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# 2D $SnX_2$ (X=S, Se) Based Heterojunctions for $NO_2$ Sensing at Low Temperatures

*Xiaogan Li**, Ding Gu, Xinyu Li, Xueyan Wang, Tingting He*
*Dalian University of Technology, School of Microelectronics, Dalian, P.R.China*

*Corresponding author's e-mail address: lixg@dlut.edu.cn*

**Abstract:**
Two dimensional nanomaterials (2D) $SnX_2$ (X=S, Se) based chemiresistive-type sensors was investigated for detecting $NO_2$ at low temperatures. It was found that $SnO_2$ nanocrystal-dotted $SnS_2$ heterojunctions formed by in-situ thermal oxidation in a controlled environment indicated a good sensitivity and selectivity to $NO_2$ at 80 $^{o}$C. The lower operating temperature was attributed to enhanced catalytic properties to $NO_2$ by the $SnO_2$ nanocrystals. With the replacement of S by Se in $SnX_2$ compound, the working temperature of $SnX_2$ based $NO_2$ sensor could be further decreased significantly to near room temperature. Theoretical calculation according to Density-Function-Theory (DFT) indicates that $SnSe_2$ has a higher $NO_2$ adsorption ability compared to $SnS_2$.

**Key words:** 2D nanomaterials, $SnS_2$ and $SnSe_2$, $NO_2$ Sensor, $SnO_2/SnS_2$ heterojunctions

## Introduction

A low-cost reliable chemical gas sensor for timely monitoring the pollutant gases in ambient is highly demanded for people to be aware of or obtain the more detail information on these pollutant gas concentrations [1]. Compared to graphene that is lack of the band gap, metal dichalcogenides seem more advantageous because of its adjustable narrow bandgap and replaceable metal cations and X anions in the compounds which would result to the variable photo- and electronic properties [2-5]. For example, among the metal dichalcogenides, $MoS_2$ is one of the most investigated $MX_2$ compounds. In particular for chemical gas sensors, it demonstrated a good sensitivity to several typical harmful or toxic gases such as $NO_2$, $NH_3$ and triethylamine at room temperature. However, the response and recovery speeds are usually slow. Nevertheless, with the substitution of the S in $MoS_2$ by Se that has a larger ion radius, the $MoSe_2$ based chemirestive sensor indicates a much improved response time [6]. The elemental X in the 2D $MX_2$ compounds clearly has a significant influence on the gas sensing properties. In this work, the gas sensing properties of the layered $SnX_2$ (X=S, Se) nanoflakes have been investigated. The $SnX_2$ based chemiresistive sensor shows a good response to $NO_2$ at a significantly decreased temperature even down to 30°C. A full faster recovery of the 2D $MX_2$ based $NO_2$ sensor was achieved.

## Experimental

The $SnS_2$ and $SnSe_2$ nanomaterial was purchased commercially. To obtain the $SnO_2/SnX_2$ heterojunctions, the $SnX_2$ samples were synthesized by the in-situ high-temperature oxidation method in a controlled oxygen environment. The samples were characterized by SEM, TEM, XPS. The gas sensing properties of the sensors were measured by using fully computer controlled gas mixing and data acquisition systems under dynamic gas flow region. The sensor response to $NO_2$ was defined as the relative change of the resistance in $NO_2$ to the one in Air. The density function theory (DFT) was used to calculate the gas adsorption energy on these 2D materials.

## Results and Discussion

Fig.1 shows the SEM images of the $SnS_2$, $SnO_2/SnS_2$ and $SnSe_2$ nanoflakes. All indicate a flake-like morphology. The $SnO_2$ nanocrystals are clearly observed for the $SnO_2/SnS_2$ heterojunction sample. Fig.2 shows the XPS of the samples. The existence of $SnO_2$ in the $SnO_2/SnS_2$ heterojunctions was confirmed as shown in Fig.2a. Fig.2b shows that with addition of $SnO_2$, the adsorbed $O_2$ on the surface increased. The small amount of adsorbed $O_2$ on

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pure $SnS_2$ may be induced by the S vacancies. Fig.2c confirms again the composition of $SnSe_2$.

