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Electrochemical Sensor Coating Based on Electrophoretic Deposition of Au-Doped Self-Assembled Nanoparticles

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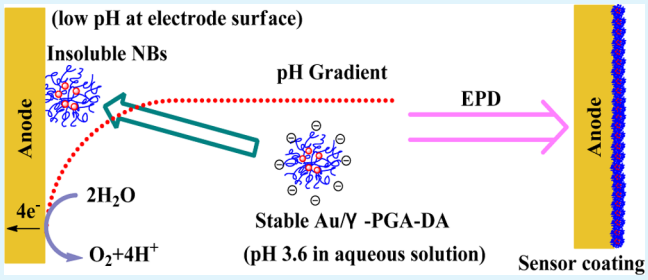
Supporting Information

ABSTRACT: The electrophoretic deposition (EPD) of self-assembled nanoparticles (NPs) on the surface of an electrode is a new strategy for preparing sensor coating. By simply changing the deposition conditions, the electrochemical response for an analyte of deposited NPs-based coating can be controlled. This advantage can decrease the difference between different batches of sensor coating and ensure the reproducibility of each sensor. This work investigated the effects of deposition conditions (including deposition voltage, pH value of suspension, and deposition time) on the structure and the electrochemical response for L-tryptophan of sensor coating formed from Au-doped poly(sodium γ-glutamate) with pendant dopamine units nanohybrids (Au/γ-PGA−DA NBs) via the EPD method. The structure and thickness of the deposited sensor coating were measured by atomic force microscopy, which demonstrated that the structure and thickness of coating can be affected by the deposition voltage, the pH value of the suspension, and the deposition time. The responsive current for L-tryptophan of the deposited sensor coating were measured by differential pulse voltammetry, which showed that the responsive current value was affected by the structure and thickness of the deposited coating. These arguments suggested that a rich design-space for tuning the electrochemical response for analyte and a source of variability in the structure of sensor coating can be provided by the deposition conditions. When Au/γ-PGA−DA NBs were deposited on the electrode surface and formed a continuous coating with particle morphology and thinner thickness, the deposited sensor coating exhibited optimal electrochemical response for L-tryptophan.



KEYWORDS: *electrophoretic deposition, electrochemical sensor, sensor coating, self-assembled nanoparticles, Au/γ-PGA−DA nanohybrids*

INTRODUCTION

Being a precursor of hormone for neurotransmitter serotonin and other relevant biomolecules, L-tryptophan is an essential amino acid for the human body and an important component of protein biosynthesis in the living organisms.[1,2] However, many side effects can be caused due to large quantity or improper intake of L-tryptophan in the body. So, it is urgent to find a simple and rapid method for determining L-tryptophan with high selectivity and sensitivity.[1,2] The electrochemical method has received considerable attention for determining L-tryptophan due to its high sensitivity, simple operation mode, low cost, and L-tryptophan's inherent electroactivity. However, the direct oxidation of L-tryptophan at bare electrode is not satisfactory because of high overpotential and slow electron transfer processes. To overcome these defects, various materials have been used to modify electrode for enhancing the selectivity and sensitivity of the electrochemical methods.[3,4]

The self-assembled nanoparticles (NPs), which combined the unique physical or chemical properties of amphiphilic polymers and the hierarchical nanophase-separated nanoeffect resulted from the self-assembly of amphiphilic polymers, have been used in electrochemical sensors.[5−7] Miao et al.[8] first used self-assembled botanical inositol hexakisphosphoric NPs and horseradish peroxidase via casting method to fabricate biosensor coating, which possessed a low detection limit (0.1 μmol·L^{-1}) and fast response (3 s) for H_2O_2. Sigolaeva et al.[9] used self-assembled polybutadiene-*block*-poly(2-(dimethylamino) ethyl methacrylate) NPs as a platform for immobilizing enzyme to prepare sensor coating via layer-by-layer deposition method. In our previous work, the Au NPs were used to dope poly(sodium γ-glutamate) with pendant dopamine units (γ-PGA−DA) NPs, obtaining the Au/γ-PGA−DA nanohybrids (NBs). Through the casting method, Au/γ-PGA−DA NBs formed sensor coating on the electrode surface. The prepared sensor coating exhibited a good analytical performance for L-tryptophan. The introduction of Au NPs in NBs coating played an important role in enhancing the conductivity between NBs coating and the underlying electrode.[10] Despite all of these

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developments, it was a great challenge to controllably integrate the self-assembled NPs on the surface of electrode to prepare sensor coating.

