A room-temperature hydrogen gas sensor based on TiO$_2$/MoS$_2$ nanocomposite

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Abstract. A room-temperature hydrogen gas sensor based on TiO$_2$/MoS$_2$ nanocomposite which synthesized by the hydrothermal process was investigated. The nanocomposite was the flowerlike MoS$_2$ nanosheets adhering on end surfaces of the porous TiO$_2$ nanorods. The sensing properties of the TiO$_2$/MoS$_2$ based sensor to hydrogen were investigated at room temperature and compared with the sensing properties of the sensor based on pure TiO$_2$ nanorods. The nanocomposite-based sensor has the sensing response(S) of 4.25% to 200 ppm hydrogen at 25 °C, which was about 80 times higher than the sensing response(S) of the pure TiO$_2$ nanorod-based sensor. The response time of the nanocomposite-based sensor was about 96 s, and the recovery time was about 54 s to 200 ppm hydrogen at 100 °C. The enhanced sensing response(S), rapid response and recovery characteristics were attributed to the structural characteristics of the nanocomposite and the formed p-n junction between TiO$_2$ and MoS$_2$.

1. Introduction
With the exhaustion of fossil fuels and increasingly serious environmental problems, Hydrogen, which has high combustion heat (142 kJ/g), low minimum ignition energy (0.017 mJ), wide flammable range (4-75%vol), and high burning velocity, has drawn more and more attentions and has become one of the best clean energy sources because of its regenerated and clean final combustion product [1]. However, hydrogen is not a really safe energy source because it will explode violently when its concentration ranges from 4% to 75% (volume ratio) in the air [2]. Therefore, for safe production, storage, and application, it is extremely necessary to detect the hydrogen leakage rapidly and accurately.

So far, there are various types of hydrogen gas sensors [3-5], and among of them, those based on the different TiO$_2$ [6-8] have been widely studied and applied, due to their good stability, simple structure, low cost and simplicity of synthetic process. The nanostructured material can provide large specific surface area, e.g., a kind of uniformly distributed TiO$_2$ nanoparticle fabricated by Wang, LQ et al., whose specific surface area is 203.245 m$^2$/g [9]. The surface and size effect of the nanostructured metal oxides allow their higher sensing response. To realize low-temperature or even room-temperature gas sensors and to reduce power consumption, the TiO$_2$ materials are often prepared intentionally in the form of nanostructures and then doped. B. Lyson-Sypien et al. investigated that the
mixture of TiO$_2$ and Cr/TiO$_2$ nanopowders has good response of to H$_2$ at 350 °C [10]. However, at a lower working temperature, the gas sensors usually exhibit some disadvantages, for example, the low sensing response and long response/recovery time [11].

In order to reduce the power consumption of the hydrogen gas sensor as well as to overcome those disadvantages above, researchers attempt to find some ways of lowering the working temperature in the precondition of keeping good sensing properties. One of the most effective way is doping or coating noble metal catalysts like Pd, Pt or others on metal oxide semiconductor materials [12, 13]. Hayawa et al. reported that the TiO$_2$ doped with Pt has good gas sensing performance at 200℃ [14]. Some researchers also doped the different semiconductors for synergistic effects or forming heterojunctions to enhance the sensing properties [15-17].

Graphene has attracted much attention due to its unique thermal, electrical, biological, mechanical and sensing properties [18-20]. However, it is not beneficial to improve the gas sensing response and selectivity because of its zero band gap, limiting its application in the gas sensors. Zero band gap of graphene has inspired researchers to turn to other graphene-like materials with appropriate band gaps, such as transition-metal oxides (TMOs) or transition-metal chalcogenides (TMCs), like MoS$_2$ [21-26], GaS, GaSe [27, 28] and WSe$_2$ and so on [29, 30]. Compared with other emerging 2-D layered materials, the MoS$_2$ has been widely studied as the gas sensing material because of its high sensing response [31]. The nanosheet MoS$_2$ has better hydrogen adsorption and desorption properties, and it can be developed into a monolayer hydrogen sensor [32].

