



# High-performance acetone gas sensor based on Ru-doped SnO<sub>2</sub> nanofibers

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## ABSTRACT

We report the Ru doping effect on the gas-sensing properties of SnO<sub>2</sub> nanofibers for acetone detection in this paper. For this purpose, pure and 1, 2, 3 mol% Ru-doped SnO<sub>2</sub> nanofibers were prepared through electrospinning technique combined with calcination treatment. The fibrous microstructure of these nanofibers were maintained and the grain size of the SnO<sub>2</sub> nanoparticles were decreased from 9.2 nm (pure) to 5.1 nm (3% Ru-doped) after Ru doping. In order to confirm that Ru doping is an effective way to improve the gas sensing properties of the SnO<sub>2</sub>-based gas sensor, the gas sensing properties of the sensors based on pure and Ru doped SnO<sub>2</sub> nanofibers were investigated systematically. The results showed that the response to 100 ppm acetone of 2 mol% Ru-doped SnO<sub>2</sub> nanofibers was 118.8, which was 12 times higher than that of pure SnO<sub>2</sub> nanofibers. In the end, the role of Ru in the gas sensing mechanism of SnO<sub>2</sub> nanofibers was analyzed according to the results of the X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS).

## 1. Introduction

As one of the widely researchful chemiresistive sensors, the one adopting semiconducting metal oxides (SMOs) as sensing materials, has become the focus due to its low cost, high stability, simple operation principle and easy fabrication [1,2]. Up to now, many promising SMOs sensing materials, such as SnO<sub>2</sub> [3,4], In<sub>2</sub>O<sub>3</sub> [5,6], ZnO [7,8], α-Fe<sub>2</sub>O<sub>3</sub> [9,10], WO<sub>3</sub> [11,12], NiO [13,14] and so on, have been continuously reported for the use of detecting poisonous and flammable gases. As for the effective methods of improving gas sensing properties of SMOs sensing materials, it is particularly important to design the reasonable morphology and structure of the sensing material and adopt appropriate surface modification method. As is known to all, surface morphology and structure of the SMOs have a great influence on gas sensing properties due to the surface of the sensing materials providing the site of the interaction between gas molecules and the surface chemisorbed oxygen species. Up to now, a variety of morphologies and structures of SMOs have been synthesized through various methods such as nanoparticles [15,16], nanorods [17,18], nanosheets [19,20], nanospheres [21,22] and nanoflowers [23,24] and so on. Besides these, nanofibers have been confirmed of great potential in the application of gas sensing materials owing to their high electron mobility, large length to diameter ratio, high crystalline and uniformity [25–27]. Many sensing materials of nanofibrous structure have been widely reported. Lee et al.

synthesized pure and Fe-doped In<sub>2</sub>O<sub>3</sub> nanofibers and demonstrated that Fe-doped could change the gas selectivity [28]. Yang et al.'s work proved that SnO<sub>2</sub>/ZnO 1D fibrous hierarchical structure exhibited superior gas sensing response toward ethanol gas [29]. Kim et al. provided an evidence of enhanced CO and NO<sub>2</sub> sensing properties, using SnO<sub>2</sub>-Cu<sub>2</sub>O core-shell nanofibers [30]. Although morphology and structure have great influence on the gas sensing properties of nanomaterials, surface modification on the gas sensing materials also played a crucial role. A variety of modification methods have been applied to gas sensing materials. Such as aliovalent doping [31,32], two nanomaterial composite [33,34], noble metal loading [35,36] and so on. The above modification methods could improve the sensitivity and selectivity of gas sensing materials by adjusting the electron depletion layer on the surface of materials, constructing potential barriers, adjusting the carrier concentration of materials, changing the distribution of oxygen components on the surface and introducing catalysts [37,38].

In this work, pure and 1–3 mol% Ru-doped SnO<sub>2</sub> nanofibers were synthesized through an electrospinning process with subsequent calcination method to investigate the variation of gas sensing properties after doping. In this process, we determined the optimal Ru doping amount and investigated the effect of Ru<sup>4+</sup> doping on the gas sensing properties of SnO<sub>2</sub> nanofibers. The results showed, the sensors based on Ru-doped SnO<sub>2</sub> nanofibers exhibited improved gas sensing properties to all tested gases. Notably, the response of the 2 mol% Ru-doped SnO<sub>2</sub>

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nanofibers to 100 ppm acetone at 200 °C was 118.8, which was 12 times higher than that of pure SnO<sub>2</sub> nanofibers. In the end, the possible reasons for the improvement of gas sensing properties of Ru-doped SnO<sub>2</sub> nanofibers were analyzed and discussed with respect to the change of the electron concentration and distribution of oxygen component caused by the incorporation of Ru<sup>4+</sup> into SnO<sub>2</sub> nanocrystals.