Electrophoretic deposition (EPD) is a commonly used method for preparing coating. The deposited weight and coatings structure prepared by the EPD methods can be easily controlled by deposition conditions like the deposition time, the deposition voltage, the salt concentration in suspension, the pH value, and the concentration of the suspension.[11−13] Our previous work reported that the molecular imprinted NPs self-assembled from amphiphilic polymer and template molecule can be deposited on the surface of electrode for preparing molecular imprinted sensor coating. The resultant sensor coatings demonstrated broad linearity and good selectivity and reproducibility for detecting the template molecule.[7,14−17] The electrochemical response for an analyte of the deposited NPs-based sensor coating can be controlled by simply changing the deposition conditions. This advantage can decrease the difference between different batches of sensor coating and ensure the reproducibility of each sensor.

In this work, the Au/γ-PGA−DA NBs were deposited from the aqueous solutions onto the gold electrode (GE) surface via the EPD method for preparing the sensor coating. The effects of deposition conditions on the structure and the electrochemical response for L-tryptophan of deposited NBs coating were investigated. The deposition mechanism is shown in Figure 1. Au/γ-PGA−DA NBs were pH-responsive NPs. At high pH value, the carboxyl groups of Au/γ-PGA−DA NBs were deprotonated, making them water-dispersed anionic NBs. When a constant positive voltage was applied, the negatively charged Au/γ-PGA−DA NBs were attracted and moved toward GE; the electrochemical reactions generated the low pH conditions, which instigated the carboxylate groups (−COO^-) to undergo protonation (to form −COOH) and to be deposited at the anode surface.

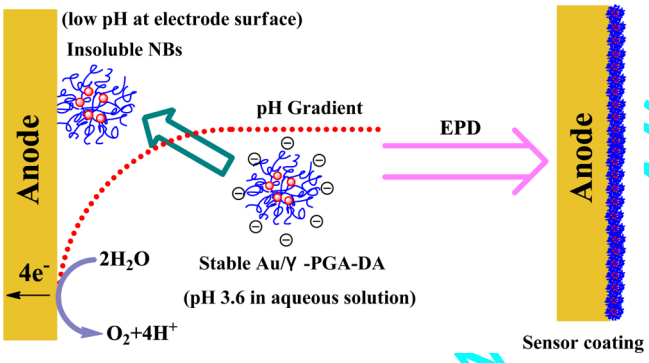

Figure 1. EPD mechanism of Au/γ-PGA−DA NBs on GE surface for fabricating sensor coating.

EXPERIMENTAL SECTION

Materials. Poly(sodium γ-glutamate) (γ-PGA, M_w 700 000−100 000 KDa) was supplied by AMRESCO. Dopamine (DA), hydrochloric acid (HCl), sodium hydroxide (NaOH), phosphate, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), sodium chloride (NaCl), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$), *N*-hydroxysuccinimide, and L-tryptophan were purchased from Aladdin Chemistry Co. Ltd., China.

EPD of Au/γ-PGA−DA NBs for Preparing Sensor Coating. The preparation of Au/γ-PGA−DA NBs has been reported in our previous published work.[10] Herein, the Au/γ-PGA−DA NBs suspension prepared from the molar ratio (Au^{3+} to the repeated units of γ-PGA−DA) of 0.3 was used as a deposition bath for EPD. The concentration of Au/γ-PGA−DA NBs suspension was 0.1 mol·L^{-1}.

The EPD was performed under a constant positive voltage using a three-electrode system. A bare GE, which was first treated by polishing cloth with some alumina particles and then cleaned by ultrasonication in ethanol and ultrapure water, was used as the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode. A platinum electrode served as the counter electrode. The potentials applied to the working electrode were in reference to the SCE. The distance between any two electrodes was 3 cm. The effective area of GE was 28.26 mm^2.

After EPD, the GE coated with Au/γ-PGA−DA NBs was removed from the deposition bath. It was then rinsed and kept under conditions that prevented the coating from redissolving. To form a uniform sensor coating, a beaker was used to cover the electrode, slowing the evaporation rate of water in air at room temperature. The effects of the deposition voltage, the pH value of Au/γ-PGA−DA NBs suspension, and the deposition time on the structure and the electrochemical response for L-tryptophan of sensor coating were investigated, respectively.

Characterization. The ζ potential and the particle size of Au/γ-PGA−DA NBs were determined by a Nano-ZS instrument (Malvern Instruments) at 20 °C. Atomic force microscopy (AFM) measurements were conducted on a CSPM3300 (Benyuan Co.) with a horizontal resolution of 0.2 nm and a vertical resolution of 0.1 nm. The morphology of Au/γ-PGA−DA NBs coating was confirmed by a field emission scanning electron microscopy (SEM) (Hitachi S-4800) operating at 1 kV. The pH value of the solution was detected by a precision digital pH meter (pHS-3C). All of the electrochemical experiments were conducted on an Epsilon electrochemical workstation (BAS) using a three-electrode system. The GE coated with Au/γ-PGA−DA NBs was used as the working electrode. A SCE was used as the reference electrode. A platinum electrode served as the counter electrode. The potentials applied to the working electrode were in the reference to the SCE.

