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Selective determination of arsenic (III) using a Nafion/α-MnO_2@polydopamine modified electrode

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ABSTRACT

A simple strategy for reliable determination of As(III) without strongly acidic media is described by using the gold disk electrode modified with the water-dispersible polydopamine-coated α-MnO_2 (α-MnO_2@PDA) composites and the Nafion layers. The composites have been synthesized by the in-situ polymerization of dopamine and used to improve the sensitivity for detection of As(III). In this case, the α-MnO_2 microrods are used as inorganic matrixes with strong adsorption abilities towards As(III) and the permeable PDA layers are prepared to enhance such adsorption effects by plenty of amino and hydroxyl groups that could work as the active adsorption sites. Nafion has been employed based on its excellent film-forming ability, by which the α-MnO_2@PDA modified layer can be tightly attached to the sensor surface. Such a designed electrode shows a remarkably improved analysis performance to As(III). The electrode has a linear range of 10–150 μg L^{-1} with a sensitivity of 0.13 μA μg^{-1} L. Moreover, the proposed sensor exhibits a favorable stability and reproducibility in the determination of As(III). Additionally, interferences from co-existing ions can be effectively diminished. Therefore, we believe that the combination of α-MnO_2@PDA composite and Nafion could be used to develop electrochemical sensors for the sensitive and selective analysis of As(III).

1. Introduction

The contamination of arsenic in drinking water has been a serious water quality problem in many countries [1–4]. Exposure to arsenic by the consumption of contaminated drinking water may lead to a variety of adverse health effects in humans. The most toxic forms of arsenic are its inorganic species, especially trivalent arsenic (As(III)), which has been classified as a human carcinogen [5]. Several techniques have been developed for reliable detection of As(III) in water samples, such as inductively coupled plasma mass spectroscopy (ICP-MS) [6,7], atomic absorption spectrometry (AAS) [8], and X-ray fluorescence spectroscopy (XRF) [9]. Compared to these spectroscopic methods, stripping voltammetry is more popular for environmental monitoring due to its short analysis time, inexpensive equipment and low power consumption [10]. Among the solid metal substrates commonly used for working electrodes, such as mercury(Hg) [11], platinum (Pt) [12], silver (Ag) [13], and gold (Au) [14], Au has been found to be the superior substrate for electrochemical analysis of As(III). Therefore, various Au based-electrodes have been fabricated for accurate measurements of As(III) at the μg L^{-1} levels [15–21]. Although these electrodes are effective for determination of trace As(III), their applications in analysis of water samples may be limited by the use of a strongly acidic medium since the toxic arsine gas could be formed during the testing period. Additionally, the serious interference from Cu(II) could be induced in such an acidic medium because there is a rather small difference between the oxidation potentials of Cu(0) and As(0) [22].

In recent years, many micro/nano-materials have been utilized to fabricate novel electrochemical electrodes for stripping analysis of heavy metal ions (HMIs) due to their excellent adsorption abilities towards the HMIs of

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interest [23–28]. α-MnO_2 micro/nano-particles have attracted considerable attention as adsorbents for the removal of As(III) from aqueous environments due to their high surface area and good adsorption ability towards As(III) [29–31]. Unfortunately, like most of micro/nano-structured materials, α-MnO_2 particles may suffer from their instinct tendency to aggregate and could not be dispersed well in an aqueous solution [32,33], which may limit their applications in surface modification of sensors. Since a homogeneous layer of α-MnO_2 particles could not be formed on electrode surface by drop-casting the suspension of α-MnO_2, which might cause a rather poor reproducibility of the modified electrodes.

Herein, a polydopamine (PDA)-coated α-MnO_2 (α-MnO_2@PDA) composite has been synthesized simply by the self-polymerization of dopamine with the α-MnO_2 particles used as inorganic matrixes. The hydrophilic and permeable PDA layer allows the α-MnO_2@PDA composite to be water dispersible. In addition, the PDA layer has plenty of amino and hydroxyl groups, which could work as the active sites to promote As(III) adsorption [34,35]. A layer of the α-MnO_2@PDA composite can be modified on the surface of Au disk electrode for stripping analysis of As(III). To supply the stability of such a modifying layer, Nafion has been employed as the membrane matrix due to its excellent film-forming ability. Experimental results show that the proposed sensors based on the α-MnO_2@PDA composite and Nafion can be used at alkaline solution and have promising potential for sensitive detection of As(III) in water samples.