In this paper, we proposed a room-temperature hydrogen sensor based on the TiO$_2$ / MoS$_2$ nanocomposite. The nanocomposite was prepared by a two-steps hydrothermal process and characterized by a series of methods. The gas sensor was fabricated by integrating the nanocomposite with the micro electrodes on substrate, and its sensing properties to H$_2$ were also tested. The nanocomposite-based hydrogen sensor demonstrates a higher sensing response and faster response/recovery properties compared with the sensor based on the pure TiO$_2$ nanorods.

2. Experiment

All chemicals are analytical reagent grade and used without further purification. The precursor solution was prepared by mixing 10 ml HCl with 10 ml deionized water, under vigorous stirring at room temperature to form a homogeneous solution. Then appropriate amount of cetyltrimethyl ammonium bromide (CTAB) was added into the solution and stirred continuously until the CTAB was dissolved completely. Titanium butoxide of 0.4 ml was added drop by drop. The solution was kept stirring 25 min at room temperature until it was turned into totally homogeneous, then transferred into a 25 ml Teflon-lined stainless-steel autoclave and maintained at 150 °C in an electric thermostatic drying oven for 6 h. After the hydrothermal procedure, the autoclave was cooled down to the room temperature naturally. After the above hydrothermal process, some white powder, TiO$_2$ nanorods, grew on the inside wall of the autoclave. The powder was carefully collected and washed thoroughly by centrifugation alternately with deionized water and ethanol for 3 times, of which each one lasts for 10 min. Then the solid powder was placed in an electric thermostatic oven to dry up at 80 °C for 12 h, and subsequently annealed at 600 °C in air for 2 h. Finally, the nanostructured TiO$_2$ nanorods were obtained.

The hydrothermal process was used again to prepare the TiO$_2$/MoS$_2$ nanocomposite. In the synthesis process, TiO$_2$ powder of 20 mg prepared by the above process was dispersed into 15 mL of deionized water under vigorous stirring to be a clear solution. After that, 60.5 mg sodium molybdate (Na$_2$MoO$_4$•2H$_2$O) and 4 mg oxalic acid(H$_2$C$_2$O$_4$) were added and stirred for over 10 min until all the reagent were dissolved. Then 91.125mg L- cysteine was added and then stirred for 20 min to prepare the second precursor solution.

The solution was transferred into a 25 ml Teflon-lined stainless-steel autoclave and kept at 200°C for 12 h. After this, the autoclave was cooled down to the room temperature, and black solution was obtained. It was centrifuged, washed with deionized water and ethanol for 3 times, and dried up at
60 °C in the vacuum drying oven. After keeping it at 500 °C for 1 h in the nitrogen ambient atmosphere, the TiO$_2$/MoS$_2$ nanocomposite was obtained in the end.

The prepared pure TiO$_2$ and TiO$_2$/MoS$_2$ composite were characterized by X-ray diffraction (XRD) using Cu Kα radiation at 40 kV and 40 mA at the scanning rate of 0.02° in degree, 0.1 s/step, field-emission scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

The gas sensor was fabricated by integrating sensing nanomaterial with micro interdigitated electrodes on the silicon substrate with drop-coating process. The TiO$_2$/MoS$_2$ nanocomposite of 10 mg was put into a sampling bottle, 10 ml of absolute ethyl alcohol was injected, and 20 mg of ethocel was added to improve the adhesive property. The bottle was vibrated for 10 min in an ultrasonic cleaner to mix the solution well. A syringe was used to pipet 5 μl solution, and then the solution was dropped on the surface of the interdigitated electrodes. The sample was dried up on the heating plate at the 90 °C to make the solution volatize, and a layer of sensing materials appeared on surface of the electrodes. After aging 12 h at 120 °C, the fabrication of the nanocomposite sensor was completed, as shown in Fig. 1, in which the two pads are used for connecting the wires. By taking appropriate TiO$_2$ nanorods and using the same process, the sensor based on the pure TiO$_2$ nanorod were prepared.

The sensor chip was attached to a small PCB board and put into an airtight chamber for testing. Response properties of the sensor to different concentration of H$_2$ were tested at 25 °C-150 °C. The total flow rate was 200 sccm, which was controlled by a gas delivered system and a calibrated mass flow controller, as shown in Fig. 2. The airtight chamber was full of air before measurement, and the gas concentration was changed in an interval of 5 min. A DC power supplier was used to drive the sensor at the fixed value of 5 V, and the change in the resistance of the sensor was recorded by a High Resistance Meter. The gas response of the sensor was defined as |Rg-Ra|/Ra, where Ra is the electrical resistance of the gas sensor in air and Rg the resistance in the presence of target gas.

