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Low-temperature NO_2 sensors based on polythiophene/WO_3 organic-inorganic hybrids

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Abstract: Polythiophene (PTP) was prepared by a chemical oxidative polymerization and nanosized WO_3 was prepared by a colloidal chemical method. The organic–inorganic PTP/WO_3 hybrids with different mass fractions of PTP were obtained by a simple mechanically mixing the prepared PTP and WO_3. The as-prepared PTP/WO_3 hybrids have a higher thermal stability than the pure PTP. The gas sensing measurements demonstrate that the PTP/WO_3 hybrid sensors exhibit higher response for detecting NO_2 at low temperature than the pure PTP and WO_3 sensor. The sensing mechanism is suggested to be related to the existence of p–n heterojunctions in the PTP/WO_3 hybrids. The response of the PTP/WO_3 hybrids is markedly influenced by the PTP mass fraction. The 20% PTP/WO_3 hybrid shows high response and good selectivity to NO_2 at low temperature (<90 °C). Therefore, the PTP/WO_3 hybrids can be expected to be potentially used as gas sensor material for detecting NO_2 at low temperature.
Key words: NO_2 sensor; polythiophene/WO_3; low temperature

1 Introduction

As one of the potential conducting polymers, PTP and its derivatives have attracted considerable attention for their easy polymerization and good environmental and thermal stability [1, 2]. However, there are also some disadvantages such as low chemical stability and mechanical strength that are unfavorable for conducting polymer-related applications.

WO_3, an n-type semiconductor metal oxide, has received considerable attention for use as chemical sensor because of its unique sensing properties for a series of target gases, including H_2S [3, 4], NO_2 [5, 6], H_2 [7], O_3 [8], NH_3 [9] and volatile organic compounds (VOCs) [10]. NO_2 is toxic itself, badly harmful to human life and health, and, furthermore, is a main source of acid rain and photochemical smog [11]. WO_3 has been considered a promising sensing material of solid-state semiconductor gas sensors for NO_2 monitoring because of its excellent sensitivity [12]. However, similar to other semiconductor metal oxides, the high operating temperature and bad selectivity of WO_3 for detecting NO_2 restrict its actual application.

Inorganic–organic metal oxide/conducting polymer hybrid materials are currently of great interest for exploring enhanced sensor characteristics, due to their synergetic or complementary behaviors that are not available from their single counterparts [13]. Some effort has been paid to investigating this kind of hybrids for gas sensor applications. GUERNION et al [14] reported that the 3-alkylpolypyrrole-tin oxide composites exhibited much higher sensitivity and better selectivity to volatile organic compounds than the pure inorganic and organic materials. DESHPANDE et al [15] have synthesized the tin oxide-intercalated polyaniline nanocomposite, which had better sensitivity than the SnO_2 and polyaniline with respect to ammonia gas exposure. HOSONO et al [16] prepared intercalated polypyrrole/MoO_3 hybrids, which showed good sensing properties to VOCs.

In the present work, we prepared an organic−inorganic hybrid material containing PTP as the organic part and WO_3 nanocrystalline powders as the inorganic part by a simple mechanically mixing the prepared PTP and WO_3. The gas sensors based on the hybrids were fabricated and examined for gas sensing application for

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detecting NO_2. Obtained results showed that the hybrid materials exhibited high response and good selectivity for detecting NO_2 at low temperature.

2 Experimental

2.1 Preparation of PTP

PTP polymer was prepared via an in situ chemical oxidative polymerization. A specific amount of anhydrous $FeCl_3$ (A.R., Tianjin Guangfu Fine Chemical Research Institute) was added into 50 mL ethyl glycol methyl ether (A.R., Tianjin Guangfu Fine Chemical Research Institute) under vigorous stirring. Then a certain volume of thiophene (TP) monomers (A.R., Tianjin Guangfu Fine Chemical Research Institute), with a mole ratio of TP to $FeCl_3$ (1:3), was injected into the above stirred solution. After the reaction was carried out at room temperature for 3 h, the mixture was filtered. The obtained black precipitate was dipped in methanol for 24 h. The product was filtered and washed with methanol several times. The final product was dried at room temperature under vacuum for 24 h.

