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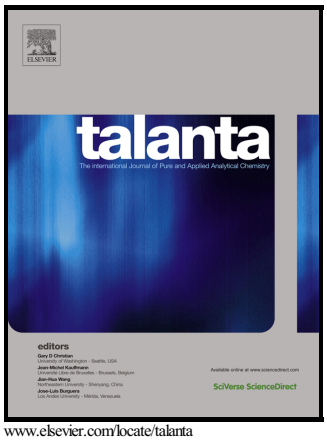

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Single Strand DNA Functionalized Single Wall Carbon Nanotubes as Sensitive Electrochemical Labels for Arsenite Detection

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Abstract

In this work, a simple and sensitive electrochemical strategy for arsenite detection based on the ability of arsenite bound to single-strand DNA (ssDNA) and the signal transduction of single wall carbon nanotubes (SWCNTs) is developed. To realize this purpose, the ssDNA/SWCNTs complexes were formed at first by making ssDNA wrapped around SWCNTs via π-stacking. In the presence of arsenite, the arsenite could strongly bind with the G/T bases of ssDNA and decrease the π-π interaction between ssDNA and SWCNTs, resulting in a certain amount of ssDNA dissociating from the complexes. The separated SWCNTs were selectively assembled on the self-assembled monolayer (SAM) modified Au electrode. Then the SWCNTs onto the SAM-modified Au electrode substantially restored heterogeneous electron

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transfer that was almost totally blocked by the SAM. The assembled SWCNTs could generate a considerably sensitive and specific tactic for signal transduction, which was related to the concentration of the arsenite. Through detecting the currents mediated by SWCNTs, a linear response to concentration of arsenite ranging from 0.5 to 10 ppb and a detection limit of 0.5 ppb was readily achieved with desirable specificity and sensitivity. Such a SWCNTs-based biosensor creates a simple, sensitive, nonradioactive route for detection of arsenite. In addition, this demonstration provides a new approach to fabrication of stable biosensors with favorable electrochemical properties believed to be appealing to electroanalytical applications.

Keywords*:* electrochemical; SWCNTs; signal transduction; arsenite; biosensor

1. Introduction

It is inorganic arsenic species that are probably best known as a poison and extremely toxic to humans who ingested it. Large doses are fatal relatively quickly, while small doses over time can be causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes such as hyperkeratosis and pigmentation changes [1, 2, 3]. In the present world, a large amount of populations are at stake for arsenic poisoning because of exposure to contaminated drinking water. It is widely distributed throughout Earth's crust, most often as arsenic sulfide or as metal arsenates and arsenides. Usually speaking, the arsenic species are most likely to present as arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) in water [4]. The two oxidative forms of arsenic play a large role in the toxicity and behavior of the metalloid.

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However, arsenite is even considered 60 times more toxic than arsenate and both of these inorganics are 100 times more toxic than their organic versions. In reducing environments such as those found in Bangladesh, West Bengal, Vietnam, China and Taiwan, ground water is polluted primarily with arsenite through the desorption of arsenic from iron surfaces after the reduction of iron oxyhydroxide by underground bacteria. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) set public drinking water standards called "Maximum Contaminant Levels" (MCL) to help reduce public health risk associated with drinking water. Also they set the arsenic MCL at 10 ppb (ppb = parts per billion or micrograms per liter) in 2006. This is due mainly to the fact that inorganic As compounds are carcinogenic to humans in reference to sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals.

There have been several methods used to detect trace levels of arsenic, and they are mainly carried out using analytical methods such as fluorescence [5, 6, 7], colorimetric assay [8, 9], resonance Rayleigh scattering [10], electrochemical method [11, 12], surface plasmon resonance (SPR) [13], surface-enhanced Raman spectroscopy (SERS) [14], electrothermal atomic absorption spectrometry (ETAAS) [15]. However, most of those methods were somewhat sophisticated, expensive or needing fluorescence labeling. Thus, to develop a simple, label-free and sensitive sensor for arsenite detection is highly expected. The electrochemical technique performs appealing merits of simple instrumentation, high sensitivity, miniaturization, and excellent compatibility with assay of colored and viscous samples so that it has been

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widely applied in various biosensors. Therefore, electrochemical technique is an important technique for arsenite detection and using various nanomaterial-based amplifications can further enhance the sensitivity of electrochemical biosensors to some extent.

Compared with other potential nanomaterial, carbon nanotubes (CNTs) are acknowledged to be promising materials that are composed of hollow graphitic cylinders. Exhibiting electronic conductivity and ability to promote electron-transfer reactions, CNTs simultaneously bear great chemical stability, large aspect ratio, excellent electrical conductivity, and high electrocatalytic activity that serve as novel and intriguing electrode modifications for the catalysis of biomolecules and inorganic compounds [16, 17]. These modified electrodes, particularly the ordered CNT arrays exemplified by CNT forests, build efficient platforms for accelerating electron transfer between the electrochemical labels and the electrodes, thus increasing the possibility of sensitivity improvement [18, 19]. In addition to the utilization of CNTs in direct electrochemical signal transduction, CNTs can also be applied as efficient carriers to load a large amount of labels, which extremely amplify the signal transduction events and yield a dramatic enhancement to the sensitivity [20]. Moreover, the CNT-based labels can be controllably assembled on an electrode modified with an insulating self-assembled monolayer, and then mediate the redox response of numerous indicator molecules [21]. All that above proved that the CNT is a novel label offering a highly efficient signal amplification style in electrochemical transduction while with a low background current [22, 23]. It has been reported that sonication of

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ssDNA with CNTs is extremely effective at dispersing the nanotubes in the aqueous solution by means of aromatic interactions between CNTs' sidewalls and nucleotide bases, and several researchers reported covalent or noncovalent functionalization of CNTs with ssDNA, indicating the great potential of CNTs for the development of biosensor [24, 25].

