Acta Microscopica Vol. 28, No.3, 2019, pp.602-610

Application Technology of Electrochemical Sensors Based on New Nanomaterials

Shaojun Zhang
College of Naval Architecture and Marine Engineering, Shandong Jiaotong University, Weihai, China
201168@sdjtu.edu.cn

Mingyu Wang*
College of Naval Architecture and Marine Engineering, Shandong Jiaotong University, Weihai, China
**Corresponding author (E-mail: 222001@sdjtu.edu.cn)*

Tianshu Wang
College of Naval Architecture and Marine Engineering, Shandong Jiaotong University, Weihai, China

Bingbing Liu
College of Naval Architecture and Marine Engineering, Shandong Jiaotong University, Weihai, China

Junsheng Meng
College of Naval Architecture and Marine Engineering, Shandong Jiaotong University, Weihai, China

Abstract
In order to study the application technology of electrochemical sensors based on new nanomaterials, AuNPs nanomaterials were prepared, and then Nafion-Ru $(bpy)_3^{2+}$-AuNPs complex solution was obtained by electrostatic interaction. The electrochemical immunosensor was prepared by electrochemiluminescence method, and its performance was analyzed by TTX (Tetrodotoxin) measurement. It was found that the new nano-materials were characterized by clear bright spots and successfully adhered. The electrochemical behavior of ECL (electro-chemiluminescent) immunosensor was analyzed. It was found that with the gradual modification of the materials, the impedance value gradually increased. The results showed that the biosensor was successfully constructed; in the optimization analysis of ECL experimental conditions, it was found that the optimum experimental conditions were PBS (Phosphate Buffered Saline) with pH of 7.5, incubation time of 60 minutes and deposition voltage of 0.6V; in TTX detection analysis, it was found that the signal of electro-chemiluminescent sensor tended to be stable after a certain scanning time, which indicated that the immunosensor was very stable, and suitable for subsequent TTX detection; in sample analysis, it was found that the RSD (relative standard deviation) was 3.4-8.1% and the recovery was 98.0-104.2% by adding different concentrations of TTX to standard samples. The experiments show that through the research on the application technology of the new nano-material electrochemical sensor, a label-free self-enhanced electrochemiluminescence immunosensor is prepared, which has good conductivity and sensitivity. Therefore, the immunosensor has good practical value. Although there are some shortcomings in the research process, it still provides a reference for the production of bio-immune labeling sensor in the future.

Key words: Nanomaterials, ECL, Electrochemical Sensors, TTX Method

1. Introduction

With the continuous improvement of people's living standards, health has become the focus of attention. With the progress of science and technology, the medical level is also developing rapidly. At the same time, the development of medical level is indispensable for the application of related materials. In recent years, the research on new nanomaterials has attracted wide attention. Graphene, as a representative of new nanomaterials, has made great progress in the fields of optoelectronics, catalysis and sensing due to its super carrier mobility, large theoretical specific surface area and good thermal conductivity [1,2]. The rapid development of graphene and the continuous progress of preparation technology have led to the emergence of many other new nanomaterials, especially transition metal dichalcogenides (TMDs) with graphene-like layered structure, which is widely concerned [3].

Although graphene has a variety of excellent properties, the untreated graphene itself has no gap. Only by changing its nanostructure or through a series of chemical functionalization methods can it change its corresponding defects, which to some extent limits the practical application and commercialization of graphene [4,5]. On the contrary, the new TMDs have abundant element reserves, unique crystal electronic structure and rich physical and chemical properties [6], which make up for the shortcomings of graphene to a certain extent, and have developed rapidly in the fields of electronic devices, catalysis, sensing and biomedicine. However, the detection methods of new nanomaterials are also very important. At present, a variety of detection methods have been developed, including chromatography, spectroscopy, chromatography-mass spectrometry, enzyme-linked immunosorbent assay, electrochemical methods, etc. [7-9]. Although these methods can detect target objects well, they still have some shortcomings, such as complex operation, time-consuming and laborious, expensive detector materials and so on, which cannot be well developed and popularized in practical application. However, electro-chemiluminescence (ECL) has been widely used in biology, medicine, environment and food analysis because of its high sensitivity, simple equipment, easy operation, high automation and low background signal [10]. The construction of ECL sensors with high sensitivity and good selectivity has become a top priority. Multifunctional nanomaterials and methods to improve the sensitivity of electrochemical sensors play an important role in the construction of sensors [11]. Nanomaterials have many excellent properties, such as good photoelectric properties, catalytic properties, large specific surface area and so on, and they show good application prospects in many fields.