## 2. Experimental section

### 2.1. Synthesis of pure and Ru-doped SnO<sub>2</sub> nanofibers

Pure and Ru-doped SnO<sub>2</sub> nanofibers with various doping amount of 1, 2 and 3 mol% were prepared by electrospinning combining with calcination treatment. As similar as our previous work [38], 5 mL DMF and 5 mL ethanol were used as a solvent to dissolve 2 mmol SnCl<sub>2</sub>·2H<sub>2</sub>O and a certain dose of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.02 mmol for 1 mol%; 0.04 mmol for 2 mol%; 0.06 mmol for 3 mol%) by magnetic stirring at room temperature. Then, we put 1 g PVP into above mixture solution with continuing magnetic stir for 5 h. After above process, we got a transparent and clear precursor, which was used to electrospinning. As for the process of electrospinning, the precursor was moved into a syringe which connecting with a spinneret. The parameters of electrospinning is as follows: the voltage was 14 ± 0.5 kV and the distance between the positive pole (needle) and the negative pole (collector) was 12 cm. The injection speed of the precursor was fixed at 0.3 mL/h by a peristaltic pump. The PVP/SnCl<sub>2</sub> or PVP/SnCl<sub>2</sub>/RuCl<sub>3</sub> composite nanofibers mats were obtained after the electrospinning process. In the end, the four obtained samples were calcined at 500 °C for 2 h in a muffle furnace with air atmosphere to remove organic polymer components completely.

### 2.2. Characterization

The phase structures of the four samples were analyzed by X-ray diffraction (XRD) through Rigaku TTRIII X-ray diffractometer with Cu K $\alpha$  radiation at a wavelength of 1.5406 Å at 40 kV and 200 mA. The external microstructures were observed by field-emission scanning electron microscopy (FESEM) (JEOL JSM-7500F, operated at an accelerating voltage of 5 kV). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEM-2200FS (JEOL) transmission electron microscope with an operating voltage of 200 kV to further observe the microstructures of the samples. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250 X-ray photoelectron spectrometer with an X-ray source (Al K $\alpha$   $h\nu = 1486.6$  eV) and the ultraviolet photoelectron spectrometer (UPS) measurements were also collected from it with an ultraviolet source.

### 2.3. Fabrication and measurement of gas sensor

Fig. 1 shows the structure diagram of the fabricated gas sensor. The sensor consists of a base and a planar electrode substrate, whose characterization was described in our previous work [38]. The size of the electrode substrate are 1.5 mm × 1.5 mm and the thickness is 0.2 mm. Fig. 1(a) and (b) are the front and back of the electrode substrate. The electrode substrate adopts alumina ceramic plate as the main body, which was coated with two “L” shape gold electrodes on the front side (electrode widths = 0.3 mm; separation = 0.15 mm) and RuO<sub>2</sub> heating layer on the back side. The as-prepared sensing materials (pure, 1, 2, 3 mol% Ru-doped SnO<sub>2</sub> nanofibers) were mixed with deionized water to form a homogeneous viscous paste, respectively. Then the pastes were coated onto the front surface of planar electrode substrate. The operating temperatures of the sensors were adjusted by changing the working current or voltage of the electrode substrate. The heating current or voltage corresponding to the operating temperature value were measured by an FLIR temperature sensor (T250, FLIR

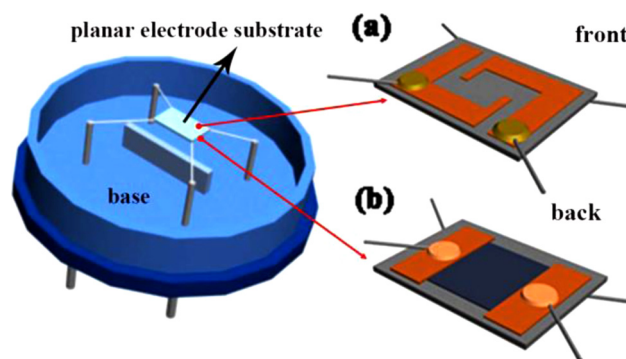


Fig. 1. Schematic diagram of the gas sensor and the (a) front (b) back of the planar electrode substrate.