In this paper, we developed a label-free and sensitive electrochemical sensing platform for arsenite detection based on the folded ssDNA bound to arsenite and controlled assembly of single wall carbon nanotubes (SWCNTs) for the first time. The wrapping of SWCNTs by ssDNA occurs when the aromatic nucleotide bases in ssDNA may be exposed to form π-stacking interactions with the hydrophobic side-wall of carbon nanotubes, whereas the hydrophilic part of the ssDNA strand is left exposed to interact with the solvent. In the presence of arsenite, the arsenite could strongly bind up with the G/T bases of ssDNA and lead to some ssDNA to dissociate from the SWCNTs [26]. The SWCNTs are selectively assembled on the self-assembled monolayer (SAM) of $C_{18}H_{37}SH$ modified Au electrode. This SWCNTs assembly can mediate efficient electron transfer between the electrode and electroactive species, generating a high faradic current due to the signal transduction, which was correlative with the concentration of arsenite. Such a SWCNTs based biosensor explores a simple, sensitive, nonradioactive route for arsenite detection. In addition, this demonstration offers a new approach to fabrication of stable biosensors with excellent electrochemical properties that are believed to be very attractive for electroanalytical applications.

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2. Experimental Section

2.1 Reagents and materials

Single wall carbon nanotubes (purity > 90%, diameter < 2 nm, length 5-15 μm) was purchased from Nanoport. Co. Ltd. (Shenzhen, China). Ferrocenecarboxylic acid (FcCOOH) and 1-octadecanethiol ($C_{18}H_{37}SH$) were purchased from Sigma-Aldrich. Other reagents were of analytical grade used without further purification. All solutions were prepared and diluted using ultrapure water (18.2 MΩ·cm) from the Millipore Milli-Q system.

The ssDNA was synthesized and purified by Shanghai Sangon Biological Engineering Technology & Services Co., Ltd. (China). The sequence of ssDNA probe used in this work was as follows:

5'- ACGCATCTGTGAAGAGAACCTGGG -3'

2.2 Instrumentation

Transmission electron microscopy (TEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) measurements were carried out on a JEOL 3010 transmission electron microscope. A CHI660A electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) was employed for differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) measurements. The electrochemical workstations have a three-electrode mode consisting of a gold working electrode (2 mm diameter, CHI101, CH Instrument Inc.), a platinum counter electrode and a saturated calomel reference electrode (SCE). All the potentials in this paper were with respect to SCE. The

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electrolyte buffer was thoroughly purged with nitrogen before experiments.

All electrochemical measurements were carried out in the electrolyte solution of 0.1 M phosphate buffer (PB buffer, pH 7.4) containing 5 mM FcCOOH and 0.1 M $NaClO_4$ at room temperature. DPV was performed within the potential range from -0.1 V to +0.7 V under modulation amplitude of 25 mV and sample width 16.7 ms. EIS was performed in the frequency ranging from 0.1 Hz to 100 kHz with 10 mV as the frequency modulation at a bias potential of 0.28V. The electrolyte buffer was purged thoroughly with high-purity nitrogen before experiments. All the measurements were performed by parallel experiments for at least five times repetitions, and the error bars have been shown.

2.3 Working electrode modification

The insulated $C_{18}H_{37}SH$ modified gold electrode can be a good platform for controlled assembly of SWCNTs as signal transduction. Before detection, the gold electrode was treated with freshly prepared piranha solution (H_2SO_4/H_2O_2, 7:3 by volume) for 10 min and rinsed with ultrapure water thoroughly, then polished carefully with 0.3 and 0.05 μm alumina powder, followed by sonication for 5 min in ultrapure water, ethanol, and ultrapure water, respectively. The clean gold electrodes electrochemically treated in 0.1 M H_2SO_4 by cycling the potential between -0.2 to 1.55 V until a stable cyclic voltammogram was obtained, washed with ultrapure water and dried with purified nitrogen for use. The pretreated electrodes were immersed in an ethanol solution containing 20 mM $C_{18}H_{37}SH$ at room temperature for 3 h to produce a dense SAM. Then the SAM-modified electrodes were rinsed completely

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using ethanol so as to remove $C_{18}H_{37}SH$ weakly adsorbed on the electrode followed by drying under mild nitrogen stream. These gold electrodes could be used for assay of the next sample via polishing to remove the adsorbates followed by the aforementioned treatments.

