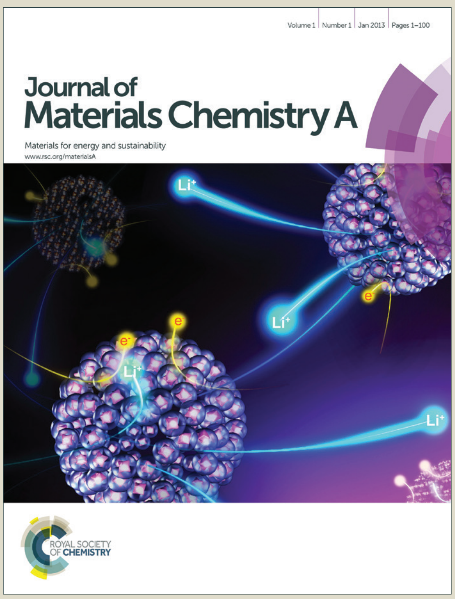
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Porous SnO_2 Nanoplates for Highly Sensitive NO Detection

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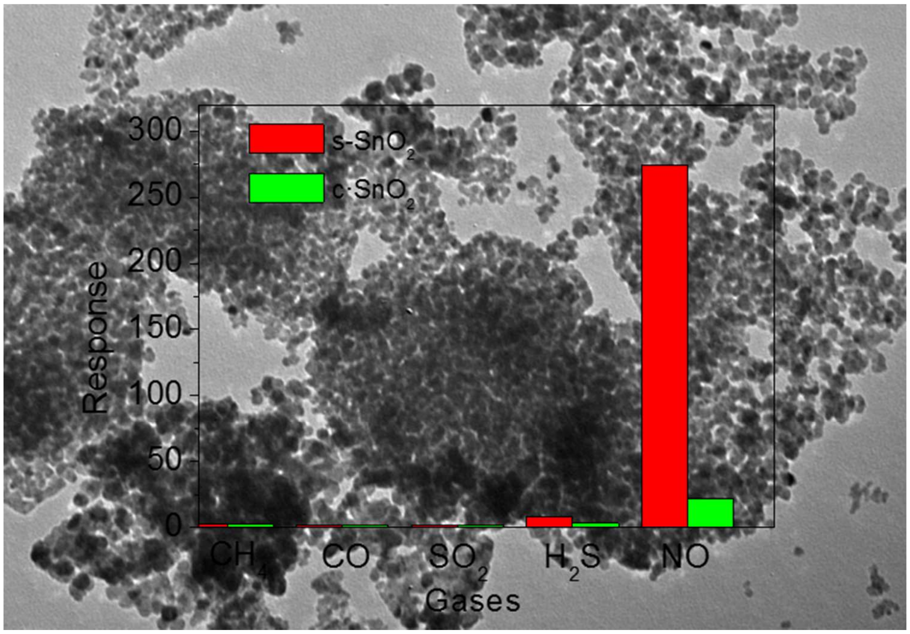

Porous SnO_2 nanoplates with high NO response have been successfully prepared by the oxidization conversion of corresponding SnS_2 nanoplates.

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Porous SnO_2 nanoplates have been successfully prepared by the oxidization conversion of hydrothermally synthesized SnS_2 nanoplates at 500 °C. When exposed to NO gas, such porous SnO_2 nanoplate sensors have exhibited the fast response, enhanced sensitivity and excellent selectivity due to their unique structural characteristics in comparision with commercial SnO_2 nanoparticles.

Gas detection has been widely studied due to its importance in many fields.[1-4] As one of the most important gas detection devices, semiconductor gas sensors have drawn great attention, and great effort has been focused on the design and synthesis of sensing materials, since the gas-sensing performance of materials strongly depends on their size, shape, components and even impurities, which are determined by synthetic methods.[5-15] Therefore, it is of interest to explore novel synthetic methods for improving the performance of sensing materials.

As an important n-type semiconductor, tin oxide (SnO_2) has obtained great attention in its application of gas sensors, since it has excellent gas-sensing characteristics.[16-18] Presently, great effort has been focused on improving its gas-sensing properties, through controlling the size, shape, morphology of SnO_2,[19-23] as well as integrating other materials into SnO_2-based composites,[24-30] respectively. Thus, it is necessary to prepare SnO_2 with novel synthetic methods for enhancing gas-sensing performance.

