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Jiang Zhang, Dong Han, Shu Wang, Xiaodi Zhang, Ruiqi Yang, Yanchen Ji,
Xin Yu

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Short communication

Electrochemical detection of adenine and guanine using a three-dimensional WS₂ nanosheet/graphite microfiber hybrid electrodeJian Zhang^{a,b}, Dong Han^b, Shu Wang^c, Xiaodi Zhang^c, Ruiqi Yang^a, Yanchen Ji^a, Xin Yu^{a,*}^a Institute for Advanced Interdisciplinary Research (iAIR), University of Jinan, Jinan 250022, China^b Université de Lyon, Ecole Centrale de Lyon, UMR CNRS 5270, Institut des Nanotechnologies de Lyon, UMR CNRS 5270, Ecully 69130, France^c Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, National Center for Nanoscience and Technology (NCNST), Beijing 100083, China

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ABSTRACT

In this work, a WS₂ nanosheet/graphite microfiber hybrid electrode has been fabricated by in situ synthesis of WS₂ nanosheets on the surface of graphite microfibers. The WS₂ nanosheets possess an excellent electrocatalytic oxidation response towards adenine and guanine that encourages the adsorption of nucleobases and charge transfer at the surface of the microfibers. The WS₂ nanosheet/graphite microfiber hybrid electrode shows high sensitivity and selectivity for the detection of adenine and guanine. This hybrid microfiber electrode represents an excellent candidate platform for development of an electrochemical biosensor due to its low cost, flexibility and 3D morphology.

1. Introduction

The analysis of nucleobases is critical in the life sciences, especially in the diagnosis of infectious diseases and the study of genetic mutations. They store and transmit biological information and can influence various genetic conditions such as metabolic disorders, blood diseases, vision and hearing loss or neurodegenerative diseases [1,2]. Electrochemical methods are considered to be the most convenient and efficacious techniques for detecting nucleobases because they exhibit excellent sensitivity, give quick results, and are cost effective [3–9]. P. Zuman et al. first reported the electrochemical activity of nucleobases in 1955 [10]. However, nucleobases have a weak direct electron transfer capacity, and exhibit quite weak electrocatalytic oxidation ability. High catalytic potentials can adversely affect detection by electrochemical means [11–13]. Therefore, nanomaterials such as graphene, metal nanoparticles and TiO₂ have been employed to modify electrodes in order to improve their electrochemical sensing performance [14–18].

Due to their unique physical and chemical properties, nanomaterials based on 2D layered transition metal dichalcogenides (TMDs) have attracted much attention in recent years, particularly for applications in sensing [19–21]. Tungsten disulfide (WS₂) consists of S-W-S sandwiches in a trigonal prism configuration. WS₂ nanosheets produced by exfoliation from the bulk material or fabricated via hydrothermal methods have been used in gas sensors and biosensors, among other

applications [22–24]. In particular, the interaction of DNA and nucleotides with TMDs has continued to attract much scientific attention. It has been reported that density function theory (DFT) calculations show that the binding energy between a single nucleotide and MoS₂ decreases in the order G > A > C > T. The average binding free energy for different single nucleotides A, T, C, G on the MoS₂ surface is about 2.29 kcal/mol [25]. In particular, strategies for detecting DNA using either a single WS₂ nanosheet or a few layers of nanosheets have been thoroughly discussed. DNA can be adsorbed onto WS₂ via van der Waals forces. WS₂ is capable of discriminating between single-stranded DNA and double-stranded DNA, which may prove useful in electrochemical or fluorescent sensors for biomedical applications. It has also been found that nucleobases could be physisorbed onto WS₂ due to van der Waals interactions [26,27]. Adsorption of nucleobases on monolayer WS₂ changes its photoluminescence emissions, which opens the door for the development of label-free optical sensing approaches for DNA sequencing [28]. To the best of our knowledge, the study of WS₂ nanosheets for electrocatalytic oxidation of nucleobases has not yet been reported, although layered WS₂ nanosheets have been widely studied as electrocatalysts due to their large surface area and excellent electron transfer processes compared to other inorganic nanomaterials [24,25].

