



UV-enhanced room temperature NO₂ sensor using ZnO nanorods modified with SnO₂ nanoparticles

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ABSTRACT

ZnO/SnO₂ composite materials are synthesized by hydrolyzing SnCl₂ on ZnO nanorods via the wet chemical method. The gas sensing studies revealed that ZnO/SnO₂ exhibits a high response to NO₂ at room temperature under UV light emitting diode illumination. The highest response to NO₂ was achieved by the ZnO/SnO₂ composite with Zn and Sn molar ratio of 1:1 (ZS3). The resistance of sensor based on ZS3 with UV light stimulation changed 1266-fold to 500 ppb NO₂ gas at room temperature. Furthermore, the selectivity, as well as response and recovery properties, of the sensor was improved remarkably by UV light irradiation. The ZnO/SnO₂ heterojunction model and the increased photo-generated electrons are proposed to elucidate the gas sensing mechanism.

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1. Introduction

Nitrogen dioxide (NO₂) is a main atmospheric pollutant that causes acid rain and photochemical smog. High performance NO₂ sensor is urgently needed for detecting or monitoring ppb-level NO₂ in the atmosphere [1]. Until recently, various NO₂ sensors have been developed such as piezoelectric quartz [2], electrochemical [3,4], and semiconductor sensors. Semiconductor gas sensors are becoming more attractive in NO₂ detection in recent years because of the simple structure, low cost, and long-term stability of these sensors. The sensors based on WO₃, NiO, In₂O₃ [5–7] and some composite materials exhibit good performance in NO₂ detection. However, these traditional semiconductor gas sensors are usually operated at a high temperature. This condition should be addressed because of the power consumption and undesirable long-term drift problems caused by the sintering effects in the metal oxide grain boundaries at a high temperature.

Some researchers have reported feasible approaches, such as doping with noble metals [8], application of electrostatic field [9], and UV light stimulation [10–13], to reduce the operating temperature. UV light stimulations have drawn increasing attention for activating the chemical reactions at a low operating temperature. Saura [10] described the gas sensing properties of tin dioxide films with and without UV irradiation. He illustrated that

the selectivity of the sensor can be modified by UV irradiation. Comini [11,12] reported UV-activated room temperature NO₂ sensors based on SnO₂ and In₂O₃ thin film sensors and demonstrated that UV light source-assisted sensors can be used to detect NO₂ in ppm-level at room temperature. Prades [13] postulated a qualitative model to explain the response of sensors towards oxidizing gaseous species as well as demonstrated the equivalency between thermal and UV light emitting diode (LED)-modulated responses. Given that single semiconductor oxides usually exhibit poor selectivity and reliability, the composite nanostructures ZnO/TiO₂ [14], In₂O₃/SnO₂ [15], and ZnO–SnO₂ have been introduced to enhance gas sensing properties at a high operating temperature. ZnO-doped SnO₂ nanoparticles exhibit a remarkably higher sensitivity to NO₂ than pure SnO₂ nanoparticles [16]. In addition, the hetero-nanostructures have the potential to enhance the sensing performance, such as gas response and selectivity [17–21]. Lee [22] synthesized ZnO–SnO₂ core-shell nanowires and found that the sensitivity and selective detection of NO₂ and C₂H₅OH are achieved at 200 and 400 °C, respectively, and respective gas responses are 33- and 6.8-fold higher than those of the ZnO nanowires, respectively. To the best of the authors' knowledge, composite material-based sensors used to detect NO₂ in the ppb level at room temperature have not been reported.

In the current paper, the composite materials of ZnO nanorods mixed with SnO₂ nanoparticles were synthesized under mild condition. The gas sensors based on as-prepared ZnO/SnO₂ exhibited a high response to NO₂ at room temperature with UV-LED stimulation.

