FlatChem 9 (2018) 21–26

Contents lists available at ScienceDirect

FlatChem

journal homepage: www.elsevier.com/locate/flatc

A highly sensitive room temperature humidity sensor based on 2D-WS_2 nanosheets

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ARTICLE INFO

Keywords:
Tungsten disulfide
WS_2 nanosheets
Humidity sensor

ABSTRACT

Ambient humidity monitoring is of outmost importance in many technological fields. For this reason, there is still a substantial interest in the development of new simple humidity sensors with high performances. Here it is presented a study to the development of a sensitive, selective and reliable conductometric humidity sensor based on two-dimensional (2D) WS_2 nanosheets. The 2D nanomaterial was synthesized by exfoliation of a bulk WS_2 with *tert*–butyllithium, and then deposited onto the interdigitated electrodes of a conductometric ceramic platform. To evaluate the sensing performances, the sensor was exposed to different relative humidity (RH) levels, recording in real time the change of conductivity of the 2D-WS_2 layer. The sensor exhibited high sensitivity to humidity at room temperature, showing an increase of the current of about 3 orders of magnitude as RH value was varied between 8% and 85% with fast response and recovery times of 140 s and 30 s, respectively. Field tests, carried out to measure the environmental humidity, demonstrated the good performances of the developed sensor as a highly sensitive and reliable relative humidity probe for environmental applications.

1. Introduction

The determination of relative humidity (RH) is of great interest in numerous fields. In fact, there is an increasing demand of accurate and highly sensitive humidity sensors because of their applications in semiconductor industry, medical field, chemical gas purification, food processing and soil moisture monitoring [1]. A variety of transduction principles and materials are widely known for humidity sensing [2]. Among them, resistive humidity sensors have been largely investigated because of their simple device structure and suitability in integrating with current microelectronic technology. Many materials have been proposed as humidity sensitive layer for such resistive devices, including metal oxides, polymers and inorganic/organic composites [3–6].

Apart the above-mentioned conventional materials, novel nanostructures have been explored as sensing materials for humidity sensors. For instance, Weiss et al. [7] investigated the humidity sensing performance of Metal–Organic Frameworks (MOFs), reporting their electrical and dielectric response to humidity. They also tested MOFs as sensitive layer for ambient capacitive humidity sensors by correlating the change in permittivity of the materials with the amount of physisorbed water. Two-dimensional (2D) nanomaterials are also receiving increased attention in the field of humidity sensing. Graphene is one of the most investigated 2D nanomaterials, as demonstrated by the large number of paper published [8–10].

Here, we want to explore the humidity sensing properties of emerging two-dimensional transition-metal dichalcogenides (2D-TMDCs) materials and nanostructures. They find many advanced applications such as field-effect transistors, photodiodes, lasers, memory devices and biomedical applications [11]. Moreover, thanks to their unique structural, electrical, physical and chemical properties, 2D-TMDCs are demonstrating great potential for gas sensor applications [12,13]. Among them, 2D MoS_2, SnS_2 and WS_2 are attracting a lot of interest because they show high sensitivity to various molecules due to the favorable properties for gas adsorption and the high surface area conferred by 2D structure [14–16]. Studies about humidity sensing characteristics of these novel nanomaterials have been reported, but investigation on their performance in field tests are generally lacking.

Here, it is proposed the use of 2D-WS_2 nanosheets for humidity sensing. The 2D nanosheets were prepared from their bulk layered counterpart through an intercalation method by exfoliation of bulk WS_2 with *tert*–butyllithium (*t*-Bu-Li). This method is reported to be of

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https://doi.org/10.1016/j.flatc.2018.05.001
Received 28 January 2018; Received in revised form 4 May 2018; Accepted 10 May 2018

general use and highly effective to produce nanosheets of inorganic materials [17]. Previously, using impedance spectroscopy, the effect of water and organic vapors on both impedance module and phase of a interdigitated gold electrode modified with WS_2 nanosheets, were studied [18]. Both impedance module and phase were found to change during the interaction of water molecules with the surface of WS_2 nanosheets. In particular, the impedance phase spectrum recorded in frequency range from 1 mHz to 100 kHz presented different resonant frequencies with maximum at 1 kHz for water vapor. Unlike, the impedance module continuously increased with reduction of frequency suggesting improved performances if it operates in direct current (DC). Significantly, this layered material was also found selective towards many other gaseous species by selecting specific frequencies.

With the aim to fabricate a simple device for humidity monitoring, here it is developed a conductometric sensor operating in DC mode, by printing the as-prepared 2D-WS_2 nanosheets onto an alumina substrate provided with interdigitated silver electrodes. At presently, very few papers deal with sensors based on 2D-WS_2 sheets for humidity sensing [19–21]. However, these previous data indicate that they do not display the high sensitivity reported for metal oxide-based humidity sensors [22]. Moreover, their sensing characteristics have been not evaluated in field tests.

The results reported in this work demonstrated that WS_2 nanosheets based conductometric sensor exhibited excellent sensing performance towards humidity at room temperature, displaying sensitivity much higher than previous 2D-disulphide based sensors. Moreover, these characteristics were confirmed comparing the performances of the 2D-WS_2 sensor developed with a commercial RH sensor during the monitoring of environmental humidity in laboratory room.

