Developments of Materials for Nonenzymatic Biosensing Applications

Yufei Ding *

Department of Shanghai University, Shanghai, China

* Corresponding author: dingyufei39@shu.edu.cn

Abstract. Nonenzymatic electrochemical biosensors, characterized by high sensitivity, good tolerance, simple preparation and low cost, have become a new research focus in recent years. Nanomaterials exhibit nonenzymatic catalytic mechanisms that enhance electrocatalytic activity and promote electron transfer, making them the popular materials used in nonenzymatic electrochemical sensors. Although catalytic activity and electrical conductivity of conductive polymers are not as good as inorganic nanomaterials, the introduction and doping of metal or carbon nanoparticles as well as the construction of composites with various modified groups can improve the performance of the sensors, and at the same time endow the sensors with the properties of lightweight, flexibility, plasticity, and better biocompatibility, which develops up a great potential opportunity of application in biosensing. This review summarizes the latest research developments of conductive polymer-based materials in nonenzymatic electrochemical sensors in recent years to provide ideas for the construction of sensors.

Keywords: Nanomaterials, conductive polymers, nonenzymatic sensors.

1. Introduction

Because the electrical signal has the characteristics of fast corresponding speed, easy to convert and obtain, simple and intuitive data analysis, electrochemical biosensors have become the sensors with early development, rich research achievements and wide application. Electrochemical biosensors primarily use electrodes as information conversion materials to transform substance-specific reaction processes into electrical signals. By using the level of the electrical signals, they can indicate the concentration of the reactants in an indirect way. Based on the type of receptor, electrochemical biosensors can be further classified into four categories: nucleic acid/DNA, enzyme, antibody-antigen, and cellular [1]. Among them, enzymatic electrochemical biosensors play a crucial role in biosensors as a result of their attractive features such as high selectivity, high efficiency, and low energy cost. However, at the same time, enzymatic biosensors also show obvious drawbacks, such as easy denaturation and inactivation of enzymes during immobilization, difficult and costly preparation process, and cumbersome operation steps [2]. Therefore, the development of a simple, effective and stable sensor has great potential for application.

Nonenzymatic electrochemical biosensors are characterized by tolerance to harsh environments, low and controllable preparation cost, and flexible structure design. Meanwhile, with the development of nanotechnology, nanomaterials also provide broad possibilities and opportunities for the research and advancement of nonenzymatic sensors. In addition to the earliest and most well-developed nonenzymatic glucose sensors, the observation of cholesterol, uric acid, dopamine, ascorbic acid, and other bio substances based on the principle of nonenzymatic sensing has also emerged one after another. Nanomaterials have enzyme-like activity, exhibit enzymatic reaction kinetics and catalytic mechanisms similar to natural enzymes, and can enhance interfacial adsorption properties and increase electrocatalytic activity [3]. Various nanomaterials such as nanoparticles, carbon nanotubes, noble metal graphene, and MXenes materials are widely applied in nonenzymatic electrochemical sensors. In recent years, composite nanomaterials have dominated the research of nonenzymatic biosensors, which have attracted great attention by virtue of the synergistic effect of two or more materials with each other to solve the shortcomings of single-phase nanomaterials, such as poor mechanical stability, susceptibility to interference, and insufficient electrical conductivity.

In composites, besides inorganic nanomaterials, another material is conductive polymers that has conductive properties. They can have metallic conductivity and be semiconductors. These polymers usually have conjugated structures. One structure is the conjugated double bond, in which π electrons are able to freely transition between adjacent double bonds. Another structure is the aromatic ring, which forms the resonance state of the electron cloud through conjugation, and realizes the free transfer of electrons [4]. The most popular conductive polymers are: polyaniline (PANI), polythiophene (PTP), polypyrrole (PPy) and their derivatives. Despite the fact that conductive polymers have preferable qualities like satisfactory electrical conductivity and high specific surface area, their electrocatalytic activity and electrical conductivity are inferior to those of typical inorganic nanomaterials, which is unfavorable for their use in nonenzymatic electrochemical sensors. This is because such sensors require high sensitivity and corresponding speed. However, compared to conventional nanomaterials, conductive polymers have the unique advantages of being flexible, biocompatible, mechanically strong, can be processed in solution, transparent, and low cost [5].

Therefore, conductive polymers are usually not used alone as electrodes for nonenzymatic electrochemical sensors, but are combined with inorganic nanomaterials to form composites. Under the premise of the complex structure and good stability of the polymers themselves, the polymer materials are able to improve the electrical performance through the introduction and doping of metal or carbon nanoparticles or a variety of modification groups. At the same time, the sensors are endowed with lightweight, flexible and malleable properties. This opens up a great potential for applications in the field of biosensing. Currently, even though conductive polymers have some attractive properties, their application in nonenzymatic electrochemical biosensors is less studied than inorganic materials.