TMD catalysts are commonly supported on carbon materials (e.g. carbon nanofibers, carbon nanotubes, graphene, mesoporous carbon, carbon foam) [29–34]. L. Wang et al. synthesized 3D carbon foam

* Corresponding author.

E-mail address: ifc_yux@ujn.edu.cn (X. Yu).<https://doi.org/10.1016/j.elecom.2019.01.007>

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electrodes coated with $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloys with different Mo/W ratios. The electrocatalytic activity towards the hydrogen evolution reaction (HER) can be tuned by varying the ratio of transition metals in the compounds [31]. B. Seo et al. investigated the growth of TMDs (WS_2 , MoS_2) on carbon surfaces inside confined nanopores. Experimental studies and adhesion energy calculations suggested that WS_2 and MoS_2 favour basal and edge bonding modes with the carbon support, respectively [32]. The electrochemical activity and catalytic properties may vary depending on the energy of adhesion between the TMDs and the various supports [34]. Graphite microfibers have attracted much attention due to their unique 1D fibrous morphology and high electronic conductivity. Small flexible fiber electrodes can potentially be used in vivo. Furthermore, instead of relying on physical adsorption of nanomaterials on glassy carbon, gold or other solid electrodes, nanostructures can be synthesized in situ on the surface of the microfibers, resulting in a larger electrochemically active surface area, higher utilization efficiency, superior electron transfer and excellent stability. Electrochemical biosensors based on nanostructured hybrid microfiber electrodes have been developed for DNA, glucose and H_2O_2 detection [35–37].

In this work, we have produced WS_2 nanosheets in situ on graphite microfibers via a hydrothermal method and obtained a WS_2 nanosheet/graphite microfiber hybrid material. The resulting WS_2 nanosheet/graphite microfiber electrode combines the electronic conductivity and fibrous morphology of graphite fibers with the high electrocatalytic ability of WS_2 , and has been used as the working electrode in the electrocatalytic oxidation of adenine and guanine. It is assumed that the WS_2 nanosheets play an important role in the enhanced charge transfer process and surface adsorption of nucleobases. The fibrous WS_2 nanosheet hybrid electrode is considered to be a promising candidate for detection of nucleic acids in in vivo diagnosis and molecular biology research.

2. Experimental

2.1. Reagents and materials

All the reagents used here are commercially available and of analytical grade. WCl_6 and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) were bought from Sigma. Adenine and guanine were obtained from Aladdin (Shanghai, China). Phosphate buffer solutions (PBS, 0.1 M) were prepared using Na_2HPO_4 and NaH_2PO_4 and were adjusted to pH 7.0. Commercial graphite microfibers were obtained from Toray (M40-JB-12K) (Japan).

2.2. Preparation of WS_2 nanosheet/graphite microfiber hybrid material

The surfaces of the graphite microfibers were first cleaned by sonicating sequentially in acetone, 3.0 M HNO_3 , 1.0 M KOH and distilled water for several minutes, followed by drying at 60 °C overnight [38]. In a typical experiment, WS_2 nanosheets were then formed on the graphite microfibers through a hydrothermal method [39]. 3 mM WCl_6 and 15 mM $\text{C}_2\text{H}_5\text{NS}$ were dissolved in 50 mL DI water and stirred at room temperature for 60 min. This solution and about 10 cm graphite microfibers were then transferred to a 50 mL Teflon-lined autoclave and heated to 265 °C and kept for 24 h. After cooling to room temperature, the hybrid graphite fibers were washed using DI water, and dried at 50 °C for 6 h, producing the WS_2 nanosheet/graphite microfiber hybrid material.