In summary, in order to study the application technology of electrochemical sensors based on new nanomaterials, AuNPs nanomaterials are prepared, and then Nafion-Ru(bpy)$_3^{2+}$-AuNPs complex solution is obtained by electrostatic interaction. The electrochemical immunosensors are prepared by ECL method, and their properties are analyzed by TTX (Tetrodotoxin), to provide reference for the preparation of electrochemical sensors.

2. Method

2.1. Electrochemical Sensor

The electrochemical sensor is based on the electrical or electrochemical properties of the substance or molecule to be measured, and it can realize quantitative and qualitative analysis of the object to be measured. It is widely used in many fields, such as medical testing, biological testing, food testing, military and environmental pollutant monitoring, etc., and the sensor is mainly studied based on nano-material modified electrode [12].

The electrochemical sensor is tested by converting the chemical or biological information generated by the interaction between the substance to be measured and sensitive nanomaterials into electrical signals. The related working principle is shown in Figure 1 [13]. According to the principle, the electrochemical sensor mainly consists of two parts: identification element system (sensitive element) and conversion element system (converter) [14]. Generally, the electrode is the conversion element in the sensor, and the nano-material modified on the electrode becomes the sensing element. The function of recognition element is to selectively combine the measured substance with the conversion element system, so as to transform the chemical information of the tested substance into electrochemical information that can be recognized by the system. However, the conversion element system is to receive the signals transmitted from the identification element system, amplify or convert the response signals (amplify or transmit in the form of potential, current, impedance, etc.) through the electrode system, thereby establishing the relationship between the chemical quantities such as concentration and composition of the substance to be measured and the output signals, and realizing the quantitative or qualitative analysis of the substance to be measured [15,16]. From the schematic diagram, it can be seen that the electrode system interacting with the object to be measured is the key sensor to determine the whole sensor. Therefore, appropriate modification of working electrodes in the electrode system, such as the development of new electrodes and sensitizer electrodes, can improve the detection sensitivity and detection limit of electrochemical sensors for target substances. In the classification of electrochemical sensors, there are different working principles according to the detection signals. The electrochemical sensors can be roughly divided into potentiometric sensors, amperometric sensors and conductometric sensors [17].

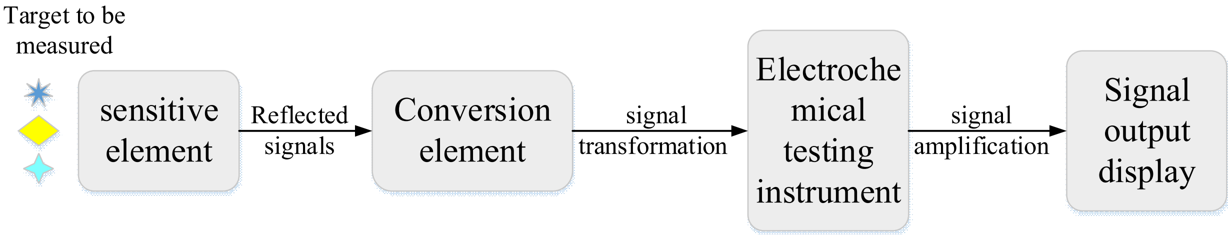


Figure 1. Principle of electrochemical sensor

2.2. Nanomaterials Commonly Used in Electrochemical Sensors

Nanomaterials generally refer to a kind of materials whose size is between atoms and macro-materials (1-100 nm). Nanomaterials have some unique effects, such as quantum effect, interface effect, small size effect, surface effect and macro tunneling effect. These unique effects make them have excellent properties (such as magnetics, thermology, optics, electricity, etc.) [18] that ordinary materials do not have. In addition, nano-materials can be modified on the surface of electrodes by dropping, electrostatic adsorption, electrodeposition or embedding, which can give full play to the excellent properties of nano-materials. It will be conducive to improving the sensitivity and detection limit of electrochemical sensors to target analytes. At the same time, it will promote the development of electrochemical sensors. At present, the widely used nanomaterials are graphene, carbon nanotubes, precious metals, metal oxides, polymers, etc. [19].