This paper reviews the applications of nonenzymatic electrochemical biosensors based on metal and its oxide nanomaterials, carbon-based nanomaterials, and conductive polymer composites, respectively, and expands on the progress of research on polyaniline, polypyrrole, polythiophene, and a few other polymers among the conductive polymers. Finally, it concludes with a discussion of the future perspectives of electrochemical biosensors relied on nanomaterials and conductive polymer materials.

2. Nanomaterial-Based Nonenzymatic Biosensors

2.1. Metal and Metal Compound Nanomaterial

Precious metals and their alloys, transition metals and their oxides have enzyme-like properties and show good physicochemical properties in the field of nonenzymatic electrochemical biosensors [3].

Pt and Au are widely used because of their high catalytic activity and excellent stability. Wang et al. reported a core sheath of Ag/Au nanowires with a morphology similar to a double-ended matchstick, as shown in Fig. 1 [6]. They fabricated a highly stable, stretchable and transparent electrode from this nano-matchstick for nonenzymatic glucose detection, with an optical transmittance of 78.7%, which can reach a maximum of 240% of the stretchability variation with high sensitivity. Metal nanoparticles can also be modified by modifying the surface morphology to obtain tunable detection capabilities.

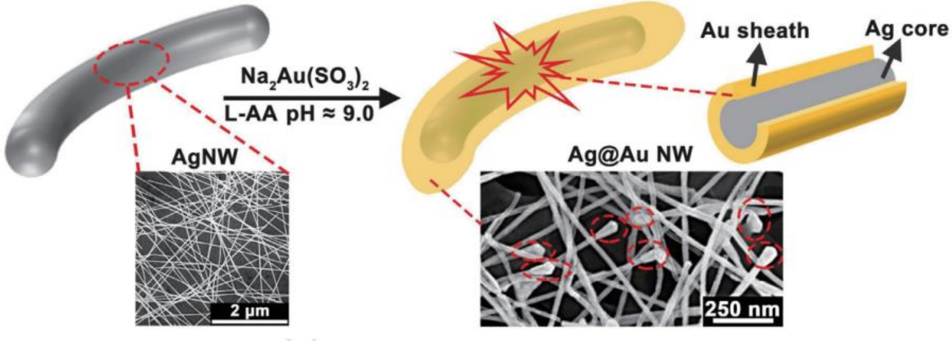

Figure 1. Images of schematic and SEM of pristine AgNWs and matchstick of synthesized Ag@Au NWs [6]

Zhang et al. were able to change the detection range of the glucose biosensor by using electrochemical etching which changed the microstructure and specific surface area of the Au electrode [7]. The biosensor obtains an arbitrarily adjustable range of glucose measurements for blood samples, sweat, and urine respectively, as shown in Fig. 2.

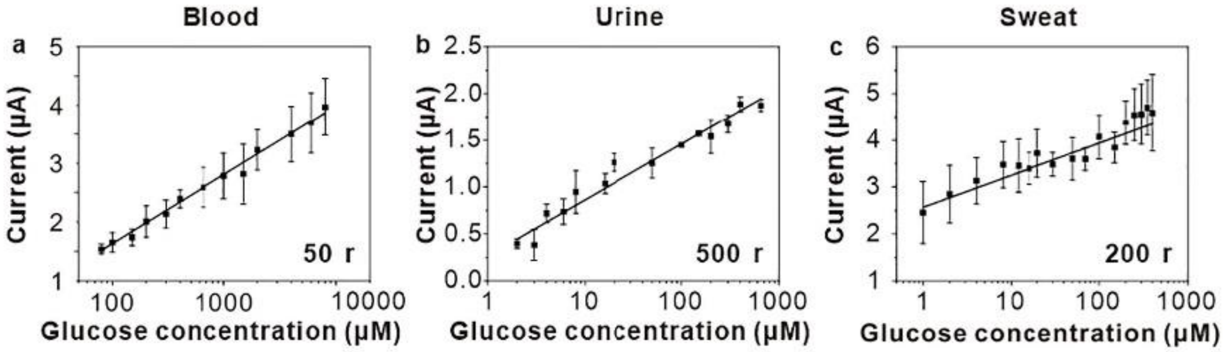

Figure 2. Current measurements correlate with glucose concentration in blood, urine and sweat which signed as a, b, c [7]

Transition metals and their oxides do not have the problems of high cost and low content of precious metals and their tendency to bind with chloride ions. Sajna et al. simply modified CuO nanoparticles onto a glassy carbon electrode in order to prepare a biosensor with a fast response to lactic acid, which can be used as an important tool for non-invasive detection of lactic acidosis caused by medical conditions [8]. Bao et al. used hydrothermal and electrochemical deposition of Ni and ZnO nanomaterials to modify the copper electrode to prepare a novel composite nonenzymatic glucose sensor with a quick response rate (<3 s) and a wide detection range (0.02-1.70 mmol/L) [9].

2.2. Carbon-Based Nanomaterial

Carbon-based nanomaterials are often utilized for the application of electrochemical biosensors because of their high electrical conductivity and electrochemical inertness. To date, a number of different carbon-based nanomaterials have been employed by nonenzymatic electrochemical biosensors, such as carbon nanotubes, graphene or graphene oxide.