![Image of the hydrogen sensor.](image1)

![The system for testing of the gas sensor.](image2)
3. Results And Discussion

Fig. 3 shows the XRD patterns of the pure TiO$_2$ nanorods and the TiO$_2$/MoS$_2$ composites, respectively. It indicates that both samples consist of high intensity fraction of the rutile phase. In terms of TiO$_2$/MoS$_2$ composites, the peak at 13.396° and 32.686° are indexed with (002) and (100) of MoS$_2$ (JCPDS No.2-1133). Besides this, the peak at 27.499°, 36.081° and 54.372° are corresponding with (110), (101) and (211) of TiO$_2$ (JCPDS No.4-551). No other diffraction peak of impurities may be observed, which indicates that the final products are the mixture of TiO$_2$ and MoS$_2$ with high purity.

As shown in Fig. 4a, the SEM image indicates that the prepared TiO$_2$ nanorods are good dispersity, and only a few short nanorods perhaps are the undeveloped nanorods. It can be seen that the nanorods are uniform and have smooth surfaces. The diameters of the TiO$_2$ nanorods are ranging from 80-100 nm and lengths are about 1.5 μm. Figs. 4b and c are the TEM and high-resolution TEM (HRTEM) images of the TiO$_2$ nanorods. As shown in Fig. 4b, the nanorods are straight and uniform, and some short nanorods also can be found, which are as the same as SEM image. Some unshaped nanorods can be found around the periphery of the nanorods, which is in accordance with the SEM image. Fig. 4c is a magnified TEM image of the area within the red rectangle in Fig. 4b. According to the image, the lattice distances are d$_{110}$ = 3.25 Å and d$_{101}$ = 2.49 Å, which are in accordance with the interplanar spacings of rutile (110) and (101), respectively. And the fast Fourier transform (FFT) image of the Fig. 4b also shows regular speckles, which indicated that the TiO$_2$ nanorods are pure rutile crystal. These imply that the TiO$_2$ nanorods grow along [001] direction.

After the second hydrothermal reaction, flowerlike MoS$_2$ nanosheets grows outward and attaches themselves onto TiO$_2$ nanorods to form the TiO$_2$/MoS$_2$ hierarchical nanocomposites. It can be found in Fig. 4d that the flowerlike MoS$_2$ microspheres appear after the second hydrothermal process. Moreover, it shows that the MoS$_2$ nanosheets wrap on the end of the TiO$_2$ nanorods. The same phenomenon can be found in the low-resolution TEM image (Fig. 4e). Besides, the end surfaces of TiO$_2$ nanorods appear much coarser, which may be a useful for MoS$_2$ nanosheet to form core and grow up. Fig. 4f is the high-resolution TEM image of selected region in Fig. 4e. The lattice fringes spacing of TiO$_2$ and MoS$_2$ are 2.5 Å and 6.6 Å, respectively, which are consist with the interplanar spacing of (101) planes of rutile TiO$_2$ and (002) planes of MoS$_2$.

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Fig. 3 XRD patterns of the pure TiO$_2$ and TiO$_2$/MoS$_2$ composites
The optimal working temperature of gas sensors was investigated by studying their sensing response to hydrogen at 200 ppm as the temperature varying from 25 to 150 °C. The results indicate that the response of the sensor based on TiO$_2$/MoS$_2$ nanocomposites reaches its maximum of 19.48% at 100 °C, as shown in Fig. 5a. However, the sensor based on the pure TiO$_2$ nanorods has the highest sensing response at 50 °C, which is only 0.56%. It can be observed that the response of the sensor based on the TiO$_2$/MoS$_2$ nanocomposites to 200 ppm hydrogen is 40 times higher than the sensor based on the pure TiO$_2$ nanorods. This indicates that the gas sensing response to hydrogen can be enhanced remarkably by the TiO$_2$/MoS$_2$ nanocomposites. Since it has a good sensing response at room temperature, the response and recovery properties of the sensors at 25°C will be investigated further in the following.

