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Synergy of glutathione, dithiothreitol and *N*-acetyl-L-cysteine self-assembled monolayers for electrochemical assay: sensitive determination of arsenic(III) in environmental and drinking water†

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A simple and efficient electrochemical assay based on self-assembled monolayers (SAMs) was developed for the highly sensitive determination of arsenic(III) in water samples. The synergy of glutathione (GSH), dithiothreitol (DTT) and *N*-acetyl-L-cysteine (NAC) mixed SAMs enhanced the detection specificity and sensitivity of As(III) in water samples, resulting from the immobilization of a large number of As(III) moieties on the gold electrode surface *via* As–O and As–S linkages. After accumulating As(III), anodic stripping voltammetry (ASV) was performed, and linear sweep voltammetry (LSV) was employed for signal recording. Several main voltammetric parameters were optimized as follows: supporting electrolyte, $1~\mathrm{mol~L^{-1}}$ HCl; deposition potential, -0.35 V; deposition time, 150 s. A good linear relationship ($R = 0.9980$) was attained between the concentration of the As(III) standard and peak current, in the range of 3–$100~\mu\mathrm{g~L^{-1}}$. The limit of detection (LOD) of this sensing system was determined to be $0.5~\mu\mathrm{g~L^{-1}}$ at a signal-to-noise ratio of 3. A variety of common coexistent ions in water samples were examined, showing no obvious interferences on the As(III) determination. The amenability of this method to the analyses of water samples was also investigated. High recovery of 90.5% with the precision of 5.1% at spiked $10~\mu\mathrm{g~L^{-1}}$, and low LOD of $0.3~\mu\mathrm{g~L^{-1}}$ were obtained in seawater. The synergy effect of GSH, DTT and NAC provided the possibility for the rapid and sensitive LSV determination of As(III) in complicated water samples.

Introduction

Arsenic is one of the most toxic elements found in nature and constitutes a main threat toward human health.[1] It is the 20th most abundant mineral in the Earth's crust. Drinking water rich in arsenic over a long period can lead to arsenic poisoning or arsenicosis. Many water areas contain excessive arsenic known to occur naturally in some regions[2] that is higher than the World Health Organization's guideline of $10~\mu\mathrm{g~L^{-1}}$.[3] At present, there are about 19 diseases associated with organism poisoning by arsenic compounds, especially after it is concentrated in the biological chain. Therefore, the sensitive determination of microscopic concentrations of arsenic compounds is a topical task.

Over the years, various analytical techniques and methods for the determination of arsenic at the trace level have been developed;[4] for instance, atomic fluorescence spectrometry (AFS),[4a–c] atomic absorption spectrometry (AAS),[4d,e] inductively coupled plasma spectrometry (ICP) with optical emission detection[4f–h] or mass spectrometry (MS),[4i] high-performance liquid chromatography (HPLC) with optical spectrometry detection,[4j,k] or MS,[4l] and HPLC-ICP-MS.[4m,n] Although these methods offer excellent sensitivity and multielement analysis, they involve costly, time-consuming procedures, sophisticated instruments, and are inappropriate for on-site field analysis.[1,4o,5] Therefore, it remains a challenge to explore a simple and inexpensive method for the determination of arsenic in environmental samples. Electrochemical sensing assays provide a possible means to this end since they are both rapid and portable.[1,5] Besides, they usually need no specific sample treatment, can preconcentrate analytes to produce very high sensitivity and low detection limits, are capable of speciation, their instrumentations are relatively simple and inexpensive and can be automated, as well as electrode devices being easily miniaturized.[1,5]

Hence, electrochemical methods, with high sensitivity, low detection limits, low costs and portable design for trace elements determination have received a great deal of interest.[6] Sarkar *et al.*[6b] reported a simple method for the estimation of arsenate in drinking water. The sensors were able to estimate arsenic below

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10 mg L^{-1} with a detection limit of 1.2–4.6 mg L^{-1}. Silvia et al.[6c] proposed platinum nanoparticle-modified carbon-based screen-printed electrodes for the electrochemical detection of arsenic (III). Good precision and accuracy were determined by analyzing the certificated and spiked tap water samples.