2.2 Preparation of WO_3

WO_3 was synthesized by a colloidal chemical method. $Na_2WO_4 \cdot 2H_2O$ (A.R., Tianjin Guangfu Fine Chemical Research Institute) was dissolved into a certain amount of deionized water. Then a certain concentration of aqueous solution of HCl was drop-wise added to the sodium tungstate solution under stirring at room temperature till no white precipitate was further formed. The pH of the solution was adjusted with an aqueous solution of HCl in the reaction process. Then the solution was aged for 24 h, after which 15 mL of 0.15 mol/L cetyltrimethyl ammoniumbromide (CTAB) (A.R., Tianjin Guangfu Fine Chemical Research Institute) solution was immediately added. The abundant white flocculent precipitate formed was treated by ultrasonication for 40 min. Then the precipitate was filtrated and centrifuged with deionized water to remove Cl^-, Br^- and any other possible remnants, dried at 80 ºC and calcined at 600 ºC for 2 h. Light yellow WO_3 powders were obtained.

2.3 Preparation of PTP/WO_3 hybrids

A series of PTP/WO_3 hybrids were prepared by mechanically mixing the above obtained PTP and WO_3 with the PTP mass fraction of 5%, 10%, 20% and 30%, respectively, denoted as PW-5, PW-10, PW-20 and PW-30.

2.4 Characterization

X-ray diffraction (XRD) analyses were performed on Rigaku D/max−2500 diffractometer operating at 40 kV and 100 mA, using Cu K_α radiation (scanning range 2θ: 10°−80°). Fourier transfer infrared (FTIR) spectra were recorded using Avatar380FT-IR spectrometer series in the wave number range of 4000−400 cm^{-1}. Thermal-gravimetry (TG) analyses were performed by ZRY−2P thermal analyzer at a linear heating rate of 10 °C/min. α-Al_2O_3 was used as reference.

2.5 Gas sensing properties test

The gas sensing measurements were performed on a commercial HW−30A system (a computer-controlled static gas sensing characterization system, Han Wei Electronics Co., Ltd., Henan Province, China). A proper account of sample powder was lightly grinded with several drops of terpineol in an agate mortar to form slurry. Then, the slurry was coated onto the outside surface of the alumina tube with 4 mm in length and 1 mm in diameter, as well as containing two Au electrodes and four Pt wires on both ends of the tube. A small Ni−Cr alloy filament was put through the tube to supply the operating temperatures by tuning the heating voltage. Finally, the Al_2O_3 tube was welded onto a pedestal with six probes. The sensor response to NO_2 gas is defined as the ratio of R_g/R_a, where R_g and R_a are the electrical resistances of the sensor in NO_2 gas and in air, respectively.

3 Results and discussion

Figure 1 shows XRD pattern of the prepared WO_3. All the diffraction peaks can be well indexed to orthorhombic WO_3 (JCPDS file no. 20—1324). No peaks for other impurities can be detected, indicating the formation of pure WO_3. The sharp peaks suggest that the crystal of WO_3 is perfect. The average crystallite size of WO_3 particles is about 29 nm, calculated by Scherrer's equation.

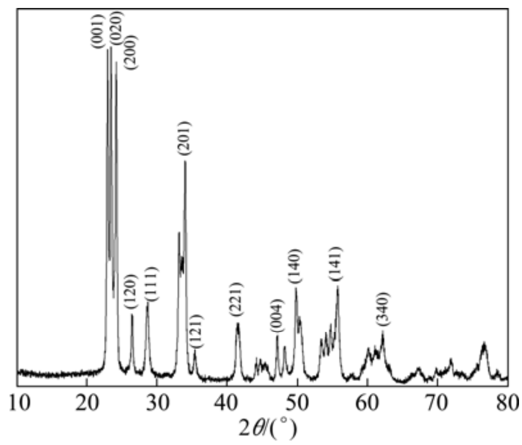

Fig. 1 XRD pattern of prepared WO_3

FTIR spectrum of the prepared PTP is shown in Fig. 2. Several weak peaks in the range of 2800−3100 cm^{-1} and 1630 cm^{-1} can be attributed to the C—H stretching vibrations and C═C characteristic peak, respectively. In the range of 600−1500 cm^{-1}, it is the fingerprint region of PTP. The peak at 784 cm^{-1} is due to the C—H out-of-plane vibration of the 2, 5-substituted thiophene ring created by the polymerization of thiophene monomer. The peak at approximately 695 cm^{-1} denotes the C—S stretching in the thiophene ring [17−20].