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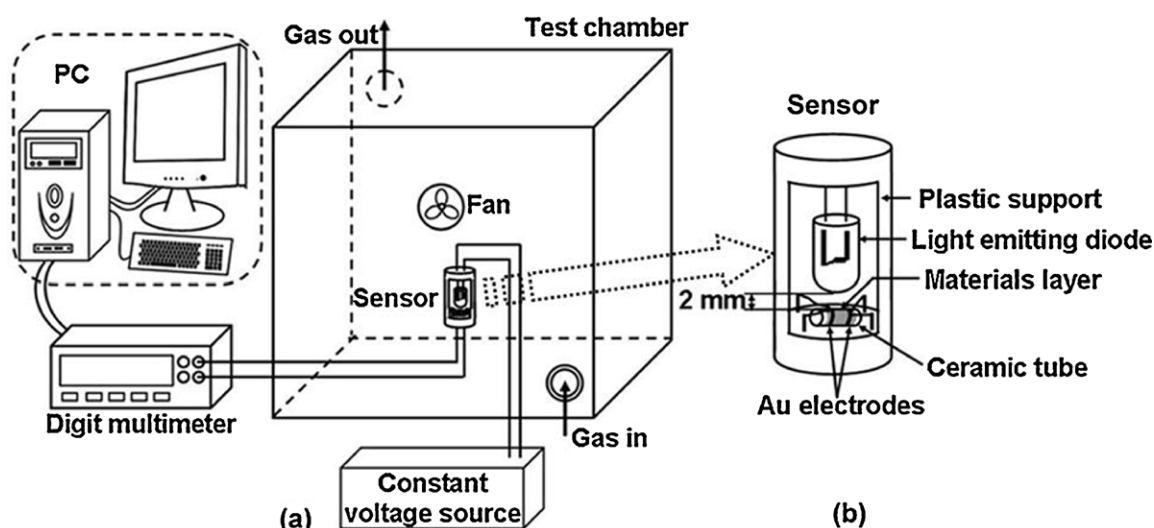


Fig. 1. (a) Measurement system for testing gas sensors. (b) Amplified schematic diagram of sensor configuration.

2. Experimental methods

2.1. Synthesis and characterization of materials

All the chemicals used were of analytical grade and purchased from Sinopharm Chemical Reagents Co., China.

The reaction solution was prepared using 0.1 M zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ as the inorganic precursor and 0.1 M hexamethylenetetramine (HMT) as the organic template as well as counter ion source. The synthesis of ZnO nanorods was described in detail as follows. The $\text{Zn}(\text{NO}_3)_2$ solution was placed in an oil bath at a constant temperature of 90°C for 10 min. Then, the HMT solution was dropped into the solution at a speed of 2 drops/s, and stirred for 1 h. The mixture solution was kept at 90°C for 16 h. The resulting products were centrifuged and washed alternately by deionized water. The products were dried at 80°C , and ZnO nanorods were obtained.

ZnO/SnO₂ composite materials were obtained by hydrolyzing Tin (II) chloride on ZnO nanorods. First, ZnO nanorod powders (0.324 g) were added into 20 ml polyvinyl pyrrolidone (PVP) aqueous solution (0.8 g/ml) and stirred for 12 h. Second, the as-obtained ZnO suspension solution was mixed with 1 mol/l SnCl₂ ethanol solution and the diluted dimethylformamide by equal volume proportion (Table 1) and stirred at room temperature for 24 h. The products were washed well, dried at 80°C , and sintered at 600°C for 2 h.

The morphology of the materials was characterized by scanning electron microscopy (SEM; SSX-550, Shimadzu, Japan) and transmission electron microscopy (TEM; Hitachi S-570, Japan). The structure of the products was confirmed by X-ray diffraction (XRD; Rigaku D/max-2500V, Japan; diffractometer with Cu K α radiation, $\lambda = 0.15406$ nm). The photo-generated charge transfer in the ZnO/SnO₂ was identified by photoluminescence (PL) emission

Table 1
Denomination and detail ingredient of the ZnO/SnO₂ composite materials.

	ZnO/PVP (ml)	1 mol/l Sn a.s. (ml)	DMF/ethanol (ml)	Zn/Sn molar ratio
ZS1	5	0.1	9.9	10:1
ZS2	5	0.5	9.5	2:1
ZS3	5	1	9	1:1
ZS4	5	5	5	1:5

spectra. The Brunauer–Emmett–Teller (BET) surface area of the nanomaterials was analyzed on a Micromeritics Gemini VII apparatus (Surface Area and Porosity System; USA).

2.2. Fabrication and measurement of gas sensor

As-prepared ZnO nanorods, four kinds of ZnO–SnO₂ composite materials, and SnO₂ nanoparticles prepared by the traditional precipitation method [23] were named as ZS0, ZS1, ZS2, ZS3, ZS4, and ZS100, respectively, according to the different molar ratios of ZnO to SnO₂ (Table 1). The gas sensors were fabricated by coating the sensing materials on the surface of the ceramic tube attached with Au belt-shaped electrodes [24]. The thickness of materials layer is approximately $150\ \mu\text{m}$. UV-LED (peak wavelength = 380 nm; operating voltage = 3 V) was chosen as the light source, and the distance between the UV-LED and gas sensors was 2 mm. The measured power of the UV-LED at this distance was $0.7\ \text{Cd}/\text{m}^2$ (PR650, California, USA). The sensors were first irradiated with UV-LED for 30 min to stabilize the electrical properties of the sensor [25].