2.4 Preparation of ssDNA/SWCNTs complex

The purchased SWCNTs were further purified before used. Briefly, 5 mL of 20 mM Tris-HCl buffer (pH 8.2) containing 2.0 mg/mL SWCNTs was sonicated (200 W) for 120 min in ice bath using an ultrasonic crasher to obtain a black dispersed suspension. Then the resulting suspension was centrifuged at 1000 rpm for 10 min to remove large SWCNTs. Consequently small pieces of SWCNTs supernatant were collected and reserved for further sensing application.

5.0 mL of aqueous solution containing 10.0 mg of purified SWCNTs, 50 μM DNA oligonucleotides, and 0.1 M NaCl was sonicated in ice bath for 120 min. The resulting suspension was centrifuged at 14 000g for 30 min to remove possible SWCNTs aggregates. The supernatant was collected and recentrifuged under similar conditions, and the sediment was again discarded. The SWCNTs in the supernatant were collected and filtered through a Millipore centrifugal filter with a molecular weight cutoff of 100 kDa (Billerica, MA) to remove excessive oligonucleotides not wrapping around the SWCNTs. After washed 3 times, the ssDNA/SWCNTs complex was resuspended in 20 mM Tris-HCl buffer (pH 8.2). Such a suspension of ssDNA/SWCNTs complex, when stored at 4 ^{o}C, was found to be stable for weeks with no appreciable aggregates and precipitates.

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2.5 Electrochemical detection of arsenite

A 4.0 μL aliquot of ssDNA/SWCNTs complex was added into 16.0 μL of sample mixture containing 20 mM Tris-HCl buffer (pH 8.2) and arsenite of a given concentration. The mixture solution with designed arsenite concentration was incubated for 60 min to allow complete interaction between the arsenite and the ssDNA/SWCNTs complex, which induces ssDNA desorption from SWCNTs. 10 μL aliquot of the resulting solution was dropped on the surface of SAM modified electrodes and incubated at room temperature for 60 min. Subsequently, the electrode was thoroughly rinsed with ethanol and ultrapure water to remove SWCNTs weakly adsorbed on the electrode surface. Then the electrodes were dried under N_2 stream before electrochemical measurements. All electrochemical measurements were conducted in 20 mM PB buffer solution (pH 7.4) containing 5 mM FcCOOH and 0.1 M $NaClO_4$ at room temperature.

2.6 Selectivity of arsenite detection

The influence of other ions on arsenite detection could be also quantitatively analyzed using this assay. For the selectivity test, ions with final concentration at 100 ppb (Fe^{3+}, Fe^{2+}, Ag^{+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Cu^{2+}) were added respectively, amounting to 10-fold higher than that of arsenite, and the electrochemical signal was recorded after 60 min. The processes were similar to the assay of arsenite.

3. Results and discussions

3.1 Design strategy

The arsenite can easily bind to the G/T ssDNA and issue in some ssDNA

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dissociate from the SWCNTs. When coupled with certain unique properties of SWCNTs, it inspires the development of a novel label-free electrochemical biosensor strategy for detecting the arsenite, the principle as illustrated in **Scheme 1**. In the design, the clean gold electrode is modified with a dense SAM of long chain alkanethiols $C_{18}H_{37}SH$. This hydrophobic SAM isolates the electrode from electroactive species in aqueous solution, and thus the electron transfer between redox probes and the electrode surface is blocked with no electrochemical signal detected. Whereas in the absence of arsenite, SWCNTs are wrapped around by ssDNA via π-π stacking interactions between nucleotide bases and SWCNTs sidewalls, forming an ssDNA/SWCNTs complex stably dispersed in the solution (**Figure 1**). Then it would not be adsorbed on the SAM due to strong electrostatic and hydration repulsions, which kept the SAM isolated with no background current signal being generated **(it is eT off state**). In addition of arsenite, the complexation of arsenite with the ssDNA yielded a folded arsenite/ssDNA complex, thus the ssDNA couldn't be adsorbed efficiently on SWCNTs, and therefore the SWCNTs would be detached from the solution. When the mixture was dipped on the SAM electrode, the released SWCNTs were assembled on the electrode by van der Waals and hydrophobic interaction. Adsorbed on the isolated SAM, the SWCNTs could mediate efficient electron transfer between the electrode and electroactive species such as FcCOOH, after which a strong redox current was generated (**it is eT on state**). As the electrochemical current boosts with the increasing concentration of arsenite, this biosensor offers a general and quantitative approach for sensitive arsenite detection.