Self-assembled monolayers (SAMs) have attracted considerable interest in the past decades owing to their chemical stability, physical robustness, versatile strategies capable of introducing diverse functional groups, as well as featuring low cost and easy preparation. Therefore, they have been widely applied to the analysis of various target compounds, such as proteins,[7a,b] metal ions,[7c–e] pharmaceutical molecules,[7f–i] hormones[7j,k] and organic compounds.[7l] Zavarise et al.[8] described devices based on mercaptoalkyl/arylsulfonates-modified gold electrodes, which resulted in the effective determination of free and labile Pb(II) in water samples by anodic stripping voltammetry (ASV). And the ASV determination of Hg(II) at sub-ppm level concentrations had also been successfully attempted on a SAMs-modified gold electrode.[9] Miah et al.[10] reported the enhanced electrochemical oxidation of uric acid at the S–Au electrode in alkaline media. The proposed electrochemical sensor not only exhibited good reproducibility, but also showed a fast amperometric response with a low detection limit.

It is well known that As(III) can bind amino acids, amines, acids, peptides and organic micromolecules through the As–O or As–S linkages.[11] Kalluri et al.[12] demonstrated a highly sensitive colorimetric assay for arsenic recognition in aqueous solution based on the As–O and As–S linkages. Based on the above-mentioned linkage and interaction, we proposed a synergy effect of three common sulfhydryl compounds including glutathione (GSH), dithiothreitol (DTT), and N-acetyl-L-cysteine (NAC), which were synchronously self-assembled on the surface of a gold electrode, for the sensitive determination of As(III) in several water samples. The monolayer proved convenient and highly effective for the preconcentration of As(III), and thus it served as an excellent interface for the following stripping voltammetric detection. To the best of our knowledge, this is the first time that As(III) was preconcentrated from a water sample and highly sensitively determined by ASV based on the synergy of the synchronously mixed SAMs.

Experimental

Apparatus

Electrochemical studies were performed with a CHI 660C instrument (Chenhua Instruments, Shanghai, China). A gold disk electrode (2 mm in diameter) with the SAMs served as a working electrode, a Ag/AgCl (saturated KCl solution) was used as a reference electrode, and a Pt wire was employed as an auxiliary electrode.

Chemicals

All chemicals were of analytical grade and were used as received. Double deionized water (DDW) (18.2 MΩ) was used in the preparation of solutions. As(III) and As(V) standards in the concentration range from 1 μg L^{-1} to 1 mg L^{-1} were prepared fresh daily by making appropriate dilutions of the As(III) stock solution (1000 mg L^{-1}, Sigma) and As(V) stock solution (1000 mg

L^{-1}, Sigma) with DDW. Glutathione (GSH), dithiothreitol (DTT) and N-acetyl-L-cysteine (NAC), were also obtained from Sigma. HCl, H$_2$SO$_4$, acetic acid and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

Procedures

The gold disk electrode (2 mm in diameter, Chenhua Instruments, Shanghai, China) was polished with Al$_2$O$_3$ powder (0.3 and 0.05 μm) and sonicated in absolute ethanol and DDW (each for 3–5 min). After rinsing with DDW, the electrode was pretreated in a piranha solution (concentrated sulfuric acid : 30% hydrogen peroxide, 3 : 7, v/v) for 15 min in order to remove possible contaminants. An electrochemical cleaning process was carried out using a cyclic voltammetry (CV) technique performed from 0.0 to +1.7 V vs. Ag/AgCl in 0.5 mol L^{-1} H$_2$SO$_4$ solution using a scan rate of 100 mV s^{-1} until a stable cyclic voltammogram was obtained. Finally, the freshly pretreated gold electrode was immersed into an aqueous solution of the mixtures (GSH, DTT and NAC at 5 mM, respectively) or individual compounds at 5 mM, with overnight incubation for the formation of SAMs on the electrode surface. That the similar monolayers were formed but not multilayers can reference related work.[13] Then, the modified electrode was rinsed with DDW to remove physically adsorbed species before use.