The sensors were operated in a static test system as diagrammed in Fig. 1. The temperature ($20^\circ\text{C} \pm 1^\circ\text{C}$) and humidity ($\sim 30\% \pm 5\%$ RH) within the testing room were well controlled during the measurement. Each sensor was connected in series to a digit precision multimeter (Fluke, 8846A) for data acquisition. The multimeter is concatenated to a personal computer for data processing. The sensor test was performed by measuring the resistance of the sensor upon controlled concentration of various gases in the dark and under UV light. A known volume of standard NO₂ gas (1000 ppm) was injected into the test chamber to obtain the desired NO₂ gas concentrations. A fan was used to uniformly distribute the gas inside the chamber. The response of the sensor was defined as $(R_g - R_a)/R_a$, here, R_a and R_g were the resistances of the sensor in the air and target gas, respectively.

2.3. Effect of water vapor on the NO₂ sensor

The responses of sensor to NO₂ were measured at various relative humidity in static test system. The correlation between the current and time was measured by using DC reversed circuit (Electrochemical Analyzer, CH611C49011, CH Instruments, Shanghai, China) according to references [26,27].

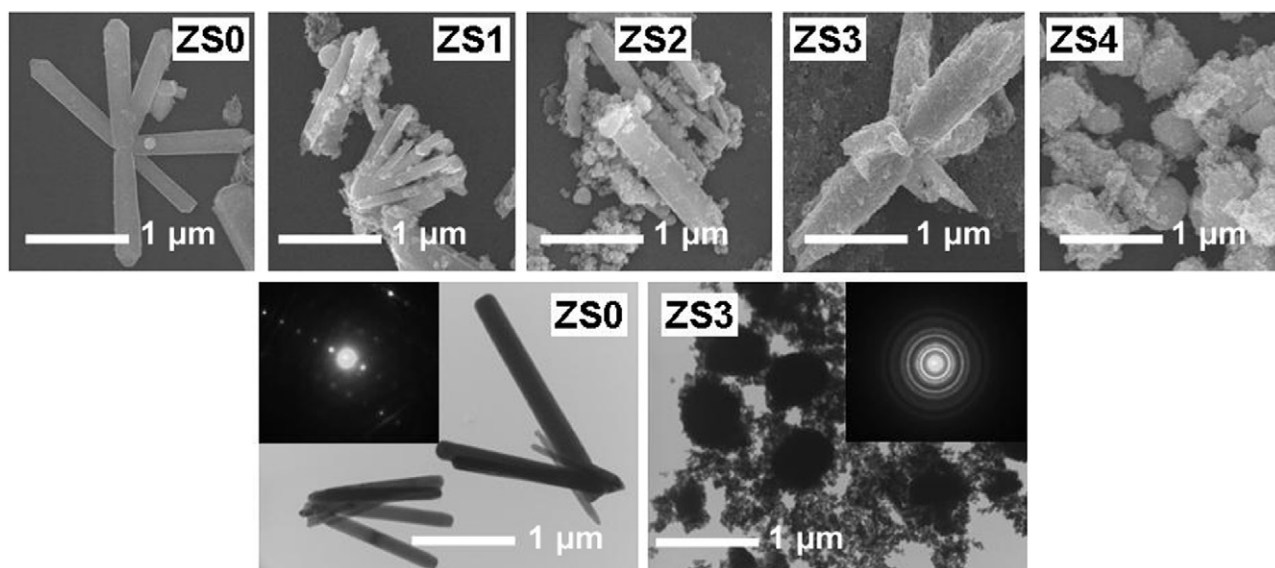


Fig. 2. SEM images (top) and TEM images (bottom) of the ZS0, ZS1, ZS2, ZS3 and ZS4. The inset of TEM is the corresponding electron diffraction patterns.

3. Results and discussion

3.1. Characteristic of the materials

The SEM and TEM images of the as-prepared ZnO and ZnO–SnO₂ composite materials are shown in Fig. 2. Uniform nanorods (average size: length = 1.5 μm and diameter = 0.5 μm) were clearly observed. The inset in Fig. 2, a TEM image of ZS0, displays dot-like pattern, indicating that the ZnO is a monocrystal nanorod. The surfaces of the ZnO nanorods were partly covered with SnO₂ nanoparticles in the composites. Moreover, the diameter of the nanorods increased with an increasing amount of SnCl₂. However, when the molar ratio of Sn to Zn was increased to 5:1, the ZnO nanorods disappeared. During this process, the pH of the isoelectric point at 25 °C for ZnO in water is in the range of 8.7–10.3 [28]. Thus, excessive acid coming from the SnCl₂ hydrolysis could have eroded ZnO.

