2D SnX₂ (X=S, Se) Based Heterojunctions for NO₂ Sensing at Low Temperatures

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Abstract:
Two dimensional nanomaterials (2D) SnX₂ (X=S, Se) based chemiresistive-type sensors was investigated for detecting NO₂ at low temperatures. It was found that SnO₂ nanocrystal-dotted SnS₂ heterojunctions formed by in-situ thermal oxidation in a controlled environment indicated a good sensitivity and selectivity to NO₂ at 80 °C. The lower operating temperature was attributed to enhanced catalytic properties to NO₂ by the SnO₂ nanocrystals. With the replacement of S by Se in SnX₂ compound, the working temperature of SnX₂ based NO₂ sensor could be further decreased significantly to near room temperature. Theoretical calculation according to Density-Function-Theory (DFT) indicates that SnSe₂ has a higher NO₂ adsorption ability compared to SnS₂.

Key words: 2D nanomaterials, SnS₂ and SnSe₂, NO₂ Sensor, SnO₂/SnS₂ 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, MoS₂ is one of the most investigated MX₂ compounds. In particular for chemical gas sensors, it demonstrated a good sensitivity to several typical harmful or toxic gases such as NO₂, NH₃ and triethylamine at room temperature. However, the response and recovery speeds are usually slow. Nevertheless, with the substitution of the S in MoS₂ by Se that has a larger ion radius, the MoSe₂ based chemiresistive sensor indicates a much improved response time [6]. The elemental X in the 2D MX₂ compounds clearly has a significant influence on the gas sensing properties. In this work, the gas sensing properties of the layered SnX₂ (X=S, Se) nanoflakes have been investigated. The SnX₂ based chemiresistive sensor shows a good response to NO₂ at a significantly decreased temperature even down to 30°C. A full faster recovery of the 2D MX₂ based NO₂ sensor was achieved.

Experimental
The SnS₂ and SnSe₂ nanomaterial was purchased commercially. To obtain the SnO₂/SnX₂ heterojunctions, the SnX₂ 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 NO₂ was defined as the relative change of the resistance in NO₂ 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 SnS₂, SnO₂/SnS₂ and SnSe₂ nanoflakes. All indicate a flake-like morphology. The SnO₂ nanocrystals are clearly observed for the SnO₂/SnS₂ heterojunction sample. Fig.2 shows the XPS of the samples. The existence of SnO₂ in the SnO₂/SnS₂ heterojunction sample was confirmed as shown in Fig.2a. Fig.2b shows that with addition of SnO₂, the adsorbed O₂ on the surface increased. The small amount of adsorbed O₂ on...
pure SnS2 may be induced by the S vacancies. Fig. 2c confirms again the composition of SnSe2.

SnO2/SnS2 heterojunction based sensor indicates an excellent selectivity to several typical gases such as alcohols, formaldehyde, acetone and methylbenzene.

As the replacement of S in SnX2 compound by Se, the SnSe2 nanoflakes based sensor exhibited a room temperature response to NO2 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 SnX2 compounds. The calculation using density function theory indicates that SnSe2 has a larger adsorption energy relative to SnS2.

Table 1 Comparison of sensing properties of SnX2 (X=O, S, Se) 2D nanomaterials based chemiresistive sensors.

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<tr>
<td>SnO2</td>
<td>3.5 eV</td>
<td>200°C</td>
<td>NO2</td>
<td>&lt;1 minute</td>
<td>-</td>
<td>[1]</td>
</tr>
<tr>
<td>SnS2</td>
<td>2.1 eV</td>
<td>120 ºC</td>
<td>NO2</td>
<td>~2 minutes</td>
<td>Good</td>
<td>[2]</td>
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<tr>
<td>SnO2/SnS2</td>
<td>-</td>
<td>80 ºC</td>
<td>NO2</td>
<td>~3-4 minutes</td>
<td>Good</td>
<td>[4]</td>
</tr>
<tr>
<td>SnSe2</td>
<td>1.1 eV</td>
<td>30 ºC</td>
<td>NO2</td>
<td>~1-2 minutes</td>
<td>Good</td>
<td>This work</td>
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References
[2] Ou et al., Physisorption-based charge transfer in two-dimensional SnS2 for selective and reversible NO2 gas sensing, ACS nano. 9, 10313-10323 (2015); doi: 10.1021/acsnano.5b04343