Physical and chemical methods are commonly used to prepare nano-catalytic materials, which are mainly divided into the following: mechanical cleavage, epitaxial growth, chemical vaper deposition, graphene oxide reduction, etc. Metals and metal oxide nano-catalytic materials have small size, excellent electrical conductivity and biocompatibility, good electrochemical window width and good chemical stability. It also has the advantages of nanomaterials (mass transfer, high effective surface area, efficient utilization of chemical or optical properties, etc.) [20]. Metals (Ag, Pt, Cu, Au, Pd, etc.), metal oxides (Fe_3O_4, CuO, MnOx, ZnO, SnO_2, TiO_2, NiO) as excellent catalysts nanoparticles, have various oxidation forms. They are modified to electrodes and combined with other nanomaterials, which will greatly improve the sensitivity of electrochemical sensors; composite nanomaterials have two or more different physical and chemical properties. Comparing with ordinary materials, composite materials not only have excellent properties (such as small size effect, interface effect, etc.) of single material, but also have synergistic function, which endows materials with unique properties and greatly broadens the application scope of composite nanomaterials in optics, electromagnetics, catalysis, medicine, sensors, etc. and many other fields. Composite nanomaterials prepared by various methods and modified electrodes by different methods can well combine the advantages of composite nanomaterials and electrochemical analysis. It can not only introduce the excellent and unique properties of composite nanomaterials into the interface of electrodes, but also provide the unique properties that traditional materials cannot provide. It can also combine the versatility of composite materials and electrodes. There will also be a large specific surface area of composite nanomaterials, which will improve the catalytic performance of the sensor.

2.3. Chemically Modified Electrode

Chemically modified electrodes are the basis of target detection by sensors and have important significance in sensor research. That is to say, by modifying the electrode with materials with specific functional groups, the surface chemical properties of the electrode can be changed so that it has the expected functions. Chemical modified electrode is the key to improve the selectivity and sensitivity of the sensor. The methods of modifying the electrode mainly include dropping coating, adsorption, covalent bonding and electrodeposition. The application of nanomaterials modified electrodes in sensor construction is illustrated by nanomaterials. As shown in Figure 2, the common zero-dimensional metal nanomaterials are AuNPs, PItNPs, AgNPs, CuNCs, etc. [21]. Metal nanometer material and its composite nanometer material have good electrical conductivity, which is one of the most widely used modified electrode materials at present. The common one-dimensional nanometer modified electrode is carbon nanotubes in sensor applications, which has a very large application prospect [22]. Graphene is a good example in two-dimensional nanomaterials, which has good electrical conductivity and mechanical properties and also has a large specific surface area. These nanomaterials can improve electrical conductivity very well [23].

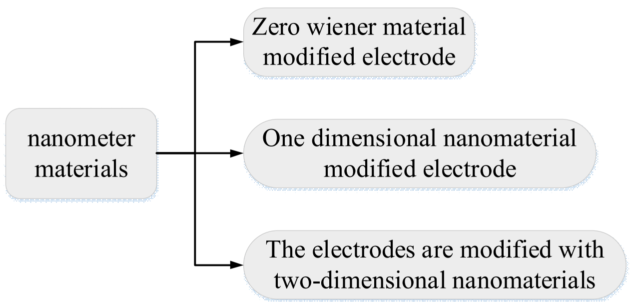


Figure 2. Classification of chemically modified electrodes with nanomaterials

2.4. Preparation of AuNPs Nanomaterials

In this experiment, we first stirred and heated 50 mL 0.01% HAuCl solution until boiling, and then quickly added 2 mL 1% sodium citrate. The solution boiled for about 10 minutes [24]. The color changed from yellow to black and then to wine red. AuNPs sol was obtained, cooled to room temperature and stored at 4°C for reserve.

2.5. Preparation of Nafion-Ru(bpy)$_3^{2+}$-AuNPs Compound

1mL above-mentioned AuNPs sol was mixed with 10μL 0.05mol·L^{-1}Ru (bpy)$_3^{2+}$ solution. The mixture was homogeneous by shaking. The static reaction lasted for about 10 minutes, which combined AuNPs with Ru (bpy) $_3^{2+}$ through electrostatic action. Then, 30μL Nafion solution were added to the mixed solution, and the mixed solution of Nafion-Ru (bpy) $_3^{2+}$-AuNPs was obtained by shaking and ultrasound for about 30 minutes[25].

2.6. Preparation of ECL Immunosensor

ECL analysis method was used, which has the advantages of high sensitivity, simple equipment, easy operation, high automation and low background signal. It has been widely used in the fields of biology, medicine, environment and food analysis. Pretreatment of glassy carbon electrode: The electrode was polished to the mirror surface with 1.0, 0.3 and 0.05m of α-Al_2O_3 powder in turn. Put them in distilled water, ethanol and distilled water for one minute respectively, then blow the surface of the electrode with nitrogen to dry. The process of electrode modification was as follows: first, 7μL Nafion-Ru (bpy)$_3^{2+}$-AuNPs complex solution was removed and dried on GCE surface at 37°C; then 10μL 100ng·mL^{-1}anti-TTX solution were dripped on the modified electrode and incubated at 4°C for 12 hours to obtain anti-TTX modified GCE/Nafion-Ru (bpy) $_3^{2+}$-AuNPs (GCE/Nafion-Ru (bpy) $_3^{2+}$-AuNPs/anti-TTX) and washed with ultra-pure water to remove the anti-TTX adsorbed physically; the washed electrodes were incubated in 100μL 1% BSA solution for 1 hour to block the non-specific binding sites and washed with distilled water[26].