The XRD patterns of ZnO nanorods and the ZnO–SnO₂ composite materials are illustrated in Fig. 3. The diffraction peaks indicate that the materials are well crystallized, and there were only two components, ZnO and SnO₂, in the mixture. There was no other characteristic peak corresponding to other compounds, such as ZnSnO₃ and Zn₂SnO₄. The average crystal sizes of ZnO and SnO₂ were calculated by Scherrer equation.

The average crystal sizes calculated from the XRD data and the BET surface area of ZnO–SnO₂ composite materials are shown in Table 2. The crystal size of ZnO gradually decreased with increasing molar ratio, similar to that of SnO₂. Pure ZnO had a lower surface area, which increased when this compound was covered by the SnO₂ nanoparticles with larger surface areas. Among these samples,

Table 2
Average particle size and BET surface area of ZnO/SnO₂ composite materials.

	Average crystal size (nm)		BET surface area (m ² /g)
	ZnO	SnO ₂	
ZS0	40	6	4
ZS1	35	10	27
ZS2	32	10	34
ZS3	17	11	50
ZS4		14	32

ZS3 provides the largest surface area. ZS4 shows a lower surface area than ZS3 because of the larger particles of the latter.

3.2. Gas sensing properties of the NO₂ gas sensor

The gas sensing properties of the sensors based on the ZnO/SnO₂ composite materials with and without UV light illumination were tested at room temperature. These sensors showed consistent performance during at least 10 testing periods. The molar ratio of ZnO to SnO₂ was a crucial factor that affected the response to NO₂. When the molar ratio of ZnO to SnO₂ was varied from 10:1 to 2:1, 1:1, and 1:10, the response of the sensor to 500 ppb NO₂ changed two orders of magnitude and was remarkably higher than those of pure ZnO (ZS0) and SnO₂ (ZS100) (Fig. 4). The maximum response can be achieved by the sensor at a molar ratio of ZnO to SnO₂ equal to 1:1 (ZS3). The results show that the NO₂ response both in the dark and under UV light initially increases and then decreases as the SnO₂ content is increased. The sensors based on ZnO/SnO₂ had an appreciable response at room temperature. This condition was attributed to the heterostructure that was advantageous to chemical interactions, adsorption of gases, and changes in electronic band energies in the composite [16].

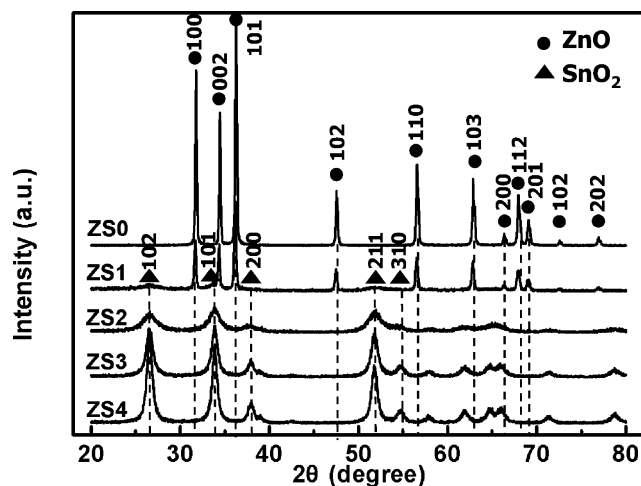


Fig. 3. X-ray diffraction patterns of ZS0, ZS1, ZS2, ZS3 and ZS4.

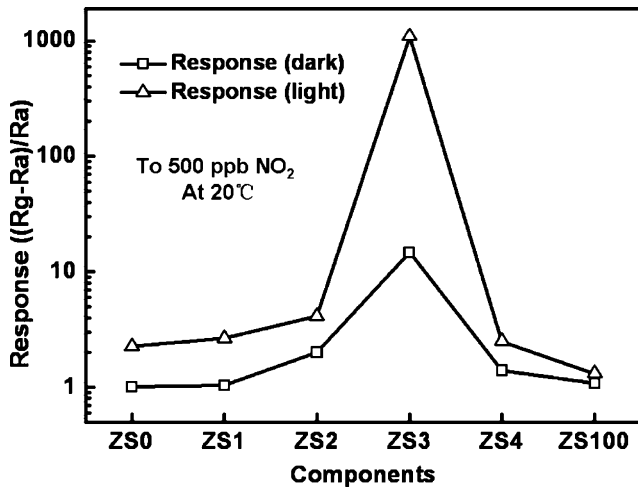


Fig. 4. Responses of the sensor based on the composite materials with the various molar ratio of ZnO to SnO₂ to 500 ppb NO₂ at room temperature with and without UV light irradiation.