Graphene oxide (GO) has excellent electrochemical properties, rich functional groups, easy chemical modification and other advantages, so it has been widely used in many fields. Sen et al. synthesized reduced graphene oxide (ERGO) by electrochemical reduction and constructed an nonenzymatic electrochemical biosensor based on this material [10]. This biosensor can be applied for the particular detection of organophosphorus pesticide (PT) residue levels in the environment or food. Such method is simple and economical, can be used for large-scale production, has a wider linear range and lower LOD compared with other nonenzymatic sensors, and is a good and feasible solution for the detection of PT in agricultural fields.

Mesoporous carbon materials such as nanoporous carbon (NC) are promising materials for nonenzymatic monitoring because of their high specific surface area (SSA), abundant oxygencontaining groups as well as optimized pore size distribution. Jia et al. employed a simple method to construct nanoporous carbon composites Ni/NCNs embedded with Ni nanoparticles, which is available for nonenzymatic determination of glucose as a sensing electrode [11]. This sensor exhibited ultra-low LOD, wide linear detection range, fast response time (<1.6s) and anti-interference capability.

Zhang et al. reported the preparation of flexible carbon nanofiber membranes by electrostatic spinning using polyacrylonitrile as a carbon source and loading Pt nanosheets on the fiber membranes to construct a flexible nonenzymatic glucose sensor [12]. Carbon nanofibers have a huge specific surface area and high porosity. Therefore, the sensitivity of the sensor is significantly improved. The electrode material is simple and low-cost to prepare and combines the advantages of flexible devices and nonenzymatic electrochemical sensors, which provides the possibility of constructing flexible glucose monitoring devices.

3. Conductive Polymer

In recent years, conductive polymers and their composites have been used in a variety of applications in the manufacture of different devices which include electrodes, sensors, coatings as well as supercapacitors. Polymer-based nanostructured composites are the main form used. In such composites, polymers are mainly used as conductive substrates or as modifying films to enhance the selectivity of the detected substance [13].

Conductive polymer composites are composites of conductive polymers with other materials to achieve different properties. Benefiting from the different physical or chemical properties of the combined materials, composites exhibit multifunctionality with enhanced mechanical properties and processability.

3.1. Polyaniline

Polyaniline (PANI) and its derivatives have become widely used conductive polymers due to their unique advantages such as easy synthesis, cheap and readily available raw materials, simple synthesis, high electronic conductivity similar to metals, and good stability [14] PANI belongs to the structural conductive polymers, which are highly controllable in conductivity and can be flexibly structured. The conductivity can be changed by altering the doping degree of PANI (Fig. 3).

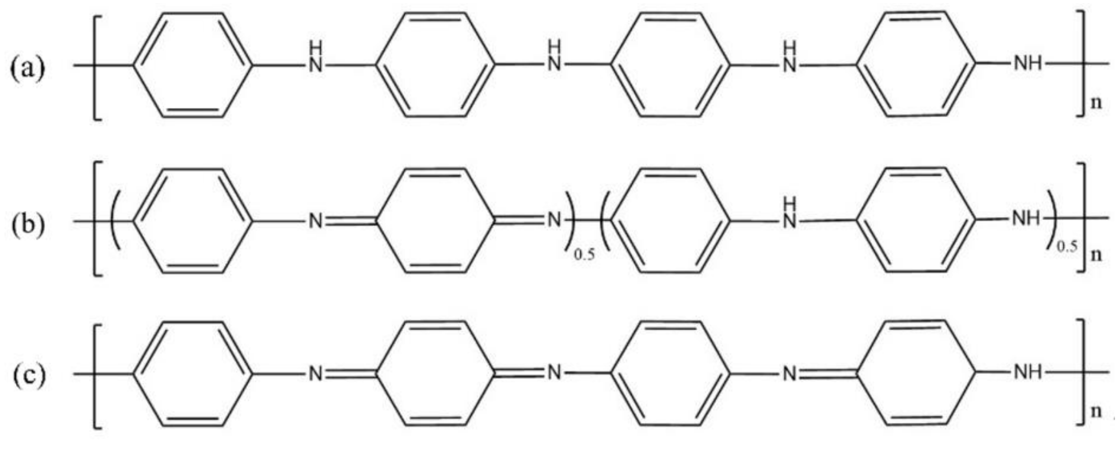

Figure 3. Three structures of PANI (a) Fully oxidized state; (b) Intermediate state; (c) Fully reduced state

Zhao et al. constructed an electrochemical immunosensor based on the nanocomposite of high carbon spheres@polyaniline (HCS@PANI) for sensitive detection of alpha-fetoprotein (AFP), with a wide linear concentration of the detected antigen (0.001-80ng/mL) [15]. They made the PANI by doping protonate and HCS to be a good conducting substance as shown in Fig. 4.