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Scheme 1

Figure 1

3.2 Feasibility investigation and characterization of the electrochemical assay

To investigate feasibility of the electrochemical assay, the DPV was performed. As shown in **Figure 2A**, there was no remarkable DPV response signal observed for FcCOOH at the $C_{18}H_{37}SH$ modified electrode (**curve a**), indicating that a densely packed isolating layer on the electrode formed by the long chain alkanethiol thoroughly blocked the effective electron-transfer of the redox probe on the electrode surface. Incubation of a SWCNTs/ssDNA complex suspension on the electrode had little effect on the DPV response, and only a tiny increase could be observed (**curve b**). It manifested that the adsorption of the SWCNTs/ssDNA complex on the SAM was precluded due to the strong electrostatic and hydration repulsion between the SWCNTs/ssDNA complex and the SAM surface. Whereas when arsenite was added, the current response considerably increased (**curve c**). This demonstrated that SWCNTs would be assembled on the SAM by the π-stacking and hydrophobic interactions, thus facilitating the electron transfer between the electrode and FcCOOH. In contrast, the bare gold electrode exhibited a high DPV response (**curve d**). These experimental datas showed that the electrochemical assay for arsenite detection could be carried out.

The EIS measurements were an efficient method to investigate the interface properties of modified electrode. Therefore, EIS measurements were also performed

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to further investigate the isolating properties of the SAM for the arsenite sensing. As **Figure 2B** showed, the bare gold electrode exhibited a very small semicircle domain whose R_{et} value was about 122.2 Ω (**curve a**), attributing to the free electron-transfer process. When the SAM modified gold electrode, the R_{et} increased to 17704.5Ω (**curve b**), because the hydrophobic isolating layer blocked electron transfer between the electrode and the electroactive indicators. Since there was trace dissociative SWCNTs in the suspension of the SWCNTs/ssDNA complex, the incubation of the SWCNTs/ssDNA complex on the electrode induced slightly decreased impedance whose R_{et} value was 15788.8 Ω (**curve c**). However, after incubation with arsenite, the substantial decrease of electrochemical impedance can be observed (**curve d**), the R_{et} value increased to 7513.6 Ω which is because the arsenite could be adsorbed on the ssDNA and the SWCNTs thus isolated from the SWCNTs/ssDNA complex. These released SWCNTs could be assembled on the SAM, thus facilitating the electron transfer between the electrode and FcCOOH. These datas agreed well with the equivalent circuit model (**inset in Figure 2B**): Rr, RSWCNT, Rsol, and RSAM were the electrochemical resistance of the soluble redox species, SWCNT/SAM, solution, and SAM respectively. CSWCNT and CSAM were for the capacitance of SWCNT/SAM and SAM respectively. EIS results demonstrated that the surface of gold electrode was successfully fabricated according to design strategy.

Figure 2

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3.3 Optimization of assay conditions

To achieve the optimal response of the assay, the effect of pH value in the reaction system, incubation time of SWCNTs/ssDNA complex and arsenite, and immobilized time of the released SWCNTs on the DPV intensity were optimized in this experiment. As seen in **Figure 3A,** the pH range was between 6.0 and 9.0, with the maximum response at pH 8.2, which was precisely the optimum pH value for the arsenite detection. The arsenite in the form of H_3AsO_3 contained three hydroxy groups, which made them easy to bind to the G/T of the ssDNA through the strong hydrogen bonds between hydroxy groups and amine groups or ketone groups of bases in DNA. The incubation time of prepared SWCNTs/ssDNA complex with target was also optimized. As indicated from **Figure 3B,** the DPV response increased with the increment of incubation time from 20 to 120 min, and tended to a maximum at 60 min. longer incubation time did not obviously change of the signal intensity. Therefore, 60 min was chosen as the optimal time for the detection. The signal of the sensor directly depended on the released SWCNTs which were assembled on the SAM modified gold electrode, so the immobilized time was also crucial in the assay. As seen in **Figure 3C**, with the increase of immobilized time, the DPV response slowly increased and tended to a maximum at 60 min, Thus 60 min was chosen for the immobilized time of released SWCNTs on the SAM modified gold electrode.

Figure 3

3.4 Arsenite detection

Under the optimum conditions, we have presented the electrochemical method to

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assay arsenite. The detection performance of the arsenite assay was carried out by exposing the sensor to series of arsenite concentrations. As shown in **Figure 4A,** it gave typical DPV responses to different concentrations of arsenite. We observed dynamically increased peak currents in response to increasing arsenite concentrations within the range from 0.5 to 1000 ppb. Linear correlation showed in the calibration plot between the peak current and arsenite concentration in the range of 0.5 to 10 ppb with a correlation coefficient of 0.983 (inset of **Figure 4B**), and the regression equation was I (A) = 0.1382x + 0.8179 (x is arsenite concentration). The detection limit was 0.5 ppb, much lower than the toxicity level of arsenite in drinking water defined by EPA and WHO. With respect to sensitivity, this electrochemical assay for arsenite detection was better than some previously reported arsenite assay [26, 27].

Figure 4

3.5 Selectivity of the arsenite detection

To verify that the assay could specifically detect arsenite, we incubated the sensor with various ions (100 ppb) including Fe^{3+}, Fe^{2+}, Ag^{+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Cu^{2+}. As shown in **Figure 5**, it presented the difference in electrochemical intensity between the solutions containing arsenite and other ions. It could be seen that all the other ions presented only slight and negligible effects on the DPV intensity of the ssDNA/SWCNTs detection system. These datas implied that the other ions could not interfere with this assay and thus these results distinctly indicated that the ssDNA/SWCNTs approach exhibited high selectivity for arsenite detection, with

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which the ssDNA/SWCNTs approach bears high potential for future use.

