**Dispersed SnO<sub>2</sub> nanoparticles on MoS<sub>2</sub> nanosheets for superior gas-sensing performances to ethanol**

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The unique properties of MoS<sub>2</sub> nanosheets make them promising supporting substrate for preventing the interparticle aggregation of metal-oxide-semiconductor nanomaterials. A novel composites were successfully obtained by a two-step low temperature hydrothermal method for the synthesis of SnO<sub>2</sub> nanoparticles dispersing on the surfaces of MoS<sub>2</sub> nanosheets. The morphology and structure of the as-prepared samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). Owing to the supporting substrate of specific two-dimensional MoS<sub>2</sub> nanosheets and the superior gas-sensing performance offered by ultrasmall SnO<sub>2</sub> nanoparticles, the sensor based on SnO<sub>2</sub>@MoS<sub>2</sub> composites exhibit high response and good selectivity to ethanol gas.
were reduced under high temperature condition, forming MoS$_2$ nanosheets without adding any 2D substrate. SnO$_2$ nanoparticles were prepared using a simple hydrothermal method and dispersed onto MoS$_2$ nanosheets. A comparative study between pure SnO$_2$ nanoparticles and SnO$_2$@MoS$_2$ composites was performed to reveal the promotion effect of SnCl$_2$ on the gas-sensing performance. Experimental results showed that SnO$_2$@MoS$_2$ composites exhibit superior gas-sensing performance to ethanol in comparison with pure SnO$_2$ nanoparticles. A possible sensing mechanism was also proposed for the SnO$_2$@MoS$_2$ composites.

**Experimental**

**Synthesis of MoS$_2$ nanosheets**

All the chemical reagents were analytical graded and used without further purification. The MoS$_2$ precursors were synthesized through a simple hydrothermal method. In a typical reaction, 2 mmol of sodium molybdate (Na$_2$MoO$_4$$\cdot$2H$_2$O) and 9 mmol of thiocarbamide (CH$_4$N$_2$S) were mixed and dissolved in 70 ml deionized water. After stirring the solution for 30 min, 2.2 mmol of citric acid (C$_6$H$_8$O$_7$$\cdot$H$_2$O) was added into the above solution. After magnetically stirring for 10 min, the homogeneous solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, sealed tightly, and maintained at 200 °C for 21 h. After the hydrothermal procedure, the autoclave cooled down to room temperature spontaneously. The black precipitates were collected by centrifugation, washed several times with deionized water and absolute ethanol, respectively, and dried at 60 °C for 12 h in air.

**Synthesis of SnO$_2$@MoS$_2$ composites**

The synthesis of SnO$_2$@MoS$_2$ composites were used by the hydrothermal method. The as-fabricated MoS$_2$ (0.1 g) was dissolved in 80 ml deionized water and ultrasonic dispersion 20 min to ensure the black powders was completely dispersed in the solution. SnCl$_2$$\cdot$5H$_2$O (0.438 g) and NaOH (0.3 g) dissolved in the solution. After magnetic stirring for 30 min, a suspension was obtained and transferred into a 100 ml stainless steel autoclave with Teflon-lined, which was heated at 180 °C for 18 h. After the autoclave was cooled down to room temperature, the precipitates were collected and washed several times with deionized water and ethanol, respectively. After drying at 60 °C for 6 h, the ashen powders were obtained.

**Characterization**

The crystal structure and phase composition of as-prepared samples were identified by X-ray diffraction (XRD, Bruker D8 Advance) using CuKα1 radiation (λ = 0.15406 nm) at 30 kV and 40 mA at a scanning rate of 2° at 2θ min$^{-1}$. The morphology and nanostructure of the products were characterized using FEI Sirion 200 field emission gun scanning electron microscope (FESEM, Hitachi S4800), and transmission electron microscopy (TEM, Hitachi H-800). More details about the structure were investigated by the selected area electron diffraction (SEAD) pattern and high resolution transmission electron microscopy (HRTEM, JEOL 2010). X-ray photoelectron spectra (XPS) were measured using a PHI 5300 X-ray photoelectron spectrometer with Al Kα radiation.