Systems Inc., USA). Subsequently, the resulting sensing device was calcined at 400 °C for 2 h to enhance the stability of the sensing materials. The gas sensing properties of sensors based on pure and Ru-doped SnO<sub>2</sub> nanofibers were investigated by a static gas sensing characterization system under laboratory conditions (30% relative humidity, 20 °C), which were shown in Fig. 2. The static gas sensing characterization system consists of a constant current source, a high precision digital multimeter, a computer and two test chambers. At first, the sensor was stayed in chamber 1, which was full of fresh air and its resistance in air maintained a certain value, noted as R<sub>a</sub>. Then, a certain amount of target test gas was injected into chamber 2 using a microsyringe which was washed by fresh air. After that, the sensor was put into the chamber 2 quickly to react with the target gas molecules and the resistance of sensor will change immediately. After a while, the resistance becomes stable again, noted the value as R<sub>g</sub>. In the end, the sensor was transferred back into the chamber 1, which was full of fresh air and the resistance of the sensor will recover. In this process, the resistance of the sensor was monitored and recorded in real time by the high precision digital multimeter, and the curve of the resistance changing continuously with time was finally displayed on the computer. The gas response of the sensor is defined as the ratio of R<sub>a</sub>/R<sub>g</sub>. In addition, when the sensor was exposed to the test gas, the time taken by the sensor for the change of resistance from R<sub>a</sub> to R<sub>a</sub> - 90% (R<sub>a</sub>-R<sub>g</sub>) was noted as the response time ( $\tau_{res}$ ). When the sensor was detached from the test gas, the time taken by the sensor for the change of resistance from R<sub>g</sub> to R<sub>g</sub> + 90% (R<sub>a</sub>-R<sub>g</sub>) was noted as the recovery time ( $\tau_{recov}$ ). According to the definition of response and recovery time, we could obtain the corresponding response and recovery time from the continuous curve of sensor resistance recorded by the high precision digital multimeter.

## 3. Results and discussion

### 3.1. Structural and morphological characteristics

The XRD patterns of the pure and 1, 2, 3 mol% Ru-doped SnO<sub>2</sub> nanofibers are shown in Fig. 3. From Fig. 3(a), we could observe that all the diffraction peaks of the four samples could be indexed to tetragonal rutile structure of SnO<sub>2</sub>, which were agreed well with the recorded values from the Joint Committee on Powder Diffraction Standards card (JCPDS 41-1445). In addition, as shown in Fig. 3(b), we could clearly observe that the diffraction peaks shifted to high angle with increasing the Ru doping amount by comparing the peaks (110) and (101) of the four samples. It could account for the difference radius of Ru<sup>4+</sup> and Sn<sup>4+</sup>. The radius of Sn<sup>4+</sup> was 0.690 Å, which was larger than that of Ru<sup>4+</sup> (0.620 Å). When the Ru<sup>4+</sup> was introduced into the SnO<sub>2</sub> lattice, Ru<sup>4+</sup> replaced the lattice position of Sn<sup>4+</sup>, causing the decrease of the interplanar spacing (d) of SnO<sub>2</sub>. According to the Bragg's Law ( $n\lambda = 2d \sin\theta$ ), when the interplanar spacing (d) decreased, Bragg diffraction

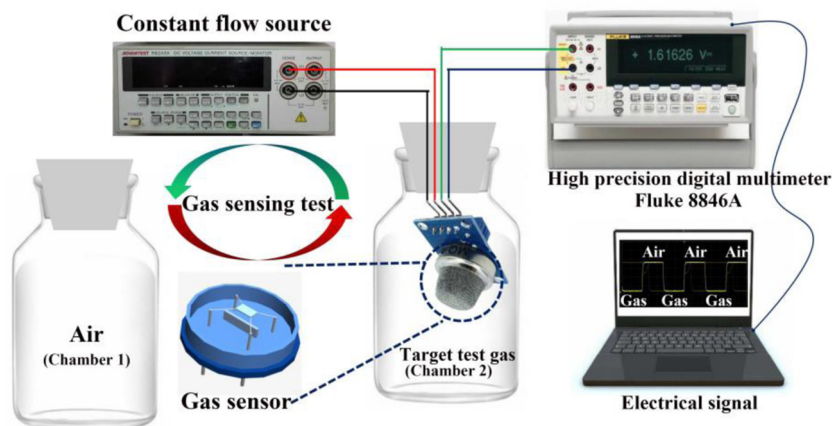


Fig. 2. Schematic diagram of static gas sensing characterization system.