2.3. Materials characterization

The crystalline structure of the WS_2 nanosheet/graphite microfiber hybrid was obtained with an X-ray diffraction (XRD) spectrometer (D8-advance, Bruker AXS, Germany). The morphology of the WS_2 nanosheet/graphite microfiber hybrid was characterized by a field emission scanning electron microscope (FESEM) (HITACHI S8020, Japan)

and transmission electron microscope (TEM) (JEM 2100F, Japan). The composition of the WS_2 nanosheet/graphite fiber hybrid was analysed by an energy-dispersion spectroscope (EDS, Oxford link system), which was equipped with SEM. Raman spectroscopy was carried out using the 532 nm excitation line (LabRAM HR Evolution, HORIBA). X-ray photoelectron spectra (XPS) were recorded using a K-alpha, Thermo Fisher Scientific (ESCALAB 250xi).

2.4. Electrochemical measurements

Electrochemical measurements were recorded on a Gamry electrochemical workstation (Gamry Reference 3000, America). A standard three-electrode system was used: Ag/AgCl (saturated KCl) was used as the reference electrode; a Pt plate (1 cm × 1 cm) was used as the counter electrode; the WS_2 nanosheet/graphite microfiber material was used as the working electrode. The enrichment of adenine and guanine was performed at the open circuit and the optimal enrichment time at the electrodes was found to be 150 s.

3. Results and discussion

The XRD patterns of the WS_2 nanosheet/graphite microfiber hybrid were recorded and compared with those of the bare graphite microfiber and WS_2 separately (Fig. 1A). The diffraction peak of the graphite microfiber (curve b) centered at $2\theta = 25.7^\circ$ can be assigned to graphite (JCPDS 65-6212). The JCPDS card of WS_2 (denoted as a) showed peaks at 14.1° , 33.0° , 58.2° corresponding to (002), (100), and (110) planes, indicating the presence of the WS_2 hexagonal phase. The XRD pattern of the crystalline phase of the WS_2 nanosheet/graphite microfiber hybrid is given in curve c. Apart from the peak at 14.1° , no other new peaks were observed in the XRD pattern, showing that the nanosheets grow in the (002) direction. The crystalline structure of the WS_2 nanosheet/graphite microfiber hybrid was further characterized using Raman spectroscopy (Fig. 1B). The Raman spectrum of the graphite fiber (curve a) showed typical G and D peaks at 1585 cm^{-1} and 1350 cm^{-1} , respectively. The Raman spectrum of the WS_2 nanosheet/graphite microfiber hybrid also showed peaks at 350 cm^{-1} and 413 cm^{-1} , which correspond to the E_{2g} and A_{1g} peaks for WS_2 (curve b) [40]. The pure graphite microfiber and the WS_2 nanosheet/graphite microfiber hybrid were also examined using SEM to check the surface morphology. The graphite microfibers are about 5 μm in diameter and have a smooth surface (Fig. 1C). The image of the WS_2 nanosheet/graphite microfiber hybrid shows that the graphite microfiber is buried in dense layers of WS_2 nanosheets (Fig. 1D, E). The WS_2 nanosheets are randomly connected with each other, forming a porous surface (Fig. 1F). WS_2 nanosheets were exfoliated from the surface of the microfibers and characterized using TEM. The TEM images show that the vertical edges of the WS_2 nanosheets possess a layered structure (Fig. 1G). Furthermore, the interplanar distance between the lattice fringes was about 0.62 nm, corresponding to the distance between the (002) planes of WS_2 crystals (Fig. 1H) [41]. The chemical composition of the WS_2 /graphite microfiber hybrid was analysed by energy-dispersion spectroscopy (EDS). The EDS spectrum is shown in Fig. 1I. The elements S, C, O, W and Al were detected, which indicated that the WS_2 nanosheet/graphite microfiber hybrid electrode had been fabricated successfully (Al and O are from the substrate). The molar ratio W:S was calculated to be 5.69:11.98 (which is approximately 1:2) from the peak intensities (see insert in Fig. 1I), confirming the stoichiometry of the product.