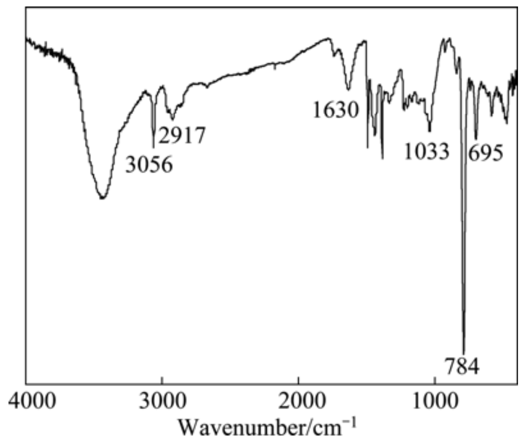

Fig. 2 FT-IR spectrum of prepared PPT

Thermal stability of the hybrid was examined by TG analysis. Figure 3 presents the TG curves of the prepared pure PTP and PW-20 hybrid. In the case of the pure PTP (Fig. 3(a)), the mass starts to decrease at approximately 170 °C, and almost decomposes completely when the temperature is up to 750 °C. Different from the pure PTP, the PW-20 hybrid is still stable at the temperature below 300 °C. The delay of decomposition process of the hybrid indicates that the thermal stability of the PTP/WO_3 hybrids is better than that of the pure PTP. As a result, these data confirm that the mass fraction of WO_3 in the PTP/WO_3 hybrids is responsible for the higher thermal stability of the hybrids, which is beneficial for the potential application of the hybrids as chemical sensors.

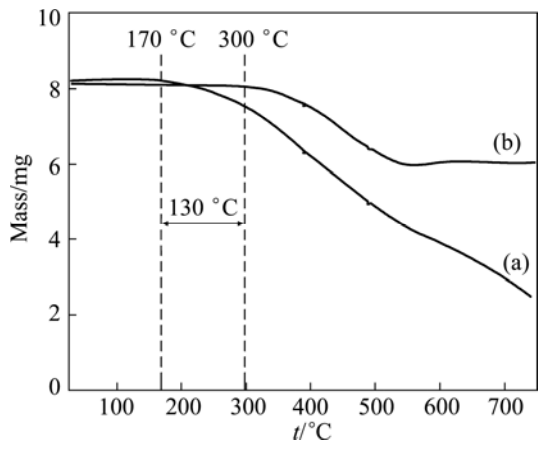

Fig. 3 TG curves of prepared pure PTP (a) and PW-20 hybrid (b)

To investigate the gas-sensing properties of the prepared PTP/WO_3 hybrids to NO_2 at low temperature, the gas-sensing test was carried at room temperature (RT), 60 and 90 °C, respectively. The gas sensing results are included in Figs. 4−8.

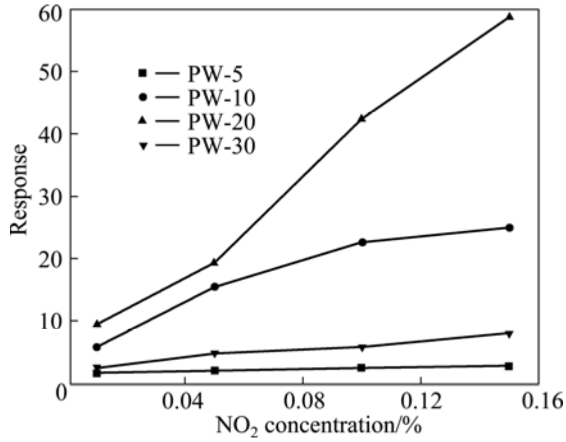

Fig. 4 Response of prepared PTP/WO_3 hybrids with different PTP mass fractions to NO_2 with different concentrations at room temperature

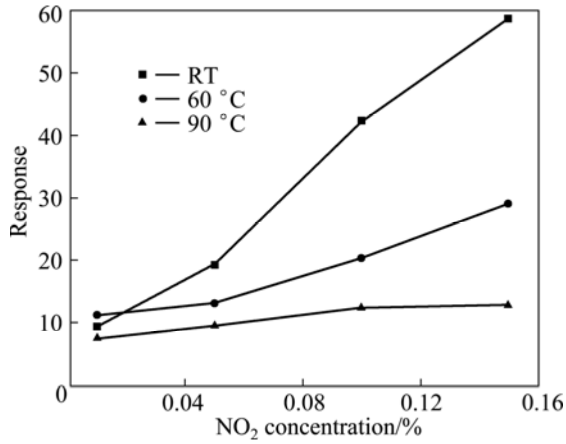

Fig. 5 Response of PW-20 hybrid to NO_2 with different concentrations at different operating temperatures