The modified electrode was immersed into 1.0 mol L^{-1} HCl solution containing the target As(III) ion. The deposition potential of −0.35 V was applied to the SAMs-modified electrode for 150 s while the solution was stirred. Following the preconcentration step, the stirring was stopped and after 30 s the voltammetry was recorded by applying linear sweep voltammetry (LSV) with a scan rate of 100 mV s^{-1}. The scan was performed in the range from −0.3 to +0.6 V. All the solutions were purged with nitrogen before use to remove the dissolved oxygen.

Results and discussion

Characterization of the GSH/DTT/NAC mixed SAMs-modified gold electrode

For the proposed procedure, the three thiolated compounds mixed SAMs were first formed (Scheme 1). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using [Fe(CN)$_6$]$^{3−/4−}$ as a redox probe were performed to characterize the SAMs. As seen from Fig. 1A, the distorted redox peaks with larger electric potential difference and lower currents indicated a more sluggish electron transfer rate, observed at the GSH/DTT/NAC/Au interface (curve a) when compared to that of the bare gold electrode (curve b). Since [Fe(CN)$_6$]$^{3−/4−}$ and the monolayer on the electrode surface are negatively charged, the charge repulsion caused the decrease in the rate of electron transfer. This phenomenon is also well established by the EIS Nyquist plot in Fig. 1B, where the charge transfer resistance (R_{ct}) was increased remarkably when the thiol groups were assembled on the gold electrode surface (curve a), while very low one was seen on the bare electrode (curve b). More interestingly, the mixed SAMs also exhibited remarkably higher electronic repulsive force toward [Fe(CN)$_6$]$^{3−/4−}$ than that of individual SAMs (curve c–e). So, the mixed SAMs-modified electrode was selected.
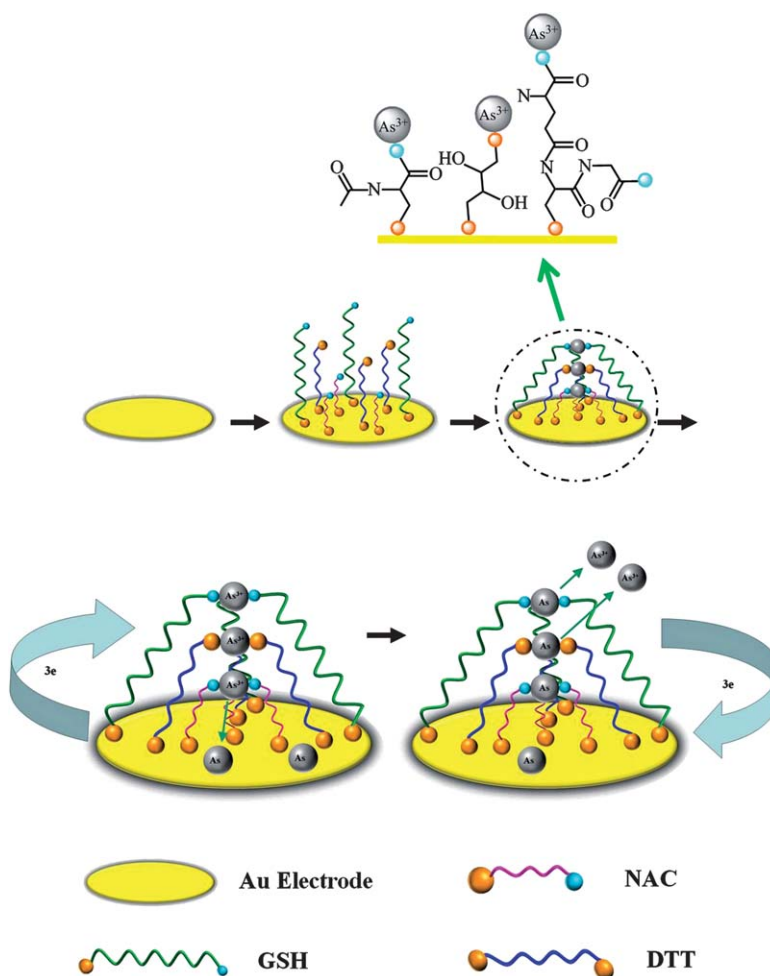
Scheme 1 Schematic representation of the amplified electrochemical detection of As(III) *via* mixed SAMs on the gold electrode. For clarity, GSH, DTT, NAC, and arsenic molecules are not drawn to scale.