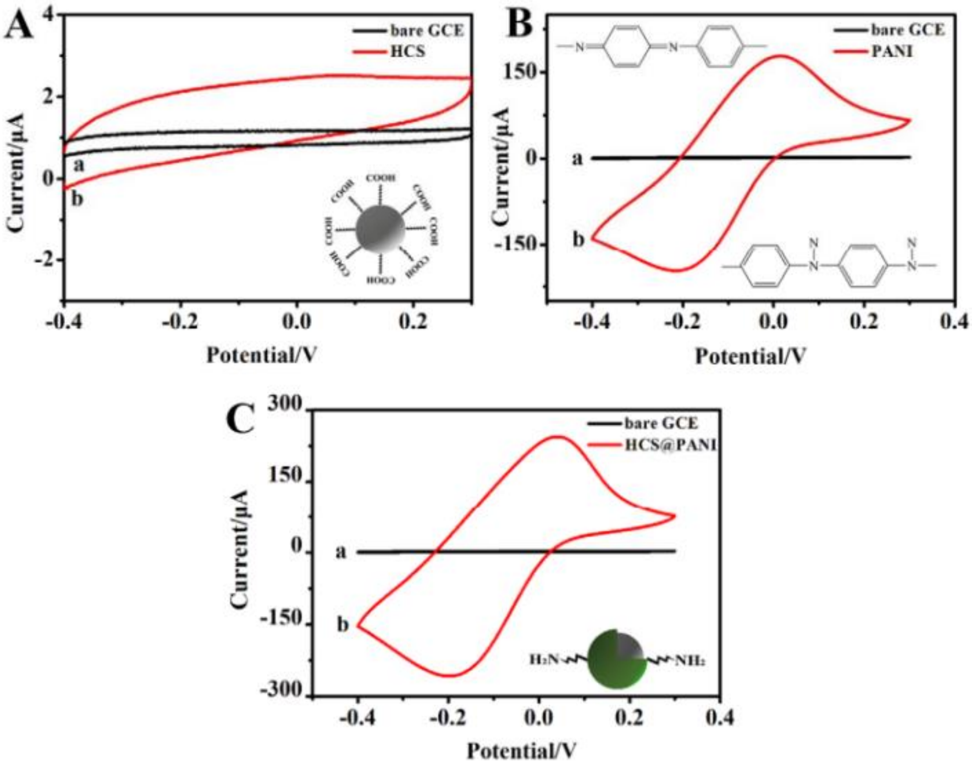

Figure 4. Electrochemical performance tests of different materials. A, B, C represent -CVs of bare GCE, HCS; CVs of bare GCE, PANI; CVs of bare GCE, HCS@PNAI respectively [15]

Specifically, PANI has shown excellent sensitivity and selectivity in composites formed with other conductive polymers, metal nanoparticles, or carbon-based nanomaterials. Yasmine et al. synthesized ZnO/PANI nanocomposites using ultrasonication for modification of carbon paste electrodes to make nonenzymatic electrochemical sensors. This biosensor can detect uric acid (UA), vitamin C (VC) and dopamine [16]. Such process was less expensive and time saving. The modified electrode's electroactive surface area, which was 0.235 cm2 instead of 0.117 cm2 for the bare electrode due to the presence of PANI, increased significantly, raising the sensitivity of the electrochemical sensor. Jia et al. deposited PANI on nickel-based hydroxyapatite (HAP/NF) electrodes by chemical in-situ polymerization for the preparation of nonenzymatic glucose sensors [14]. The findings demonstrated that the PANI-modified electrode had great immunity to interference with ascorbic acid and uric acid with only 4% of the response current to glucose and good electrochemical activity in sodium hydroxide solution of glucose. A flexible glucose monitoring system was constructed by Lu et al. who used a conductive carbon cloth as a substrate and loaded with PANI and nanogold on the electrode [17]. PANI makes the composite material more surface-loaded metal particles and improves the stability of the electrode.

3.2. Polypyrrole

Polypyrrole(PPy) is characterized by high conductivity, easy preparation, electrochemical reversibility and good stability. Polypyrrole can be used to construct modified electrode materials. PPy nanoparticle-modified electrodes with high sensitivity can be obtained by doping phosphomolybdenum heteropolyacid root-doped pyrrole solution and modifying it onto the electrode surface by nanoporous anodic alumina template electropolymerization.

Nagarajan et al. prepared glassy carbon electrodes modified with Au/NiO-PPy nanocomposites, which can be used for nonenzymatic monitoring of cholesterol (Fig.5) [18]. Simple and inexpensive to synthesize, this sensor relies on the huge specific surface area due to PPy and the excellent electrocatalytic activity of the metal nanoparticles, and this electrode has an encouraging accuracy. Since this material can detect the difficult cholesterol in a non-enzymatic manner, it is hypothesized that it has the versatility to detect other alcohols.