The sensor can work at room temperature, as the responses at ambient 25 °C, as shown in Fig. 5b, indicating that the sensor. Due to heterogeneous structure of the nanocomposites, it is impossible to keep porosity and uniform adsorption on the throughout surface sensing material. To simplify the question, assuming that the concentration of the surface species is uniform and then the sensing response of the sensors can be explained by the Freundlich isotherm processes [33]. As shown in Fig. 5c, higher the gas concentration, longer the response and recovery time at 25°C to different concentrations. The response and recovery time are the important factors of gas sensitivity. These phenomena can be attributed to the adsorption/desorption, and diffusion process. For higher concentration of H$_2$, gas molecules require longer time to diffuse into the nanostructures and adsorb/desorb on the surfaces.

The responses of the sensors based on the TiO$_2$/MoS$_2$ nanocomposites and pure TiO$_2$ nanosheets to various gases such as H$_2$, NH$_3$, and CH$_4$ are shown in Fig. 5d. It can be seen that the sensors based on the TiO$_2$/MoS$_2$ nanocomposites have enhanced responses to all gases compared with the sensor based on the pure TiO$_2$ nanorods. And the nanocomposites sensor has the strongest response to H$_2$ among the three testing GaSe, which indicate that the nanocomposites based sensor has good selectivity to H$_2$. 

Fig. 4 SEM images and TEM images of the TiO$_2$ and TiO$_2$/MoS$_2$
Fig. 5 Response properties of the sensors.

The sensing mechanism is resistance change of a semiconductor sensor due to the adsorption and desorption processes of oxygen molecules on the surface of semiconductor materials. When the n-type TiO$_2$ materials are exposed to atmosphere, oxygen molecules will be adsorbed onto the surfaces of the sensing materials and be ionized into species such as $\text{O}^2-$, $\text{O}^-$, and $\text{O}_2^-$ by transferring electrons from conduction band to valence band of the n-type semiconductor. When the materials are exposed to H$_2$, H$_2$ reaction with oxygen ion on the surface produces resultants of H$_2$O and electron. Consequently, the resistance of the sensor decreases with the increasing concentration of H$_2$.

The enhanced gas sensing properties of TiO$_2$/MoS$_2$ composites are likely to be a result of several factors. First, TiO$_2$/MoS$_2$ nanocomposites have structural characteristics of high surface area and good permeability. The surface area of TiO$_2$/MoS$_2$ composites is larger than that of pure TiO$_2$ nanorods. This will provide more adsorptive sites so that more oxygen molecules can be absorbed and ionized. Meanwhile, the nanostructures lead to effective and rapid gas diffusion toward surface regions, resulting in the strong and quick response.

Second, p-n junction between TiO$_2$ nanorod and MoS$_2$ nanosheet is the primary factor to improve sensing response of nanocomposites. Fig. 6 shows energy bending of the nanocomposites without gas molecules adsorption. TiO$_2$ is a n-type semiconductor with band gap of 2.9eV, and MoS$_2$ is a p-type semiconductor with band gap 1.9eV. The P-N junction is formed at the interface due to different work functions of two materials, which the electron may transfer from TiO$_2$ to MoS$_2$, and hole moves on the contrary direction[34]. Dynamic equilibrium of vacancy and electron appearing and merging around the p-n junction forms a depleted layer. Since the Fermi-level energy is at the same energy level for the two kinds of metal oxide semiconductor (MOS) materials, energy bending occurs at the depleted layer, and leads to greater change of resistance. When a depletion layer is formed, the barrier will increase and the initial resistance will increase, so the resistance will decrease significantly when it reacts with reducing gases such as H$_2$. Eventually an enhanced response will be observed.
4. Conclusion

TiO$_2$/MoS$_2$ composites consisted of TiO$_2$ nanorods and flowerlike MoS$_2$ nanosheets were successfully synthesized by hydrothermal method. Based on the nanocomposites, the gas sensor was developed successfully, and it had better sensing properties to hydrogen compared with the sensor based on pure TiO$_2$ nanorods and MoS$_2$ nanosheets. Improvement of the gas sensor properties could be primarily attributed to depleted layer, large specific area and heterojunction of nanocomposites.

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