For EIS, the Randles circuit model[14] was used with slight modification in the fitting (inset of Fig. 1B), where R_s is the electrolyte solution resistance, R_{et} the electrode surface electron transfer resistance, Z_w the Warburg impedance resulting from the diffusion of ions, and C_{dl} the double layer capacitance. In EIS, the semicircle diameter of the Nyquist diagram is equal to the surface electron transfer resistance (R_{et}) of the electrode. The immobilization of thiolated compounds on the electrode surface can change the R_{et} value. Therefore, the properties of modified electrodes may be known by the EIS measurement (Fig. 1B).

The electrode coverage (θ) is a key factor, which can be used to estimate the surface state of the electrode, and the charge-transfer resistance is also related to it. Assuming that all the currents are passed by pinholes on the electrode, the electrode coverage can be calculated[15] as:

$$(1 - \theta) = \frac{R_{ct}^0}{R_{ct}} \qquad (1)$$

where, R_{ct}^0 and R_{ct} are the charge-transfer resistances at the gold electrodes without and with the modification of SAMs under the same conditions, respectively. The charge-transfer resistances for the bare electrode and for the GSH/DTT/NAC-modified electrode, established through the impedance-plot, were 695 Ω and

28330 Ω, respectively. Using these values and eqn (1), the electrode coverage was estimated to be 97.5%. The large electrode coverage meant that huge amounts of molecules were immobilized onto the electrode's surface. Therefore, the formed mixed SAMs would greatly favour the following capturing and redox process of As(III), and the modified electrode could serve as the free interface for As(III) analysis in aqueous solutions.

Electrochemistry of As(III) on the mixed SAMs-modified electrode

LSV responses for the stripping analysis of As(III) were recorded from different electrodes, as shown in Fig. 2. The freshly prepared GSH/DTT/NAC Au electrode was immersed in a 1 mol L^{-1} HCl solution containing 0.1 mg As(III), obtaining a well-defined peak corresponding to the reduction of captured As(III) at 0.21 V (curve a). Meanwhile, no peak was observed in the absence of As(III) (curve b). It is noted that a peak with much lower peak current also appeared at approximately 0.21 V for the same conditions as described in curve 'a' except on the bare electrode (curve c). It is well known that, the surface of the bare gold electrode is easily oxidized and contaminated, and therefore causes the effective electrode area to become smaller and smaller, so current efficiency
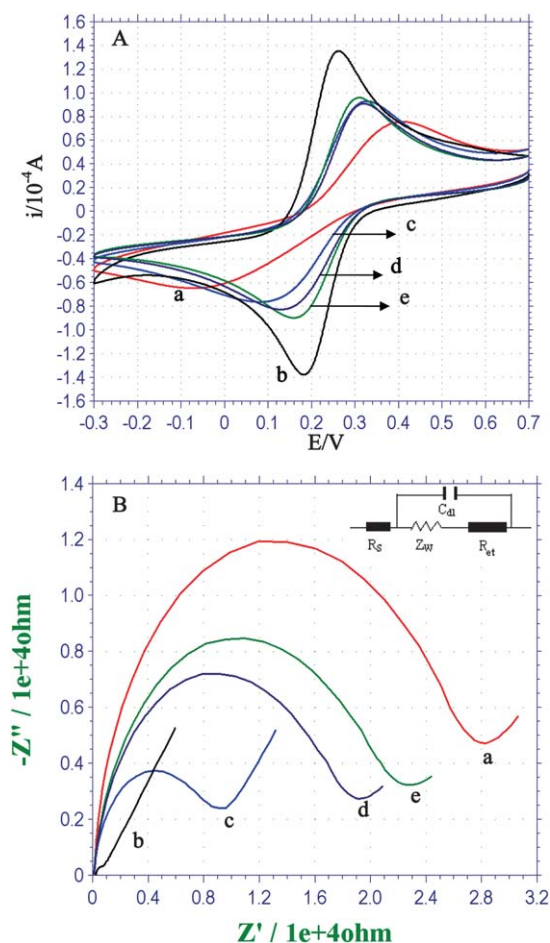
Fig. 1 Electrochemical characterization of GSH/DTT/NAC Au electrode (a), bare Au (b), NAC Au electrode (c), GSH Au electrode (d) and DTT Au electrode (e) in 1 mM of $[Fe(CN)_6]^{3-/4-}$ containing 0.1 mol L^{-1} KCl. (A) Cyclic voltammograms at a scan rate of 100 mV s^{-1}. (B) Electrochemical impedance spectroscopy Nyquist plot. (Inset) Equivalent circuit used to model impedance data in the presence of redox couples; R_s is the electrolyte solution resistance, R_{et} the surface electron transfer resistance, Z_w the Warburg impedance resulting from the diffusion of ions, and C_{dl} the double layer capacitance.