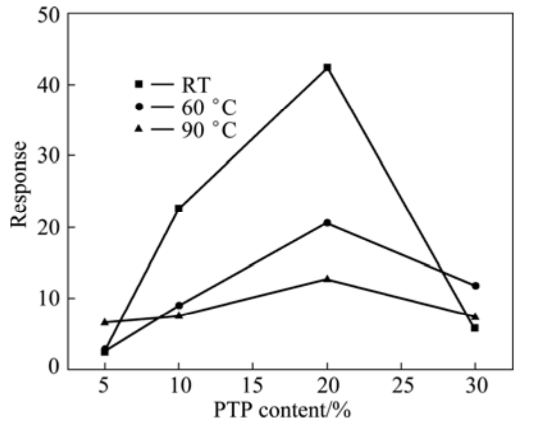

Fig. 6 Response of PTP/WO_3 hybrids with different PTP contents to 0.1% NO_2 (volume fraction) at different operating temperatures

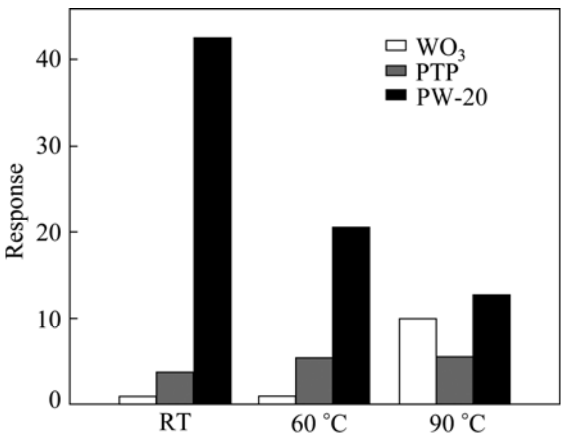

Fig. 7 Response of PW-20 hybrid, pure WO_3 and pure PTP to 0.1% NO_2 (volume fraction) at different operating temperatures

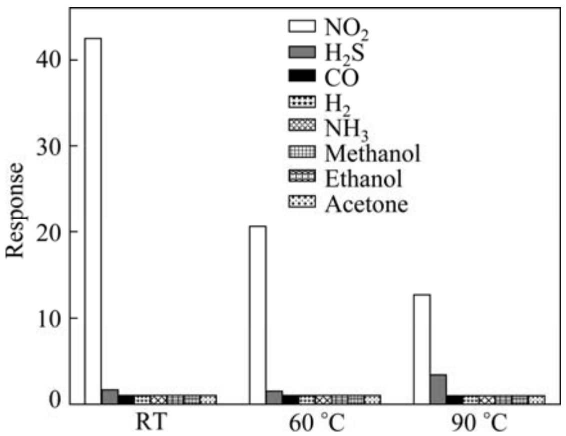

Fig. 8 Response of PW-20 hybrid to various gases with same concentration of 0.1% at different operating temperatures

Figure 4 shows the response of the PTP/WO_3 hybrids with different PTP mass fractions (5%, 10%, 20% and 30%) to different concentrations (0.01%, 0.05%, 0.1% and 0.15%, volume fraction) of NO_2 at room temperature. All the four PTP/WO_3 hybrids show a similar response pattern to NO_2. From Fig. 4, it can be concluded that the gas response is a function of NO_2 concentration. The gas response increases generally to a certain extent with an increase in concentration of NO_2 from 0.01% to 0.15% (volume fraction). The maximum response can be observed when the NO_2 gas concentration is 0.15% (volume fraction). Meanwhile, the response of PTP/WO_3 hybrids enhances with the increase of PTP mass fraction from 5% to 20%, and the 20% PTP/WO_3 hybrid shows the highest response to NO_2. However, further increase of the PTP mass fraction results in the decrease of the response.

Figure 5 illustrates the response of the PW-20 hybrid to NO_2 with different concentrations at different operating temperatures. It can be observed that, similar to at room temperature, at the operating temperature of 60 and 90 °C the response increases with the increase of NO_2 concentration, and all the hybrids show the maximum response to 0.15% NO_2 (volume fraction). It is also found that the PTP/WO_3 hybrid exhibits much higher response to NO_2 at RT than at 60 or 90 °C. Therefore, it is suggested that this kind of hybrids can be potentially used for gas sensor material for detecting NO_2 at RT.