**Fabrication and measurement of gas sensor**

The obtained samples were firstly mixed with distilled water to form slurry through milling, and then pasted onto a prefabricated alumina tube (7 mm in length and 1.5 mm in diameter, attached with a pair of gold electrodes and platinum wires) by a small brush to form a thick film. The thickness of sensing films was about 100 µm. A Ni-Cr resistor (diameter = 0.5 mm, resistance = 35 Ω) in the inner alumina ceramic tube, as a heater, was used to provide the working temperature for the sensor device. After dried in the air and aged at 300 ℃ for 2 days, it has been an indirectly-heated gas sensor, and then the gas sensor was putted into the test chamber in a measuring system of WS-30A (Winsen Electronics Co. Ltd., Zhengzhou, China) by a static process. A typical testing procedure was as follows: The sensors were put into a glass chamber (18 L) at the beginning. When the resistances of all the sensors were stable, the calculated amount of the target gas or liquid was injected into glass chamber by a micro-injector and mixed with air. For the target gases obtained from liquid, the concentration of target gas was calculated by the following formula,

$$ C = \frac{(22.4*ρ*d*V_l)}{(V_{\text{testing}}*M*V_p)} \quad (1) $$

where $C$ (ppm) is the target gas concentration, $ρ$ (g/mL) is the density of the liquid, $d$ is the purity of the liquid, $V_l$ ($\mu$L) is the volume of the liquid, $V_p$ (L) is the volume of the glass chamber, and $M$ (g/mol) is the molecular weight of the liquid. The working temperature of the sensor can be controlled by adjusting the heating voltage ($V_{\text{heating}}$) across a Ni-Cr alloy resistor inside the ceramic tube. A reference resistor ($R_{\text{ref}}$) is put in series with the sensor to form a complete measurement circuit. In the test process, a working voltage of 5 V ($V_{\text{working}}$) was applied. By monitoring the voltage across the reference resistor ($V_{\text{ref}}$), the response of the sensor in air or in a test gas could be measured. The sensor response was defined as,

$$ \text{Response} = \frac{R_{\text{load}}}{R_{\text{air}}} \quad (2) $$

where $R_{\text{air}}$ is the resistance of the sensor in air and $R_{\text{gas}}$ is the resistance of sensor in the presence of the test gas.

**Results and discussion**

The purity and crystalline phase of as-synthesized pure MoS$_2$, SnO$_2$ nanoparticles and SnO$_2$@MoS$_2$ composites were analyzed by a powder X-ray diffractogram. Fig. 1 shows the XRD patterns of the samples, which displays diffraction peaks in the range of 10-80°. As for the pure MoS$_2$ sample, the detected peaks at 2θ = 26.1°, 46.5°, 50.7°, 54.7°, 68.1° and 74.9° can be assigned to the (002), (101), (103) and (110) planes in the hexagonal phase of MoS$_2$ (JCPDS 37-1492). Moreover, the diffraction peaks of SnO$_2$ can be easily indexed to a pure tetragonal rutile structured tin dioxide, which was consistent with the standard data file (JCPDS file no. 41-1445). No other diffraction peaks were observed. In additional, the crystallite size of SnO$_2$ is about 8.2 nm, which is estimated using the Scherrer formula,

$$ D = \frac{Kλ}{β \cosθ} \quad (3) $$
The as-synthesized MoS\(_2\) nanoflower. A few SnO\(_2\) nanoparticles aggregations are observed in FESEM image. The intriguing structure is also elucidated under TEM to provide further insight about the morphology and microstructure. Fig. 2(c) is the TEM image of typical MoS\(_2\) nanosheets inlayed with several dispersive SnO\(_2\) nanoparticles. It can be seen that the sizes of the SnO\(_2\) nanoparticles are less than 10 nm, which is in accord with the results of XRD patterns. Under a higher magnification, the ultrasmall SnO\(_2\) nanoparticles attached on MoS\(_2\) nanosheets can be well observed. The cross-sections of MoS\(_2\) nanosheets can be observed. As shown in Fig. 2(d), the distance between two adjacent atomic planes were calculated to be around 0.64 nm, corresponding to the interplanar distance of (002) plane of hexagonal MoS\(_2\) crystalline structure. The lattices of SnO\(_2\) nanoparticles can be also clearly observed with the interplanar distance of 0.34 nm, matching the (110) plane of cubic SnO\(_2\) crystalline structure (JCPDS 41-1445).