falls continuously. As a result, it is impossible to accurately and sensitively determine As(III) by using the bare electrode. To solve this problem, the proposed SAMs formed an excellent protective layer on the electrode surface (Scheme 1). More importantly, the SAMs captured more As(III) from the solution due to the two types of specific coordination interactions of As–O and As–S (Scheme 1), leading to amplified current responses (curve a).

Possible detection mechanism for the SAMs-modified electrode

The illustration for As(III) reduction detection based on the chelation interactions of As–O and As–S of the mixed SAMs is shown in Scheme 1. The three kinds of molecules of GSH, DTT and NAC containing sulfhydryl were first immobilized on the electrode surface *via* the strong bonding interaction of Au–S[13c] to form the stable and compact mixed SAMs. On the other end of the SAMs, there are sulfhydryl or hydroxyl groups exposed in the solutions, which are apt to capture As(III) from the solutions to
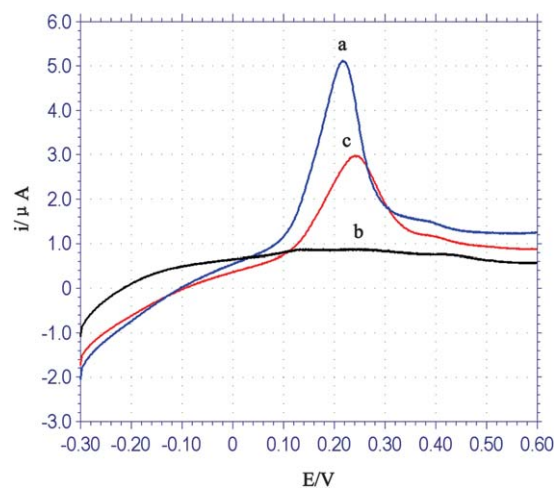
Fig. 2 Linear sweep voltammograms of As(III) collected at electrodes modified with the mixed SAMs in the presence (a) and absence (b) of 0.1 mg L^{-1} As(III), and at bare electrodes in the presence of 0.1 mg L^{-1} As(III) (c). Experimental conditions: supporting electrolyte, 1 mol L^{-1} HCl; deposition potential, −0.35 V; deposition time, 150 s.

the electrode surface by virtue of the chelation interactions of both As–S and As–O bonds, and these linkages have been validated by mass spectrometric method[16] and inductively coupled plasma atomic emission spectrometer (ICP-AES),[17] and surface plasmon resonance (SPR),[18] respectively. The chelated As(III) was reduced and deposited on the gold surface. And then the emptied exposed sulfhydryl or hydroxyl groups rebind As(III) from solutions. The As(III) moieties are easily positioned in close proximity to the underlying electrode, allowing facile electron transfer to occur. More As(III) in the solutions were brought to the electrode surface and reduced, resulting in amplified voltammetric responses. Notably, herein the electron transfer was promoted by some factors such as the suitable distance, small steric hindrance and enough electron/hole acceptors, or *vice versa* insulated. The similar electron transfer mechanism about SAMs has been well documented.[19]

Additionally, for the mixed SAMs, a three-dimensional structure was formed on the surface of the gold electrode. Due to the different lengths of the chains, a three-layer hierarchy might be shaped and would co-contribute to the amplified detection of As(III) by a synergetic effect. This synergy was further confirmed by comparing the analytical performance with other individual SAMs-modified electrode or bare electrode, as shown in Table S1.† From the table, although a comparable LOD was obtained on the NAC-based SAMs electrode, the poor anti-interference was a headache. Comprehensively considering the sensitivity and the selectivity, a proportional mixture of the three compounds was adopted. It would prefer to capture a large number of As(III) in sequence and then exhibit the excellent electron transfer property. Also, the surface coverage of SAMs *ca.* 97.5% supported the approaching and reduction of more As(III), and higher current responses.