RESULTS AND DISCUSSION

Deposition Voltage Effect on the Structure and Electrochemical Response of Sensor Coating. Deposition voltage is a key parameter affecting the EPD kinetics and the coating structure. Figure 2 shows the current−time curves of the coatings formed from the Au/γ-PGA−DA NBs suspension with the pH value of 3.6 under different deposition voltages. The deposition time is 30 s. It can be seen that during the EPD process, prolonging the deposition time leads to the current values first decreasing significantly and then becoming stable when the deposition voltage is in the range of 0.5−1.5 V. In

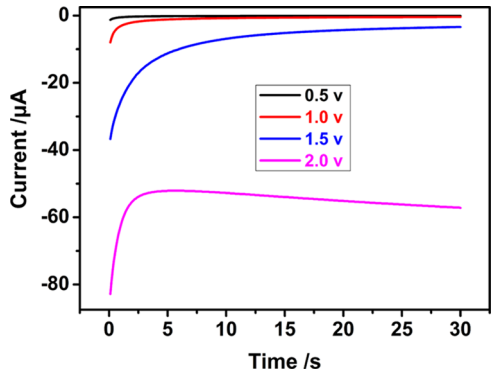

Figure 2. Current−time curves during the Au/γ-PGA−DA NBs EPD process under different deposition voltages. The pH value of NBs suspension and the deposition time were 3.6 and 30 s, respectively.

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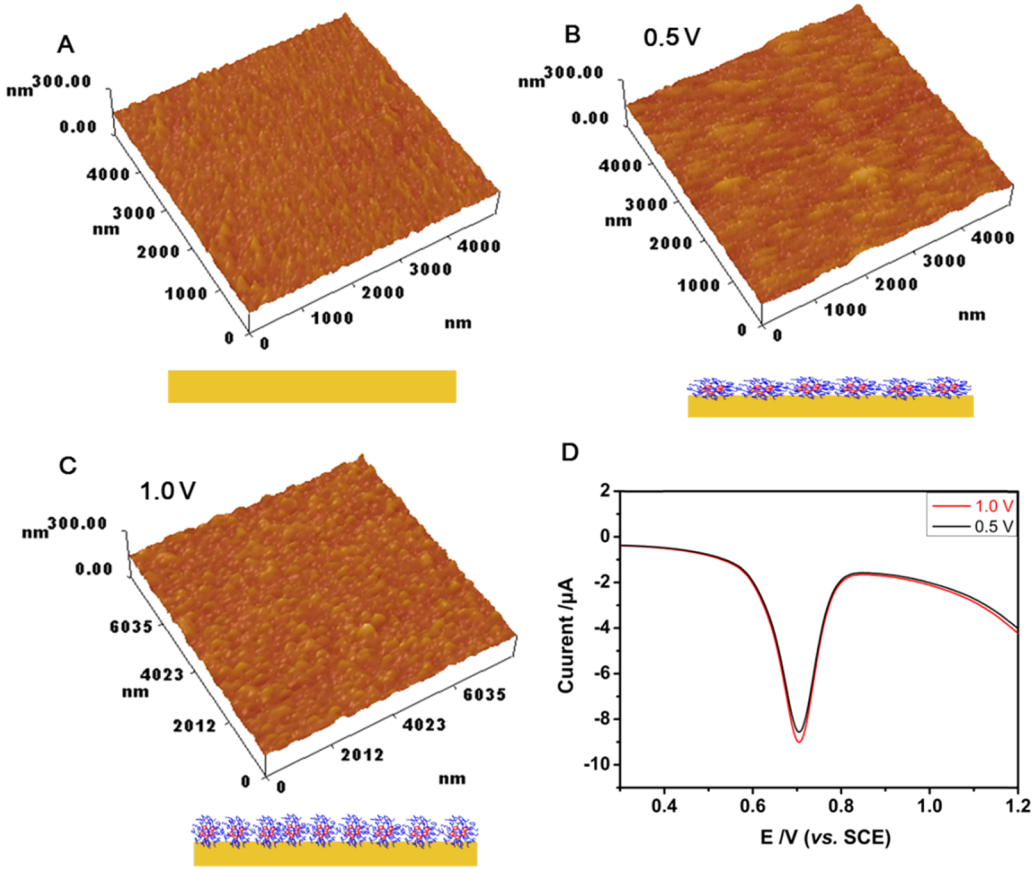