On the basis of the results stated above, the formation process of SnO\(_2\)@MoS\(_2\) composites in hydrothermal system is concluded. First, sodium molybdate was chosen as the precursor for molybdenum thioacetamide was used as the sulfur source. During the hydrothermal treatment, MoO\(_4^{2-}\) anions were reduced under high temperature condition, forming MoS\(_2\) nanoparticles. Second, these nanoparticles grow up into nanosheet structures in order to reduce the high surface energy through the process known as oriented aggregation. As the reaction further proceeds, the nanosheets tend to merge together to well-defined MoS\(_2\) nanoflowers through a self-assembly process. In addition, the formation of SnO\(_2\) nanoparticles adhering on the MoS\(_2\) can be expressed as follows:

\[
\text{Sn}^{4+} + 6\text{OH}^- \rightarrow \text{Sn(OH)}_6^{2-} \tag{4}
\]
\[
\text{Sn(OH)}_6^{2-} \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \tag{5}
\]
To explore the advantages of the SnO$_2$@MoS$_2$ composites, the as-prepared product was evaluated as sensing material to investigate its gas sensing performance. For comparison, the sensing properties of the pure SnO$_2$ nanoparticles prepared by hydrothermal method were also studied. It is well known that the gas response of semiconductor gas sensors is greatly influenced by the operating temperature. In order to determine the optimum operating temperatures of sensors based on SnO$_2$@MoS$_2$ composites and pure SnO$_2$ nanoparticles, the response of two sensors to 200 ppm ethanol were tested as a function of operating temperature. As shown in Fig. 3, both sensors exhibit peak-shaped dependence on the operating temperature. It can be clearly observed that the ethanol response first increased with working temperature, and then gradually decreased when the temperature further increases. The relative optimum working temperature can be explained as follows: Normally, the reactivity between the target gas and adsorption oxygen needs certain activation energy, which is provided by increasing reaction temperature. At low working temperature, the adsorbed methanol molecules are not activated enough to overcome the activation energy barrier to react with the adsorption oxygen species, while at high temperatures the gas adsorption is too difficult to be adequately compensated for the increased surface reactivity. Moreover, it can be observed that the pure SnO$_2$ nanoparticles have the maximum gas response at 340 °C, whereas SnO$_2$@MoS$_2$ composites have the maximum gas response at 280 °C. Compared with pure SnO$_2$ nanoparticles, SnO$_2$@MoS$_2$ composites exhibit superior gas-sensing performances to ethanol.

The response and recovery time is an important factor to evaluate the gas sensing properties of the sensor. The response time was defined as the time required for the variation in resistance to reach 90% of the equilibrium value after a test gas was injected, and the recovery time as the time necessary for the sensor to return to 10% above the original resistance in air after releasing the test gas. Fig. 4(a) shows the dynamic response transient of the SnO$_2$@MoS$_2$ composites gas sensor to different concentrations of ethanol at its optimum operating temperature of 280 °C. It is clear that the response curves of the sensor increases sharply with increasing concentration of ethanol and then returns to the baseline quickly with the ethanol exhausted out in the closed testing chamber, indicating their quick and reversible response and recovery time. Moreover, it can be seen that the response of the sensors increases with the increasing of the ethanol concentrations. The sensor response can be empirically represented as $S = a[C]^b + 1$, where $a$ and $b$ are the constants and $S$ is the gas response, $C$ is the concentration of the test gas. Fig. 4(b) shows a chart of logarithm of the response of the sensor (S-1) versus the logarithm of methanol concentration (C). It can be found that the response of the sensor based on SnO$_2$@MoS$_2$ composites has a good linear relationship with the ethanol concentration (50-1000 ppm range) in logarithmic forms. As shown in Fig. 3(c), the straight line is the calibration curve and the experimental data were fitted as: $y = 0.4717x + 0.9561$, where $y$ is $\log (S-1)$ and $x$ is $\log (C)$. The results highlighted the potential applications of SnO$_2$@MoS$_2$ composites in...
monitoring ethanol gas. The selectivity of gas sensors is the ability that a sensor can distinguish different kinds of gases, which is also important for the gas sensing properties. Fig. 5 demonstrated that the gas sensor show responses to various gases of 200 ppm, including ammonia, ethanol, formaldehyde, and acetone. Significantly, the sensor based on SnO₂@MoS₂ composites displayed a much higher response and better selectivity to ethanol as opposed to any other test gases at the working temperature of 280 °C.