Figure 6 shows the response of 5%, 10%, 20% and 30% PTP/WO_3 hybrids to 0.1%NO_2 (volume fraction) at RT, 60 or 90 °C. It is found that the PW-20 hybrid has higher response to 0.1%NO_2 (volume fraction) at RT than at 60 °C or 90 °C, and at all the three operating temperatures, the PW-20 hybrid shows the highest response among the PTP/WO_3 hybrids.

Figure 7 presents the response of the PW-20 hybrid, pure WO_3 and pure PTP to 0.1% NO_2 (volume fraction) at different operating temperatures. Obviously, compared with the pure WO_3 and PTP, the sensor response has been significantly improved by constructing hybrid materials. Therefore, the PTP/WO_3 hybrid can be one of the most promising materials due to its high response at low temperature. It is well known that PTP behaves as a p-type semiconductor and WO_3 behaves an n-type semiconductor. It is expected that the p–n heterojunctions are formed in the PTP/WO_3 hybrids [21], which could generate a unique electron donor–acceptor system, increasing the depletion barrier height and thus improving the response of the sensor [22]. The test gas can adjust the conductivity of the junction by changing the depletion region. When the NO_2 gas is introduced, the width of the depletion region decreases and the conductivity of the PTP channel increases [23−25]. Therefore, the PTP/WO_3 hybrid shows much higher response in comparison to pure PTP and WO_3 at low operating temperature. However, it can also be observed from Figs. 4−6 that the concentration of the PTP is as high as 30% which leads to the decrease in the response of the PTP/WO_3 to NO_2, which should be related to the fact that the p-n heterojunctions are covered with the excessive PTP. As a result, the effective p-n heterojunctions are reduced and the response decreases.

For practical use, the selectivity of the chemical sensor is also an important consideration. Figure 8 shows the response of the PW-20 hybrid to various gases including NO_2, H_2S, CO, H_2, NH_3, ethanol, methanol and acetone with the same concentration of 0.1% NO_2 (volume fraction) at RT, 60 and 90 °C, respectively. It is found in Fig. 8 that the PW-20 hybrid exhibits high response to NO_2, but less to H_2S, and no gas response to CO, H_2, NH_3, ethanol, methanol and acetone, illuminating that the sensor based on the as-obtained PTP/WO_3 hybrid has good selectivity to NO_2.

4 Conclusions

1) The as-prepared PTP/WO_3 hybrids have a higher thermal stability than the pure PTP, confirming that the presence of WO_3 in the PTP/WO_3 hybrid is responsible for the higher thermal stability of the hybrid, due to a certain synergetic interaction between the inorganic WO_3 and organic PTP components, which is beneficial for the potential application of the hybrid as chemical sensors.

2) The gas sensing measurements demonstrate that the sensors based on the PTP/WO_3 hybrids exhibit higher gas response for detecting NO_2 at low temperature than the sensor based on pure PTP or WO_3. The sensing mechanism is suggested to be related to the existence of p–n heterojunctions in the PTP/WO_3 hybrids.

3) The response of the PTP/WO_3 hybrids is markedly influenced by the PTP mass fraction. Among the hybrids, the 20% PTP/WO_3 hybrid shows the highest response to NO_2. Moreover, the 20% PTP/WO_3 hybrid shows higher response at room temperature than at 60 or 90 ^{o}C. Meanwhile, the PTP/WO_3 hybrid exhibits much higher sensor response to NO_2 compared with other gases including H_2S, CO, H_2, NH_3, ethanol, methanol and acetone, illuminating that the sensors based on the as-obtained PTP/WO_3 hybrids have good selectivity to NO_2.

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基于聚噻吩/WO_3的有机−无机复合材料低温 NO_2 传感器

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摘 要：通过化学氧化聚合法和胶溶法分别制备了聚噻吩(PTP)和纳米 WO_3，通过简单机械共混和 PTP 和 WO_3 制备不同 PTP 质量分数的有机−无机 PTP/WO_3 复合物。所制备的 PTP/WO_3 复合物比纯的 PTP 具有更高的热稳定性。气敏测试结果表明，在低温检测 NO_2 时，PTP/WO_3 复合物具有比纯的 PTP 和 WO_3 更高的响应，这可能与 PTP/WO_3 复合物中 p–n 异质节的存在有关系。PTP/WO_3 复合物的响应受 PTP 质量分数的影响显著，20% PTP/WO_3 复合物在低温(<90 °C)时对 NO_2 显示出高的响应和好的选择性。因此，PTP/WO_3 传感器有望被用于低温检测 NO_2

关键词：NO_2 传感器；聚噻吩/WO_3；低温

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