Optimization of voltammetric parameters

In order to obtain the optimum determination performance, several main voltammetric parameters remarkably affecting the

stripping responses of the SAMs-modified electrode were examined, including supporting electrolyte, deposition potential, and deposition time.

Effect of supporting electrolyte. Selection of a suitable supporting electrolyte is important for good electrochemical responses towards As(III) on the GSH/DTT/NAC-modified electrodes. Three electrolyte solutions including HCl, H_2SO_4 and acetic acid were tested, at two concentration levels of 0.1 and 1 mol L^{-1}, respectively. Among these, the better shape and higher intensity of the reduction peak of As(III) in 1 mol L^{-1} HCl was obtained than that in others (Fig. S1†). So, 1 mol L^{-1} HCl was chosen as the supporting electrolyte in the following work. The SAMs-modified electrode will be working stably in the strong acid solution under the applied potential. The same strong acid solution was also employed as the supporting electrolyte for similar SAMs-based electrochemical detections.[20]

Deposition potential. The effect of deposition potential on the LSV response for As(III) on the SAMs electrode is shown in Fig. S2.† As can be seen, the peak current increased as the deposition potential became more negative. That As(III) carried positive charges favored the accumulation of As(III) at more negative potentials. However, a too negative potential would cause the progressive reductive desorption of the SAMs. Therefore, a deposition potential of −0.35 V was chosen for all the subsequent work.

Deposition time. Linear responses with deposition time at −0.35 V for 0.1 mg L^{-1} As(III) is shown in Fig. S3.† As the deposition time increased, the peak current rose gradually, till up to 150 s. Then the peak current began to level off at longer deposition time, probably due to the saturation of As(III) on the electrode surface. Hence, 150 s was selected for further experiments.

Analytical performance for determination of As(III)

Under the optimum experimental conditions mentioned above, the LSV responses of the SAMs-modified electrode were recorded with varying As(III) concentrations in the range from 3 to 100 µg L^{-1} as shown in Fig. 3. The peak current was used for As(III) quantification. LSV and current peak height were adopted over differential pulse voltammetry (DPV) and current peak area, respectively (data not shown). As shown in the inset, the peak current goes up with increasing concentration of As(III) standard, with a good linear correlation ($R = 0.9980$) of 2 orders of magnitude. The error bars (relative standard deviation, RSD, ranging from 2.13 to 7.32%) were relatively small, indicating that the method is quite reproducible. Based on a signal-to-noise ratio of 3 (S/N = 3), the limit of detection (LOD) was estimated to be 0.5 µg L^{-1}, which is much lower than the maximum level of As(III) (10 µg L^{-1}) permitted by the WHO. The developed sensing assay proved promising in environmental monitoring of the exposure of As(III).

The comparisons of the analytical performances with other reported electrochemical methods for As(III) determination were shown in Table S2.† As can be seen, this voltammetry-based method is very sensitive and accurate for As(III) analysis. We
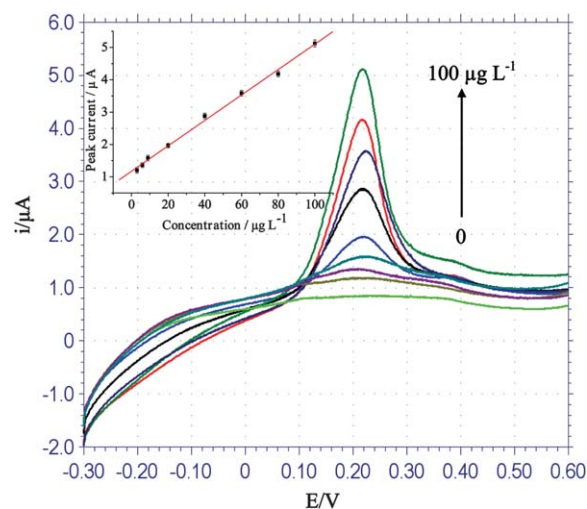
Fig. 3 Anodic stripping voltammetric responses of the mixed SAMs-modified electrodes to the addition of various concentrations of As(III) (0, 3, 6, 9, 20, 40, 60, 80 and 100 µg L^{-1}) in 1 mol L^{-1} HCl solutions. (Inset) Plots of the value of anodic peak currents as a function of the concentration of As(III). The error bars denote standard deviation from 5 independent measurements. The experimental conditions were the same as those described in Fig. 2.