2. Experimental section

2.1. Reagents and chemicals

Nafion (5% *w*/w solution in a mixture of lower aliphatic alcohols and water), dopamine hydrochloride, tris(hydroxymethyl) aminomethane (Tris) were obtained from Sigma-Aldrich. $KMnO_4$, $MnSO_4{\cdot}H_2O$, hexadecyl trimethyl ammonium bromide (CTAB), *N, N*-dimethylformamide (DMF) and the stock solution of 1000 mg L^{-1} As(III) were purchased from Shanghai Chemical Reagent Co., Ltd. (China). All other chemicals were analytical reagents and used without further purification. Deionized (DI) water (18.2 MΩ cm specific resistance) was obtained with a Pall Cascada laboratory water system.

2.2. Instrumentation

A three-electrode system controlled by an electrochemical workstation (CHI 660D, Shanghai Chenhua Apparatus Corporation, China) was applied for all electrochemical experiments. The system consisted of a bare/modified Au disk working electrode (3 mm in diameter), a 0.5 mm diameter platinum wire counter electrode, and a Ag/AgCl (3 M KCl) reference electrode.

The scanning electron microscopy (SEM) image and the energy dispersive spectrometer (EDS) pattern of the as-synthesized α-MnO_2@PDA composite were obtained from the field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). The surface microstructures of these composites were characterized by the transmission electron microscopy (TEM, JEOL-1400Plus, Japan) operated at 120 kV.

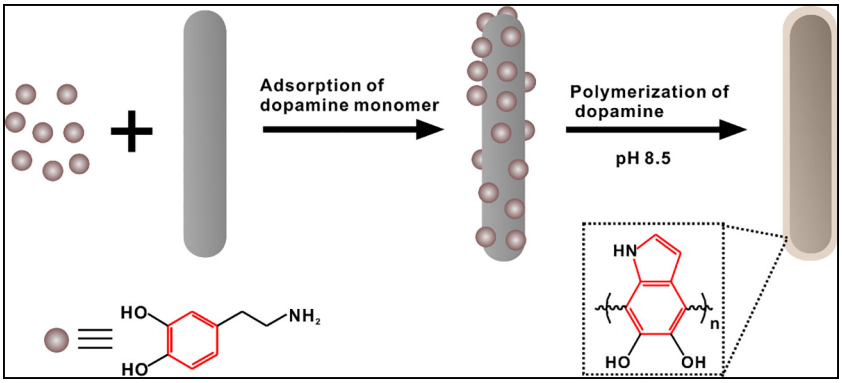
2.3. Synthesis of the α-MnO_2@PDA composite

The α-MnO_2 particles were prepared by hydrothermal synthesis, as described before [36]. In brief, 0.8 g of CTAB was dissolved in 46 mL of DI water with vigorous stirring. 1.0 g of $KMnO_4$ and 0.4 g of $MnSO_4{\cdot}H_2O$ were then added to the resulting solution. The mixture solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 160 °C for 24 h. Finally, a brown product was collected by centrifugation, washed with DI water and dried at 75 °C for further experiments.

The procedures for synthesizing the α-MnO_2@PDA composite are shown in Scheme 1. The dopamine monomer was first attached on the surfaces of α-MnO_2 particles via noncovalent interactions, such as the hydrogen bonding and electrostatic interactions. The oxidative polymerization of these dopamine monomers was then triggered in an alkaline solution, so that a hydrophilic PDA layer was deposited on the surfaces of α-MnO_2 particles, which could improve their water-dispersible properties. For preparation of such a PDA layer, 20 mg of the as-prepared α-MnO_2 was dispersed in 5 mL of DI water containing 20 mg of dopamine hydrochloride by ultrasonication for 30 min. Then, 10 mL of 0.1 M Tris-HCl buffer (pH 8.5) was added into the mixture, and the resulting suspension was stirred for 12 h in air. After the self-polymerization of dopamine, the obtained α-MnO_2@PDA product was washed by DI water for three times and dried at 75 °C.

2.4. Preparation of the Nafion/α-MnO_2@PDA-modified Au disk electrodes

The procedures for preparation of the Nafion/α-MnO_2@PDA-modified Au disk electrode are described as follows: (1) a bare Au disk electrode was successively polished with 0.3 and 0.05 μm alumina slurries to obtain a mirror shiny surface and sonicated thoroughly in absolute ethanol and DI water, respectively. The electrode was then transferred to an electrochemical cell for the electrochemical cleaning process by cycling between 0.0 and 1.7 V in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1} until a stable profile was obtained. (2) 10 mg of the α-MnO_2@PDA composite was dispersed in 1 mL of DI water and sonicated for 1 h to obtain a homogeneous α-MnO_2@PDA suspension. (3) The original 5% *w*/w Nafion solution was diluted to 0.5% w/w solution with DMF. (4) 5 μL of the resulting α-MnO_2@PDA suspension was pipetted onto the surface of the bare Au disk electrode and dried under an infrared lamp. Then, 2 μL of the diluted Nafion solution was dropped on the surface of the α-MnO_2@PDA-modified electrode and dried in air to form a transparent Nafion membrane, by which α-MnO_2@PDA could be tightly attached to the surface of Au disk electrode. For comparison, the Nafion/α-MnO_2-modified Au disk electrodes were prepared in the same manner.



