DOI 10.5162/IMCS2018/P1NM.2

Electrochemical hydrazine sensor based on atomically-thin sub-nanometer WO_3 developed by atomic layer deposition

Zihan Wei[1], Serge Zhuiykov[1], Zhenyin Hai[1], Mohammad Karbalaei Akbari[1]
[1]Ghent University Global Campus, Department of Applied Analytical & Physical Chemistry 119 Songdomunhwa-ro, Yeonsu-gu, Incheon 21985, South Korea
E-mail: serge.zhuiykov@ugent.be

Abstract:
Wafer-scale two-dimensional (2D) WO_3 films with the different thicknesses of 0.78, 1.4, 3.6 and 6.5 nm were fabricated on Au-SiO_2/Si substrates by atomic layer deposition (ALD) technique. The surface morphologies and chemical components characterization results showed that WO_3 films were aggregated with nanoparticles with the average diameter of 40 nm. The electrochemical behaviors of 2D WO_3 films with the different thicknesses towards the hydrazine detection at various conditions and the effect of the thickness on electrochemical performance were investigated using cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). Significant improvement in hydrazine sensing capabilities was obtained for monolayer WO_3 (0.78 nm) with the high sensitivity of 1.24 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$, linear hydrazine concentration detection ranged from 0.2 μM to 2100 μM, great long-term stability, excellent selectivity and the lowest limit of detection (LOD) of 0.015 μM reported to date. All these facts confirmed that ALD technique can provide a great potential for the nanomaterials fabrication in the development of high performance hydrazine sensor.

Key words: WO_3, two-dimensional materials, atomic layer deposition, hydrazine, sensing capabilities

Introduction

Owing to the fact that sluggish kinetics and high over-potential at bare metal or glassy carbon electrode result in the poor sensing performance, electro-catalysts are the key component in the application of electrochemical detection of hydrazine [1]. Therefore, the development of nanomaterials with superior electrochemical sensing capabilities towards hydrazine is of great importance.

Although transition metal oxides nanostructures have been explored for the sustainable hydrazine detection, in order to improve the hydrazine detection at very low concentration, the specific nanostructure in 2D form should be explored due to its quantum-confined effects [2]. Among these 2D transition metal oxides, tungsten oxide (WO_3), has already demonstrated the great potential in various fields [3]. However, the utilization of 2D WO_3 for the determination of hydrazine has not yet been explored.

In the wide range of approaches for the fabrication of 2D WO_3, ALD technique can enable the self-limiting growth of 2D films from one fundamental layer to multi-layer by controlling over the deposition rate. Therefore, in this work, 2D WO_3 with the thicknesses varied from 0.78 to 6.5 nm were developed by ALD technique. Their electrochemical capabilities for the determination of hydrazine and the thickness effect on electrochemical performance were comprehensively studied.

Experimental

All 2D WO_3 films with the thicknesses of 0.78, 1.4, 3.6 and 6.5 nm were performed on the Au-SiO_2/Si wafers by ALD technique using $(^tBuN)_2(Me_2N)_2W$ as the metal precursor along with H_2O vapor as the source of oxygen and the optimum growth conditions were as follow: at 350°C, $(^tBuN)_2(Me_2N)_2W$ pulse 2 s, N_2 purge 10 s, H_2O pulse 50 ms, N_2 flow 5 s without pumping and then 10 s with pumping. After deposition, all wafers were annealed in air at 200°C for 1 h with the heating rate of 0.5°C/min.

Results and Discussion

Fig. 1 depicts the CVs of 2D WO_3 films with different thicknesses and bare Au electrode in 0.1 M PBS at the presence of 500 μM hydrazine. With the introduction of hydrazine into the PBS, obvious oxidation peaks were observed during the anodic scanning at 0.14 V with the current value of 221 μA, 183 μA, 128

μA, and 98 μA corresponding to 0.78, 1.4, 3.6 and 6.5 nm WO_3 films, respectively. On the contrary, bare Au electrode exhibited low oxidation peak current of 45.8 μA at overpotential of 0.35 V. The measured results indicated that 2D WO_3 films possessed low oxidation potential and high oxidation peak current for hydrazine electro-oxidation, and the oxidation current values increased with the decreasing of WO_3 films thickness.