It is well known that WS_2 nanosheets can form not only the usual semiconducting prismatic structure (2H- WS_2) but also the less common distorted octahedral structure (1T- WS_2), which exhibits metallic behavior [42]. The 1T- WS_2 form has recently been shown to be very efficient in redox reactions [43]. The chemical composition of the as-prepared WS_2 nanosheets on the graphite fiber was further analysed by X-ray photoelectron spectroscopy (XPS). Fig. 2A shows two peaks at 32.0 eV and 34.1 eV for $\text{W}4f_{7/2}$ and $\text{W}4f_{5/2}$ of 1T- WS_2 , respectively. The

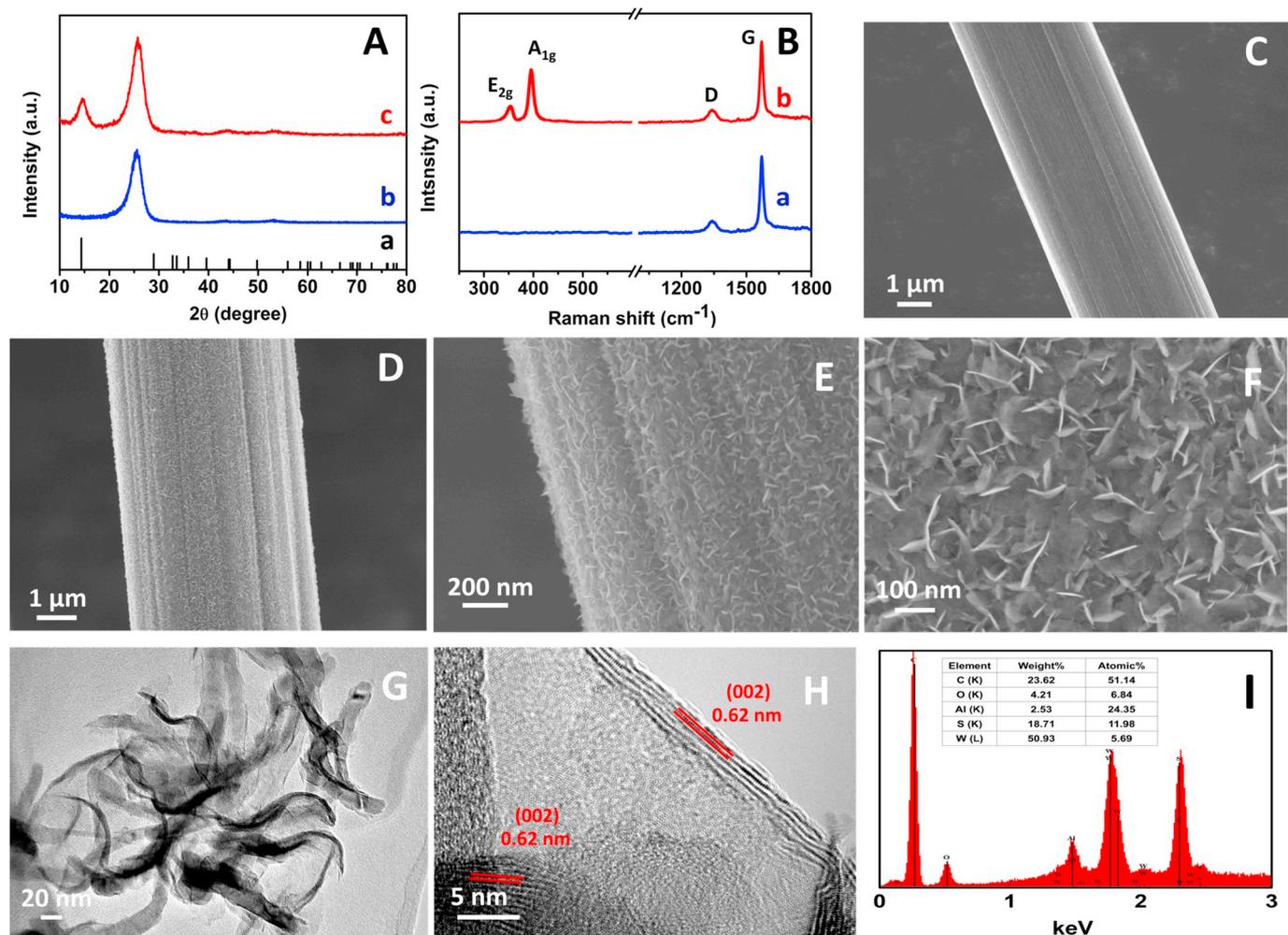


Fig. 1. (A) XRD patterns of (a) WS₂ (JCPDS 84-1398), (b) graphite microfiber (JCPDS 65–6212) and (c) WS₂ nanosheet/graphite microfiber. (B) Raman spectra of (a) graphite microfiber and (b) WS₂ nanosheet/graphite microfiber hybrid. SEM images of (C) graphite microfiber, (D, E) WS₂ nanosheet/graphite microfiber hybrid and (F) high resolution SEM image of WS₂ nanosheets. (G, H) TEM images of WS₂ nanosheets. (I) EDS spectrum of WS₂ nanosheet/graphite microfiber on Al substrate.

characteristic peaks of 2H-WS₂ are shifted by about 0.9 eV to a higher binding energy compared to those of 1T-WS₂, being located at 32.9 eV and 35.0 eV, respectively. In addition, WS₂ is partially oxidized, as evidenced by the characteristic peaks of W⁶⁺ at 36.0 eV and 38.1 eV. Fig. 2B shows the high-resolution XPS S2p spectrum. Two peaks are located at 161.8 eV and 163.5 eV, corresponding to the S2p_{3/2} and S2p_{1/2} of 1T-WS₂, respectively. Similarly, it is found that the S2p peaks of 2H-WS₂ are shifted to a higher bonding energy compared with those of 1T-WS₂. The 1T-WS₂ and 2H-WS₂ coexist in the sample with a ratio of 2.5/1 (1 T/2H) [31,44]. Furthermore, the composition after the electrochemical oxidative treatment was also investigated. As shown in Fig. 2C and D, the XPS peaks show no obvious change compared with those recorded before the electrochemical oxidative treatment, indicating that the WS₂ nanosheet/graphite microfiber hybrid electrode has excellent stability.