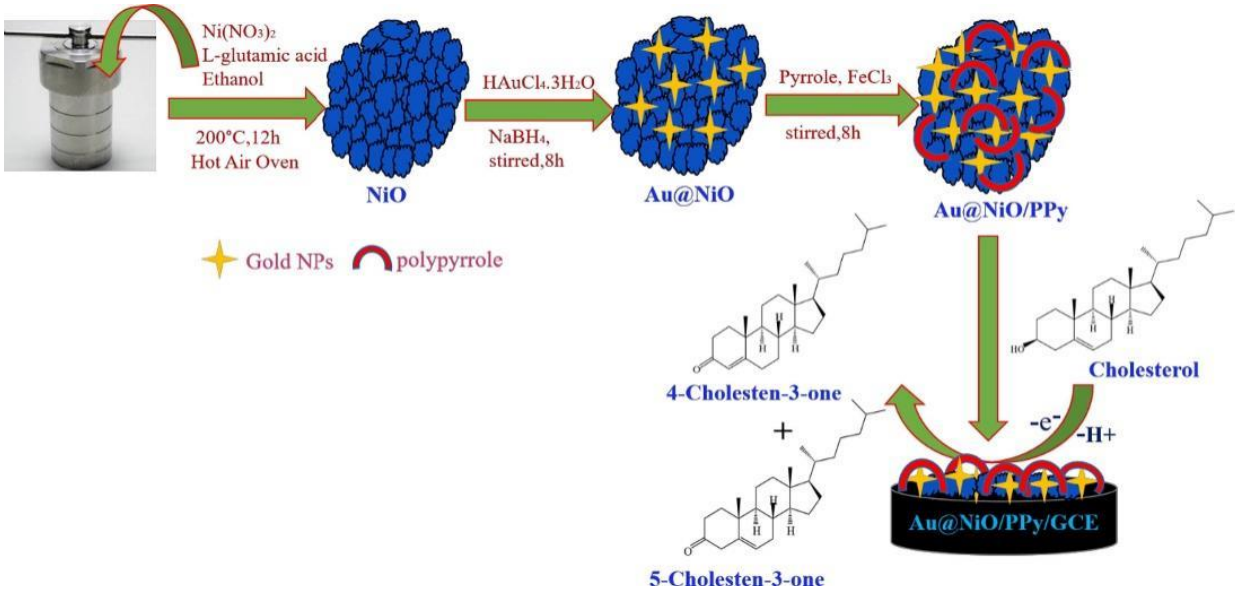

Figure 5. Schematic representation of the electrocatalytic oxidation of cholesterol under Au@NiO/PPy/GCE [18]

Although PPy has better electrochemical properties, it also suffers from the problems of difficult processing and poor flexibility. Combining PPy with other flexible polymers (chitosan, collagen, etc.) can be a good solution to these kinds of problems. Xu et al. prepared polypyrrole-polycaprolactone nanofibers using electrostatic spinning and combined them with nanometal oxides, such as CuO/NiO, to construct metal oxide/PCL@PPPy/ITO electrodes to determine uric acid (UA) and glucose in blood [19]. The detection device has good performance and can detect UA in the linear range of 6 μM-830 μM or glucose in 2 μM-6 mM.

3.3. Polythiophene

In recent years, researches on polythiophene (PTP) and its derivatives have gained a lot of interest. Although its demanded oxidation potential is higher compared to the previous two conducting polymers, low cost and adjustability are not its main advantages. However, the thiophene ring has a sulfur-containing five-membered ring, which helps the electron conduction, and this makes it and some of its derivatives natively better conductive than polyaniline and polypyrrole.

An electrochemical sensor for the nonenzymatic detection of glucose was developed by doping AgBr nanoparticles into the polythiophene framework by the research team of Hashemi [20]. Approximately 97.1% of glucose from human plasma was recovered by the biosensor based on PT-AgBr with little influence from interfering substances in the solution. The team found that the ideal conductive polymer structure of PTP helps to improve the conductivity of the sensor and achieve better sensing sensitivity, and the integration of PTP with metal particles can further improve its electrocatalytic performance, ultimately enabling the sensor to achieve lower LOD and wider linear range.

3.3.1. PEDOT

Poly(3,4-ethylenedioxythiophene;PEDOT) derives from polythiophene, and PEDOT obtained by ferric chloride polymerization reaction almost immediately shows the special properties of being highly conductive and stable, especially in the doped state. Masood et al. synthesized the imidazolium acidic skeleton ZIF-67 and prepared a sensing electrode for the detection of dopamine by attaching PEDOT to its surface [21]. PEDOT provided a smooth conducting substrate (LOD=15.240 μM) for the precise detection of ZIF-67 and simultaneously protected the electrode from interference and damage. The sensor they developed was successfully used to monitor dopamine in the blood of COVID-04 isolates.