Scheme 1. Synthesis procedure for the water-dispersible polydopamine-modified α-MnO_2.

2.5. Electrochemical measurements

Square wave anodic stripping voltammetry (SWASV) was used to detect As(III) in 0.1 M Na_2CO_3-$NaHCO_3$ solution with a pH value of 9.0 under optimized conditions. A potential of −1.1 V was applied to the Nafion/α-MnO_2@PDA-modified Au disk electrode for 140 s with stirring to electrochemically reduce As(III) to As(0). The anodic stripping of As(0) was performed to scan from −0.6 V to 0.1 V (frequency of 25 Hz, step potential of 4 mV and amplitude of 25 mV). The obtained stripping peak current (i_p) was used for the quantitative analysis of As(III). After each measurement, the Nafion/α-MnO_2@PDA-modified Au disk electrode was regenerated at +0.8 V for 120 s with stirring to remove the previous residual As(0).

2.6. As(III) adsorption experiments

The adsorption abilities of the α-MnO_2@PDA and α-MnO_2 microrods towards As(III) were determined with a sorbent dose of 1.0 mg mL^{-1} at pH 9.0. In brief, 10 mg of the prepared α-MnO_2@PDA or α-MnO_2 microrods was dispersed in 10 mL of 0.1 M Na_2CO_3-$NaHCO_3$ solution (pH 9.0) with different As(III) concentrations (2, 4 mg L^{-1}). The obtained suspensions were shaken (200 rpm) at room temperature for 24 h for adsorption equilibrium. Then, the sorbents were isolated from the aqueous dispersions by centrifugation (8000 rpm, 5 min), and the As(III) concentrations in the supernatant were determined by inductively coupled plasma mass spectroscopy (ICP-MS, PE Elan DRC II, Canada). The removal efficiency (%) was calculated by establishing a mass balance of As(III) before and after adsorption experiments:

$$Removal\ efficiency = \frac{C_0 - C_e}{C_0} \times 100\%.$$

Where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the As(III) concentrations in the original and equilibrium conditions, respectively.

3. Results and discussion

3.1. Characterization of the α-MnO_2@PDA composite

The as-prepared α-MnO_2@PDA composite was characterized by FE-SEM and TEM, respectively (Fig. 1). As illustrated in Fig. 1a, the α-MnO_2@PDA composite exhibits rod-like structures with a particle width of 170–206 nm, while the α-MnO_2 materials have a similar appearance with a particle width of 111–178 nm (Fig. S1). Besides, a slightly rougher surface can be observed after the modification with PDA layers. The increases in particle width and surface roughness are probably due to the deposition of the PDA layers on the surfaces of α-MnO_2 microrods. Indeed, the C and N elements attributed to PDA layers can be observed in the EDS pattern of the α-MnO_2@PDA composite (Fig. S2). Moreover, the layers have a thickness of 37 nm measured by TEM (Fig. 1b).

To confirm the water-dispersible properties of the as-prepared α-MnO_2@PDA composite, the dispersibility characteristics of the composite and the α-MnO_2 microrods were compared. As shown in Fig. S3, the α-MnO_2 microrods cannot be dispersed well in DI water and quickly precipitate from the aqueous dispersion within 10 min; in contrast, the suspension of the α-MnO_2@PDA composite is rather stable during the test period, indicating their good water-dispersible properties, which could be attributed to the presence of hydrophilic groups (e.g., hydroxyl and amine groups) on the surface of the α-MnO_2@PDA composite.

3.2. Electrochemical characterization of the Nafion/α-MnO_2@PDA-modified electrode

The electrochemical characterizations of the bare, α-MnO_2@PDA-modified and Nafion/α-MnO_2@PDA-modified Au disk electrodes were carried out by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in a solution of 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl. As shown in Fig. S4a, the anodic and cathodic peaks significantly decrease after the subsequent coatings of the α-MnO_2@PDA composite and Nafion layer, which is probably due to their smaller conductivities. Indeed, the increased electron transfer resistance can be observed at these modified electrodes when compared to the bare electrode, suggesting the decrease in the capability of electron transfer (Fig. S4b). Therefore, it can be predicted that the electrochemical redox process of As(III) may occur on the surface of Au disk electrode, rather than the surface of the α-MnO_2@PDA composite. In this case, As(III) can be efficiently adsorbed by the α-MnO_2@PDA composites due to the interaction between the amino/hydroxyl groups and As(III) [34,35], and subsequently be released to the Au electrode surface where the reduction/oxidation of As(III)/As(0) occurs and gives the voltammetric signals [37,38].