The electrocatalytic oxidation of adenine and guanine at the WS₂ nanosheet/graphite microfiber electrode was explored by cyclic voltammetry (CV). Fig. 3A shows the CVs recorded at a graphite microfiber electrode and a WS₂ nanosheet/graphite microfiber electrode in 0.1 M PBS at pH 7.0 containing 1×10^{-5} M adenine and 1×10^{-5} M guanine at a scan rate of 100 mV s⁻¹. At the graphite microfiber electrode, two broad oxidation peaks were observed at +0.73 and +1.03 V, corresponding to the electrochemical oxidation of adenine and guanine, respectively. However, two well-defined oxidation peaks for adenine and guanine were observed when using the WS₂ nanosheet/graphite

microfiber electrodes. Note that these two peak potentials are about 90 mV and 70 mV more negative than those at the graphite microfiber electrode, indicating the catalytic activity of the WS₂ nanosheets towards the oxidation of adenine and guanine. In addition, the peaks with higher currents at the WS₂ nanosheet/graphite microfiber electrode are much sharper than those at the graphite microfiber electrode, indicating the good electrocatalytic oxidation behaviour of WS₂ nanosheets towards adenine and guanine. The highly electrocatalytic activity of the WS₂ nanosheet/graphite microfiber electrode may be due to the layered WS₂ nanosheets increasing the surface area of the microfiber electrode and promoting electron transfer. The CVs of adenine and guanine at the WS₂ nanosheet/graphite microfiber electrode were then recorded at various scan rates (Fig. 3B). The oxidation peak currents increase linearly with the scan rate from 50 mV s⁻¹ to 300 mV s⁻¹, which suggests that the electrocatalytic oxidation of adenine and guanine at the WS₂ nanosheet/graphite microfiber electrode is a surface-controlled process (Fig. 3C) [13].

