



Electrochemically Exfoliated 2D MoS₂ for ppb-level NO₂ Sensing

Kusuma Urs¹, Tian Carey², Shixin Liu², Kevin Synnatschke², Jonathan N. Coleman², Subhajit Biswas¹, Justin D. Holmes¹

¹School of Chemistry, University College Cork, Cork T12 YN60, Ireland

AMBER Centre, Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland

²Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) and Advanced Materials Bio-Engineering Research Centre (AMBER) Trinity College Dublin, Dublin, Ireland

³Tyndall National Institute, University College Cork, Cork T12 YN60, Ireland

Corresponding author: s.biswas@ucc.ie

Summary:

We demonstrate proof-of-concept Molybdenum sulphide (MoS₂) sensors for environmental monitoring of ultra-low concentration of NO₂. Robust detection in a wide range of NO₂ concentrations, 100 ppb-50 ppm, was achieved, highlighting the great potential for electrochemically exfoliated MoS₂-based NO₂ sensors. The measurements were performed in a complex environment, combining NO₂/synthetic air, traces of other pollutant gases, and in room temperature to achieve fully deployable sensor for the environmental conditions. It is shown; with the aid of density functional theory (DFT) calculations; that the performance of the electrochemically exfoliated MoS₂ sensor can outperform sensors based on mechanically exfoliated MoS₂ owing to their large surface defects and vacancies.

Keywords: MoS₂; 2D material; Electrochemical exfoliation; NO₂ sensor

Introduction

Two dimensional (2D) materials with high surface area and high reactivity have attracted the attention in the field of sensors [1]. Nitrogen dioxide (NO₂) is an oxidizing gas which is toxic and dangerous for environment. NO₂ at levels greater than 1 ppm can cause serious damage to the human respiration system and lung tissues and contributes to the formation of ozone, which is the major cause of photochemical smog and acid rain [2]. So far, most NO₂ electrical sensors are mainly based on metal oxide materials, which usually require high operating temperatures [3]. This shortcoming, coupled with their poor selectivity, severely hampers their application in target gas detection. Therefore, room-temperature operation, portability, low power consumption, sensitive and highly selective gas sensors are of immediate requirement.

Molybdenum disulphide (MoS₂) have grabbed the attention due to the tunable layer-dependent electronic and optical properties [4]. Since 2D MoS₂ has a large surface area with sulphur vacancies and edge states, it has a potential to show a large change in the surface conductivity on exposure to the target gases. Herein, we demonstrated an ideal MoS₂ 2D material synthesized via electrochemical exfoliation for high-performance (~ 100 ppb) NO₂ sensing at room temperature.

Method

For the electrochemical exfoliation, the bulk MoS₂ is inserted in the electrochemical cell and negative voltage is applied, which results in the expansion of the bulk crystal due to the insertion of solvent ion into the crystal. The solution on immediate sonication in presence of stabilizing agent yield dispersed MoS₂ flakes. These sheets collected by centrifugation were dispersed in isopropyl alcohol to form an ink. MoS₂ nanosheet films were then deposited onto PET substrate with Inter-Digitated Electrodes (IDEs) with 100nm gold electrodes. Two terminal electrical characterization and sensor tests of the MoS₂ devices was performed using Keithley 2450 Source Meter interfaced with the semi customized Nextron probe station.

Results & Discussion

Deposited MoS₂ film has the thickness of the film is about 25-30nm. To understand the electrical structure and the oxidation states of the MoS₂, XPS measurements showed atomic percentage ratio between Mo⁴⁺ and S²⁻/S₂²⁻ is 1: 1.8 (± 0.1) which deviates from the stoichiometric ratio (1:2) for ideal MoS₂, indicating the fabrication of the sulphur-deficient MoS₂ nanosheets prepared by the electrochemical exfoliation method.

Sensor characterization of the MoS₂ device were performed towards a range of NO₂ concentration (100 ppb-100 ppm). Two terminal electrical measurements were carried out on the MoS₂ devices under the ambient, synthetic air and NO₂/synthetic air mixed

environment. The device shows a non-linear I - V behavior with the current in the order of nano-ampere range (Fig. 1a). The same device was then exposed to different concentrations of the target pollutant gas of NO_2 . It is evident from Fig. 1b that on exposure to NO_2 for 10 min, the sensor current decreases while it comes back to the initial state when NO_2 gas flow is

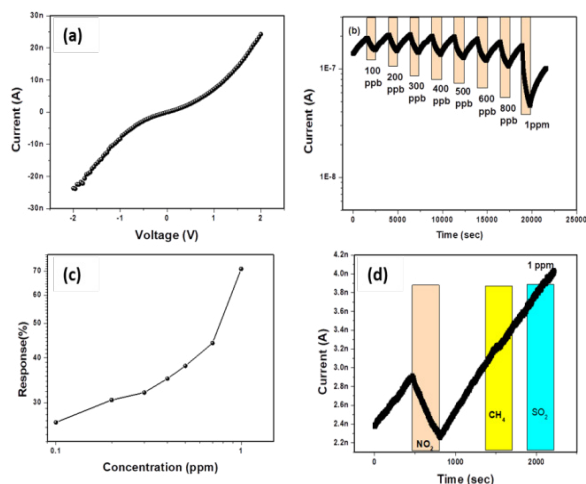


Fig. 1. (a) I - V curve of the two-terminal device. (b) The transient response of the device for NO_2 gas at 1V bias. (c) Response curve from minimum to maximum concentration of NO_2 gas. (d) The response curve for individual gases.

stopped. The decrease in current with NO_2 exposure is attributed to the sulphur vacancies in the system that causes n-type behavior. These sensors showed ~90 % response to 1 ppm of NO_2 with a room temperature response and recovery time of approximately 6 and 20 minutes, respectively. By employing UV irradiation, we enhanced the recovery time of the sensors from 20 minutes to under 1 minute. We have achieved significant response even for 100 ppb at room temperature. The average response and recovery times were estimated as 7 min and 15 min respectively. The sensor response is about 24% even for concentration as low as 100 ppb (Fig. 1c). Evaluation of the sensors was also performed within a 6.5 m³ atmospheric simulation chamber yielding a consistent performance in response and recovery times similar to the smaller scale set up.

DFT calculation have identified three primary possible mechanisms for the detection of NO_2 through electron trapping of electrons: (i) NO_2 physisorption on defective MoS_2 -x layers, (ii) the passivation of sulphur vacancies of MoS_2 -x and (iii) the formation of nitrate radical anions.

Sensor tests in a binary and ternary mixture of gases (CH_4 , SO_2 , NO_2) depicts the primary response only from NO_2 in a binary and tertiary mixture (Fig. 1d). This clearly indicates that the byproducts obtained in mixture of gases are also not interfering with the sensor signal. The device shows good stability (within

5% difference between subsequent NO_2 pulse) at the highest (1 ppm) and lowest (100 ppb) concentration of NO_2 . Electrochemically exfoliated MoS_2 shows much better performance compared to mechanically exfoliated.

In summary, we have found that electrochemically exfoliated MoS_2 with a large density of defects is an ideal candidate for room temperature NO_2 sensing with high sensitivity NO_2 (~100 ppb) and selectivity at room temperature with fast recovery. MoS_2 thin film device can clearly discriminate NO_2 from a mix gaseous environment.

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