In the composites of ZnO/SnO₂, ZnO nanorods acted as active light absorption centers. SnO₂ nanoparticles on the surface increased surface area and chemisorption ability to NO₂. The responses of all sensors to NO₂ were obviously enhanced under UV light illumination. In particular, the response of the sensor using ZS3 to 500 ppb NO₂ increased from 13.4 without UV light illumination to 1266 under UV light illumination.

The dependence of the response on the NO₂ concentration for the sensor based on ZS3 with and without UV light illumination at room temperature is shown in Fig. 5. The response to NO₂ increased with increasing gas concentration. ZS3 showed a high response to NO₂ at room temperature, which may facilitate the application of semiconductor NO₂ sensors operated at room temperature.

The selectivity of the sensor was investigated, and results are shown in Fig. 6. The sensor based on ZS3 exhibited a remarkably higher response to NO₂ than the other gases with UV light stimulation. These results prove that the sensor based on ZS3 has a high response and selectivity to NO₂ gas at room temperature under UV light illumination and may be applied to detect or monitor the NO₂ gas in the atmosphere. The normalized resistance change with time under different NO₂ gas concentrations is shown in Fig. 7, demonstrating that UV light illumination accelerates the response and

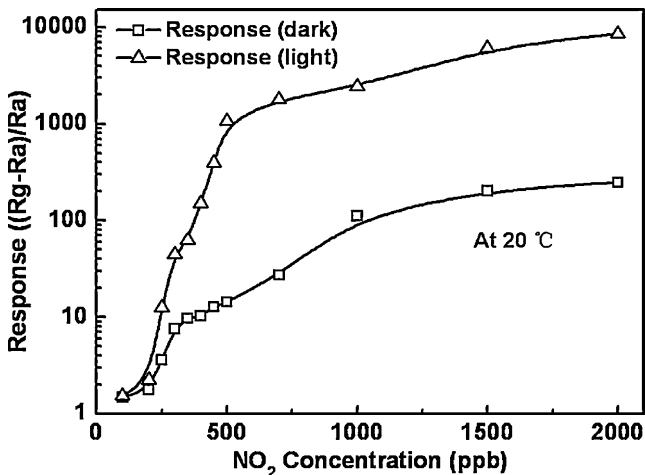


Fig. 5. Response of the ZS3 sensor vs. NO₂ concentration at room temperature with and without UV light irradiation.

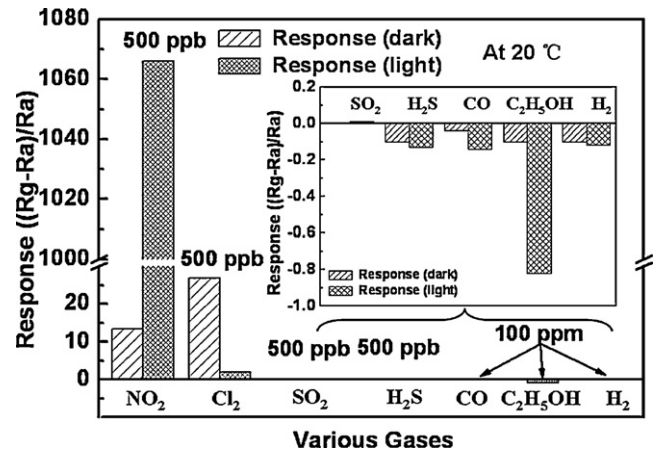


Fig. 6. Cross-response of the sensor based on ZS3 to various gases at room temperature (20 °C) with and without UV light irradiation.

recovery speeds of the sensor. For example, the response time of the ZS3 sensor to 200 ppb NO₂ was reduced from 12 min (without UV) to 7 min (with UV), and the recovery time was shortened from 14 min (without UV) to 8 min (with UV) (inset of Fig. 7).

3.3. Effect of water vapor on the response

The effect of humidity on the response of the sensor based on ZS3 to 500 ppb NO₂ at room temperature is illustrated in Fig. 8(a). The responses almost have a linear relationship with relative humidity, and moisture evidently has a negative influence on the response to NO₂. The active site on the material surface was covered gradually by water vapor [29], leading to a decrease in the response to NO₂ in dark. Under UV light illumination, the physisorbed water on the surface was decomposed by the photo-generated charges as reaction (1) [30], so the response to NO₂ is higher than that in dark at the same relative humidity.