The electron transfer kinetics and electrocatalytic ability of transition metal dichalcogenides can be improved using carbon supports or electrochemical treatments. X. Chia et al. demonstrated an electrochemical method to alter the electron transfer kinetics and catalytic properties of MoS₂ films, in which a 2H-1T transition was observed on applying an electrochemical potential. We therefore investigated the composition of the WS₂ nanosheets after the electrochemical detection of adenine and guanine. High-resolution XPS spectra recorded in the

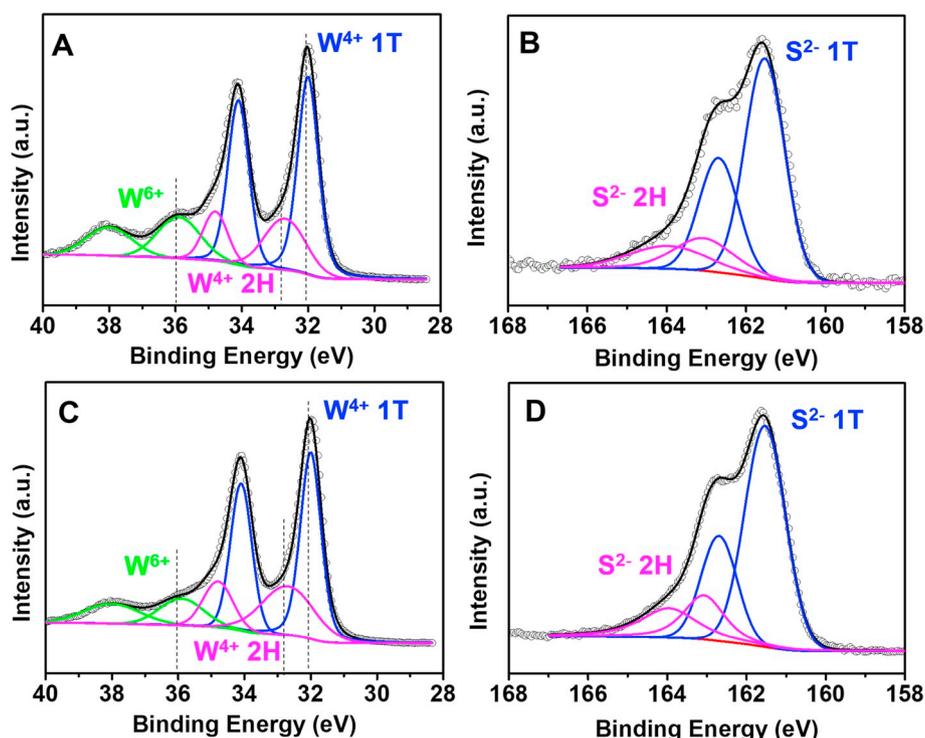


Fig. 2. High-resolution XPS W4f and S2p spectra of as-prepared WS₂ nanosheet/graphite microfiber (A, B) and after the electrochemical detection of adenine and guanine (C, D).

W4f and S2p regions are shown in Fig. 2C and D. From the XPS results, it is evident that the surface chemistry remains practically unaltered during the electrochemical treatments, which suggests that the variation in electrocatalytic behaviour is caused by electronic changes rather than surface changes [45]. Electrochemical treatment of the WS₂ nanosheets/graphite microfiber electrode may be a good topic for future research.

Fig. 4A displays the differential pulse voltammograms (DPV) of 2×10^{-5} M adenine and 2×10^{-5} M guanine in 0.1 M PBS solution (pH 7.0). The DPV peak potential of guanine at a graphite microfiber electrode is located at 0.75 V. In the case of the WS₂ nanosheet/graphite microfiber electrode, the peak potential is negatively shifted to 0.66 V. For adenine, the oxidation peak potential on WS₂ nanosheet/graphite microfiber electrodes is also negatively shifted to 0.96 V. Compared to the current response of a bare graphite microfiber electrode (curve c), the oxidation peak currents of adenine and guanine obtained at a WS₂ nanosheet/graphite microfiber electrode (curve d) are obviously higher. The enhancement in the peak current and the negative shift of

the oxidation potential are clear evidence of the electrocatalytic activity of WS₂ nanosheets towards the oxidation of guanine and adenine.