Figure 3. AFM three-dimensional (3D) images and illustrations of bare GE (A) and sensor coatings formed from Au/γ-PGA−DA NBs under 0.5 V (B) and 1.0 V (C). (D) Differential pulse voltamograms (DPVs) for L-tryptophan (1×10^{-5} mol·L^{-1}) of sensor coatings formed from NBs under different deposition voltages. The pH value of Au/γ-PGA−DA NBs suspension and the deposition time were 3.6 and 30 s, respectively.

addition, the current values increase with increase in the deposition voltage at the same deposition time. However, when the deposition voltage is set as 2.0 V, the current values decrease significantly first and then increase gradually with prolonging of the deposition time. It is reported that an unstable current can affect the quality and properties of the deposited coating.[18] It may be necessary that the deposition voltage for EPD of Au/γ-PGA−DA NBs should be lower than 2 V.

The structure of the dried sensor coatings formed from Au/γ-PGA−DA NBs under different deposition voltages are investigated by SEM. It can be observed from Figure S1 in the Supporting Information that more continuous coatings are formed at the lower deposition voltages (0.5 or 1.0 V), whereas the coatings quality deteriorate and are porous or sponge-like when relatively higher deposition voltages (1.5 or 2.0 V) are used. The reason may be that the deposition of Au/γ-PGA−DA NBs on the electrode surface is a kinetic phenomenon. The packing behavior of the Au/γ-PGA−DA NBs in the coating can be influenced by their deposition rate. Under higher deposition voltage, the fast electrolysis of water may cause gas evolution and turbulence at the electrode. The flows in the surrounding medium may disturb the coating during the process of deposition.[19] Additionally, under higher deposition voltage, the deposition rate of Au/γ-PGA−DA NBs is fast. It is difficult for Au/γ-PGA−DA NBs to find enough time to sit in their best positions for forming a close-packed structure.[19] The structures of dried coatings formed from Au/γ-PGA−DA NBs under 0.5 and 1.0 V are further investigated by AFM. The AFM images were plotted with the height scale of 300 nm. As shown in Figure 3A−C, it is apparent that Au/γ-PGA−DA NBs have been deposited on the GE surface. Compared with the morphology of the sensor coating formed under 0.5 V ($SC_{0.5V}$), the particle morphology of $SC_{1.0V}$ is more uniform. The thickness estimated from the AFM increases from 187.5 to 305.9 nm with increase in the deposition voltage from 0.5 to 1.0 V, which can be ascribed to the increase in the deposition rate at a higher deposition voltage.[20]

The electrochemical responses of coatings formed under 0.5 and 1.0 V are investigated by differential pulse voltammetry (DPV) in a phosphate buffer solution (PBS, pH 7.0) containing 1×10^{-5} mol·L^{-1} L-tryptophan. The differential pulse voltamograms (DPVs) are shown in Figure 3D. An anodic peak potential is observed at 0.673 V, which corresponds to the oxidation peak of L-tryptophan.[10] Compared with the $SC_{0.5V}$, the response current value of $SC_{1.0V}$ increases due to large surface-to-volume ratio. In the following experiment, the deposition voltage is set as 1.0 V.

pH Value of Suspension Effect on the Structure and Electrochemical Response of Sensor Coating. Besides the deposition voltage, the size and ζ potential of NPs play important roles in the structure and the properties of coating.[20] With many carboxyl groups in Au/γ-PGA−DA NBs, the size and ζ potential of NBs can be remarkably influenced by the pH value of Au/γ-PGA−DA NBs suspension. Compared with inorganic NPs, the structure of self-assembled Au/γ-PGA−DA NBs in the solution also can be affected by the pH value of the solution. So, the size, ζ potential, and structure of Au/γ-PGA−