Fig. 8(b) gives the effect of humidity on the sensor resistance in air (R_a). It can be seen that R_a decreases in dark and increases under UV light with the increasing of the relative humidity.

In order to deduce which kind of the carriers (ion or electron) in the sensing materials is domain in different humidity conditions,

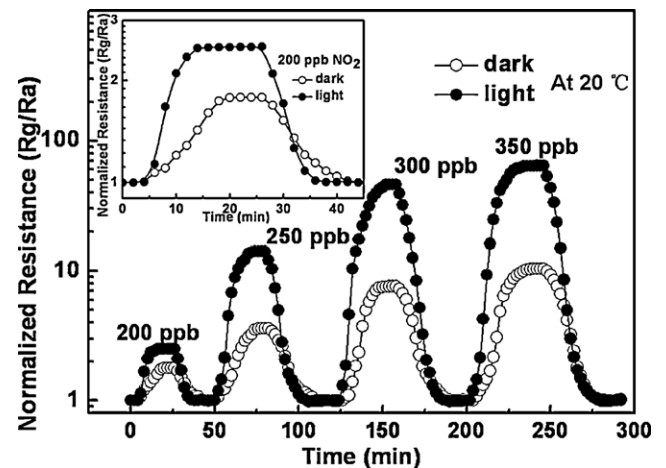


Fig. 7. Transient response and recovery characteristic of ZS3 sensor under continuous operation mode at various concentrations from 200 to 350 ppb of NO₂ diluted in air at room temperature (20 °C) under UV light irradiation. The inset is the response and recovery of ZS3 sensor to 200 ppb of NO₂ with and without UV light.

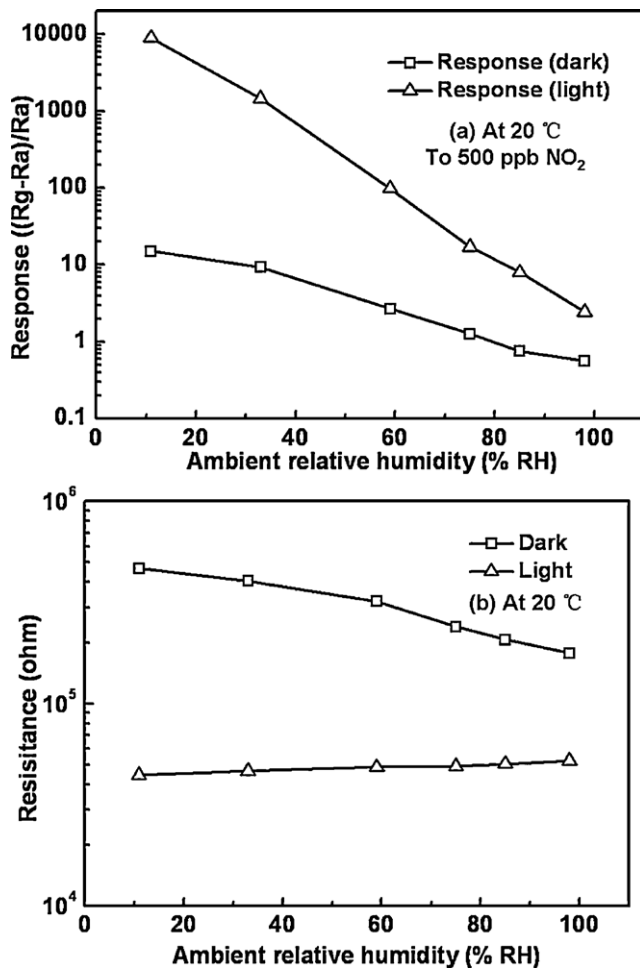


Fig. 8. (a) Response of the sensor based on ZS3 to 500 ppb of NO_2 shift with various relative humidity at room temperature (20°C) in dark and under UV light. (b) Relative humidity vs. resistance plots at 20°C for the sensor based on ZS3.

the correlation between current and time was investigated by using the DC reversed circuit, according to references [26,27]. When a DC voltage is applied to the semiconducting oxide in wet atmosphere, the ions, such as H^+ , OH^- and NO_3^- , will be driven to the two electrodes and form fixed charges. When the DC voltage is reversed, these fixed charges will be released and result in the decreasing of the current with time. The result of measurement is shown in Fig. 9. In the case of dark, the current is almost independent on time in dry air, but in wet air, the currents significantly change with time. Such behavior can be attributed to the polarization of the physisorbed water on the surface of the sensing material and ion accumulations in the electrodes. In other word, the sensing material and the two electrodes formed a capacitance which was charged and discharged when a plus and minus DC voltages were applied. The changing current can be ionic current. On the other hand, the residual current can be electronic current. It can be concluded that the mixing conductivity for the sensor using SnO_2 - ZnO composited oxide exists without illumination in wet air.