The determination of adenine and guanine at a WS₂ nanosheet/graphite microfiber electrode was explored by DPV. The peak currents increased with the increasing concentration of adenine and guanine (Fig. 4B). Fig. 4C shows the linear relationship between the peak currents and the concentration of adenine and guanine. A good linear response to either adenine or guanine concentrations is obtained within the range from 0.5 μ M to 20 μ M (correlation coefficient 0.993). The detection limits based on S/N = 3 for adenine and guanine were calculated to be 5×10^{-8} M and 9×10^{-8} M, respectively. The proposed WS₂ nanosheet/graphite microfiber electrode may therefore be used for the sensitive determination of adenine and guanine.

The effect of interfering species was investigated by adding different types of ions into the PBS containing 2×10^{-5} M adenine and 2×10^{-5} M guanine (Fig. 4D). It can be seen that inorganic ions such as Mg²⁺, Ca²⁺, Zn²⁺, Cl⁻, NO₃⁻ and SO₄²⁻ had almost no effect on the determination of guanine and adenine (signal change < 5.0%).

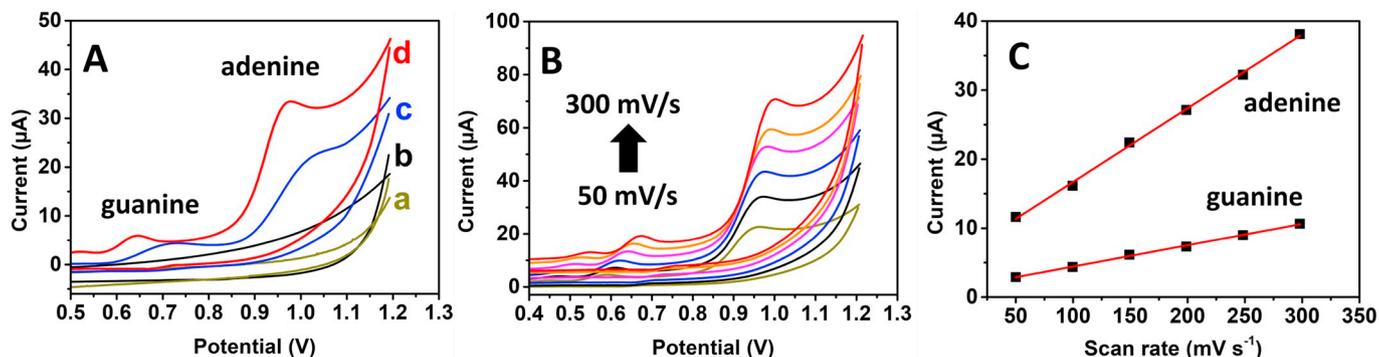


Fig. 3. (A) CV of 0.1 M PBS (pH 7.0) without guanine and adenine at the graphite microfiber electrode (curve a) and WS₂ nanosheet/graphite microfiber electrode (curve b). CV of 0.1 M PBS (pH 7.0) with 1×10^{-5} M guanine and adenine at the graphite microfiber electrode (curve c) and WS₂ nanosheet/graphite microfiber electrode (curve d) (scan rate 100 mV s^{-1}). (B) CV of 0.1 M PBS (pH 7.0) with 1×10^{-5} M guanine and adenine at the WS₂ nanosheet/graphite microfiber electrode at different scan rates; (C) variation of peak currents with potential scan rates.