attribute the sensitivity improvement to the signal amplification associated with the introduction of a large number of As(III) moieties to the electrode surface, owing to the synergy of the mixed SAMs.

Interference study

To study the selectivity of this SAMs-based ASV method for As(III), some commonly found alkali and alkaline earth metal ions (Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}), heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}), and several anions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$) in water were chosen for their possible interference investigation. The peak current of 100 µg L^{-1} of As(III) was recorded in the presence of 10, 100, and 1000 times excess amount of various potential interfering ions, respectively. Results showed that more than a 1000 times excess of Ca^{2+}, K$^+$, Na$^+$, Mg^{2+}, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$, a 100 times excess of Pb^{2+} and Cd^{2+}, and 10 times excess of Cu^{2+} and Hg^{2+} had no obvious influences on the determination of As(III), as seen from Fig. S4.† In fact, the alkali metal ions, alkaline earth ions and anions are inert in the present ASV analysis using LSV, and their effects on ASV of As(III) can be neglected. Besides, the tested transition metal ions would not interfere with the determination of As(III) considering the large difference in peak potentials between them and As(III), respectively. The present SAMs-based ASV detection showed high specificity and reliability for As(III) assay.

Determination of As(III) in environmental and drinking water samples

To demonstrate the feasibility of the method for real water sample analysis, we further subjected the SAMs to measure As(III) in several environmental and drinking water samples including tap water, bottled water, mineral water, river water and seawater. Tap water samples were collected from our laboratory

Table 1 Linear correlations and detection limits for As(III) determination in several water samples ($n = 5$)

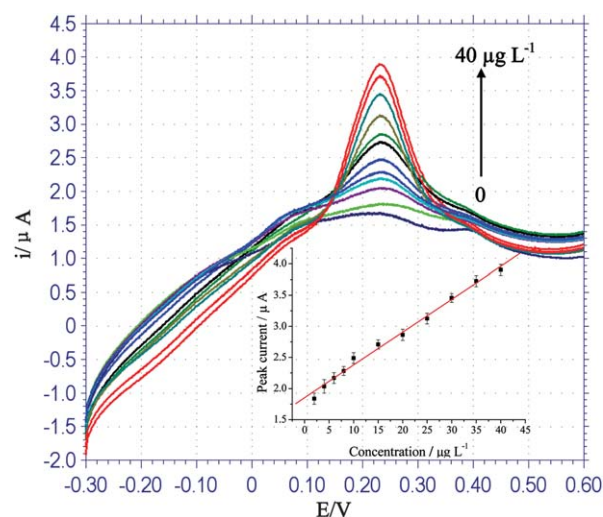| Samples	Linear range/μg L^{-1}	Slope	Intercept	R	LOD/μg L^{-1}
Tap water	8–50	0.039	1.171	0.9971	0.9
Bottled water	8–60	0.041	1.329	0.9956	0.7
Mineral water	6–50	0.049	1.636	0.9963	0.6
River water	6–60	0.046	1.563	0.9935	0.6
Seawater	2–40	0.052	1.852	0.9916	0.3

after flowing for about 5 min. The bottled purified water samples were purchased from a local supermarket, a well-known brand. Mineral water from a local pond, river water from Dagujiahe River and seawater from a bathing beach of Huanghai (Yantai, China), were collected and filtered through a 0.45 μm Nuclepore filter for removing the silt soil and sand grain. And then, hydrochloric acid was used to acidulate the tested water samples for certain acidity. The water samples were directly analyzed or stored at 4 °C for use. Before the spiking procedure, the samples were analyzed and were found to be free of arsenic contamination.