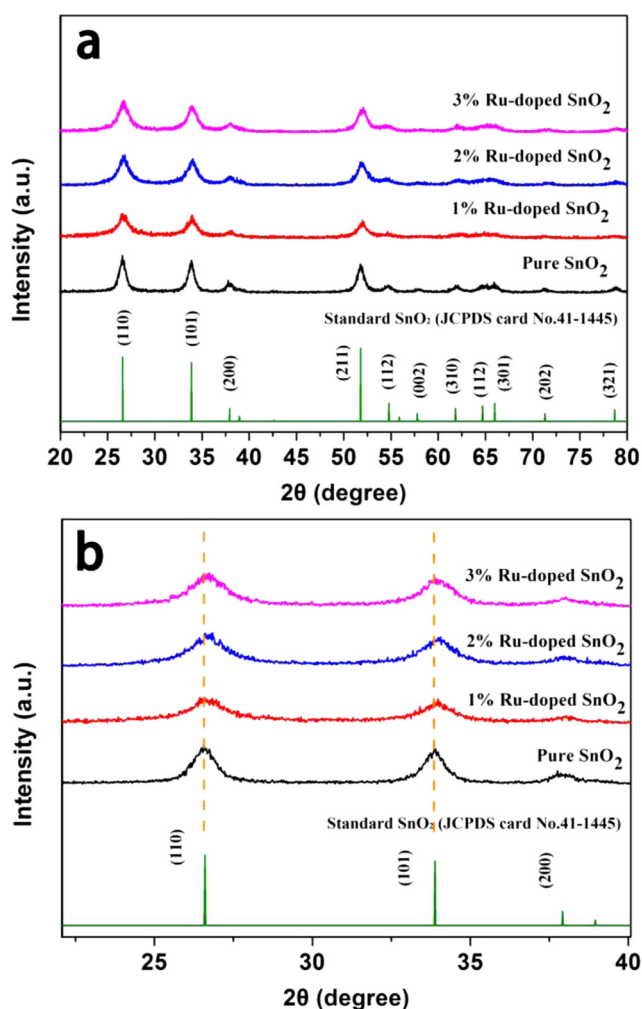


Fig. 3. (a) XRD patterns of Ru-doped SnO<sub>2</sub> nanofibers with different doping amount, (b) Comparison of (110) and (101) peaks from XRD patterns.

angle ( $\theta$ ) would increased. Therefore, the diffraction peaks shifted to high angle with Ru doping, which confirmed that Ru<sup>4+</sup> was incorporated into the SnO<sub>2</sub> lattice, successfully. Moreover, according to the Debye-Scherrer formula,

$$D = \frac{0.89 \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where  $\lambda$  is the X-ray wavelength (0.154056 nm),  $\theta$  is the Bragg diffraction angle and  $\beta$  is the peak width at half maximum, using the results of the XRD characterization, we calculated the average grain size of pure, 1, 2 and 3 mol% Ru-doped SnO<sub>2</sub> samples as 9.18, 6.74, 6.12, and 5.05 nm, respectively, which indicated that the incorporation of Ru<sup>4+</sup> could effectively prevent the grain growth of SnO<sub>2</sub>.

FESEM images of pure and 1–3 mol% Ru-doped SnO<sub>2</sub> nanofibers were shown in Fig. 4(a)–(d). We could observe that all the samples showed fibrous nanocrystalline morphology with a uniform diameter about 120–150 nm. The samples exhibited a net structures of nanofibers, which was advantageous for the target gas to easily diffuse or overflow between the surface and the internal of sensing materials. In addition, we could observe that all the samples were composed of a lot of small nanoparticles. The insets of the figures are the enlarged details of the four samples. We could observe from the insets that the SnO<sub>2</sub> nanofibers became more compact and the porosity reduced with increasing the Ru doping amount. Based on the results of XRD characterization, we analyzed that the decreased porosity of SnO<sub>2</sub> nanofibers may be due to the reduction of the grain size of the nanoparticles which consist of the nanofibers. XRD results confirmed that with the increase of Ru doping amount, the grain size of SnO<sub>2</sub> gradually reduced. It is easy to understand that the smaller size of the nanoparticles consisting of the nanofibers, the more compact and smoother of the surface of the nanofibers exhibited.

