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Limited Anodic and Cathodic Electrochemical Potential Window of MoS_2: Limitations in Electrochemical Applications

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Abstract: Molybdenum disulphide has been touted as a good material with diverse possible applications such as energy storage and sensing platform. However, we demonstrate here the limitation of MoS_2 as analytical sensing platform due to the limited potential window in both the anodic and cathodic regions attributed to the inherent electrochemistry (oxidation of Mo^{4+} to Mo^{6+}) and catalytic hydrogen evolution reaction due to H_3O^+ reduction on MoS_2 surface, respectively. Electrochemical window of MoS_2 lies in the region of ~-0.6V to +0.7 V (vs. AgCl). We show that such limited working potential window characteristic of MoS_2, precludes the detection of important analytes such as nitroaromatic explosives, pesticides and mycotoxins which are instead detectable on carbon surfaces. The limited potential window of MoS_2 has to be taken into consideration in the construction of electroanalytical devices based on MoS_2.

Keywords: Molybdenum disulphide, transition metal dichalcogenides, voltammetry, electrocatalysis

1. INTRODUCTION

Transition metal dichalcogenides (TMDs) have gained increasing interest among scientists recently[1,2] due to their special features and possible future applications.[3,4] TMDs have layered structures, similar to graphite, held by weak Van der Waal's forces of attraction between each layer.[5] TMDs exhibit desired properties for many applications such as lubricants[6], capacitors[3,7,8], energy storage devices[3,9] and sensing platforms.[10,11]

TMDs are prepared in a similar fashion to graphene due to the similarities of the layered structures. Mechanical exfoliation, such as lithium intercalation[12,13] and ultrasonication[14], is one of the common methods of producing single-layered TMD films.

The electrochemical potential window is the potential range in which the electrode is stable which is limited by the inherent electrochemistry (change in electrode surface properties) of the electrode material and redox behaviour (decomposition) of the solvent. Some examples include the dissolving of mercury from mercury electrodes into the solution at potentials greater than 0 V (*vs.* saturated calomel electrode) and the oxidation of Au electrodes at high anodic potentials.[15] We have previously showed the limitation of graphene oxides at cathodic potentials as a result of the electroactive oxygen-containing groups present.[16]

Here we demonstrate the limitation of the electrochemical working window of molybdenum disulphide both in the anodic and cathodic regions, which significantly limits the detection of oxidation and reduction processes of important analytes of interest. This is largely due to the inherent electrochemical activity of molybdenum disulphide in the anodic region and catalytic hydrogen evolution in the cathodic region.

2. EXPERIMENTAL

Zearalenone (ZEA), uric acid (UA), ascorbic acid (AA), sodium tetraborate decahydrate, 2-(N-morpholino)ethanesulfonic acid (MES) monohydrate, paraoxon, perchloric acid, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride and potassium chloride were obtained from Sigma-Aldrich (Singapore). 2-nitrotoluene (2-NT) was obtained from Alfa Aesar (Ward Hill, MA). Acetonitrile (ACN) was obtained from Merck (Singapore). MoS_2 bulk powder (< 2 μm) and *tert*-buthyllithium (1.7M in pentane) were obtained from Sigma-Aldrich, Czech Republic. Hexane was obtained from Lach-ner, Czech Republic. Deionised water of conductivity 18.2 MΩ cm (at 25^{o}C) was used.

Stock solution of ZEA and paraoxon were prepared in ACN. 10 mM stock solutions of uric acid and ascorbic acid were prepared in PBS buffer. 20 mM 2-nitrotoluene stock solution was prepared in borate buffer. All stock solutions were stored at 4°C.

3 g of bulk MoS_2 powder was suspended in 20 mL of t-BuLi. The suspension was stirred for 72 hours at 25°C under argon atmosphere in order to intercalate the MoS_2 with Li. The Li-intercalated material was separated by suction filtration under argon atmosphere and washed thoroughly with hexane (dried over Na). Repeated centrifugation (10 000 g) was carried out after placing the separated Li-intercalated material in water (100 mL). The exfoliated MoS_2 was eventually dried in vacuum oven at 50°C for 48 hours before use. It was later dispersed in water at a concentration of 1 mg mL^{-1} and ultrasonicated for 30 minutes. The exfoliated MoS_2 was examined by XPS (see Figure S1, Electronic Supplementary Information); according XPS survey scan, it contained Mo and S but not lithium (note that detection limit of XPS is ~0.1%). 1 μL of the colloidal suspension was drop-coated onto the glassy carbon electrode surface and left to dry at room temperature. The buffers used were purged with nitrogen gas for 15 minutes before each measurement was taken.