In this work, we have successfully developed an interesting synthetic route to prepare porous SnO_2 nanoplates by combining the hydrothermal synthesis and further moxidation of SnS_2 nanoplates. When porous SnO_2 nanoplates were used as the sensing material, the gas sensor displayed the excellent gas-sensing characteristics, such as the low work temperature as low as 200 °C, fast recovery time, and high sensitivity towards NO (494 for 20 ppm), and good selectivity to NO than other gases (CO, CH_4, H_2S and SO_2).

The porous SnO_2 nanoplates were synthesized by annealing hydrothermally obtained SnS_2 nanoplates using our previous synthetic method with slight modification.[31] The phase and purity of the as-obtained SnO_2 nanoplates can be confirmed by the X-ray diffraction (XRD) and energy dispersive X-ray (EDX). The XRD patterns of SnO_2 nanoplates (Fig. 1) could be well indexed with the standard card (PDF: 41-1445). There is no impurities observed in the XRD patterns, which indicates that SnS_2 nanoplates can completely transferred into SnO_2 *via* the annealing and washing processes. The EDX spectrum of as-obtained SnO_2 was investigated (Fig. S1), which indicates there is no residue sulfur.

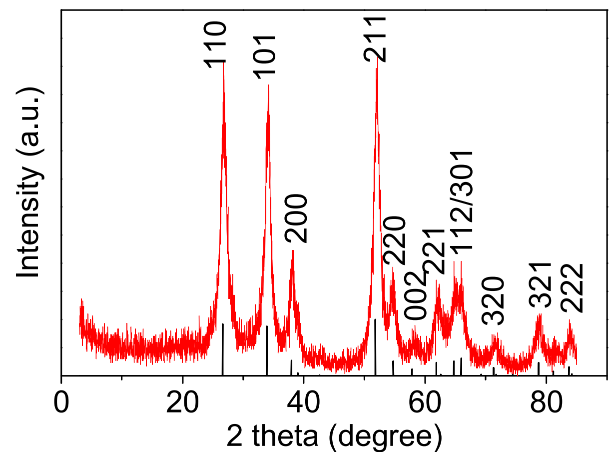

Fig. 1 XRD pattern of the as-obtained porous SnO_2 nanoplates.

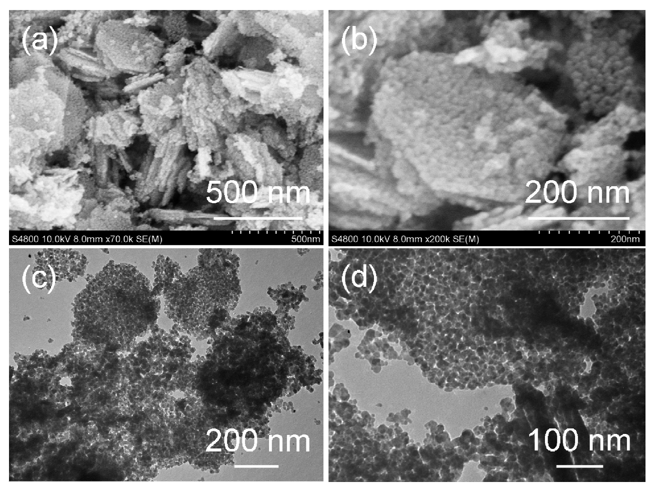

Fig. 2 (a and b) SEM images and (c and d) TEM images of the as-obtained porous SnO_2 nanoplates.