3.3. Optimization for electrochemical measurement of As(III) at the Nafion/α-MnO_2@PDA-modified electrode

Since the voltammetric parameters (i.e., supporting electrolyte, pH, deposition time, deposition potential and the loading amount of the α-MnO_2@PDA composite on electrode surface) play important roles in the analytical performance of the Nafion/α-MnO_2@PDA-modified electrodes, these parameters were optimized in the presence of 40 μg L^{-1} As(III) (Fig. 2). The effect of supporting electrolyte was investigated by comparing the obtained SWASV responses towards 40 μg L^{-1} As(III) in three different supporting electrolytes (i.e., Tris-HCl solution, Na_2CO_3-$NaHCO_3$ solution, and phosphate buffer solution (PBS)) with a concentration of 0.1 M and a pH value of 9.0, and the results are shown in Fig. 2a. As illustrated, a well-defined stripping peak with the strongest signal can be obtained

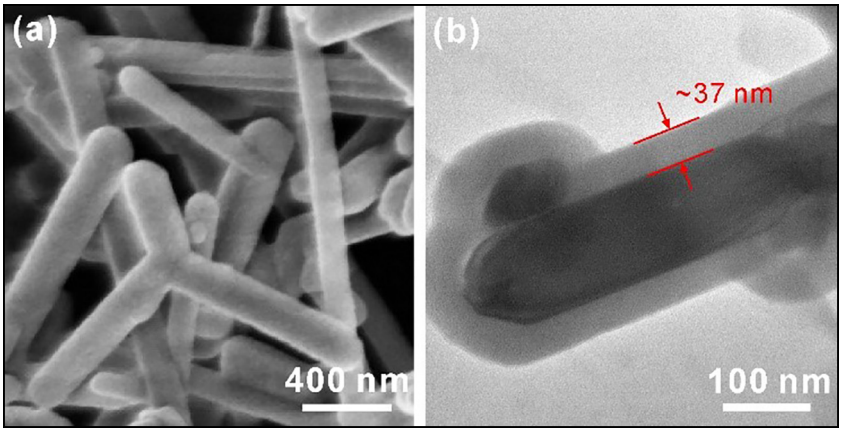


Fig. 1. (a) FE-SEM and (b) TEM images of the α-MnO_2@PDA composites.

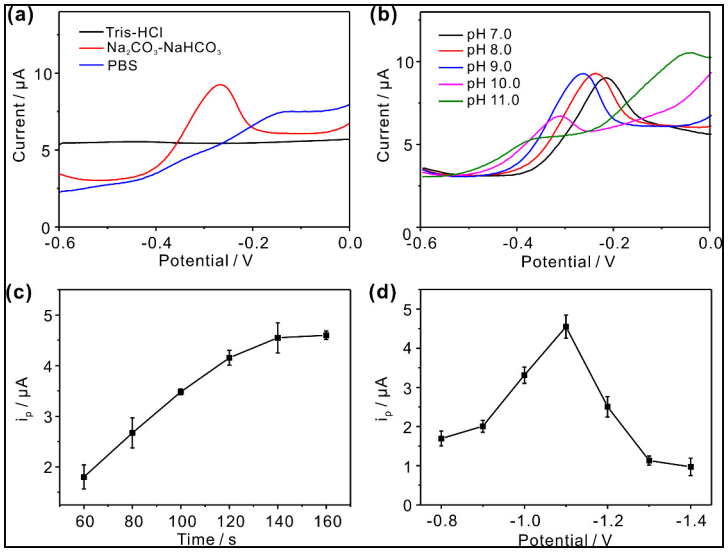


Fig. 2. Influences of (a) supporting electrolyte, (b) pH, (c) deposition time, and (d) deposition potential on the SWASV responses of the Nafion/α-MnO_2@PDA-modified Au disk electrodes to 40 μg L^{-1} As(III). Testing conditions: frequency of 25 Hz, step potential of 4 mV and amplitude of 25 mV. Error bars represent one standard deviation of three measurements.

with the Na_2CO_3-$NaHCO_3$ solution. Therefore, 0.1 M Na_2CO_3-$NaHCO_3$ solution was selected for further experiments.