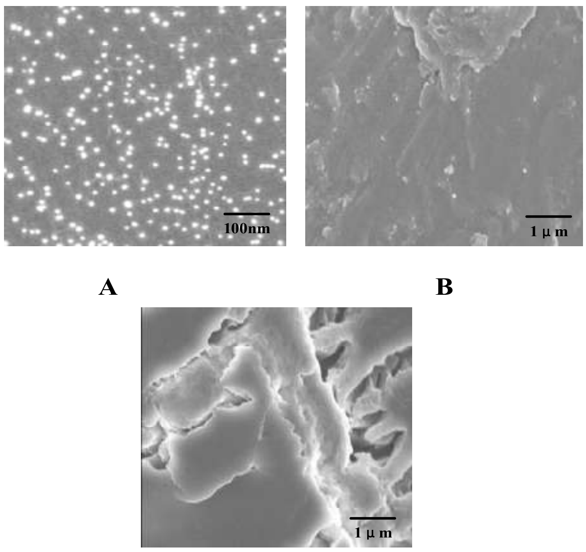
2.7. TTX Determination

The ECL immunosensor was incubated for 1 hour in 100μL TTX sample solution of different concentration at 37°C, then washed with distilled water and placed in 0.1mol·L^{-1} PBS (pH=7.4) test solution for ECL determination and the data were recorded. Scanning voltage ranges from 0 to 1.2V. The sweep speed is 100mV·s^{-1}. All data measurements are repeated at least three times to get the average [27].

3. Results and Discussion

3.1. Characterization and Analysis of New Nanomaterials

From Figure 3, it is seen that the appearance of AuNPs, Nafion-Ru (bpy)$_3^{2+}$-AuNPs and Nafion-Ru (bpy)$_3^{2+}$-AuNPs-anti-TTX are characterized by SEM. It is found that AuNPs are well dispersed and the particle size is uniform, about 11 nm. From Figure 3B, it can be seen that the Nafion Ru (bpy)$_3^{2+}$-AuNPs complex presents a thick plate-like membrane structure, and can clearly see that there are uniform and bright spots scattered on it, which indicates that Ru (bpy)$_3^{2+}$-AuNPs successfully attaches to the Nafion composite membrane and provides a good binding site for the antibody. From Figure 3C, it can be further seen that the thickness of the film increases when Anti-TTX is fixed on the surface of Nafion-Ru (bpy)$_3^{2+}$-AuNPs.



A B

C

Figure 3. SEM charts of new nanomaterials (A. AuNPs; B. Nafion-Ru (bpy)$_3^{2+}$-AuNPs; C. Nafion-Ru(bpy)$_3^{2+}$-AuNPs-anti-TTX)

3.2. Analysis of Electrochemical Behavior of ECL Immunosensor

The electrochemical characteristics of the ECL immunosensor constructed in this study are shown in Figure 4. It can be seen that the electrochemical impedance is also an effective means to characterize the change of electron transfer rate on the surface of the sensor. The impedance values of the modified electrodes were measured in the PBS ($0.1mol \cdot L^{-1}$, pH=7.5) solution containing $5.0mmol \cdot L^{-1}[Fe (CN)6]^{3-/4-}$ and $0.1mol \cdot L^{-1}$ KCl. The larger the semicircle diameter of the curve in the figure is, the greater the barrier ability of the electrode surface to $[Fe (CN)6]^{3-/4-}$ electron transfer is. As shown in the figure, the impedance value of curve A-E increases gradually with the gradual modification of the material. This result is consistent with the result of cyclic voltammetry, indicating that the biosensor has been successfully constructed [28].