2. Material and methods

2.1. Synthesis and characterization

2D-WS_2 nanosheets were prepared by exfoliation of a bulk WS_2 (obtained from Alfa Aesar, Germany) following the protocol previously described [23]. First, a suspension of 3 g of bulk WS_2 powder in 20 ml of 1.7 M *tert*–butyllithium (Sigma-Aldrich, Czech Republic) in pentane was prepared and then stirred for 72 h at 25 °C under argon atmosphere. The Li-intercalated material was separated by filtration under argon atmosphere and the intercalation compound was washed several times with hexane (dried over Na). The separated WS_2 with intercalated Li was placed in water (100 ml) and repeatedly centrifuged. The obtained material was dried in vacuum oven at 50 °C for 48 h prior to further use.

The as prepared material was characterized by SEM analysis and Raman spectroscopy. SEM images of the samples surface were acquired by a Zeiss CrossBeam 540 instrument, equipped with an electron-dispersive x-ray (EDX) spectrometer. Raman spectra were collected by using a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a charge coupled device (CCD) detector, a 514.5 nm Ar laser, and a 100 × objective mounted on a Olympus optical microscope. The calibration was made using a silicon reference at 520 cm^{-1} and gives a peak position resolution of less than 1 cm^{-1}.

2.2. Sensor preparation

2D-WS_2 humidity based sensor (see a picture of a prototype in Fig. 1) was fabricated employing a commercial alumina substrate (7 mm × 3 mm) provided with a pair of Ag interdigitated electrodes (width 200 µm, spacing 150 µm). Then, 1 µl of the exfoliated WS_2 dispersed in deionized water at concentration of 1 mg ml^{-1}, has been deposited by drop-casting on the interdigitated electrodes. The deposited drop was then dried under a IR lamp for 20 min, leaving a randomly deposited material film on the interdigitated area bridging the two Ag electrode bands. The deposited film area is well visible (Fig. 1b). The fabricated sensor was then mounted on the top of a ceramic holder (Fig. 1a) inserted in the package ensuring the electrical connections.

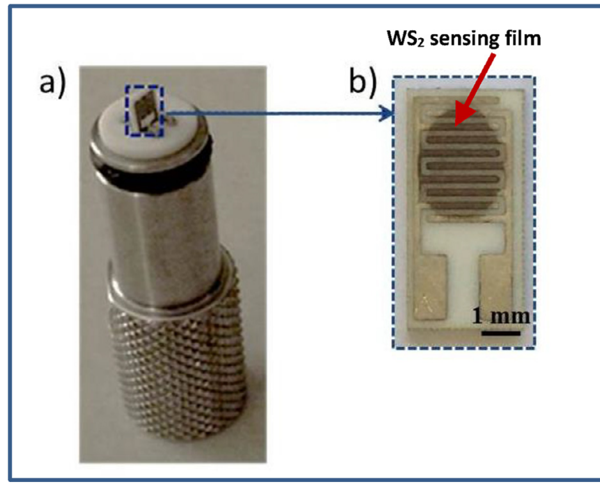

Fig. 1. a) Image of the humidity sensor mounted on the top of the ceramic holder; b) structure of the interdigitated sensor.

2.3. Apparatus and sensing tests

The electrical measurements under different humidity values were carried out at room temperature (RT ~ 26 °C) in a Teflon chamber equipped with a temperature/humidity sensor. The chamber operates at constant atmospheric pressure and can be filled with water vapor to vary the humidity from approximately 8–85 RH%, through the setup shown in Fig. 2. A real time electrical readout GUI Matlab shows the signal of the sensor under test and both temperature and humidity in the chamber during the measurement. RH and temperature were continuously monitored using a commercial sensor (Sensirion SHT21). The whole sensing setup is also schematized in Fig. 2.

The sensor response was evaluated as the variation of the current which flow through the sensitive film, at a fixed applied bias voltage of 5 V. A Keithley 6487 Picoammeter/Voltage Source was used for this purpose. The response, τ_{res}, and recovery τ_{rec}, times are defined as the times taken by the sensor to achieve 90% of the signal change in the case of water vapor adsorption and desorption, respectively. Cross-interference was also investigated exposing the sensor to different gaseous species at a fixed humidity in air. In this case the cross-response was evaluated as current ratio, $S = i_{gas}/i_0$, where i_{gas} is the current recorded during the exposure of the senor to each gas and i_0 is the current recorded at 30 RH% in air in absence of interfering gases.

During environmental measurements, the WS_2-based sensor is directly exposed to ambient air close to the SHT21 device.

3. Results and discussion

3.1. Characterization of exfoliated 2D-WS_2 nanosheets

The preparation method of the layered material and the characterization have been described in details in previous papers [18,23]. As varying the number of layers may causes change in chemical and physical as well as electrical properties, great attention should be payed to the synthesis process in order to control the quality and layer number of the nanosheets produced.

A SEM image of the sensitive film collected directly on the interdigitated electrodes is showed in Fig. 3a. 2D-WS_2 is observable as sheet-like structures, which uniformly cover the alumina substrate. This confirms that the method adopted for the preparation of the material favors the exfoliation of bulk WS_2. EDX elemental analysis (see inset