Figure 5

3.6 Practical application of the arsenite sensing assay

To further investigate the potential practical application of this electrochemical assay, we tried to detect arsenite in simulated polluted samples (by adding arsenite into drinking water). Before the addition of arsenite into drinking water, all samples were first filtered by a 0.22 μm membrane to remove particulate matters. The arsenite dissolved in drinking water resulting in a detection sample (at a final concentration of 10 ppb). And then the concentration of arsenite in the samples was analyzed by the proposed method (**Table 1**). The recoveries ranging from 101% to 104% after standard additions are satisfactory. This result manifested that this sensor could be challenged by real water samples and had great potential in practical applications.

Table 1

4. Conclusions

In summary，we developed a novel electrochemical strategy for detection of arsenite based on SWCNTs and ssDNA. The arsenite triggered the SWCNTs precipitated from ssDNA/SWCNTs complex, and the SWCNTs assembly mediated the electron transfer between the electrode and FcCOOH, creating an extraordinarily sensitive and specific strategy for signal transduction. The biosensor exhibited the linear response ranging from 0.5 to 10 ppb with detection limit at 0.5 ppb. Compared

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with the conventional techniques, this electrochemical strategy does not need to label the ssDNA, but offers a sensitive, label-free, nonradioactive, and efficient platform for quantitatively arsenite. It is believed that this method has the potential to be competitive for the detection of arsenite in aqueous biological and environmental samples with high selectivity and sensitivity.

Acknowledgments

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Figures Caption

Scheme 1. The schematic representation of the electrochemical strategy for arsenite detection based on ssDNA/SWCNTs.

Figure 1. The TEM (left) and HAADF-STEM (right) images of ssDNA/SWCNTs complex. The ssDNA wrapped the SWCNT is obviously disclosed.

Figure 2. A) Typical DPV responses of electrochemical assay for a) bare gold electrode, b) $C_{18}H_{37}SH$ blocked gold electrode, c) the blocked electrode after treated with ssDNA/SWCNTs complex, d) the complex after treated with arsenite. B) Nyquist plots obtained with a) bare gold electrode, b) $C_{18}H_{37}SH$ blocked gold electrode, c) the blocked electrode after treated with ssDNA/SWCNTs complex, d) the complex after treated with arsenite. All potentials are referenced to the SCE. Measurements were performed in 20 mM PB buffer (pH 7.4) containing 0.1 M $NaClO_4$ and 5 mM FcCOOH. Inset: The equivalent circuit of prepared SWCNT/SAM electrodes.

Figure 3. The optimization of the assay conditions. A) the effect of pH value in the reaction system; B) incubation time of arsenite and SWCNTs/ssDNA complex; C) immobilized time of the released SWCNTs.

Figure 4. A) Typical DPV response of the electrochemical assay with different concentrations of arsenite. The concentrations of arsenite were 0, 0.5, 2, 5, 10, 50, 100, 200, 500, 1000 ppb, respectively. B) The response curve obtained with different concentrations of arsenite. All potentials are referenced to SCE. Measurements were performed in 20 mM PB buffer (pH 7.4) containing 0.1 M $NaClO_4$ and 5 mM FcCOOH.

Figure 5. Selectivity of the electrochemical assay. The concentration of arsenite was

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10 ppb, and all other competing ions were 100 ppb.

Table.1. Detection of arsenite in simulated polluted samples (n = 5).

Table 1

Sample	Added (ppb)	Found (ppb)	Recovery	RSD (%)
Drinking water				
	25	26	104%	4.8
	35	36	103%	5.9
	80	81	101%	5.8
	100	104	104%	6.1

Highlights

1. A label-free and sensitive electrochemical strategy for the arsenite detection was developed.
2. The method was based on the ability of arsenite bound to ssDNA and signal transduction of SWCNTs.
3. The SWCNTs-based biosensor creates a simple, sensitive, nonradioactive assay for the arsenite detection.
4. It provides a new approach to fabrication of stable biosensors.

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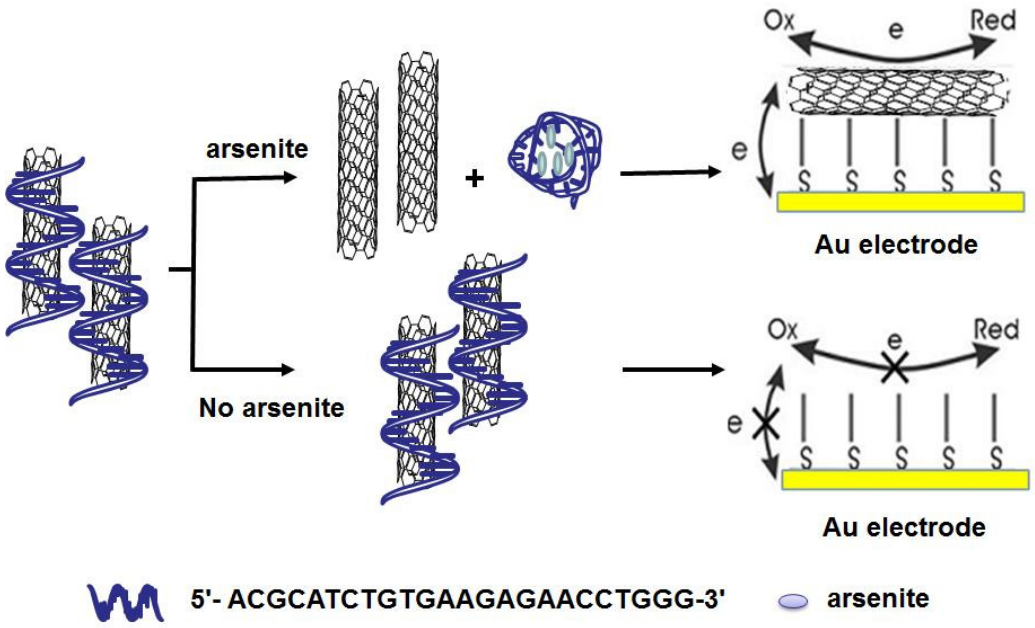
Scheme 1