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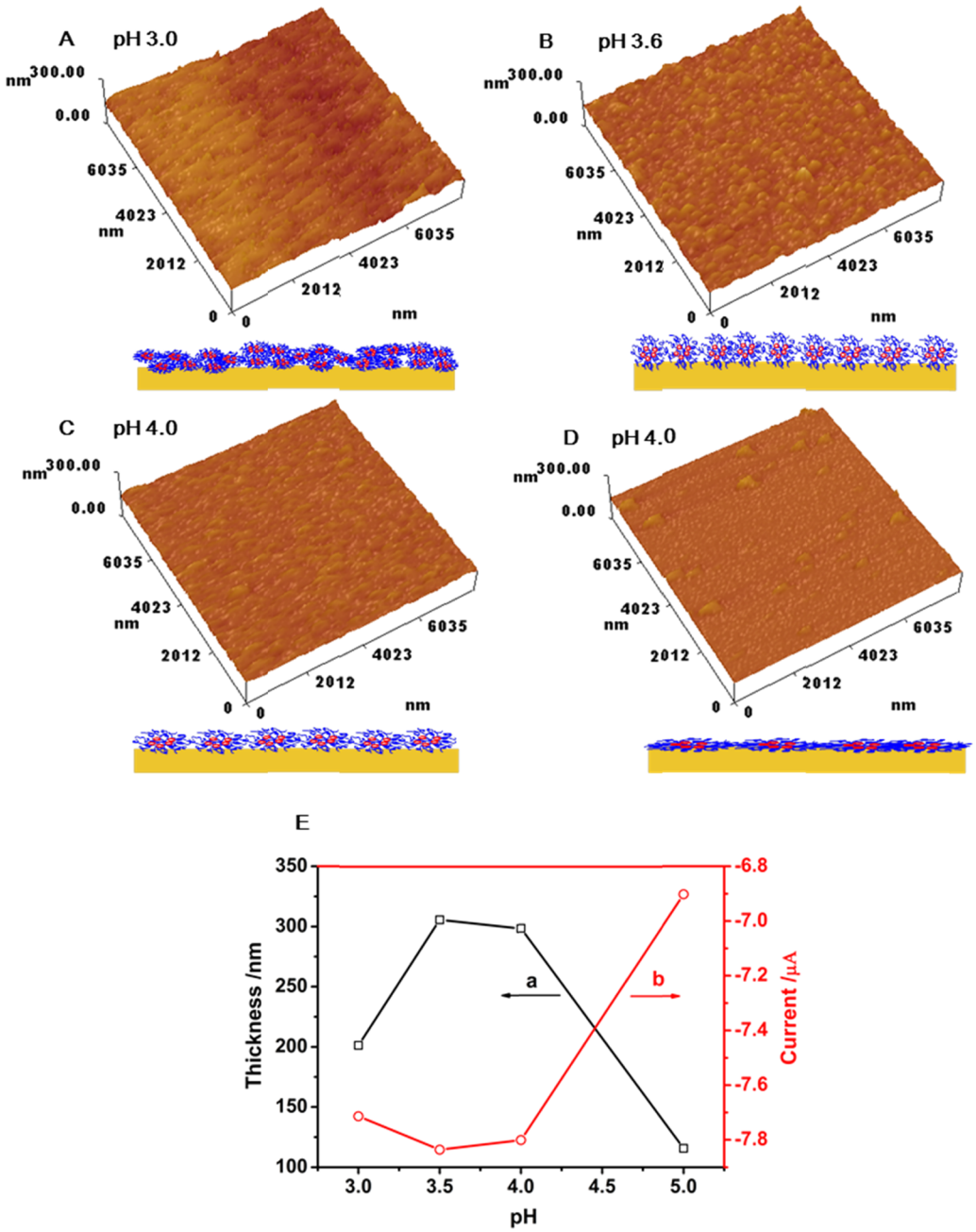

Figure 4. AFM 3D images and illustrations of sensor coating formed from NBs suspension with various pH values: (A) pH 3.00; (B) pH 3.60; (C) pH 4.00; and (D) pH 5.00. (E) Thickness (a) and response currents for L-tryptophan (1×10^{-5} mol·L^{-1}) (b) of sensor coatings formed from NBs suspensions with various pH values. The deposition voltage and deposition time was 1.0 V and 30 s, respectively.

DA NBs all can affect the structure and the electrochemical response of sensor coating. The ζ potential and the average size of Au/γ-PGA−DA NBs varying with the pH value of suspension are shown in Figure S2. With the increase in the pH values from 3.6 to 5.0, the average size of Au/γ-PGA−DA NBs increases slightly due to the swelling of the polymer chain resulting from the deprotonation of the carboxyl groups, gradually forming a loose structure. When the pH values decrease from 3.6 to 3.0, the protonation of the carboxylate groups weakens the repulsive force between NBs, leading to the coalescence of Au/γ-PGA−DA NBs and a compact structure. The ζ potential value of Au/γ-PGA−DA NBs gradually increases from 20.2 to 39.4 V due to the deprotonation of the carboxyl groups when the pH value is increased from 3.0 to 5.0. Figure S3 shows the current−time curves during the formation of sensor coating deposited from the Au/γ-PGA−DA NBs suspension with various pH values. The deposition voltage and deposition time are 1.0 V and 30 s, respectively. During the EPD process, the current values decrease first and then tend to become stable with the prolonging of the deposition time in the pH range of 3.0−5.0, indicating that Au/γ-PGA−DA NBs are deposited on the surface of GE.