The effect of pH on the stripping peak of As(0) was investigated in 0.1 M Na_2CO_3-$NaHCO_3$ solution with different pH values ranging from 7 to 11. As shown in Fig. 2b, the As(0) stripping peak current remains almost constant when increasing the pH value up to 9 and thereafter decreases with the increase of pH value. It can be explained by the fact that the dominant species of As(III) in solution is anionic $H_2AsO_3^-$ (not neutral H_3AsO_3) when pH is higher than 9.0 [39,40], the anion sites of the α-MnO_2@PDA composite (e.g., the deprotonated hydroxyl groups) and of the Nafion layer (i.e., sulphonate groups) can inhibit the adsorption of $H_2AsO_3^-$ by electrostatic repulsion, thus causing a poor stripping response. Interestingly, experiments also show that the potential of As(0) stripping peak is shifted negatively with the increase in pH. This can be explained by the fact that the shift in the stripping peak potential is proportional to the concentration of H^+ in the analyzed solution that follows the Nernst Eq. [41]. It has been found that the stripping peak of Cu(0) is commonly observed at slightly more positive potential than the As(0) stripping peak [19]. Considering a larger difference between their stripping peak potentials and a more sensitive response to As(III), the pH value of 9.0 was selected.

The effects of deposition time and potential on the stripping peak current of As(0) were investigated. As shown in Fig. 2c, the SWASV peak current of 40 μg L^{-1} As(III) at the proposed electrode increases rapidly with increasing the deposition time up to 140 s and then remains almost constant. Additionally, the stripping peak current increases as the deposition potential decreases, and a maximum current value can be obtained at −1.1 V (Fig. 2d). When potentials more negative than −1.1 V are applied, the remarkable decreases in the stripping peak signal can be observed due to the H_2 evolution. Therefore, the deposition time of 140 s and deposition potential of −1.1 V were selected for the following experiments.

Since the α-MnO_2@PDA composite plays an important role in the performance of the proposed electrode, the effect of its loading amount on electrode surface was studied, and the results are shown in Fig. S5. As illustrated, the stripping current value increases with increasing the loading amount of the α-MnO_2@PDA composite on Au electrode surface, and a maximum stripping current value can be obtained when the modified volume increases up to 5 μL. The excrescent α-MnO_2@PDA composite may affect the transport of As(III) from the modified layer to Au electrode surface [10], so that a modified volume of 5 μL was selected.

3.4. Electrochemical detection of As(III)

To clarify the functions of the modifying layers of the α-MnO_2@PDA composites and Nafion in the proposed electrode, the SWASV responses of various electrodes towards As(III) were recorded under the optimal experimental conditions. As illustrated in Fig. 3, a weak stripping peak of As(0) appears at the bare Au disk electrode, while the slightly larger peaks are observed at the α-MnO_2-modified and α-MnO_2@PDA-modified electrodes due to their adsorption abilities to As(III). However, the stripping peak current of the α-MnO_2@PDA-modified electrode is much smaller than that obtained at the Nafion/α-MnO_2@PDA-modified electrode. The large difference between the signals of the two modified electrodes is probably due to the fact that α-MnO_2@PDA could easily peel off from electrode surface without the Nafion layer, therefore leading to the decrease in the amount of accumulated As(III). These results demonstrate that the combination of the α-MnO_2@PDA composite and Nafion layer can largely improve the sensor's performance for determination of As(III). Besides, the proposed electrode has a significantly increased baseline compared with the bare and α-MnO_2@PDA-modified electrodes, which might be due to

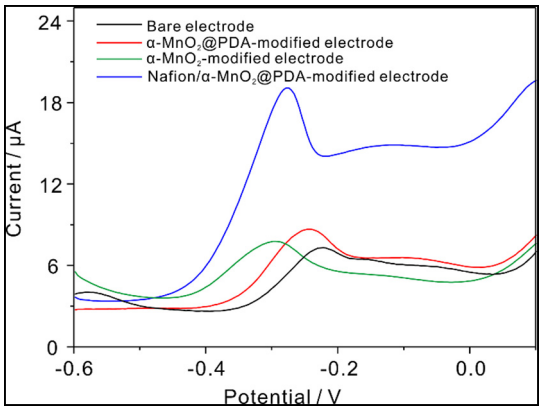


Fig. 3. Typical SWASV curves of 50 μg L^{-1} As(III) in 0.1 M Na_2CO_3-$NaHCO_3$ solution (pH 9.0) at the bare, α-MnO_2-modified, α-MnO_2@PDA-modified and Nafion/α-MnO_2@PDA-modified Au disk electrodes. SWASV parameters: deposition potential of −1.1 V for 140 s, frequency of 25 Hz, step potential of 4 mV and amplitude of 25 mV.

the increased capacitance after the modification of α-MnO_2@PDA and Nafion, while the α-MnO_2@PDA-modified electrode shows a CV curve similar to that of the bare electrode ascribed to the loss of the α-MnO_2@PDA composite from electrode surface without the membrane matrix of Nafion (Fig. S6).