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Scheme 1

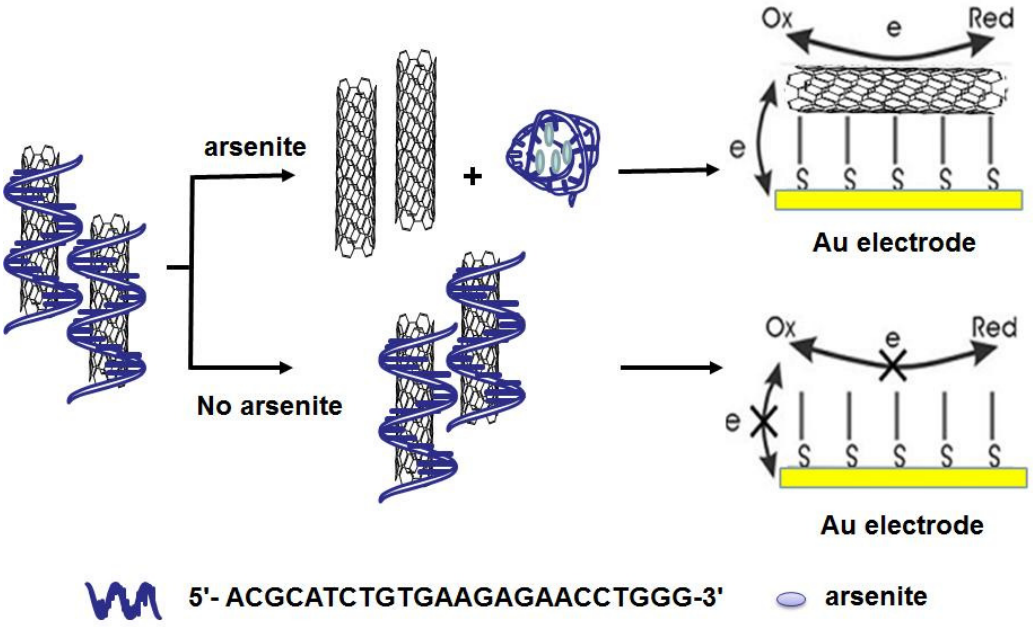

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Figure 1

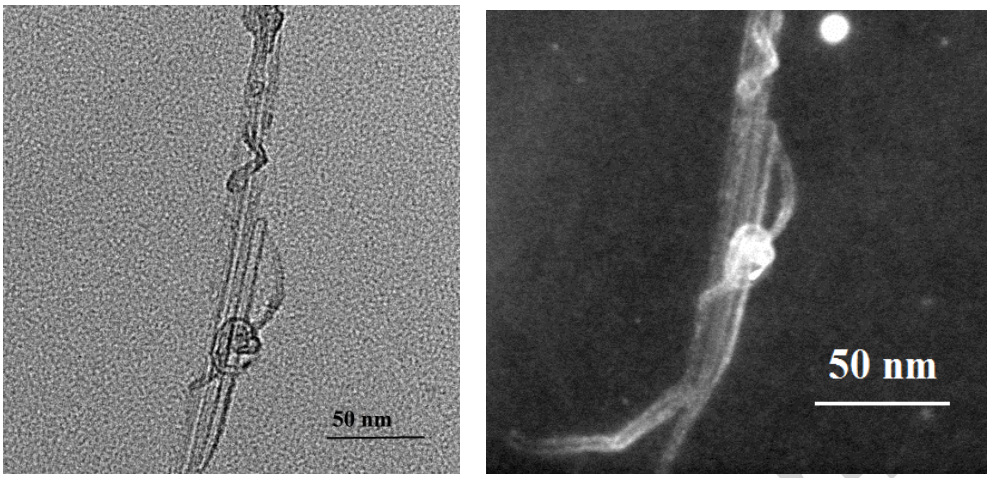

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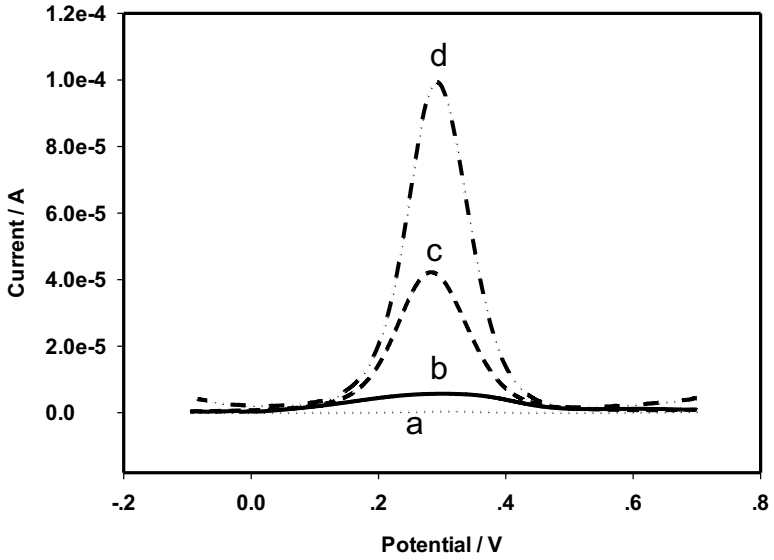