The structure of dried deposited sensor coatings formed from Au/γ-PGA−DA NBs suspension with various pH values are investigated by AFM (shown in Figure 4A−D). The AFM images reveal that when the pH value is in range of 3.0−5.0, NBs are deposited on the GE surface and form a continuous sensor coating. The sensor coating formed from the Au/γ-

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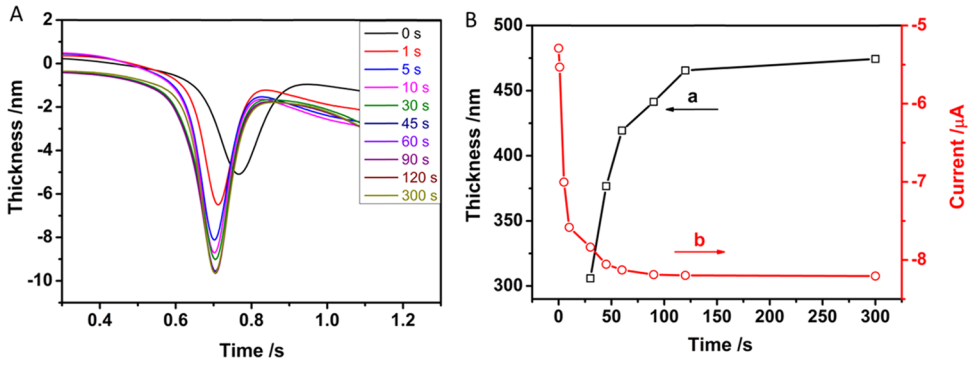

Figure 5. (A) DPVs for L-tryptophan (1×10^{-5} mol·L^{-1}) of sensor coatings formed from NBs suspension with various deposition time. (B) Thickness (a) and response currents for L-tryptophan (1×10^{-5} mol·L^{-1}) (b) of sensor coatings formed from NBs suspension with various deposition time. The deposition voltage and the pH value of NBs suspension were 1.0 and 3.6 V, respectively.

PGA−DA NBs suspension with pH 3.6 ($SC_{pH3.6}$) maintains its particle morphology and is more uniform. The thickness estimated from the AFM images is shown in Figure 4E,a. It can be seen, as the pH value of suspension increases from 3.6 to 5.0, the thickness of the coating gradually decreases. The morphology and the thickness of Au/γ-PGA−DA NBs coating are influenced by several factors. First, with an increase in the pH value from 3.6 to 5.0, the electrostatic repulsion between charged Au/γ-PGA−DA NBs increases due to the increase in the ζ potential value, which can prevent the deposition of Au/γ-PGA−DA NBs on the surface of the electrode.[21] Second, the increase in the particle size resulting from the swelling of the polymer chain in Au/γ-PGA−DA NBs decreases the EDP rate and the amount of deposit on the electrode surface. Third, the swelled Au/γ-PGA−DA NBs are easily deformed to form a flat coating on the surface of the electrode during the drying process, also leading to a decrease in the coating thickness. When the pH valve is decreased from pH 3.6 to pH 3.0, the coating thickness and homogeneity are decreased. The reason may be that the coalescence and flocculation of Au/γ-PGA−DA NBs in the suspension result from the a decrease in ζ potential during the EPD process.

The electrochemical responses for L-tryptophan (1×10^{-5} mol·L^{-1}) of sensor coating formed from the Au/γ-PGA−DA NBs suspensions with various pH values are investigated by DPV in PBS (pH 7.0). As shown in Figure 4E,b, the response current values slightly change when the pH value of the suspension is in the range of 3.0−4.5. However, the response current value of $SC_{pH5.0}$ for L-tryptophan decreases due to its flat morphology and a thinner thickness.

These results reveal that a uniform sensor coating with particle morphology can be formed on the GE surface when the size of Au/γ-PGA−DA NBs is smallest and the structure of Au/γ-PGA−DA NBs is compact. So, in the present experiment, the pH value of the suspension is set as 3.6.

Deposition Time Effect on the Structure and Electrochemical Response of Sensor Coating. When the properties of the particle suspension and the deposition voltage are fixed, the thickness and the structure of the coating can be readily controlled by the deposition time in the EPD method. The EPD process of Au/γ-PGA−DA NBs on the surface of GE is traced by SEM investigation. It can be seen in Figure S4B, after deposition for 5 s, many Au/γ-PGA−DA NBs are deposited and form a discontinuous coating on the GE surface. With prolonging of the deposition time to 30 s, a continuous coating with particle morphology is formed (Figure S4D).