It is noteworthy that the current is stable under UV light in wet air. As we know, When ZnO was illuminated by UV light, the electron and hole were generated in the sensing materials. These photo-generated carriers will enhance the decomposition of the physisorbed water on the surface as reaction (1) and greatly reduces the physisorption of water vapor. The increasing of the resistance for the sensor has been examined with the increase of the relative humidity under UV light [Fig. 8(b)]. Therefore, the reversed current

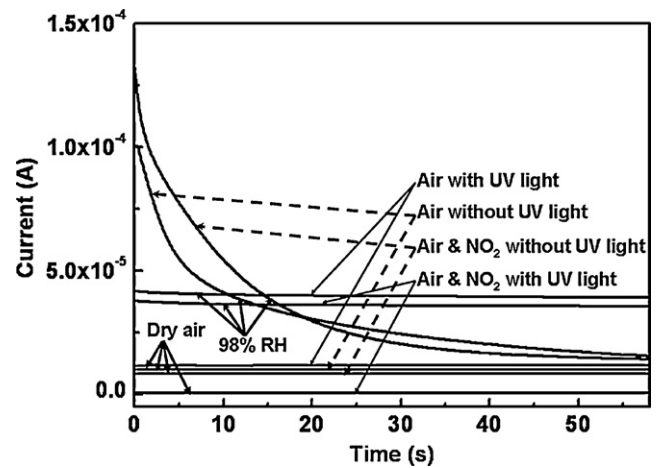


Fig. 9. Correlation between the current and time measured by using DC reversed circuit under different conditions.

is almost unchangeable under UV illumination in wet air and can be considered to be electronic current.

Although a part of the photo-generated electron and hole have been used for decomposing the adsorbed water, the residual part of them can activate the NO_2 molecule and partly enhance the response to NO_2 even in high humidity atmosphere under UV illumination. However, the response to NO_2 decreases with the increasing of the relative humidity under UV light. From the above descriptions, it can be concluded that in the case of dark, ionic conductivity of water and HNO_3 greatly affected the sensing properties of the obtained sensor at room temperature, but in the case of UV light, the ionic conductivity of the water and HNO_3 is negligible.

3.4. Mechanisms of gas sensing under UV light

A proposed mechanism for the enhanced NO_2 response of the ZnO/SnO_2 composite under UV light illumination is shown schematically in Fig. 10(a). When the sensor based ZnO/SnO_2 composite is exposed to NO_2 , the electrons on the surface of SnO_2 will be captured by the NO_2 gas, resulting in the increasing resistance of SnO_2 . This phenomenon indicates that an abundance of electrons on the surface of SnO_2 will be beneficial to the chemisorptions of NO_2 [31,32]. After the semiconductor absorbs the UV light, photogenerated carriers will be produced. When the photogenerated electrons

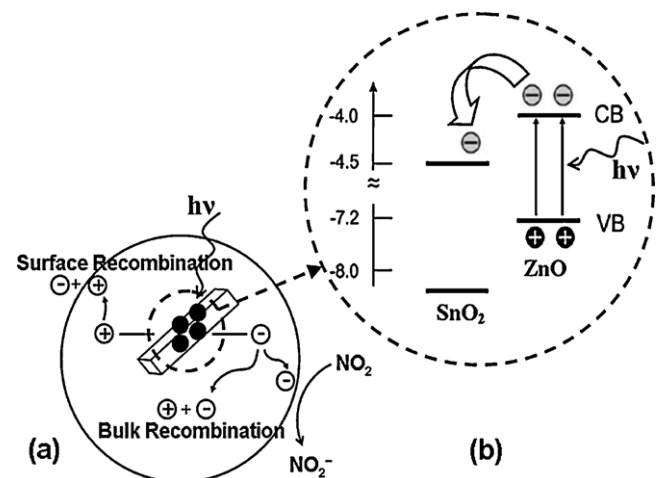


Fig. 10. Schematic diagram: (a) the carriers transport with UV light stimulated, (b) energy band structure and electron-hole pair separation in the ZnO/SnO_2 heterostructure in the area marked with a dashed circle.