Quantitation correlations assessed using samples spiked at different concentration levels were obtained between peak current height and the corresponding concentrations of As(III), listed in Table 1. LODs for As(III) in the several water samples, calculated as the analyte concentration for which the peak current height was three times the background noise (3S/N), were attained within 0.3–0.9 μg L^{-1}, respectively. Taking the seawater example, as shown in Fig. 4, remarkable peak current height and its changes could be observed for the spiked seawater with As(III). The magnitude of the peak current height was found to be dependent on the As(III) concentration, presenting an excellent linear relationship within 2–40 μg L^{-1}. The LOD was determined, namely 0.3 μg L^{-1} of As(III) in seawater matrix. It is noted that the LOD was slightly lower than that of 0.5 μg L^{-1} in the standard solution of 1 mol L^{-1} HCl. In a certain sense, the results from seawater samples also suggested that the developed SAMs-based ASV determination had wide applicability without significant matrix interferences.

The recoveries obtained in different water samples spiked with 1, 10 and 100 μg L^{-1} As(III), respectively, were from 83.5–98.5% with the RSDs of 3.5–5.7%, shown in Table 2. For the seawater samples, the recoveries of spiked As(III) ranged from 83.5–96.8% with the precision of 3.6–5.1%, indicating the great applicability of the mixed SAMs-based voltammetric method for As(III) quantification in aqueous media. The results also indicated that the matrix effect had no significant effects on the SAMs-based ASV determination. Therefore, the developed method was validated applicable to environmental and drinking water samples analysis for As(III).

Fig. 4 Anodic stripping voltammograms responses of the mixed SAMs-modified electrodes to the addition of various concentrations of As(III) (0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35 and 40 μg L^{-1}) in spiked seawater samples.

Table 2 Method recoveries for the determination of As(III) in spiked water samples ($n = 5$)

Samples	Spiked/μg L^{-1}	Recovery (%)	RSD (%)
Tap water	1	97.9	5.6
	10	91.3	4.2
	100	87.1	5.3
Bottled water	1	95.8	3.8
	10	89.6	5.3
	100	82.9	5.6
Mineral water	1	98.5	4.6
	10	93.6	5.7
	100	90.1	3.5
River water	1	96.1	3.9
	10	90.3	5.2
	100	85.2	4.6
Seawater	1	96.8	3.6
	10	90.5	5.1
	100	83.5	4.7

Determination of As(v)

The developed electrochemical sensor was further investigated about its capability of speciation. As shown in Fig. S5,† there is no apparent voltammetric response when the SAMs-modified electrode was scanned in As(v) solution (curve b), while a marked peak was obtained when Na$_2$SO$_3$ was added (curve c) showing the production of As(III) *via* the reduction of As(v). The observations indicated the sensor capable of speciation of As(III) but not As(v), and also the determination of As(v) can be realized by valence conversion to As(III). Reduction of As(v) was performed as described.[1] The method was illustrated satisfactory to determine the species of arsenate. Furthermore, the total arsenic contents could be obtained.

Conclusions

A novel type of mixed SAMs composed of GSH, DTT and NAC was immobilized on the gold electrode surface and applied to amplified electrochemical assays of As(III) in both standards and real environmental and drinking water samples. This study demonstrated a simple and efficient method for electrode modification and its application in the detection of As(III) in aqueous media via ASV. The SAMs were well constructed and characterized by CV and EIS. Several main parameters including supporting electrolyte, deposition potential and deposition time were optimized. Excellent analytical performances were attained, especially a low LOD of 0.3 μg L^{-1} in seawater matrices. The synergy of GSH, DTT and NAC made the SAMs-modified electrode possible to serve as an excellent interface for As(III) preconcentration by As–S and As–O linkages, and therefore the SAMs-based voltammetric method for trace Au(III) analysis is simple, selective, sensitive and reproducible. Given the advantages, we can foresee a strong potential for this approach in the routine monitoring of trace As(III) present in environmental and drinking water samples.

Acknowledgements

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