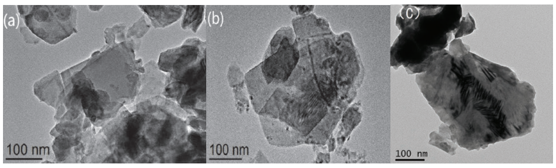


*Fig.1.Morphology of (a) $SnS_2$; (b) $SnO_2/SnS_2$; (c) $SnSe_2$.*

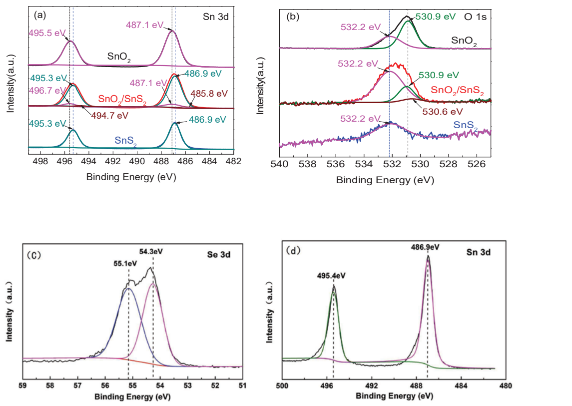


*Fig.2.XPS of (a-b) $SnS_2$ and $SnO_2/SnS_2$; (c-d) $SnSe_2$.*

Fig.3 shows the sensing performance of $SnS_2$, $SnO_2/SnS_2$ and $SnSe_2$ based chemiresistive-type gas sensors to $NO_2$. Fig.3a-b shows that with the in-situ formed $SnO_2$ nanocrystals on $SnS_2$ flakes, the operating temperature of the sensor can be lowered. This can be attributed the extra attraction of oxygen on the surface of the $SnO_2/SnS_2$ heterojunctions (as confirmed in Fig.2b). The adsorbed oxygen can help enhancing the extra response through the conventional redox reactions between $NO_2$ and $O_2$. Moreover, as displayed in Fig.3c, the $SnO_2/SnS_2$ heterojunction based sensor indicates an excellent selectivity to several typical gases such as alcohols, formaldehyde, acetone and methylbenzene.

As the replacement of S in $SnX_2$ compound by Se, the $SnSe_2$ nanoflakes based sensor exhibited a room temperature response to $NO_2$ with a fast response and full recovery within 1-2 minutes as shown in Fig.3d-e. The sensor also demonstrated a good selectivity (Fig.3f). Table 1 summarizes the comparison of the sensing features of these series of $SnX_2$ compounds. The calculation using density function theory indicates that $SnSe_2$ has a larger adsorption energy relative to $SnS_2$.

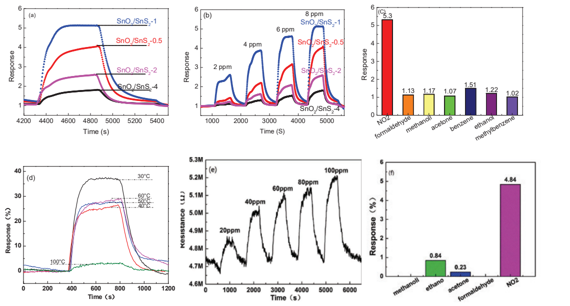

*Fig. 3. (a-b) Comparison of response of $SnO_2/SnS_2$ oxidized for different times to $NO_2$ at 80 °C; (c) Selectivity of $SnO_2/SnS_2$ based $NO_2$ sensor; (d) Temperature-dependent response, (e) Response curve and (f) Selectivity of $SnSe_2$ based sensor to $NO_2$ at 30 °C.*

In Summary, $SnX_2$ and its formed heterojunctions could be tuned systematically to achieve a low temperature $NO_2$ sensor with a good recovery feature. These sensing materials also indicated an excellent selectivity.

*Table 1 Comparison of sensing properties of $SnX_2$ (X=O, S, Se) 2D nanomaterials based chemiresistive sensors.*

| 2D Materials | $E_g$ | Temp. | Target Gases | Res./Rec. Time | Selectivity | Refs. |
|---|---|---|---|---|---|---|
| $SnO_2$ | 3.5 eV | 200°C | $NO_2$, | <1 minute | - | [1] |
| $SnS_2$ | 2.1eV | 120 °C | $NO_2$ | ~2 minutes | Good | [2] |
| $SnO_2/SnS_2$ | - | 80 °C | $NO_2$ | ~3-4 minutes | Good | [4] |
| $SnSe_2$ | 1.1eV | 30 °C | $NO_2$, | ~1-2 minutes | Good | This work |

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