors

The most common application of nanotechnology for glucose sensors is the use of nanomaterials to aid in the standard method of non-enzymatic electrochemical detection due to their simple and effective catalytic properties. Nanostructures show higher surface areas (larger currents and faster reactions) and improve catalytic activity. Mineral nanorods, for example, are at the heart of one-dimensional nanostructures and have received much attention because of their unique physicochemical properties that are directly related to their structural properties. The catalytic effects of these nanostructured electrodes are considered from three aspects, namely the creation of electrocatalytically active sites, the increment of the surface area and the formation of nanospaces enclosed by conductive surfaces. Glucose oxidation involves adsorption sites or reactive radical species of OH_{ads}, both of which play a role in facilitating the slow electrochemical kinetics of glucose oxidation. High-index plates, adsorbed edges, and atoms that are more common in nanoparticles, nanowires, and nanotubes serve as active sites for electrocatalysis at the electrode surface. Zhang et al. [16] synthesized an enzyme-free electrochemical sensor for glucose based on one-dimensional Fe_3O_4 array nanowires, which improved glucose sensitivity. The high performance of this array is attributed to the improved electron transfer pathway as well as the electrochemical oxidation of glucose by species Fe(III) and Fe(II). The array showed a wide linear range for glucose determination with a maximum sensitivity of 406.9 $\mu A.cm^{-2}.mM^{-1}$ and a detection limit of 0.1 μM. This glucose sensor had little interference from symbiotic species such as uric acid and ascorbic acid in human blood serum and provided good reproducibility and stability.

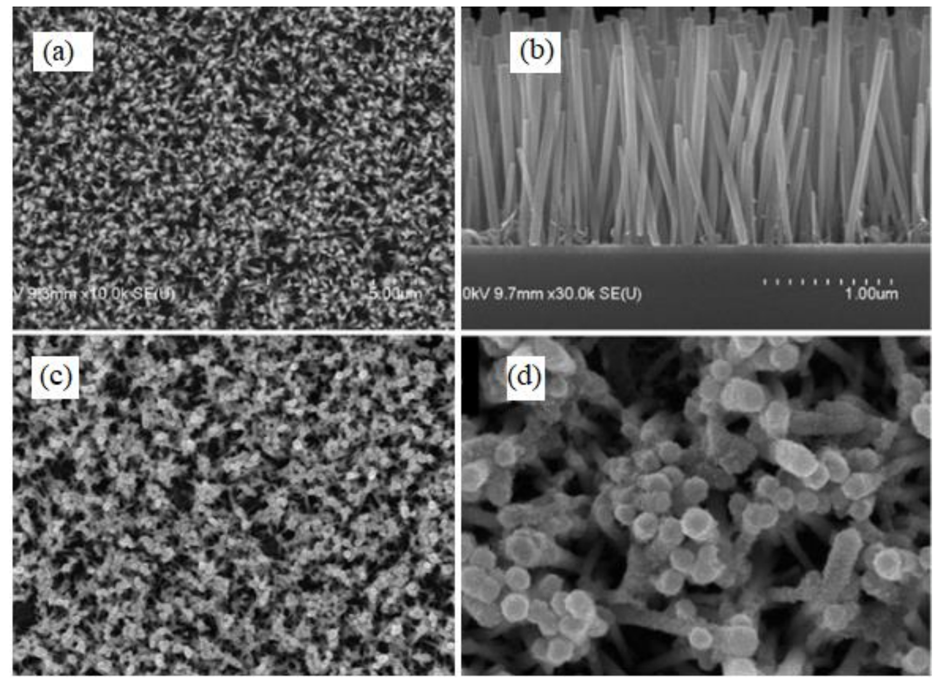


ELECTROCHEMICAL DETECTION OF GLUCOSE

Non-enzymatic sensors are based on the direct oxidation of glucose on the electrode surface. Potentiometry and amperometry are two common electrochemical methods that are suitable for measuring the potential or current of a working electrode, which itself is proportional to the concentration of glucose. Some metals (Pt, Au, Cu, Ni, Co), metal oxides (CuO, Co_3O_4), other metal compounds (CuS) and carbon-based materials due to their electrocatalytic activity are very promising options for non-enzymatic glucose sensors.

In addition to the composition and morphology of the electrode surface, the pH value or the presence of coatings such as Nephion, polyethylene glycol, or polyurethane may significantly affect the assay process. Detection of glucose in acidic, neutral, and alkaline solutions has been investigated and it has been shown that glucose is not reactive in an acidic solution. In addition, the adsorption of chloride ions on the electrode surface was very strong in acidic solution and very weak in alkaline solution. In this regard, many non-enzymatic sensors have been developed to detect glucose in neutral and alkaline environments. The development of biosensors requires the simulation of a neutral solution using a phosphate buffer solution (pH = 7.4) to simulate the physiological state.