The morphology of SnO_2 nanoplates was characterized by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Fig. 2a and b show the SEM images of SnO_2 sample. As shown in Fig. 2a, nanoplates can be observed, together with some particles. In the enlarged SEM image (Fig. 2b), one could find that the surface of SnO_2 nanoplate was not smooth. The structure of SnO_2 nanoplates were further analyzed by TEM. The TEM image (Fig. 2c) clearly indicates that SnO_2 sample is composed of nanoplates, together with some nanoparticles. In the enlarged TEM image (Fig. 2d), one could find that the nanoparticles on the surface of SnO_2 nanoplates have a size ranging from 5 to 8 nm. The above results indicate that it is effective to synthesize SnO_2 nanoplates by annealing SnS_2 at 500 °C for 2 h. Other experimental results also proved this effectivity of such annealing technique.[32-34]

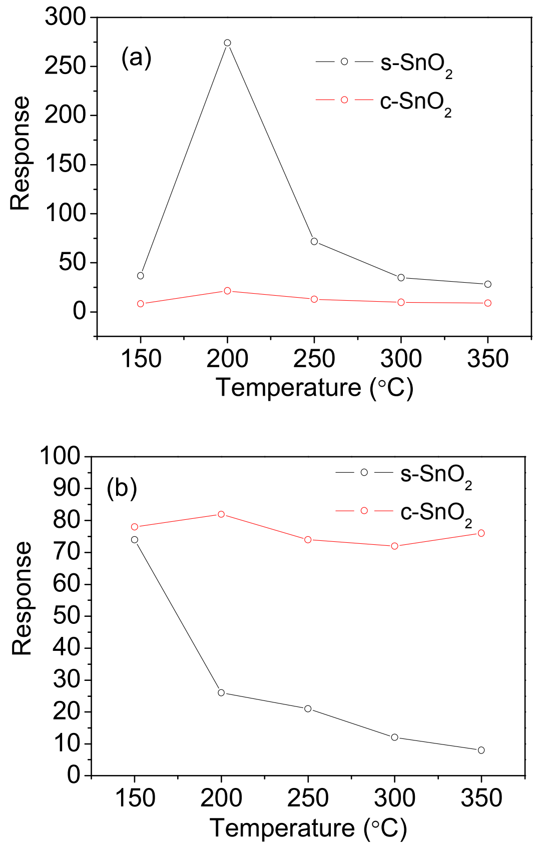

Fig. 3 (a) Sensitivity and (b) Response time of s-SnO_2 and c-SnO_2 sensors to 10 ppm NO gas at different working temperature.

Owing to their unique structure combining the plate-like shape and excellent porous characteristics, porous SnO_2 nanoplates are expected to demonstrate superior gas-sensing properties. Here, NO gas was chosed as the tested gas due to its high toxicity. Fig. 3a shows the response of the as-synthesized SnO_2 (s-SnO_2) and commercial SnO_2 (c-SnO_2 with a diameter of about 40 nm in Fig. S2) sensors towards 10 ppm of NO gas as a function of the operating temperature. For NO gas detection, the optimum working temperature should be about 200 °C, at which two sensors achieve the highest response towards NO gas from 150 to 350 °C. For s-SnO_2 and c-SnO_2 sensors in Fig. 3a, their highest response towards 10 ppm NO gas could reach 274 and 21.5, respectively. Moreover, the recovery time of both s-SnO_2 and c-SnO_2 sensors was studied, as shown in Fig. 3b. In Fig. 3b, one could find that the recovery time for the s-SnO_2 sensor can drop quickly from 74 s at 150 °C to 8 s at 350 °C. However, the recovery time for the c-SnO_2 sensor is always as long as above 70 s.