The effect of the PDA layers on the proposed sensor's performance was also investigated. The SWASV responses of the Nafion/α-MnO_2-modified and Nafion/α-MnO_2@PDA-modified Au disk electrodes were recorded from −0.6 to 0.1 V in the As(III) concentration range of 10–150 μg L^{-1} under the optimized experimental conditions. As shown in Fig. 4a, a well-defined stripping peak (at −0.28 V) attributed to the oxidation of As (0) to As(III) can be observed at the Nafion/α-MnO_2@PDA-modified electrode, and the stripping peak current is proportional to the concentration of As(III) in the range of 10–150 μg L^{-1} with a sensitivity of 0.13 ± 0.001 μA $μg^{-1}$ L (Fig. 4b). In this case, the limit of detection (LOD) can be calculated to be 3.2 μg L^{-1} (3σ method), which is below the maximum permissible limit for As(III) concentration in drinking water (10 μg L^{-1}) provided by World Health Organization (WHO) [9,42]. Such a detection limit could allow the application of the proposed electrode for analysis As (III) in contaminated freshwater and drinking water samples. For comparison, the Nafion/α-MnO_2-modified electrodes were also applied for the stripping analysis of As(III) under the same conditions, and the results are shown in Fig. 4c and d. Experiments show that these electrodes exhibit poor SWASV responses to the low As(III) concentration (lower than 90 μg L^{-1}) with a sensitivity of 0.056 ± 0.002 μA $μg^{-1}$ L. Interestingly, it has been shown that the α-MnO_2-modified electrodes have a SWASV response towards 50 μg L^{-1} As(III) (Fig. 3), which is probably due to the loss of α-MnO_2 from electrode surface without the Nafion layer, leading to the decrease in the baseline, and thus improving the response to low As(III) concentration. The remarkable difference in electrochemical behaviors of the Nafion/α-MnO_2@PDA-modified and Nafion/α-MnO_2-modified electrodes could be attributed to the introduction of the PDA nanolayer, which could provide more adsorption sites (i.e. amine and hydroxyl groups) that allow preconcentration of As(III) to promote sensitivity [43,44]. Indeed, the α-MnO_2@PDA composite exhibits a stronger adsorption ability towards As(III) compared to the α-MnO_2 material at pH 9.0, and a lower removal efficiency is obtained at the higher As(III) concentration due to the adsorption saturation (Fig. 5). To date, several electrodes

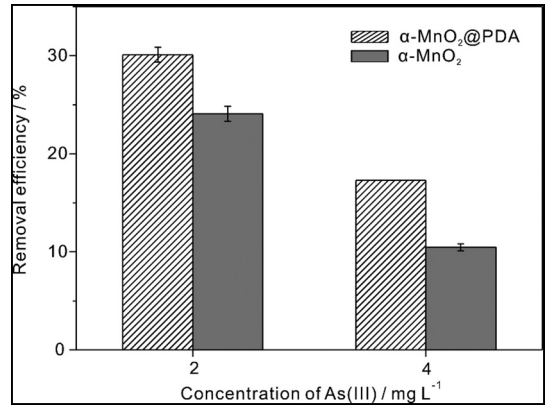


Fig. 5. Removal efficiency of As(III) by the α-MnO_2@PDA and MnO_2 microrods from 0.1 M Na_2CO_3-$NaHCO_3$ solution (pH 9.0) containing different concentrations of As(III).

have been designed and applied for electrochemical determination of As (III) in neutral and alkaline media. The comparison of the proposed electrode with other electrodes for determination of As(III) is summarized in Table S1. As illustrated, the response characteristics of the proposed Nafion/α-MnO_2@PDA-modified Au disk electrode are comparable or even superior to most of these electrodes in terms of linear detection range and sensitivity [40,45–53]. However, the proposed electrode has a relatively higher LOD, it might be due to the large baseline current of this electrode, which could overlap the stripping peak current of trace As(III). Even so, the LOD of the proposed electrode is sufficient enough for the early warning of As(III) contamination in drinking water.

3.5. Interference study

The stripping analysis of As(III) could be affected by the interferences from the coexisting metal ions. It has been found that Cu(II) exhibits the most serious influence on the current response to As(III). Since the overlapping stripping peaks, caused by the similarity in oxidation potentials of Cu (0) and As(0), could interfere with the determination of As(III) [19,22,54].