The thickness of the sensor coatings estimated from AFM varying with the deposition time is shown in Figure 5B,a. The results reveal that the thickness of the sensor coating increase first and then become stable with prolonging of the deposition time due to a decrease in the conductivity of the deposited coating.[22,23] The response currents for L-tryptophan (1×10^{-5} mol·L^{-1}) of sensor coatings formed from the Au/γ-PGA−DA NBs suspension with different deposition time are shown in Figure 5B,b. It can be observed that the response current values significantly increase during the initial 30 s. But as more time is allowed, the rate of increase of the response current values become slow and attain a plateau at a high deposition time. The results reveal that the thickness and homogeneity of the sensor coating play important roles in the electrochemical response.

To further investigate the effect of thickness of sensor coating on the electrochemical response for L-tryptophan, the sensor coatings formed with the deposition time of 30, 45, and 60 s (SC_{30s}, SC_{45s}, and SC_{60s}, respectively) are used for sensing L-tryptophan with different concentrations. Figure S5 shows the DPVs and the linear calibration curves for detecting L-tryptophan. The linear range, linear regression equation, and correlation coefficient (R^2) are shown in Table S1. Compared with SC_{45s} and SC_{60s}, SC_{30s} exhibits a wider detection range for L-tryptophan sensing, indicating that a thinner coating has more excellent detection performance. The detection limit of SC_{30s} is estimated to be 3×10^{-10} mol·L^{-1} based on the signal/noise (S/N) = 3. Additionally, we compare SC_{30s} with other previously reported sensors for sensing L-tryptophan. As can be seen in Table S2, SC_{30s} shows a wider detection range and a lower detection limit for sensing L-tryptophan than other sensors in the previous reports.[1,2,10,24,25]

To assess the applicability of SC_{30s} prepared via the EPD method, SC_{30s} is used to determine L-tryptophan in human blood serum samples. The human blood serum samples without any special treatment are diluted to 100 times with PBS (pH 7.0, 0.1 mol·L^{-1}). SC_{30s} was then used to detect the human blood serum samples with spiked L-tryptophan.[10] As shown in Table 1, the recoveries of the L-tryptophan determination in human blood serum samples via SC_{30s} are

Table 1. Detecting L-Tryptophan in Blood Samples

blood sample	added (mol·L^{-1})	found (mol·L^{-1})	recovery (%)
1	1×10^{-7}	1.02×10^{-7}	102
2	5×10^{-7}	4.93×10^{-7}	98.6
3	1×10^{-6}	0.99×10^{-7}	99

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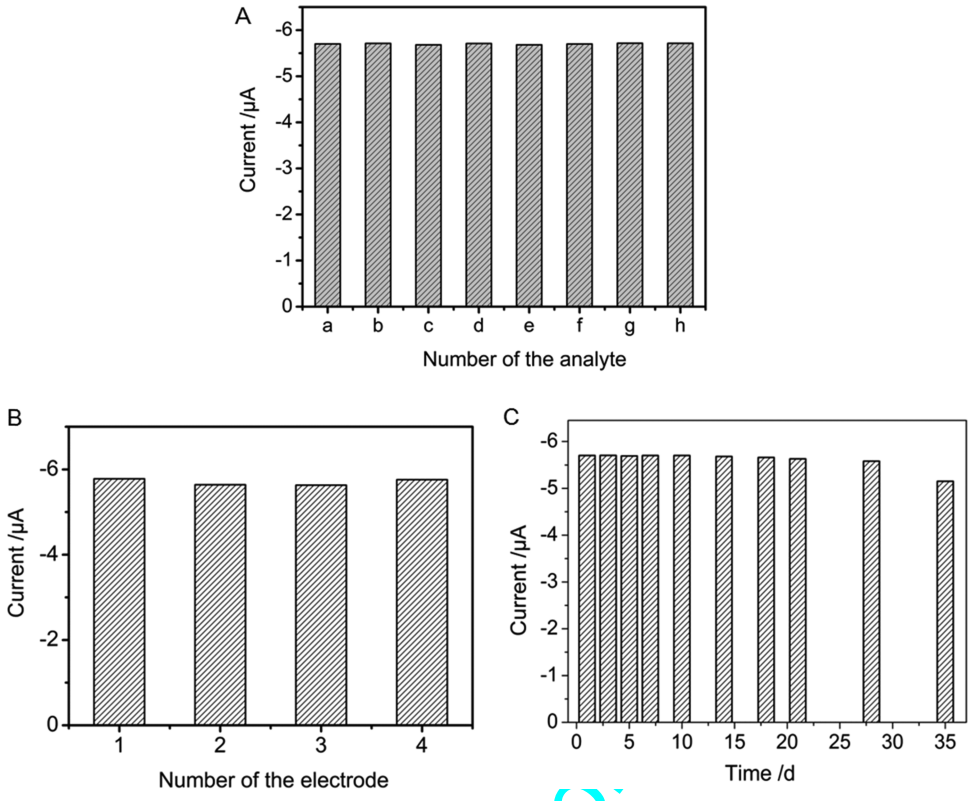