The main problem of some glucose sensors is the high absorption of toxic compounds which stick to the surface of the electrode and prevent the absorption of glucose molecules. To prevent undesirable absorption of toxic compounds, various coating materials such as nephion, polyethylene glycol and polyurethane are used. Nephion membrane is used in fuel cells, sensors, electrochemical devices, selective electrodes, etc. and is the most suitable protective layer due to its high chemical stability, biocompatibility, and excellent thermal stability, which increases the stability of biosensors



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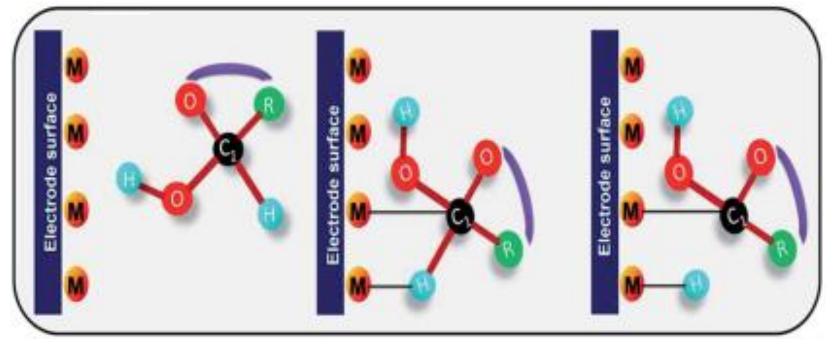
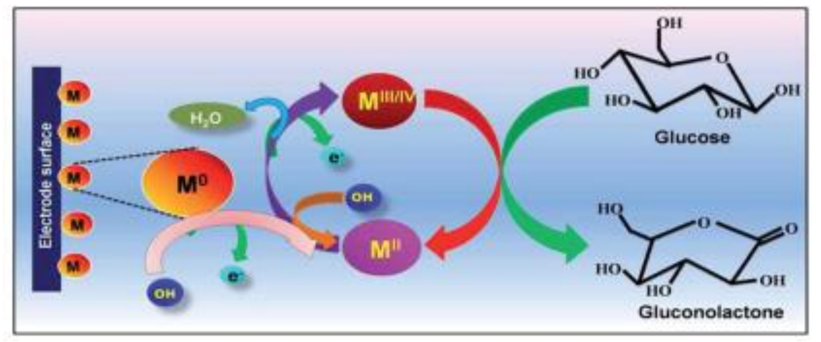
Electrochemical principles and sensing mechanisms

In general, two main theories have been proposed to explain the electrocatalytic process in non-enzymatic glucose sensors:

Activated chemisorption model: This model assumes that the oxidation process begins with the adsorption of glucose molecules on the electrode surface due to unpaired electrons and "d" unfilled orbital of the transition metal atoms which are available to form bonds with attractions. The catalysis process may occur through the accumulation step, i.e., the removal of hydrogen atoms occurs simultaneously with the adsorption of mineral species, as shown below. In fact, the removal of the hydrogen atom is considered as the reaction control step in most glucose electrooxidation experiments, and the chemical adsorption of glucose usually occurs simultaneously. Hence, the active metal centre of the adjacent metal is occupied each time by an adsorbent, which implies that adsorption sites with sufficient distance on the surface of electrocatalysts with suitable geometry can play a role in kinetically amplifying the glucose oxidation process



Primary hydrous oxide adatom mediator model: The chemical adsorption model explains only the adsorption process at the electrode interface but is incapable of considering the oxidizing role of hydroxyl radicals. Numerous papers have shown that electro-oxidation of glucose and many organic molecules coincides with the onset of adsorbed hydroxyl (OHads). Bruke therefore proposed another theory based on these observations that the active metal atoms on the surface undergo a single monolayer initial oxidation step and form a primary hydrous oxide layer of reactive OHads. This layer of OHads acts as a mediator and inhibitor in the oxidation and reduction processes, respectively. Active atoms on the electrode surface have low coordination numbers and lack the usual lattice stability energy. Polycrystalline surfaces are more reactive at discontinuous surfaces such as grain boundaries and edges because they are directly exposed to electrolytes relative to the internal components and undergo monolayer oxidation. Figure below shows this proposed process of how both oxidation and reduction processes are catalysed on the metal surface.



CONCLUSION

Diabetes is a disease caused by insufficient production of insulin by the pancreas or inability to use insulin effectively, the prevalence of which has steadily increased in recent decades. Because low-income countries, in particular, show a higher rate of diabetes and the quality of care varies greatly from country to country, it has been identified as one of four non-communicable diseases that need to be addressed. According to the International Diabetes Federation (IDF), the number of diabetics has increased from 151 million in 2000 to 382 million in 2013 and 415 million in 2015, meaning that 8.8% of adults between Ages 20 to 79 are diabetic. The IDF also predicts that the number of people with diabetes will reach 642 million by 2040, representing 10.4% of the world's population and the seventh leading cause of death in the world. But studies have shown that careful control of blood sugar can improve the lives of diabetics and prevent the complications of type 1 and type 2 diabetes. Likewise, blood sugar control devices are commonly used as medical devices in the management of diabetes. The most important component of a blood glucose control device is a diagnostic technology that measures glucose concentration. Much effort has been made to improve the performance of this technology over the past 40 years. So far, various methods have been used to detect glucose concentration, such as colorimetric method, optical method and electrochemical method, among which, electrochemical sensors, due to their simplicity, low cost and high sensitivity, as the most effective and convenient tool. Enzyme-based biosensors and enzyme-free biosensors are the two main categories of electrochemical glucose sensors and, non-enzymatic sensors have attracted a lot of attention as an attractive alternative to overcome the inherent limitations of enzyme sensors and are expected to provide a solution to the stability problem as well as a complex and unusable process for mass production of enzyme sensors. Rapid advances in nanotechnology and nanomaterials over the past ten years have led to progress and diversification in this area

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