Pt, Ag/AgCl and glassy carbon (GC) electrode (diameter of 3 mm), was obtained from CH Instruments (Texas, USA). Voltammetric measurements were conducted using μAutolab Type III electrochemical analyser (Eco Chemie, The Netherlands) controlled by a NOVA 1.10 software (Eco Chemie) at room temperature by using a three-electrode configuration. The electrochemical measurements were performed at room temperature (25±2 ^{o}C).

3. RESULTS AND DISCUSSION

We investigate here the electrochemical potential window of molybdenum disulphide (MoS_2) using cyclic voltammetry. We first looked into the anodic region of the electrochemical potential window followed by the cathodic region.

A voltammetric scan was carried out in blank buffer which resulted into the oxidation of MoS_2 starting at +0.6V and peaking at +1.0 V.[17-19] This is the result of oxidation of Mo^{4+} to Mo^{6+}.[16] Subsequent scans with analytes were carried out. Important biomarkers, ascorbic acid (AA) and uric acid (UA) were selected as the analyte of interest to investigate whether inherent oxidation peak of MoS_2 interferes with electrochemical signal provided by them. Figure 1 shows the voltammograms obtained for ascorbic acid and uric acid scanned with MoS_2-modified GC. The voltammograms obtained showed oxidation peaks corresponding to the target biomarkers (+ 0.45 V) which were easily distinguishable and did not overlap with the oxidation peak of MoS_2. In this scenario, MoS_2 exhibits excellent property as a sensing platform of such. One can note that the shoulder in the voltammograms of ascorbic and uric acids at about +1.0 V which corresponds to the oxidation of MoS_2.

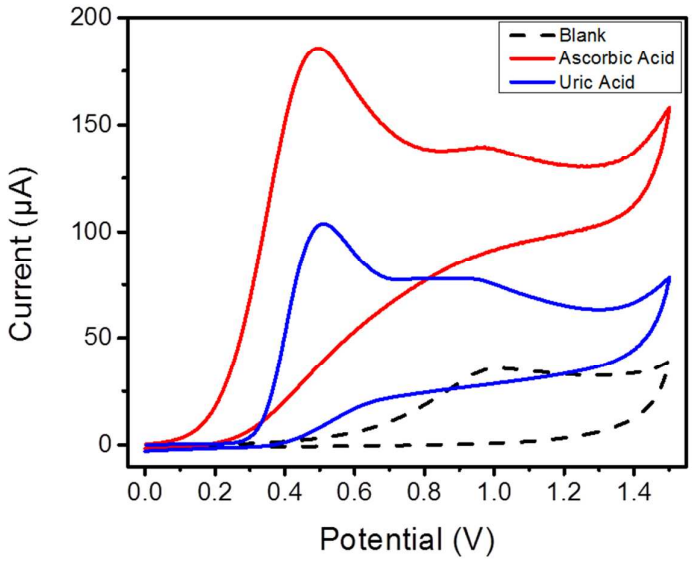
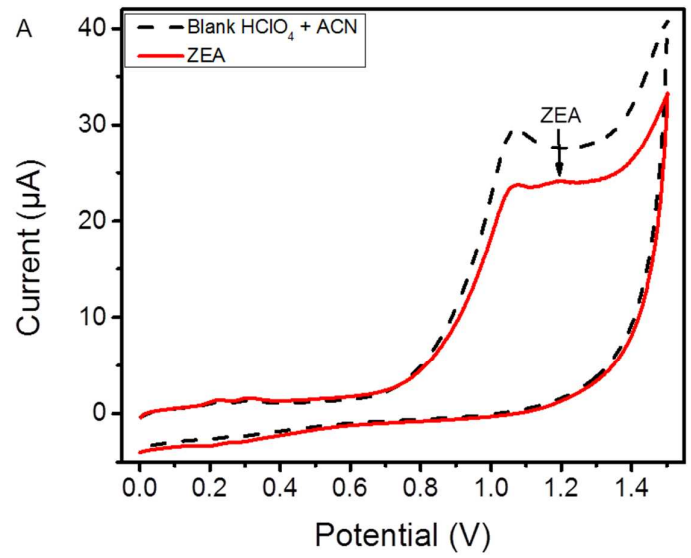


Figure 1. Cyclic voltammograms of blank buffer, 10 mM ascorbic acid (AA), and 10 mM uric acid (UA) with MoS_2-modified GC in phosphate buffer (50 mM, pH 7.2). Buffer solution purged with N_2 for 15 minutes before each measurement, scan rate of 0.1 V s^{-1}.