Figure 6. (A) Response currents for L-tryptophan of SC_{30s} in PBS of 0.1 mol·L^{-1} (pH 7.0) with different kinds of interferents. (a) 1×10^{-7} mol·L^{-1} L-tryptophan, (b) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-lysine, (c) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-phenylalanine, (d) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-serine, (e) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-histidine, (f) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-alanine, (g) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1}, L-proline, and (h) 1×10^{-7} mol·L^{-1} L-tryptophan and 5×10^{-6} mol·L^{-1} L-glycine. (B) The response currents for 1×10^{-7} mol·L^{-1} L-tryptophan in PBS of 0.1 mol·L^{-1} (pH 7.0) of different four electrodes coated with SC_{30s}. (C) The response currents for 1×10^{-7} mol·L^{-1} L-tryptophan in PBS of 0.1 mol·L^{-1} (pH 7.0) of SC_{30s} at various intervals.

good and in the range of 98−102%, indicating that SC_{30s} is a promising system for detecting L-tryptophan.

Analytical selectivity is one of the important parameters affecting the accuracy of the analysis. The selectivity of the SC_{30s} for the determination of L-tryptophan is studied by adding 5×10^{-6} mol·L^{-1} various foreign amino acids (L-lysine, L-serine, L-histidine, L-alanine, L-glycine, L-proline, or L-phenylalanine) into PBS (pH 7.0, 0.1 mol·L^{-1}) containing 1×10^{-7} mol·L^{-1} L-tryptophan. The response currents for L-tryptophan with different kinds of interferents are shown in Figure 6A. The results reveal that the response currents for L-tryptophan of SC_{30s} is not significantly affected by all of the conventional amino acids, indicating that SC_{30s} can be used to detect L-tryptophan with good selectivity.

To test the reproducibility of the method, four electrodes coated with SC_{30s} are constructed under identical experimental conditions. For sensing L-tryptophan, the current is obtained by using each of the electrodes coated with SC_{30s} to detect L-tryptophan (1×10^{-7} mol·L^{-1}) in PBS of 0.1 mol L^{-1} (pH 7.0). The response currents for 1×10^{-7} mol·L^{-1} L-tryptophan of different electrodes coated with SC_{30s} are shown in Figure 6B. The results reveal that the relative standard deviation of the responsive currents is lower than 3%, indicating that the method exhibits a good reproducibility.

The stability of the SC_{30s} is also investigated through sensing 1×10^{-7} mol·L^{-1} L-tryptophan in PBS (pH 7.0, 0.1 mol L^{-1}). The response currents for L-tryptophan of SC_{30s} at various intervals are shown in Figure 6C. The relative standard deviation is approximately 2.3% (n = 8). The response currents for L-tryptophan of SC_{30s} are kept well within 4 weeks and decrease by approximately 10% after the GE coated with SC_{30s} is stored for 5 weeks, demonstrating a good stability of SC_{30s}.

CONCLUSIONS

A sensor coating was prepared from Au/γ-PGA−DA NBs via the EDP method. By simply altering the deposition conditions, the structure and the electrochemical response of the sensor coating can be controlled. When Au/γ-PGA−DA NBs of 0.1 mg·L^{-1} (pH 3.6) were deposited under the deposition voltage of 1.0 V for 30 s, a uniform coating with a nanoparticle morphology was formed on the surface of GE. The electrochemical response currents of the prepared sensor coating increased with increasing L-tryptophan concentration and showed linear relationships ranging from 1×10^{-9} to 1×10^{-5} mol·L^{-1}. The detection limit was as low as 3×10^{-10} mol·L^{-1}. Compared with other previously reported electrochemical sensors, our prepared sensor coating exhibited a wider detection range for the determination of L-tryptophan. The prepared sensor coating also revealed good applicability, selectivity, reproducibility, and stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b13543.

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SEM images of bare GE (Figure S1); mean diameters and ζ potentials of Au/γPGADA NBs (Figure S2); current−time curves (Figure S3); SEM images of sensor coatings (Figure S4); DPVs of sensor coatings (Figure S5); comparison of sensor coatings formed from Au/γPGA−DA NBs (Table S1); comparison of the sensing performance of SC_{30s} (PDF)

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Notes

The authors declare no competing financial interest.

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