Most of the electrodes are prepared by mechanical mixing of polymers with metal-based or carbon-based nanoparticles to make composites, and another preparation method mentioned here is the choice of chemical coupling to access the detection substances on the modifiable groups of polymers. Bao et al. reported the synthesis of Poly(EDOT-FPBA) thin films for glucose detection with high specificity for the inhibition of non-specific proteins, by electropolymerization of Poly(EDOT-FPBA) using methylene chloride as the solvent for the monomers, and the synthesis of Poly(EDOT-FPBA) with a side-link branch of 4-carboxy-3-fluorophenylboronic acid (FPBA) of PEDOT, Poly(EDOT-FPBA) films were prepared as electrochemical biosensors for glucose detection and inhibited non-specific proteins with high detection specificity (Fig. 6a) and exhibited stable Art signals at set test nodes (Fig. 6b) [22].

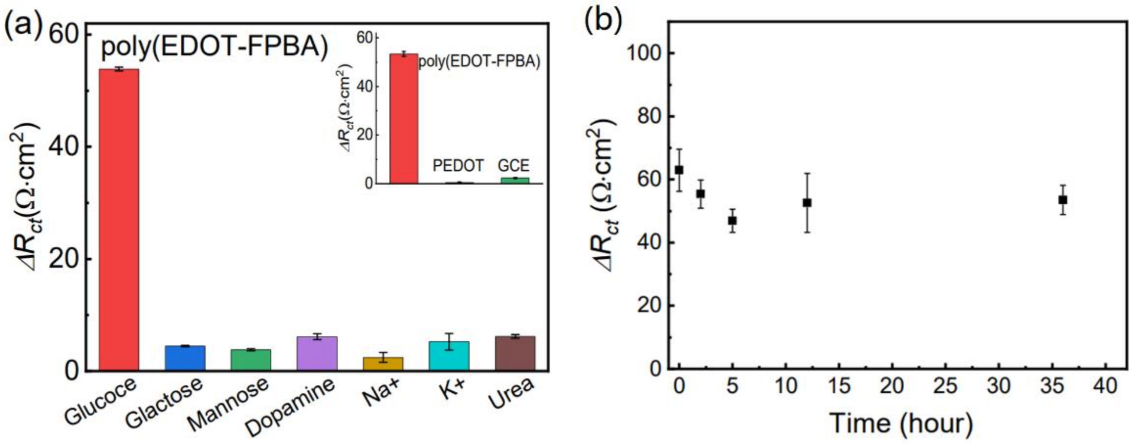

Figure 6. (a) Specificity test of Poly (EDOT-FPBA) film; (b) Stability test of Poly (EDOT-FPBA) film [22]

3.3.2. PEDOT:PSS

PEDOT, a derivative of polythiophene: PSS is a conductive polymer material with flexibility, high conductivity, excellent biocompatibility, and good stability at elevated temperatures, and is therefore often used to make flexible electrodes for sensor applications.

Epinephrine (EP) is an important hormone and neurotransmitter. Abnormal levels of its content are associated with diseases such as hypertension, hyperthyroidism and heart disease. At the same time, EP-related drugs are one of the drugs banned by the World Anti-Doping Organization. Therefore, rapid and accurate detection of EP in human blood has an important and practical significance. Hu et al. used the solution-coating and electropolymerization to construct an electrochemical sensor [23]. The materials of this sensor are poly(L-dopa)/PEDOT:PSS homogeneous material doped with reduced graphene (rGO). The biosensor has a wide linear detection range (0.10-16.50 μM) and low LOD (0.02 μM). It has good potential in the application of clinical monitoring of EP in human body, and broadens the field of electrochemical biosensors

Human sweat contains metabolites such as glucose, urea, lactic acid, and so on. By detecting the concentration of these molecules, the body's energy metabolism, diabetes management, and exercise endurance can thus be assessed. A microfluidic electrochemical sensor based on a PEDOT:PSS hydrogel is prepared by the research team of Xu, which enabled real-time monitoring of uric acid (UA) remained in human sweat [24]. The sensor has a sensitivity of 0.875 μA. According to Zhang [25], a sensor with two-terminal based on the use of silver/silver-chloride nanoparticles and bromo muscovite phenol blue-modified PEDOT:PSS has been prepared by Luca et al. for the selective determination of chloride ion concentration as well as pH. The feasibility of this biosensor has been demonstrated in the detection of human sweat.

3.4. Other Conductive Polymers

The importance of biocompatibility in biosensors is self-evident, and the development of biocompatible polymers as conductive substrates for composites has a broad application prospect.

Melanin is a natural polymer widely found with human skin, mucous membranes, etc., with a conjugated backbone. Ozlu et al. synthesized highly conductive melanin-like polymers (eMLP) using electrochemical polymerization and coated them on bare gold electrodes, which can be applied to non-enzymatic glucose biosensors (Fig. 7a) [26]. After coating with eMLP, the impedance of the electrode was reduced by 2 orders of magnitude and possessed a linear range of up to 70 μM.