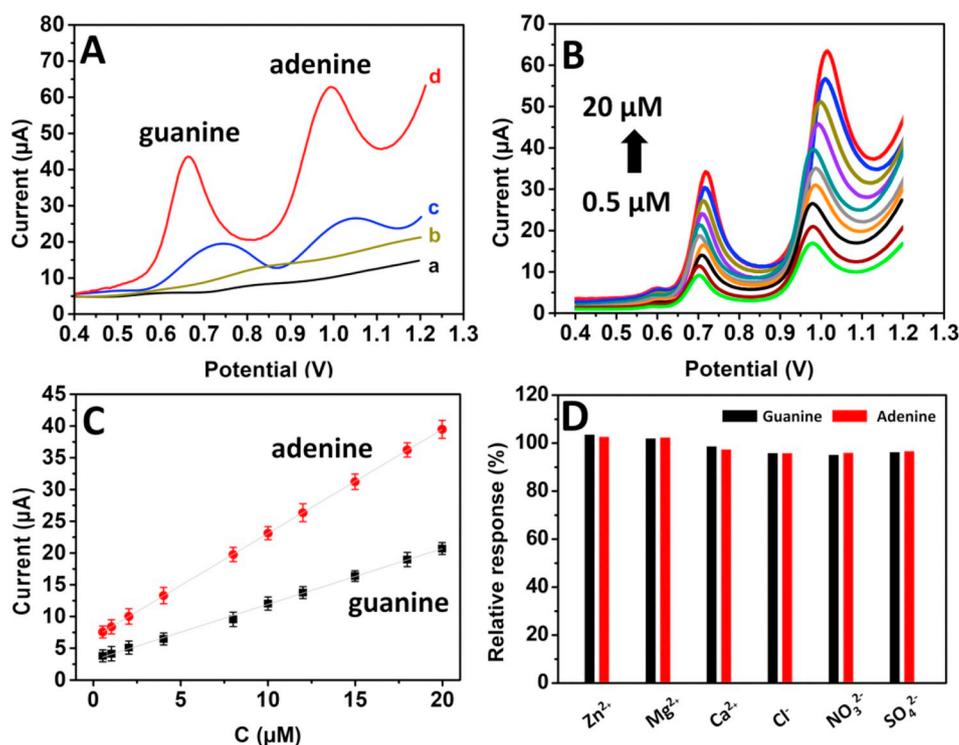


Fig. 4. (A) DPV of 0.1 M PBS (pH 7.0) without guanine and adenine at a graphite microfibre electrode (curve a) and a WS₂ nanosheet/graphite microfibre electrode (curve b). DPV of 0.1 M PBS (pH 7.0) with 2×10^{-5} M adenine and 2×10^{-5} M guanine at a graphite microfibre electrode (curve c) and a WS₂ nanosheet/graphite microfibre electrodes (curve d). (B) DPV of guanine and adenine in 0.1 M PBS (pH 7.0) at a WS₂ nanosheet/graphite microfibre electrode with the concentration ranging from 0.5 to 20 μ M. (C) Calibration plots of the peak currents versus the concentration of guanine and adenine. (D) The influence of some ions and important biological substances on the peak currents of adenine and guanine in 0.1 M PBS (pH 7.0) at the WS₂ nanosheet/graphite microfibre electrode.

The long-term stability of the WS₂ nanosheet/graphite microfibre electrodes was also investigated. These electrodes retained 93% of their initial current response after 2 weeks stored in pH 7.0 PBS at 4 °C, demonstrating that the microfibre electrode retains an acceptable detection performance for a reasonable time.

4. Conclusions

In this work, WS₂ nanosheets were successfully prepared in situ on the surface of graphite microfibres to form a hybrid WS₂ nanosheet/graphite microfibre material, which was used as the working electrode for electrocatalytic oxidation of adenine and guanine. The WS₂ nanosheet/graphite microfibre electrode exhibits good electrocatalytic oxidation activity towards adenine and guanine due to its good adsorption ability and the charge transfer provided by the WS₂ nanosheets. The hybrid WS₂ nanosheet/graphite microfibre electrode could detect adenine and guanine with high sensitivity, high selectivity and good stability. Furthermore, because of its fiber morphology and flexibility, the electrode has the potential to monitor nucleobases in some difficult environments, even within a targeted cell or in vivo. We believe that this hybrid WS₂ nanosheet/graphite microfibre electrode offers a significant new platform for biosensing applications.

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