However, not all analytes are oxidised at low potentials. Important phenolic compounds can be oxidised only at higher potentials such as mycotoxins.[20] Therefore, the experiment was repeated using another target sample which is zearalenone (ZEA). ZEA is a common mycotoxin found in food. A voltammetric scan was initially carried out with MoS_2-modified GC in blank buffer which showed a sharp peak at +1.0 V (Figure 2A), similar to that observed in Figure 1. From the scan with bare GC (Figure 2B), the oxidation peak of ZEA is expected at +1.15 V. However, when the experiment was repeated using MoS_2-modified GC, the oxidation peak for ZEA overlaps with the oxidation peak from MoS_2 and is masked by it (Figure 2A). A very broad peak was produced which makes it difficult to distinguish the peak from oxidation of ZEA. This does not make MoS_2 suitable as a sensing platform for mycotoxins in food analysis. Most mycotoxins have phenolic structures.[21] The oxidation potential of most phenolic compounds are expected beyond the potentials of +0.7

V.[22-24] This range appears to overlap with the inherent oxidation peak of MoS_2 in the different types of buffers used. It is therefore not possible to utilise MoS_2 as a screening platform for rapid detection of mycotoxins in food supply. It is clear that MoS_2 exhibits limited anodic potential window due to its inherent electrochemistry at about +0.7 V and higher potentials.



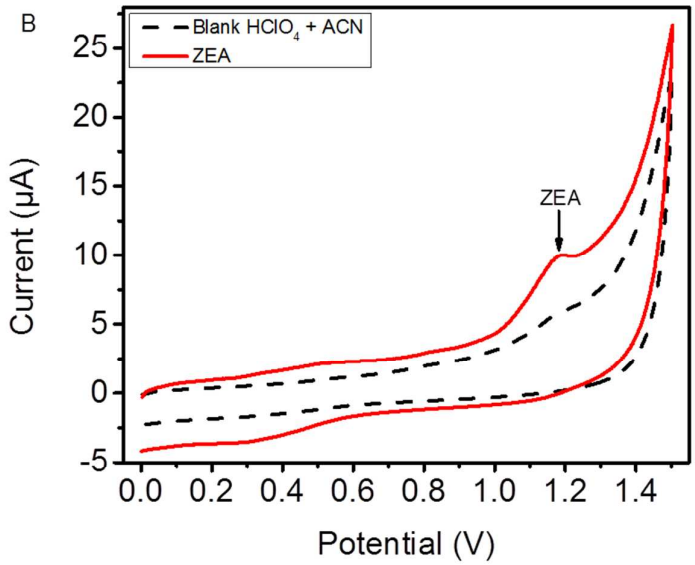


Figure 2. Cyclic voltammograms of 20 μM mycotoxin zearalenone (ZEA) in 20% ACN + 80% 1 M $HClO_4$ buffer (pH* = 0.15) with (A) MoS_2-modified GC and (B) bare GC. Buffer solution purged with N_2 for 15 minutes before each measurement, scan rate 0.1 V s^{-1}.

It was observed that changing from a neutral phosphate buffer to a more acidic buffer (20% ACN + 80% $HClO_4$) did not shift the position of the peak for the blank scans significantly. This might suggest that the oxidation of MoS_2 is not greatly dependent of the pH of the buffer used and the inherent oxidation of the material is pH insensitive.[25]

We investigated also the suitability of MoS_2 surfaces in the cathodic region by choosing two classes of compounds relevant for environmental analysis which are nitroaromatic explosives and pesticides, more specifically 2-nitrotoluene (2-NT)[26] and paraoxon.[27] Figure 3 shows the voltammograms obtained for the reduction of 2-NT and paraoxon in bare GC and MoS_2-modified GC. From the voltammetric scans of the blank buffers, no observable peaks were observed on GC electrode. However, hydrogen evolution reaction can be observed at about -1.2 V at GC electrode and at much lower potentials (~-0.6 V) in the case of MoS_2. Figure 3A showed distinguishable reduction peaks for 2-NT and paraoxon on bare GC as they are reduced at -0.66 V and -0.8 V while cathodic electrochemical window of GC is up to -1.2 V. MoS_2 is known to be catalytic to hydrogen evolution reaction in aqueous solutions. The hydrogen gas evolved is a limiting factor for the potential window in the cathodic region in general. We will see that it is pronounced in MoS_2 (Figure 3B). One can note on Figure 3B that hydrogen evolution reaction is indeed taking place as early as at ~-0.6V (pH 5.0) while at GC electrode the hydrogen evolution starts at ~-1.2V. Clearly, MoS_2 shows limited MoS_2 potential window as a result of early hydrogen evolution.