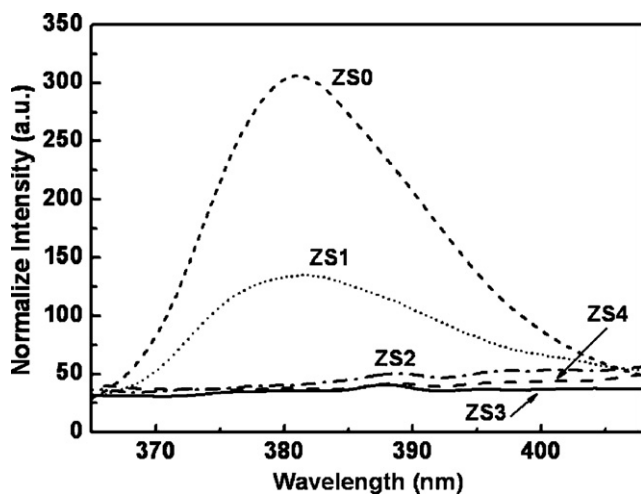
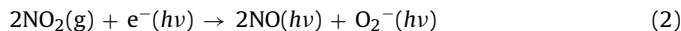


Fig. 11. PL emission spectra of ZS0, ZS1, ZS2, ZS3 and ZS4.

and holes move to the surface of semiconductor, some of these particles will recombine at bulk and/or on the surface. The remaining part of photogenerated electrons and holes will participate in the reaction with testing gas.

Generally speaking, because the sensors are operated in ambient air, oxygen molecules will trap the electron on the surface of the semiconductor materials and turn to oxygen ions O_2^- [31,33]. When the O_2 chemisorption becomes balanced, many photogenerated electrons remain on the surface of the semiconductor material under UV light illumination. During the exposure of the sensor to NO_2 gas, the remaining photogenerated electrons will be trapped by NO_2 , and the reaction occurs as Eq. (2) [25]. Thus, the resistance of the sensor increases with an increase in NO_2 concentration.



The photoinduced $NO(h\nu)$ and $O_2^-(h\nu)$ are weakly bound to the materials and can be easily removed. Thus, the UV light used in the present study has sufficiently large energy to cause the adsorption and desorption of NO_2 , resulting in the improved response and recovery rate.

A type of heterojunction that formed in the ZnO/SnO₂ interface is depicted in Fig. 10(b). Considering that ZnO has a smaller band gap (approximately 3.2 eV) than SnO₂ (approximately 3.8 eV) [34], ZnO will absorb fully the UV light emitted from the light source and play a role as photo catalyst. The Fermi energy level of ZnO is higher than that of SnO₂ because of its smaller work function, so that electrons will transfer from the conduction band of ZnO to that of SnO₂. Conversely, the hole will transfer from the valence band of SnO₂ to that of ZnO [35]. The efficient charge separation increases the lifetime of the charge carriers, enhances the efficiency of the interfacial charge transfer to SnO₂, and accounts for the higher NO_2 response of the composite ZnO/SnO₂. The enhanced separation of electrons and holes in the ZnO/SnO₂ heterostructures was confirmed by PL emission spectra of the ZnO/SnO₂ composite materials shown in Fig. 11. The ZnO/SnO₂ composite materials exhibited remarkably lower emission intensity than ZS0, indicating that the recombination of photogenerated charge carriers is inhibited greatly in the ZnO/SnO₂ heterostructures. ZS3 has the highest efficiency of the interfacial charge transfer. Therefore, the ZnO/SnO₂ heterostructures reduced bulk recombination and increased the conductivity of materials. Photogenerated electrons migrated to the surface of SnO₂ and enhanced the chemisorptions of NO_2 , contributing to a higher response to NO_2 under UV light.

Generally, NO_2 response increased with an increase in SnO₂ content in the nanocomposites for the heterojunctions,

favoring electrons to flow from ZnO nanorods to SnO₂ nanoparticles. However, excessive SnO₂ nanoparticles coverage on ZnO surface decreases the photo active sites of the ZnO surface, reducing the charge carrier density of the composite materials. Moreover, the BET surface area of ZS4 is lower than that of ZS3 (Table 2), consistent with well-known reports that the surface area of the sensing materials is an important factor that affects the gas properties. Therefore, the NO_2 response of ZnO/SnO₂ composites will decrease when the SnO₂ content is loaded up to a certain level.

4. Conclusions

The ZnO/SnO₂ heterostructure gas sensing materials have been prepared via moderate synthesis. SEM and TEM reveal a uniform distribution of SnO₂ nanoparticles on the surface of ZnO nanorods and an intimate contact between these nanomaterials. The experiments on the gas sensing properties show that the ZS3 sensor exhibits a higher response to NO_2 gas at room temperature under UV light irradiation. The resistance of sensor based on ZS3 with UV light stimulation changed 1266-fold to 500 ppb NO_2 gas at room temperature. The ZnO/SnO₂ heterojunction model and the increased photo-generated electrons are beneficial for testing NO_2 gas.

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