Electrochemical sensors have the advantages of short detection time and high detection accuracy, which are widely used in the field of food safety testing. However, there are not many applications of polymers in the nonenzymatic electrochemical sensors involved, and one of the more typical ones is chitosan (CHI). Chitosan has good film-forming ability and harmless biocompatibility, such performance can be a unique advantage in an immobilization platform for biomolecules. According to Petrucci et al., an electrochemical sensor based on an AuNPs/CHI nanocomposite film-modified electrode successfully determined caffeic acid in a complex matrix [27]. Among others, the microstructure and surface functional groups of this modified electrode are also important. As seen in Fig. 7b, AuNPs and CHI films combine to form a collaborative network. The addition of AuNPs significantly improves the electron transfer ability of the conductive polymer. The NH3+ group on the surface of CHI can be specifically combined with the coffee molecules to achieve the purpose of detection.

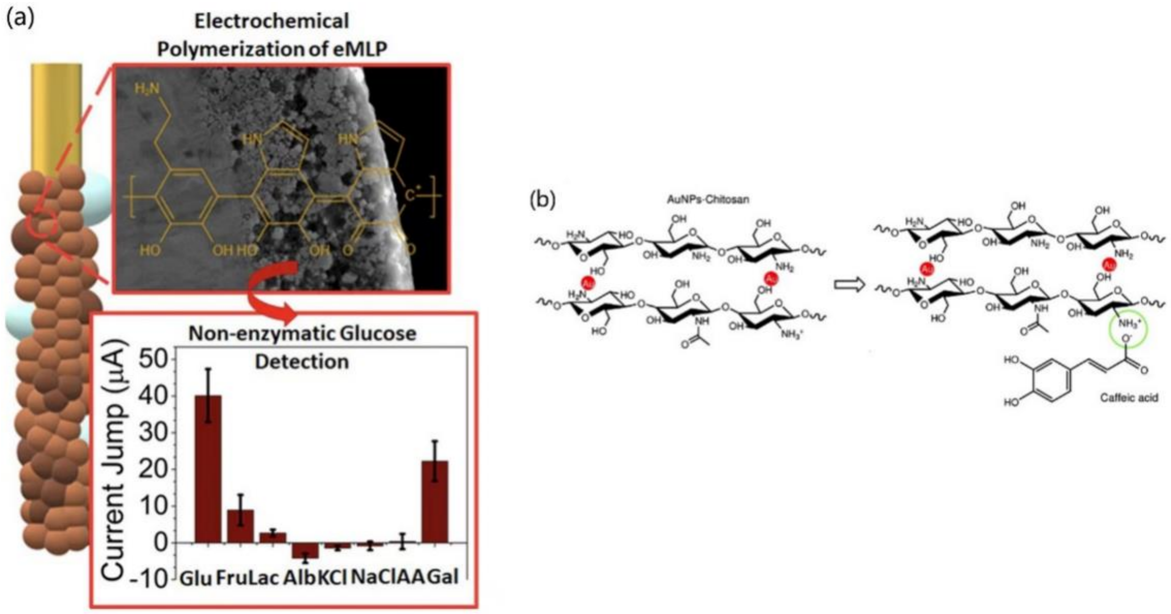

Figure 7. (a) Schematic of the coating of eMLP and the specificity of the detection of glucose [26]; (b) Schematic of the interaction between AuNPs/chitosan nanocomposites and caffeic acid [27]

4. Summary

This paper reviews recent research advances in materials used on nonenzymatic electrochemical biosensors in recent years and highlights several popular conducting polymers for electrode modification, including polyaniline, polypyrrole, polythiophene and its derivatives, and other special polymers. These types of electrochemical sensors break through the limitations of traditional enzyme-based sensors and promise to be more sensitive, faster and more specific sensing tools. Nanomaterials, with their own excellent properties as metals or carbons, enable them to become popular electrode materials for electrochemical biosensors, while conductive polymers, although not electrochemically outstanding enough, are able to enhance the specific properties of the sensors when compounded with nanomaterials. With the booming development of wearable electronic devices, based on the good biocompatibility and structural properties of polymers, one of the hotspots in the future is the use of conductive polymers to study wearable and flexible electronic sensor devices, and this material provides another direction for the application of nonenzymatic electrochemical biosensors.

References

[1] Yang Xuanyu, Qiu Pengpeng, Yang Jianping, et al. Mesoporous materials–based electrochemical.

[2] biosensors from enzymatic to nonenzymatic. Small, 2021, 17 (9): 1904022.

[3] Muhammad B, Muhammad A, Cheng Hairong, et al. multi-point enzyme immobilization, surface chemistry, and novel platforms: a paradigm shift in biocatalyst design. Critical Reviews in Biotechnology, 2019, 39 (2): 202 - 219.

[4] Xia Haiyan, Wang Xintian, Liu Lixia, et al. Research progress of nanomaterials applied to enzyme-free electrochemical biosensors. Journal of Analytical Science, 2023, 39 (02): 240 - 247.

[5] Inzelt G, Scholz F. Conducting polymers: A new era in electrochemistry. Germany: Springer Science & Business Media, 2008.

[6] Zhong Yanyu, Wang Zhengyun, Liu Hongfang. Progress in electrochemical sensing of ascorbic acid. Progress in Chemistry, 2023, 35 (2): 219 - 232.