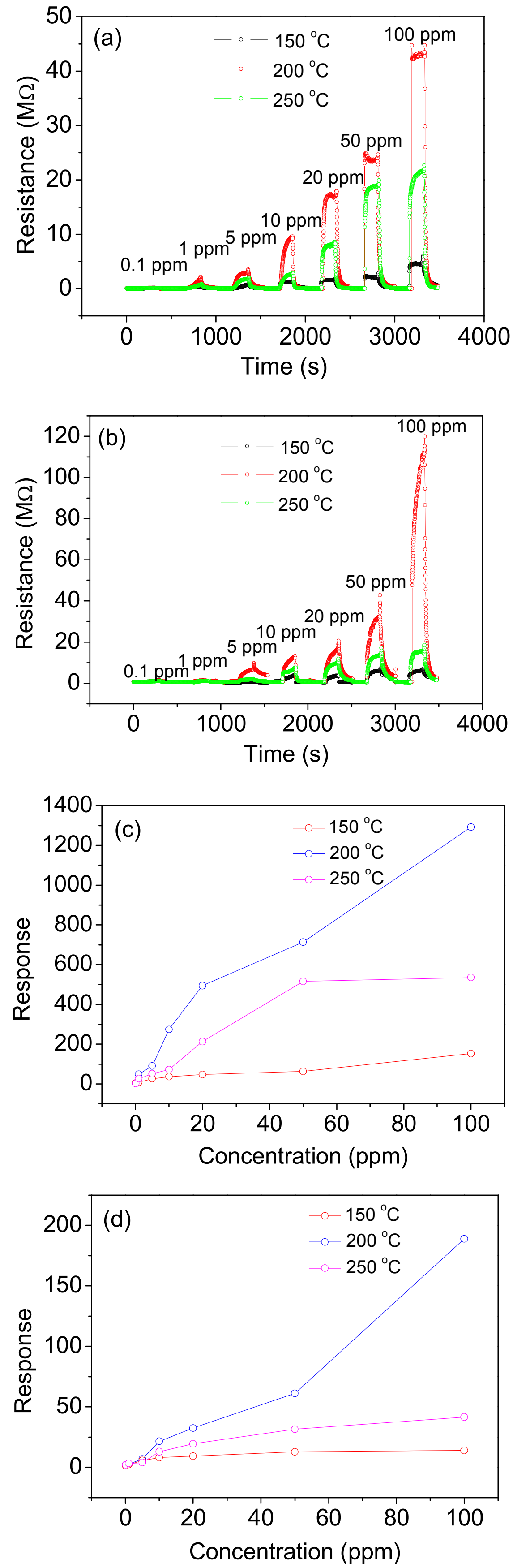

Fig. 4 (a and b) The real-time response curves of s-SnO_2 and c-SnO_2 sensors to NO gas with increased concentration at a working temperature of 200 ºC, respectively; (c and d) The relationship between the sensitivity and NO gas concentration for s-SnO_2 and c-SnO_2 sensors, respectively.

To understand the NO gas sensing characteristics, the dynamic responses of both s-SnO_2 and c-SnO_2 sensors were investigated at three different temperatures (150 ^oC, 200 ^oC and 250 ^oC), respectively. The dynamic responses of both s-SnO_2 and c-SnO_2 sensors at 150 ^oC, 200 ^oC and 250 ^oC with various concentrations (0.1, 1, 5, 10, 20, 50 and 100 ppm) of NO gas are displayed in Fig. 4a and b, respectively. In Fig. 4a and b, one could find that the response amplitudes of both s-SnO_2 and c-SnO_2 sensors were increased with increasing the concentration of NO gas, respectively. In Fig. 4c and d, the corresponding response of both s-SnO_2 and c-SnO_2 sensors towards NO gas were found to be highest at 200 ^oC and enhanced with increasing the concentration of NO gas. Compared with the c-SnO_2 sensor (Fig. 4d), the response of s-SnO_2 sensor (Fig. 4c) is obviously higher. In Fig. 4c, the corresponding response of the s-SnO_2 sensor at 200 ^oC are 3.3 for 0.1 ppm, 49 for 1 ppm, 90.6 for 5 ppm, 274 for 10 ppm, 494 for 20 ppm, 713 for 50 ppm and 1292 for 100 ppm, respectively. The enhanced performance of porous SnO_2 nanoplates might be attributed to their unique plate-like structure and porous characteristics, which facilitate the process of NO oxidizing surface oxygen species of as-used SnO_2 material.[35] It is well known that SnO_2 is a n-type semiconductor. When SnO_2 sensor expose to oxidizing gas (NO, NO_2), the oxidizing gas will capture the free electron in SnO_2, resulting higher resistance.[36, 37] Higher BET specific area of pore SnO_2 nanoplates may be also an important factor governing their better NO gas sensing performance. As shown in Fig. S3, the BET specific area of both s-SnO_2 and c-SnO_2 materials is 60 and 5.9 m^2/g, respectivly. The pore-size distribution was also further examined by using the Barrett–Joyner–Halenda (BJH) method, as shown in Fig. S4. The average pore diameter of the s-SnO_2 is approximately 6.27 nm, which is close to that obtained from the TEM observations.