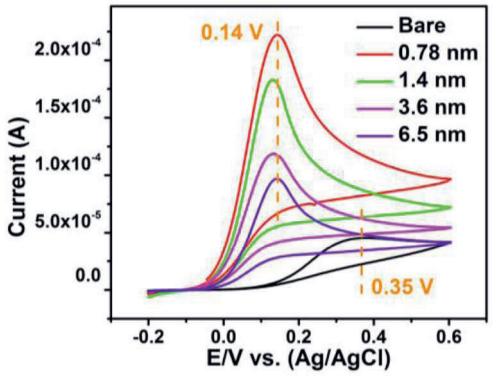

Fig. 1. CVs of Au electrode and WO_3 films in the presence of 500 μM hydrazine at the scanning rate of 10 mV/s.

Fig. 2(a) shows typical current time dynamic response for different thicknesses WO_3 films with successive addition of hydrazine at an applied potential of 0.14 V. All of the 2D WO_3 showed fast response and all steady-states were achieved within 2 s. As expected, the monolayer WO_3 films exhibited the largest catalytic current under the different hydrazine concentrations. The corresponding calibration curves are presented in Fig. 2(b). All WO_3 films demonstrated great linearity from 0.2 μM to 2100 μM with the correlation coefficient higher than 0.99. According to the equation of "*sensitivity = slope/surface of the electrode*" and "*low detection limit = $3S_b$/sensitivity*" [4], where S_b is the standard deviation of the blank signal. The 0.78 nm WO_3 films showed the greatest sensitivity of 1.24 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$ with the low detection limit of 0.015 μM at the signal to noise ratio of 3. As for 1.4, 3.6 and 6.5 nm WO_3 films, the sensitivity was 1.18, 0.74 and 0.48 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$ with the detection limit of 0.022, 0.035 and 0.07μM, respectively. The obtained measured results confirmed that ALD-fabricated monolayer WO_3 films possess the superior sensing capabilities for electrochemical detection of hydrazine with high sensitivity, wide linear range and low detection limit.

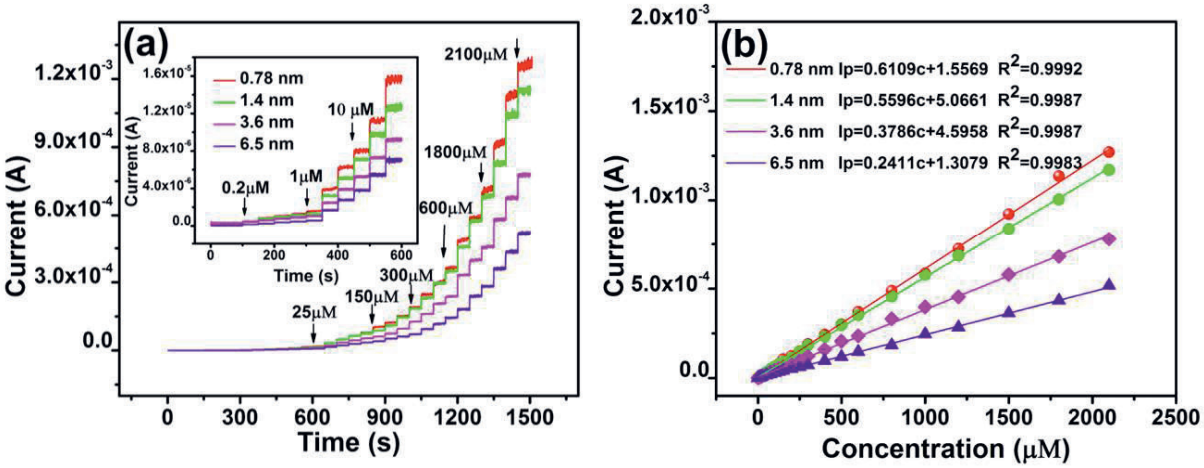

Fig.2. (a) Chronoamperometric current response of 2D WO_3 with different thicknesses under different hydrazine concentration from 0.2 μM to 2100 μM in o.1M PBS; (b) Corresponding linear plot of the current versus hydrazine concentration.

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