[7] Wang Yangyang, Kong Jingyi, Xue Ruifang, et al. Highly stable, stretchable, and transparent electrodes based on dual-headed Ag@Au core-sheath nanomatchsticks for non-enzymatic glucose biosensor. Nano Res, 2023, 16 (1): 1558 - 1567.

[8] Zhang Jing, Kuang Zhujun, Li Hui, et al. Electrode surface roughness greatly enhances the sensitivity of electrochemical non-enzymatic glucose sensors. Journal of Electroanalytical Chemistry, 2022, 919: 116541.

[9] Sajna M S, Cabibihan J J, Malik R A, et al. Nonenzymatic electrochemical lactic acid sensor using CuO nanocomposite. Materials Science and Engineering: B, 2023, 288: 116217.

[10] Bao Lifeng, Wu Jian, Dong Mingjian, et al. Preparation of enzyme-free glucose sensor by nickel and zinc oxide nanomodified copper electrode. Journal of Materials Science and Engineering, 2020, 38 (2): 194 - 200.

[11] Sen S, Roy A, Sanyal A, et al. A nonenzymatic reduced graphene oxide-based nanosensor for parathion. Beilstein J. Nanotechnol, 2022, 13: 730 – 744.

[12] Jia Huixian, Shang Ningzhao, Feng Yue. Facile preparation of Ni nanoparticle embedded on mesoporous carbon nanorods for non-enzymatic glucose detection. Journal of Colloid and Interface Science, 2021, 583: 310 - 320.

[13] Zhang Jiaojiao, Wang Xiaojun, Zhang Zhuoya. Construction of flexible electrodes using carbon nanofibre/Pt nanosheets for glucose detection. Materials Guide, 2022, 36 (9): 21010143 - 6.

[14] Kun Tian, Prestgard M, Tiwari A. A review of recent advances in nonenzymatic glucose sensors. Materials Science and Engineering: C, 2014, 41:100 - 118.

[15] Jia Linan. Preparation of PANI/HAP/NF composites and research on enzyme-free glucose biosensor. Northeastern University, 2022.

[16] Zhao Chulei. Research on biosensors based on polyaniline composite nanomaterials. Shihezi University, 2020.

[17] Kadri Y, Bekri-Abbess I, Herrasti P. Highly sensitive enzyme-free sensor based on a carbon paste electrode modified with binary zinc oxide/polyaniline nanocomposites for dopamine, ascorbic acid and uric acid sensing. Electroanalysis, 2023, 35 (4): e202200248.

[18] Lu Yao, Wang Wenlian. Enzyme-free glucose detection system using flexible conductive carbon cloth as electrode substrate. Electronic Technology Application, 2020, 46 (6):101 - 104.

[19] Nagarajan A, Sethuraman V, Sridhar T M, et al. Development of Au@NiO decorated polypyrrole composite for non-Enzymatic electrochemical sensing of cholesterol. Journal of Industrial and Engineering Chemistry, 2023, 120: 460 - 466.

[20] Xu Ting. Electrochemical sensors constructed by polypyrrole@polyhexanolactone electrospun fibres and metal oxide nanocomplexes and their applications. Shanghai Normal University, 2018.

[21] Hashemi S A, Mousavi S M, Bahrani S. Polythiophene silver bromide nanostructure as ultra-sensitive non-enzymatic electrochemical glucose biosensor. European Polymer Journal, 2020, 138: 109959.

[22] Masood T, Asad M, Riaz S. Non-enzymatic electrochemical sensing of dopamine from COVID-19 quarantine person. Materials Chemistry and Physics, 2022, 289: 126451.

[23] Bao Wenji. Synthesis and electrochemical biosensing study of poly(vinylenedioxythiophene) derivatives. Inner Mongolia University for Nationalities, 2023.

[24] Hu Yile, Yang Hui, Li Wei, et al. Screen-printed electrochemical sensor based on reduced graphene doped poly (l-dopa)/pedot: pss composites for epinephrine detection. International Journal of Electrochemical Science, 2021, 16 (12): 211224.

[25] Possanzini L, Decataldo F, Mariani F, et al. Textile sensors platform for the selective and simultaneous detection of chloride ion and pH in sweat. Scientific Reports, 2020, 10 (1): 17180.

[26] Zhang Haowei, Wang Yidong, Xuan Xueting, et al. Conducting polymer PEDOT: PSS and its research progress in flexible biomedical sensors. Beijing Biomedical Engineering, 2023, 42 (3): 322 - 326.

[27] Ozlu B, Shim B S. Highly conductive melanin-like polymer composites for nonenzymatic glucose biosensors with a wide detection range. ACS Applied Polymer Materials, 2022, 4 (4): 2527 – 2535.

[28] Petrucci R, Pasquali M, Scaramuzzo F A, et al. Recent advances in electrochemical chitosan-based chemosensors and biosensors: applications in food safety. Chemosensors, 2021, 9 (9): 254.