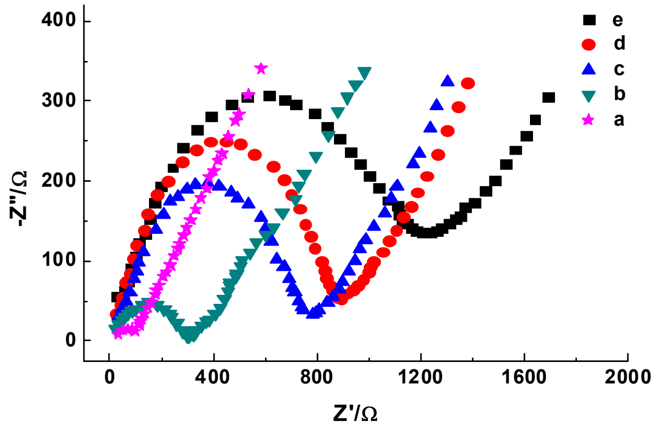


Figure 4. Impedance maps of different biosensor modified electrodes ((a) bare GCE, (b) GCE/Nafion-Ru $(bpy)_3^{2+}$-AuNPs, (c) GCE/Nafion-Ru(bpy) $_3^{2+}$-AuNPs/anti-TTX, (d) GCE/Nafion-Ru(bpy) $_3^{2+}$-AuNPs/anti-TTX/BSA, (e) GCENafion-Ru(bpy) $_3^{2+}$-AuNPs/anti-TTX/BSA/TTX)

3.3. Optimal Analysis of ECL Experimental Conditions

In order to obtain the best test conditions and improve the detection sensitivity of TTX, the pH of buffer solution and incubation time of target were optimized, respectively. Figure 5 investigates the effect of buffer solution pH in the range of 6.0-8.5 on ECL strength. Fig. 5A shows that the strength of ECL increases with the increase of pH in the range of 6.0-7.5, but decreases with the increase of pH in the range of 7.5-8.5. When the pH is 7.5, the strength of ECL reaches the maximum. The reason for this result may be that pH of the test solution affects the activity of protein molecule, which leads to the inactivation of protein molecule under strong acid and alkali conditions. Therefore, the pH of PBS used in this experiment is 7.5.

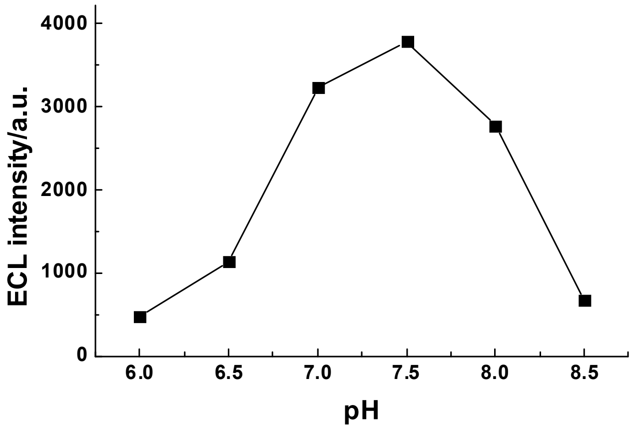


Figure 5. Effect of pH on ECL during the experiment

In the experimental study, time is also an important factor affecting the strength of ECL. The effects of incubation time from 15 min to 90 min on ECL strength were investigated. As shown in Figure 6, the strength of ECL increases with the extension of time within 15 min to 60 min, and there is no significant change in the strength of ECL between 60 min and 90 min. This may be due to the limited number of antibodies on the electrode surface and the saturation of target binding. Therefore, 60 min is the best incubation time.

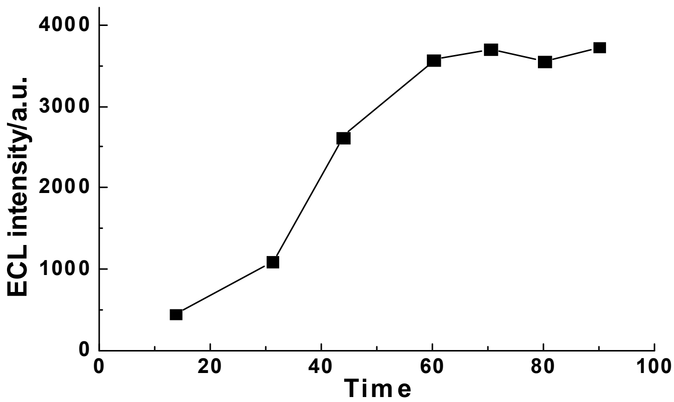


Figure 6. Effect of Time on ECL during the experiment

In experimental studies, the full deposition potential of composite nanomaterials is also very important for achieving optimal sensitivity. Therefore, in the solution with pH 7.5, the effect of deposition potential on peeling peak current was studied in the range of 0 to 1.2V. From Figure 7, it can be seen that the strength of ECL increases with time in the deposition voltage range of 0 to 0.6V, and decreases gradually in the range of 0.6 to 1.2V. This may be due to the limited number of antibodies on the electrode surface and the saturation of target binding. Therefore, 0.6V is the best deposition voltage [29].