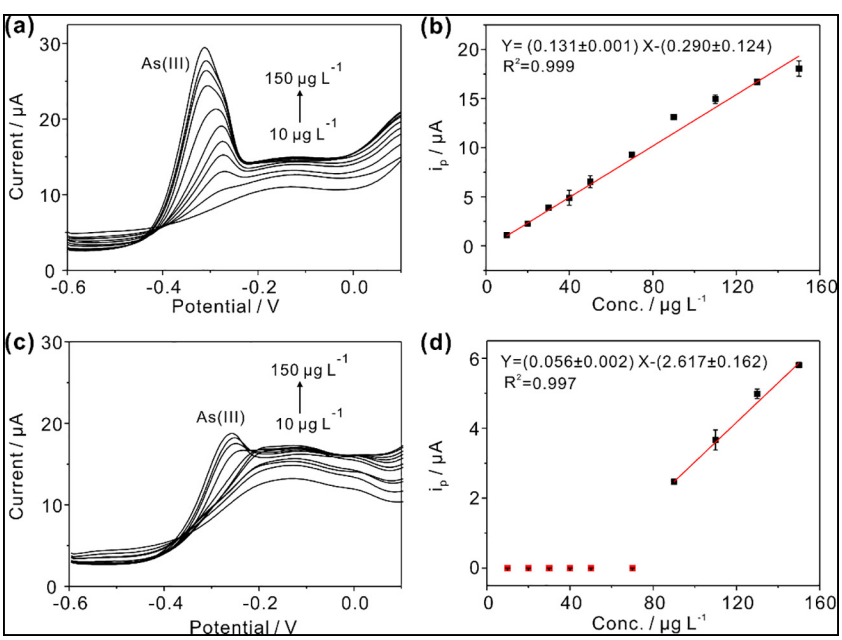


Fig. 4. Typical SWASW responses of (a) the Nafion/α-MnO_2@PDA-modified and (c) Nafion/α-MnO_2-modified electrodes to As(III) in the concentration range of 10–150 μg L^{-1} in 0.1 M Na_2CO_3-$NaHCO_3$ solution (pH 9.0). The testing parameters are given as in Fig. 3. The corresponding calibration plots of stripping peak current with As(III) concentration obtained at (b) the Nafion/α-MnO_2@PDA-modified and (d) Nafion/α-MnO_2-modified electrodes. Error bars represent one standard deviation for three measurements.

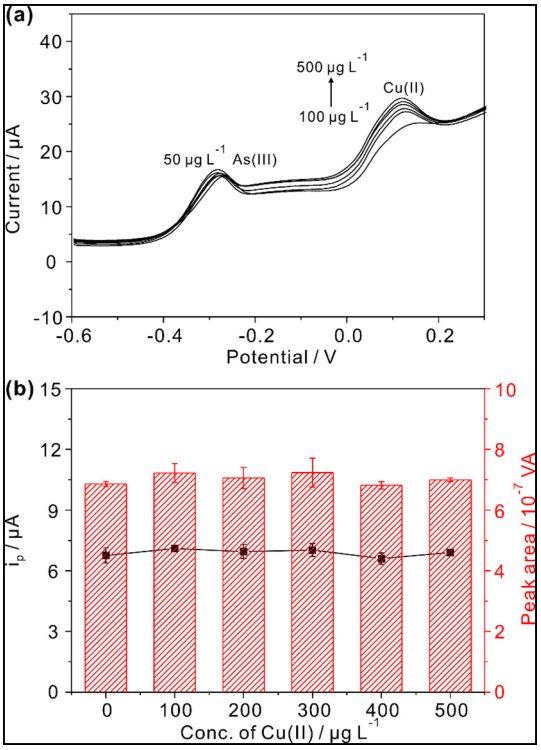


Fig. 6. (a) SWASV responses of the Nafion/α-MnO_2@PDA-modified electrodes to 50 μg L^{-1} As(III) with the Cu(II) concentration ranged from 0 to 500 μg L^{-1} (Cu (II) concentration increases by 100 μg L^{-1} for each addition) in 0.1 M Na_2CO_3-$NaHCO_3$ solution at pH 9.0. (b) Effect of the Cu(II) concentration on the stripping peak currents (points) and the corresponding peak areas (columns) of 50 μg L^{-1} As(III).

Herein, we used the proposed sensor in an alkaline medium (pH 9.0) for a larger difference between the stripping potentials of As(0) and Cu(0) to prevent the interference from Cu(II) (as discussed above). Indeed, the presence of Cu(II) ions does not influence the stripping peak of As(0) in terms of peak area, potential and current response, even at the concentration of Cu(II) 10 times higher than that of As(III) (Fig. 6a, b). Additionally, a stripping peak of Cu(0) can be observed at 0.12 V and the peak current increases as the Cu (II) concentration increases up to 500 μg L^{-1}.

The effects of other interfering ions on the SWASV response of the proposed electrode to As(III) were also investigated, and the obtained results are shown in Fig. S7. Negligible changes in the SWASV response can be observed in the presence of these interfering ions with a concentration of 500 μg L^{-1}. These results indicate the excellent anti-interference properties of the Nafion/α-MnO_2@PDA-modified electrodes under the optimized experimental conditions.