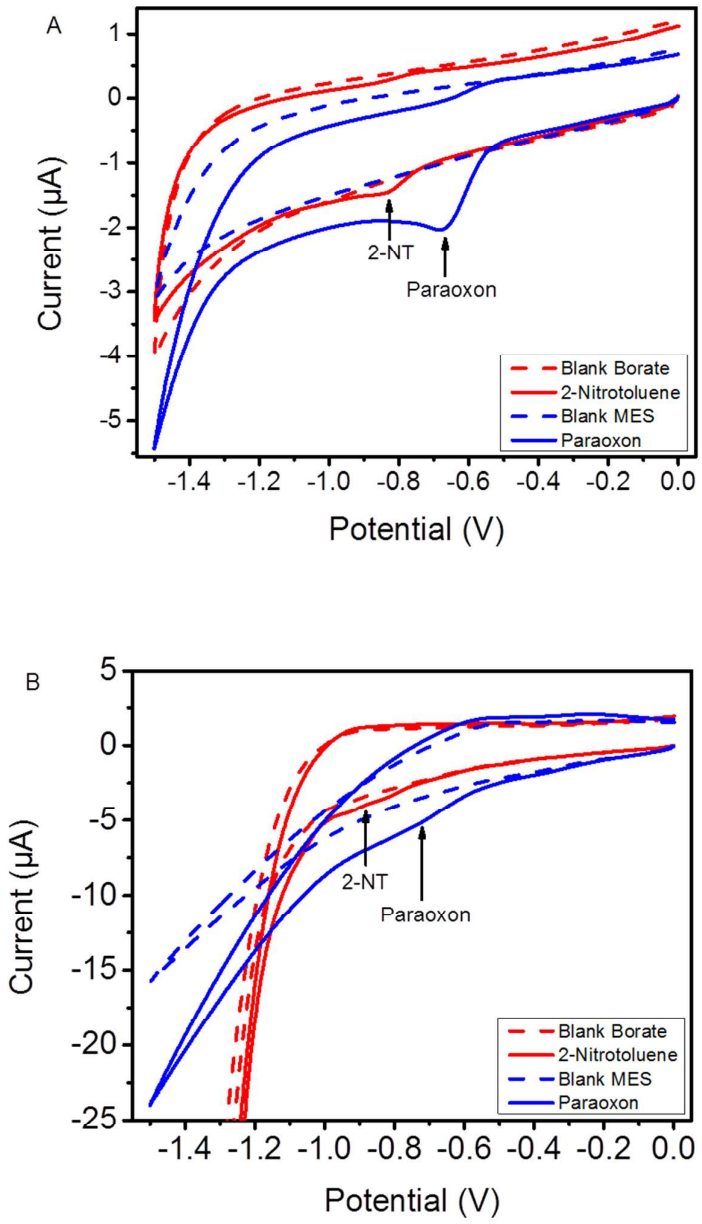


Figure 3. Cyclic voltammograms of 10 mM paraoxon in MES buffer (20 mM, pH 5.0) and 20 mM 2-nitrotoluene (2-NT) in borate buffer (20 mM, pH 9.3) with (A) bare GC and (B) MoS_2-modified GC. Buffer solution purged with N_2 for 15 minutes before each measurement, scan rate 0.1 V s^{-1}.

The usability of MoS_2 as an electrode material for sensing is also limited at the cathodic region as demonstrated. The anodic region of MoS_2 potential window is greatly restricted by the inherent oxidation of the material at about +0.7 V while cathodic potential window is limited at ~-0.6 or ~-0.9 V, depending on the used pH. It is of interest to compare electrochemical window of MoS_2 to other layered materials. For an example, electrochemically reduced graphene shows window of -1.6 to +1.2 V[16,28], fluorographite -1.0 to +1.1 V[29] due to proton reduction and water oxidation, respectively. It should be noted that while the ability of MoS_2 to act as catalyst for hydrogen evolution is unwanted for analytical applications, it is highly useful for "clean energy" applications.[30]

4. CONCLUSION

We have demonstrated that the electrochemical potential window of MoS_2 is limited in both the anodic and cathodic regions. This is a result of the oxidation of MoS_2 at anodic potentials and the electrocatalytic hydrogen evolution in cathodic potentials. As a result, it limits the possible electrochemical sensing applications of MoS_2 only to those analytes with redox potentials between ~-0.6 (due to electrocatalytic hydrogen evolution from H_3O^+ present in the solvent) to +0.7 V (due to oxidation of electrode material itself, from Mo^{4+} to Mo^{6+}) (vs. AgCl); this has a profound effect on the sensing applications as large amount of molecules are reducible at lower potentials or oxidizable at higher potentials than is the potential window of MoS_2.

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