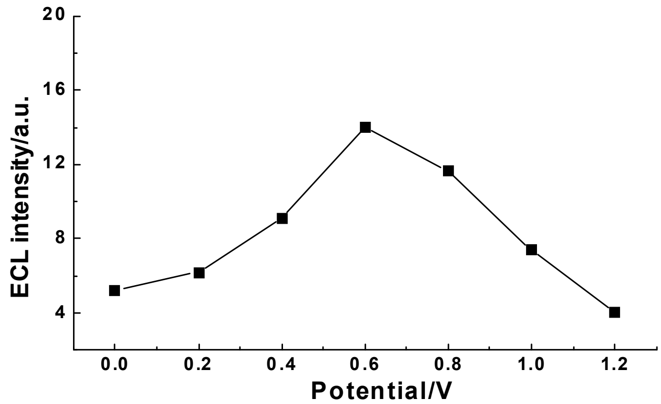


Figure 7. Effect of deposition voltage on ECL during experimental process

3.4. TTX Detection and Analysis

The stability of ECL signal is the most basic condition for sensor to be used in detection. The modified electrodes were incubated in 100μL 1000 ng·mL^{-1}TTX standard solution for 60 minutes and the stability of ECL signals was tested [30]. The changes of ECL signals in 9 cycles of continuous scanning from 0V to 1.2V were investigated. As shown in Figure 8, after a certain scanning time, the ECL signals tended to be stable, which indicated that the immunosensor had good stability and was suitable for subsequent TTX detection.

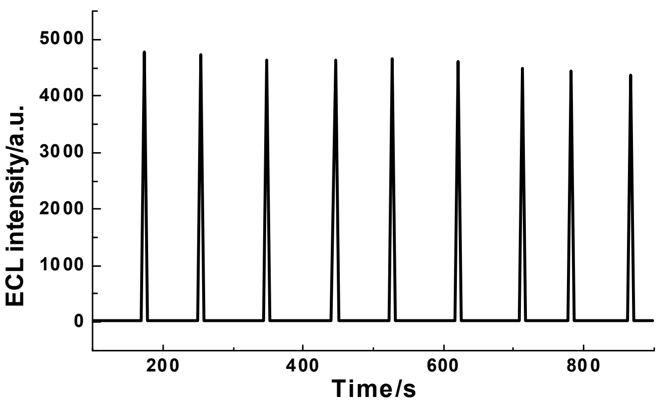


Figure 8. ECL intensity of ECL immunosensor scanning for 9 cycles in 0.1mol·L^{-1}PBS with pH=7.5.

3.4. Sample Analysis

Different concentrations of TTX labeled samples were added to the solution. The results in Figure 9 show that the RSD is 3.4-8.1% and the recovery is 98.0-104.2%. This shows that the immunosensor has good practical value.

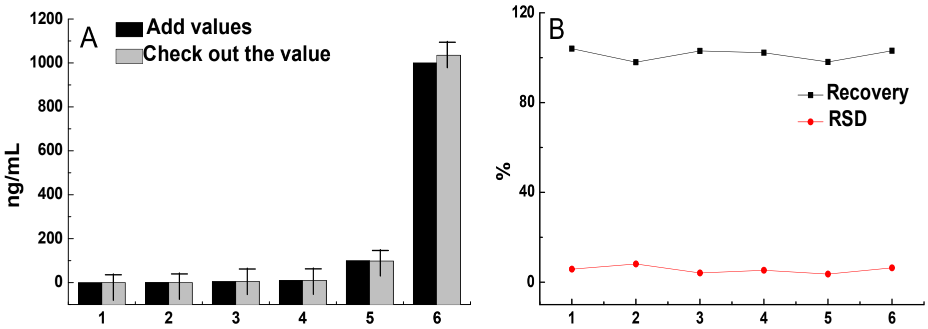


Figure 9. Detection of TTX in real samples (A. Marking value and detection value; B. Recovery rate and RSD)

4. Conclusions

In order to study the application technology of electrochemical sensors based on new nanomaterials, AuNPs nanomaterials were prepared, and then Nafion-Ru(bpy)$_3$$^{2+}$-AuNPs complex solution was obtained by electrostatic interaction. The electrochemical immunosensor was prepared by ECL method, and its performance was analyzed by TTX measurement [31]. Through the research, it was found that the new nano-materials had clear appearance and good adhesion. The electrochemical behavior of the ECL immunosensor showed that the impedance value increased gradually with the gradual modification of the materials, which indicated that the biosensor was successfully constructed [32]. In the optimization analysis of ECL experimental conditions, it was found that the pH of PBS was 7.5 and incubation time was 60 min, and it was the best experimental condition when the deposition voltage was 0.6V. The ECL signal tended to be stable after a certain scanning time was reached in TTX analysis, which indicated that the immunosensor had good stability and was suitable for subsequent TTX detection. In sample analysis, it was found that the RSD was 3.4-8.1% and the recovery was 98.0-104.2% by adding different concentration of TTX standard samples, and the immunosensor made had good practical value [33].