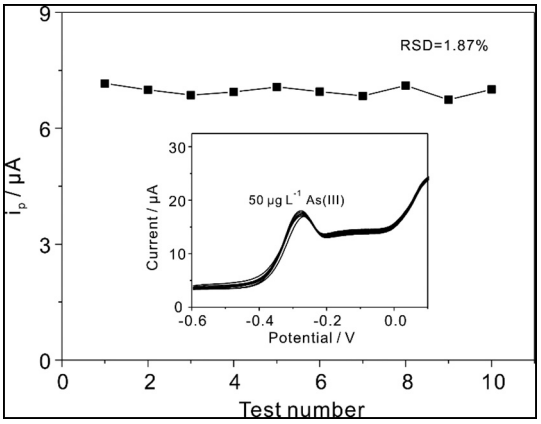


Fig. 7. Stability measurements on the Nafion/α-MnO_2@PDA-modified electrode for the repeated analysis of 50 μg L^{-1} As(III) in 0.1 M Na_2CO_3-$NaHCO_3$ solution at pH 9.0. The testing conditions are given as in Fig. 3.

Table 1
Determination of As(III) in different spiked water samples using the Nafion/α-MnO_2@PDA-modified electrode.

Samples	Added (μg L^{-1})	Found by SWAV (μg L^{-1})[a]	Recovery (%)
Lake water	50.0	49.1 ± 5.5	98.2%
	100.0	100.3 ± 1.9	100.3%
Tap water	50.0	51.0 ± 6.2	102.0%
	100.0	99.6 ± 5.1	99.6%

[a] Average value of three determination ± standard deviation.

3.6. Stability and reproducibility studies

The stability and reproducibility of the proposed Nafion/α-MnO_2@PDA-modified electrode were explored, the results are shown in Fig. 7 and Fig. S8, respectively. For 50 μg L^{-1} As(III), the relative standard deviation (RSD%) was found to be 1.87% for one electrode with ten repeated measurements and 2.67% for ten electrodes prepared with identical procedures. Additionally, the proposed electrode could be stored at room temperature for 9 days with no obvious change in its analysis performance (Fig. S9). For comparison, the reproducibility of the Nafion/α-MnO_2-modified electrode was also studied. Since experiments have shown that such an electrode exhibits a poor SWASV response to the As(III) concentration lower than 90 μg L^{-1} (Fig. 4c, d), a As(III) concentration of 110 μg L^{-1} was selected for the reproducibility study. As illustrated in Fig. S10, the RSD % is found to be 15.98% for ten Nafion/α-MnO_2-modified electrodes prepared with identical procedures. The large difference between the reproducibilities of the two modified electrodes is probably due to the good water-dispersible properties of the α-MnO_2@PDA composite.

3.7. Electroanalysis of As(III) in real water samples

To illustrate the accuracy in practical analysis using the proposed electrode, two different freshwater samples were collected from Yantai, Shandong. All water samples were used directly without pretreatment. It should be noted that the concentration of As(III) in these samples is very low, so the samples were spiked with 50 or 100 μg L^{-1} As(III) for the application evaluation. Prior to electrochemical measurements, the spiked water samples were diluted 10 times with 0.1 M Na_2CO_3-$NaHCO_3$ solution (pH 9.0). The resulting diluted samples were analyzed by the standard addition method, and the obtained results are shown Table 1. As illustrated, the data obtained at the proposed electrodes agrees well with the added concentration. These results demonstrate that the proposed electrode has promising potential for determination of As(III) in complex environmental samples.

4. Conclusion

In this work, we propose a simple strategy for determination of As(III) with the improved analysis performance in a weakly alkaline medium by using the Au disk electrode modified with the PDA-coated α-MnO_2 composites and Nafion layer. The introduction of the hydrophilic PDA layer can significantly improve the water-dispersible properties of α-MnO_2 microrods and their adsorption capabilities towards As(III) with plenty of amino and hydroxyl groups; Nafion have been employed as the membrane matrix, by which the α-MnO_2@PDA composites can be tightly attached to the sensor surface, therefore leading to the high sensitivity, good reproducibility and stability of the proposed sensor for detecting As(III). Moreover, such modified electrodes show the good anti-interference abilities even exposure to a high concentration interfering ion solution (10 times higher than the concentration of As(III)). We believe that this strategy has potential to be employed for quantification of As(III) for environmental monitoring and

drinking water quality purposes. Furthermore, the simple and robust surface modification method based on PDA layer can be extended to improve the water-dispersible properties of other micro/nanomaterials without the destruction of their structures.

Declaration of Competing Interest

None.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2020.114562.

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