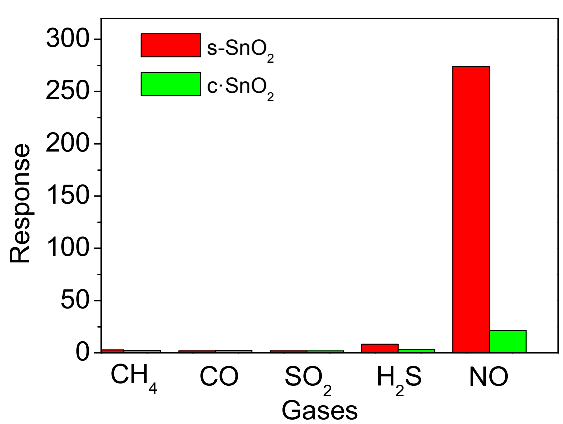

Fig. 5 Sensor response to various gases with 10 ppm at 200 °C.

The gas selectivity of both s-SnO_2 and c-SnO_2 sensors was also investigated in this work. Here, the response of both SnO_2 sensors towards other gases with 10 ppm was conducted, and the related results are shown in Fig. 5. In Fig. 5, one could find that two kind of SnO_2 sensors had a largely higher sensitivity towards NO than other gases, such as CH_4, CO, SO_2 and H_2S. In addition, we also studied the reproducibility of both s-SnO_2 and c-SnO_2 sensors. In Fig. 6a and b, the reproducibility of both s-SnO_2 and c-SnO_2 sensors demonstrates that the sensor maintains its initial response amplitude without a clear decrease upon ten successive sensing tests to 20 ppm NO gas. These results demonstrate that the s-SnO_2 sensor has better selectivity and stability than c-SnO_2 sensor towards NO gas.

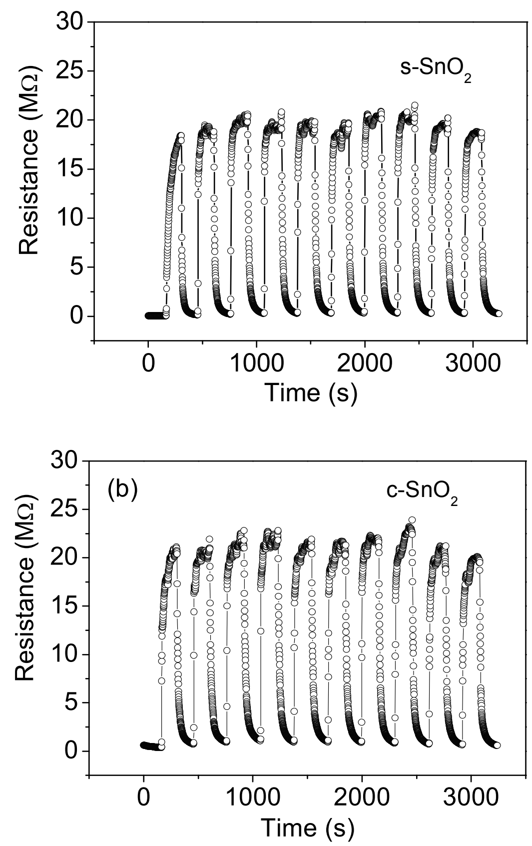

Fig. 6 (a and b) Reproducibility of s-SnO_2 and c-SnO_2 sensors on successive exposure (10 cycles) to 20 ppm NO gas.

In conclusion, we have successfully prepared the porous SnO_2 nanoplates by annealing the SnS_2 nanoplates obtained from the hydrothermal system. The structural characteristics and conversion of the as-synthesized SnO_2 nanoplates have also been studied. Gas-sensing results have demonstrated that the as-synthesized porous SnO_2 nanoplates had excellent gas-sensing characteristics towards NO gas with the lower working temperature, high selectivity, fast response and recovery, and high sensitivity. The as-synthesized porous SnO_2 nanoplates are expected to be a promising NO gas sensing material.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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