In summary, through the research on the application technology of the new nano-material electrochemical sensor, it is found that we have prepared a self-enhanced ECL immunosensor without label. TTX as Ru (bpy)$_3$$^{2+}$ co-reactant is directly modified to the surface of the electrode, assisted by good conductivity of AuNPs, which further improves the sensitivity of the immunosensor. It can provide a basis for the fabrication of bio-immune labeling sensor in the future. However, there are also some shortcomings in the research process. For example, Au used in the experiments belongs to one of precious metals. Therefore, more metal materials can be tried in the later research process in order to prepare nano-material sensors with more reference value.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51609131); Shandong Provincial Natural Science Foundation, China (ZR2017MEE031); Shandong Provincial Higher Educational Science and Technology Foundation, China (KJ2018BBA015); Weihai Science and Technology Development Plan (2017GNS18); Shandong Jiaotong University Doctoral Research Initiation Fund, and Shandong Jiaotong University “Climbing” Research Innovation Team Program.

References

[1] Zafarani H R, Mathwig K, Sudhölter E J R, et al. (2017) “Electrochemical amplification in side-by-side attoliter nanogap transducers”, *ACS Sensors*, 2(6), pp. 724-728.

[2] Li Y, Zhang P, Ouyang Z, et al. (2016) “Nanoscale Graphene Doped with Highly Dispersed Silver Nanoparticles: Quick Synthesis, Facile Fabrication of 3D Membrane - Modified Electrode, and Super Performance for Electrochemical Sensing”, *Advanced Functional Materials,* 26(13), pp. 2122-2134.

[3] Engel M, Bryant P W, Neumann R F, et al. (2017) “A Platform for Analysis of Nanoscale Liquids with an Array of Sensor Devices Based on Two-Dimensional Material”, *Nano Letters,* 17(5), pp. 2741-2746.