Figure 2

(A)



(B)

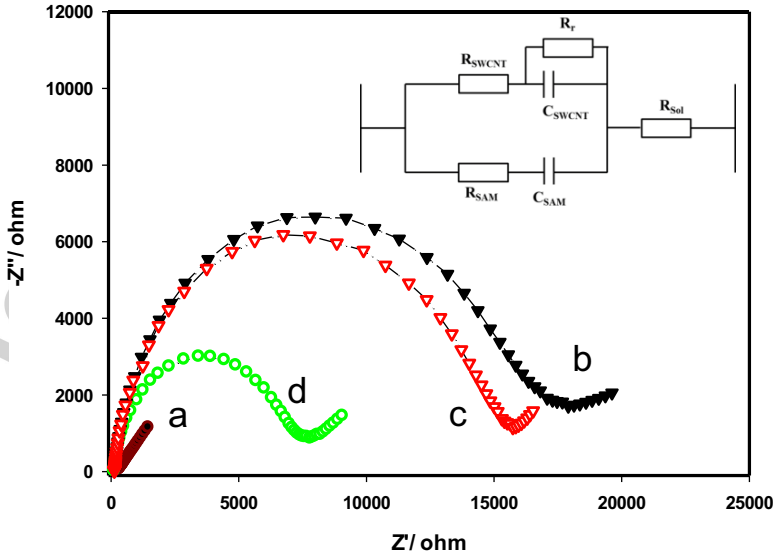


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Figure 3.

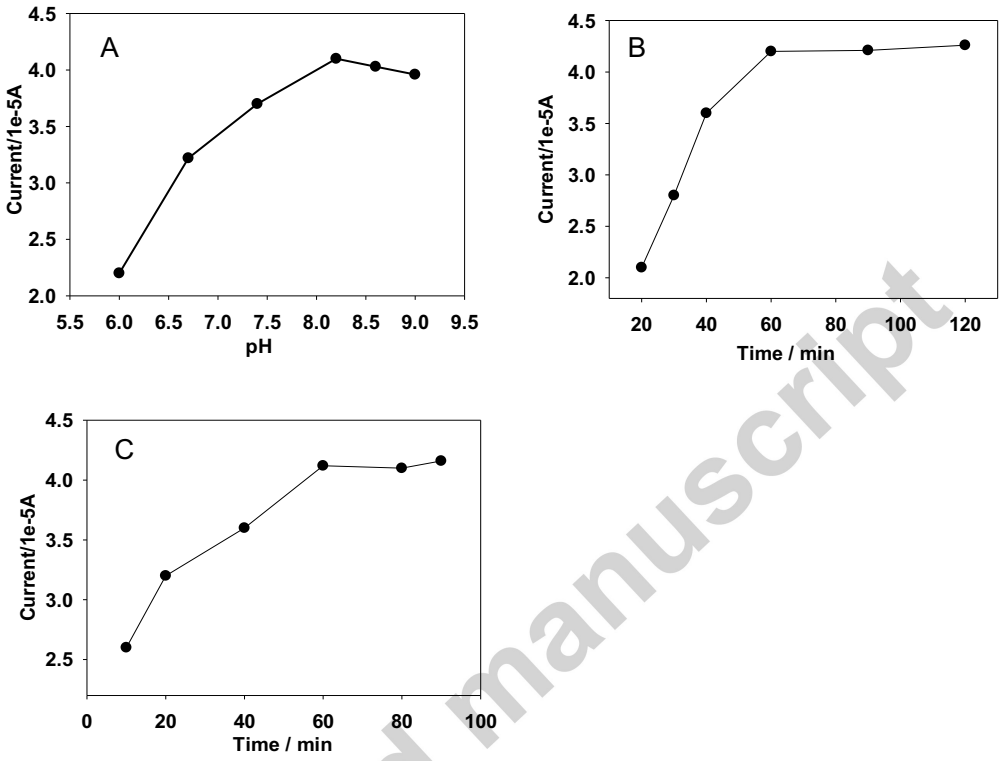

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Figure 4.