SnO₂ is well-known as an n-type gas sensing material and its gas sensing mechanism belongs to the surface-controlled type, the change of resistance is due to the species and the amount of chemisorbed oxygen on the surface. Meanwhile, the tests of gas sensing mechanism belongs to the surface-controlled type, controlled by the concentration of adsorbed oxygen species (O₂⁻, O⁻ or O²⁻) that trap electrons and act as scattering centers effectively reducing the semiconductor conductivity. When the sensor is exposed to ethanol vapor at higher temperature, ethanol reacts with the adsorbed oxygen ions reducing their concentration and thereby increasing the semiconductor conductivity. The possible reactions took place on the surface of tin oxide as follows:⁴¹-⁴³

$$\text{CH}_3\text{CH}_2\text{OH} + 6\text{O} \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \quad (6)$$

The SnO₂ sensors change to the initial electronic structure when exposed to air again. The SnO₂@MoS₂ composites exhibit superior gas-sensing performances to ethanol, which is better than that of its counterpart of SnO₂ nanoparticles. That is, there exists a beneficial effect of dispersing SnO₂ nanoparticles on MoS₂ nanosheets. As shown in Fig. 6, the improvement of sensing performance of SnO₂@MoS₂ composites may be attributed to the following reasons. Firstly, MoS₂ nanosheet with high surface area provides a platform for attaching the SnO₂ nanoparticles, preventing their interparticle aggregation. This kind of nanostructure can provide a large specific surface area, which is of great benefit to numerous oxygen molecules adsorbed onto SnO₂ nanoparticles, and facilitate the diffusion of ethanol gas, improving the reaction of the ethanol gas with surface adsorbed oxygen.⁴⁴,⁴⁵ Besides, the operating temperature of SnO₂@MoS₂ composite sensor has a significant decrease, compared to the pure SnO₂ nanoparticles, indicating the surface reaction occurred at a lower operating temperature, which can be attributed to that the activation energy of the surface reaction is lowered by mixing MoS₂ nanosheets. In this work, MoS₂ nanosheet with high surface area provides a platform for attaching the SnO₂ nanoparticles, preventing their interparticle aggregation. The crystallite size of SnO₂ is less than 10 nm, which is estimated by XRD patterns and TEM image. Under this conditions, very low activation energy for the grain growth has been calculated for SnO₂ nanocrystallites within the size range of 3–20 nm. While, above this size range (20–300 nm), the activation energy for the grain growth increases exponentially.⁴⁶,⁴⁷ Secondly, the significant increase of the gas-sensing performance for SnO₂@MoS₂ composites can be attributed to the active site provided by the MoS₂ nanosheets and also the good interaction between the two materials,⁴⁸ therefore improving the electron transfer rate, and thus enhancing gas-sensing response. Thirdly, the MoS₂ nanosheet in this work exhibits a p-n type semiconducting behavior in air, which is similar to literatures.⁴⁹-⁵³ Thus, at the interface between the SnO₂ nanoparticles and the MoS₂ nanosheets, there forms a p-n junction, which will result in the MoS₂ and SnO₂ having a same Fermi energy level at the interface. Thus a staggered band offset and a built-in internal electric field was formed near the interface. When SnO₂@MoS₂ composites are exposed to ethanol vapor at higher temperature, electrons generate in the reaction can easily cross the interface and transfer to the conductive band of SnO₂ nanoparticles. Because the conduction band and the valence band of SnO₂ both lie below the energy band of MoS₂ in this composite. As a result, the gas-sensing performance can thus be improved eventually in the composites of dispersing SnO₂ nanoparticles on the surfaces of MoS₂ nanosheets. Furthermore, to reveal the influence of the content of SnO₂ in composites, the study of morphology and gas response of SnO₂@MoS₂ composites with different reaction conditions was investigated by changing the MoS₂/SnO₂ molar ratios, while temperature and reaction time were kept at 200 °C and 21 h, respectively (Fig. S3).
Conclusions

In summary, a simple solution route was successfully promoted to synthesize novel gas-sensing composite by dispersing SnO$_2$ nanoparticles on the surfaces of MoS$_2$ nanosheets. Importantly, it is found that MoS$_2$ nanosheets play an important role for enhancing the gas-sensing performance. The SnO$_2$/MoS$_2$ composite sensor exhibits better gas-sensing performance in comparison with pure SnO$_2$ nanoparticles, indicating the potential applications as gas sensor material toward ethanol detection.

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Notes and references