[4] Wolfrum B, Kätelhön E, Yakushenko A, et al. (2016) "Nanoscale electrochemical sensor arrays: redox cycling amplification in dual-electrode systems", *Accounts of Chemical Research,* 49(9), pp. 2031-2040.
[5] Park J K, Kang T G, Kim B H, et al. (2018). "Real-time humidity sensor based on microwave resonator coupled with PEDOT: PSS conducting polymer film", *Scientific Reports*, 8(1), pp. 439.
[6] Zhou H, Zhang L, Zhang D, et al. (2016) "A universal synthetic route to carbon nanotube/transition metal oxide nano-composites for lithium ion batteries and electrochemical capacitors", *Scientific Reports,* 6, pp. 37752.
[7] Zhang Z, Schwanz D, Narayanan B, et al. (2018) "Perovskite nickelates as electric-field sensors in salt water", *Nature*, 553(7686), pp. 68.
[8] Morales ‐ Narváez E, Baptista ‐ Pires L, Zamora ‐ Gálvez A, et al. (2017) "Graphene ‐ Based Biosensors: Going Simple", *Advanced Materials*, 29(7), pp. 1604905.
[9] Velmurugan J, Agrawal A, An S, et al. (2017) "Fabrication of scanning electrochemical microscopy-atomic force microscopy probes to image surface topography and reactivity at the nanoscale", *Analytical Chemistry*, 89(5), pp.2687-2691.
[10] Park M, Park Y J, Chen X, et al. (2016) "MoS2 ‐ based tactile sensor for electronic skin applications", *Advanced Materials*, 28(13), pp. 2556-2562.
[11] Liu W, Liu N, Yue Y, et al. (2018) "Piezoresistive pressure sensor based on synergistical innerconnect polyvinyl alcohol nanowires/wrinkled graphene film", *Small,* 14(15), pp. 1704149.
[12] Kim J, Kumar R, Bandodkar A J, et al. (2017) "Advanced materials for printed wearable electrochemical devices: A review", *Advanced Electronic Materials*, 3(1), pp. 1600260.
[13] Nag A, Mitra A, Mukhopadhyay S C. (2018). "Graphene and its sensor-based applications: a review", *Sensors and Actuators A: Physical*, 270, pp. 177-194.
[14] Patel G, Pillai V, Vora M. (2019) "Liquid Phase Exfoliation of Two-Dimensional Materials for Sensors and Photocatalysis—A Review", *Journal of Nanoscience and Nanotechnology*, 19(8), pp. 5054-5073.
[15] Qi D, Liu Y, Liu Z, et al. (2017) "Design of architectures and materials in in ‐ plane micro ‐ supercapacitors: current status and future challenges", *Advanced Materials*, 29(5), pp. 1602802.
[16] Chae J, An S, Ramer G, et al. (2017) "Nanophotonic atomic force microscope transducers enable chemical composition and thermal conductivity measurements at the nanoscale", *Nano letters*, 17(9), pp. 5587-5594.
[17] Wang H, Zhang S, Li S, et al. (2018) "Electrochemical sensor based on palladium-reduced graphene oxide modified with gold nanoparticles for simultaneous determination of acetaminophen and 4-aminophenol", *Talanta*, 178, pp. 188-194.
[18] Chen M, Gan N, Zhou Y, et al. (2017) "A novel aptamer-metal ions-nanoscale MOF based electrochemical biocodes for multiple antibiotics detection and signal amplification", *Sensors and Actuators B: Chemical*, 242, pp. 1201-1209.
[19] Gautam V, Singh K P, Yadav V L. (2018) "Preparation and characterization of green-nano-composite material based on polyaniline, multiwalled carbon nano tubes and carboxymethyl cellulose: For electrochemical sensor applications", *Carbohydrate Polymers*, 189, pp. 218-228.
[20] Maduraiveeran G, Jin W. (2017) "Nanomaterials based electrochemical sensor and biosensor platforms for environmental applications", *Trends in Environmental Analytical Chemistry*, 13, pp. 10-23.
[21] Zhang W, Zong L, Geng G, et al. (2018). "Enhancing determination of quercetin in honey samples through electrochemical sensors based on highly porous polypyrrole coupled with nanohybrid modified GCE", *Sensors and Actuators B: Chemical*, 257, pp. 1099-1109.
[22] Zhou, D., Wu, Y., Gao, F., Breaz, E., Ravey, A., & Miraoui, A. (2017) "Degradation Prediction of PEM Fuel Cell Stack Based on Multiphysical Aging Model with Particle Filter Approach", *IEEE Transactions on Industry Applications*, 53(4), pp. 4041-4052.
[23] Song, Y., & Deng, Y. (2019) "A new method to measure the divergence in evidential sensor data fusion", *International Journal of Distributed Sensor Networks*, 15(4), https://doi.org/10.1177/1550147719841295.
[24] Xiao, F. (2019). "Multi-sensor data fusion based on the belief divergence measure of evidences and the belief entropy", *Information Fusion*, 46, pp. 23-32
[25] CHEN, J., WANG, S. Q., & YANG, G. Q. (2015) "Nonlinear Optical Limiting Properties of Organic Metal Phthalocyanine Compounds", *Acta Physico-Chimica Sinica*, 31(4), pp. 595-611.
[26] Shan, P. F., & Lai, X. P. (2018) "Numerical Simulation of the Fluid–Solid Coupling Process During the Failure of a Fractured Coal–Rock Mass Based on the Regional Geostress", *Transport in Porous Media,* 124(3), pp. 1061-1079.
[27] Yang, A. M., Yang, X. L., Chang, J. C., Bai, B., Kong, F. B., & Ran, Q. B. (2018). "Research on a fusion scheme of cellular network and wireless sensor for cyber physical social systems", *IEEE Access*, 6, pp. 18786-18794.
[28] Fu, H., Li, Z., Liu, Z., & Wang, Z. (2018). "Research on big data digging of hot topics about recycled water use on micro-blog based on particle swarm optimization", *Sustainability*, 10(7), pp. 2488.
[29] Liu, Z., Wang, F., Zhang, Y., & Chen, C. P. (2016) "Fuzzy adaptive quantized control for a class of stochastic nonlinear uncertain systems", *IEEE Transactions on Cybernetics*, 46(2), pp. 524-534.
[30] Liu, R., Li, B., & Jiang, Y. (2016) "A fractal model based on a new governing equation of fluid flow in fractures for characterizing hydraulic properties of rock fracture networks", *Computers and Geotechnics*, 75, pp. 57-68.

[31] Liu, W., Du, Y., & Yan, C. (2012) "Soundness preservation in composed logical time workflow nets", *Enterprise Information Systems*, 6(1), pp. 95-113.
[32] Du, Y., Jiang, C., Zhou, M., & Fu, Y. (2009) "Modeling and monitoring of E-commerce workflows", *Information Sciences*, 179(7), pp. 995-1006.
[33] Du, Y., Qi, L., & Zhou, M. (2011) "A vector matching method for analysing logic Petri nets", *Enterprise Information Systems*, 5(4), pp. 449-468.