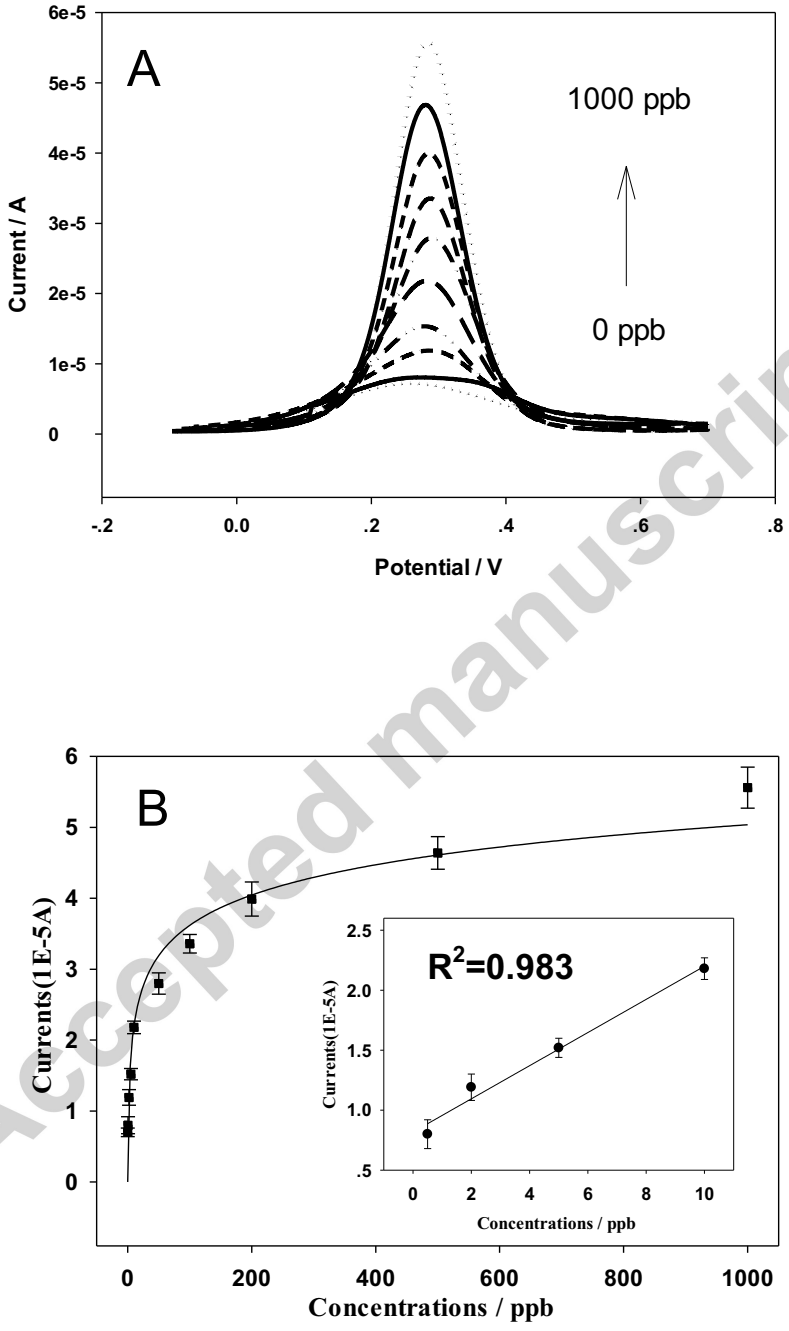

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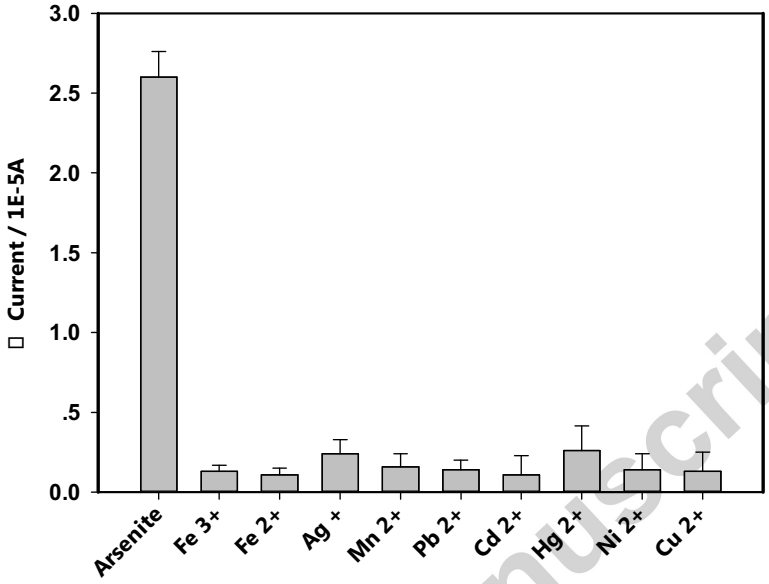
Figure 5



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