TEM characterization was carried out to further explore the internal structure of pure SnO<sub>2</sub> and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers, as shown in Fig. 5. Fig. 5(a) and (d) are the TEM images of pure and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers, while Fig. 5(b) and (e) are the high-magnification TEM images of the corresponding two samples. From the images we could clearly observe that the microstructures of the two samples were similar to the FESEM results. The two samples were all of nanofibrous structure and formed a network. In addition, the sample doped with 2 mol% Ru was a little tighter than the pure one, which was as same as the FESEM results. According to the XRD results, we knew that the average grain size of pure SnO<sub>2</sub> was 9.18 nm, which was larger than the 2 mol% Ru doped one (6.12 nm). So, the smaller grain size resulted in the tighter of the samples. TEM results further confirmed that Ru doping changed the microstructures of SnO<sub>2</sub> nanofibers. The HRTEM images and SAED patterns of the two samples were shown in Fig. 5 (c) and (f), which indicated that the SnO<sub>2</sub> nanofibers were composed of highly crystalline nanoparticles and polycrystalline in nature. We could observe the lattice fringes clearly in the insets of Fig. 5(c) and (f) and the interplanar spacings were 0.334 nm, corresponding to the (110) planes of SnO<sub>2</sub>, indicating the two samples are all SnO<sub>2</sub>. Figs. 5(g)–(j) show the EDS elemental mapping images, indicating these nanofibers were comprised of Sn, O and Ru, and the Ru elements were evenly distributed among the SnO<sub>2</sub> nanofibers.

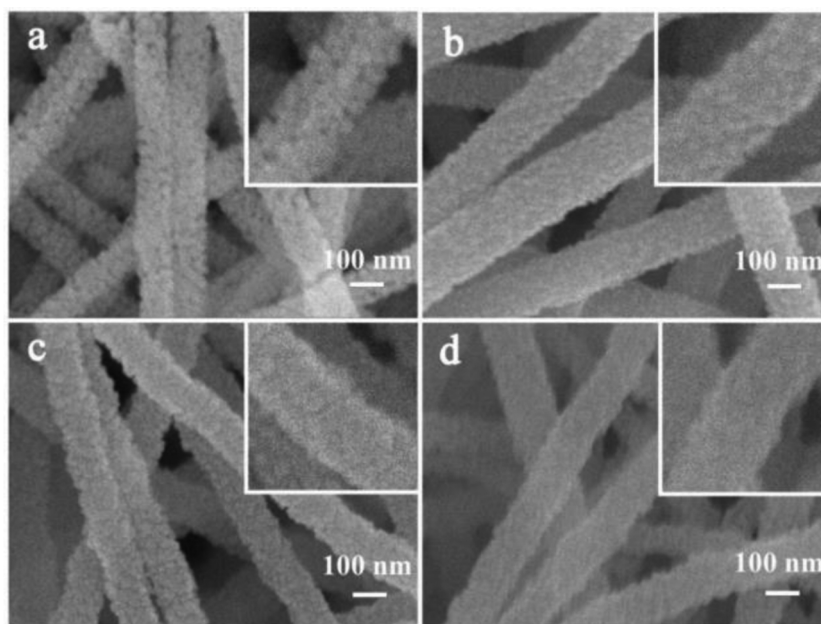


Fig. 4. FESEM images of (a) pure (b) 1 mol% (c) 2 mol% (d) 3 mol% Ru-doped  $\text{SnO}_2$  nanofibers.

### 3.2. Gas sensing characteristics

First, we investigated the influence of operating temperature and doping amount on gas sensing properties of pure, 1, 2, 3 mol% Ru doped  $\text{SnO}_2$  nanofibers. The gas responses of the sensors based on the four samples to 100 ppm acetone were tested at different operating temperatures from 167 to 239 °C, as shown in Fig. 6. Obviously, the relation curves of response to operating temperature of all samples exhibited a volcano-shaped, and the optimal operating temperature of every sample was 200 °C. In addition, we could observe that the gas response was greatly improved after Ru doping. The gas responses of the sensors based on the pure, 1, 2 and 3 mol% Ru-doped  $\text{SnO}_2$  to

100 ppm acetone at 200 °C were 10.0, 33.6, 118.8, and 52.0, respectively. The results indicated that the optimal doping amount was 2 mol% according to the highest response (118.8) to 100 ppm acetone of sensors based on 2 mol% Ru-doped  $\text{SnO}_2$ , and the response value was about 12 times higher than that of pure  $\text{SnO}_2$ . The maximum response to 100 ppm acetone decreased to 52.0, while increased the Ru doping amount to 3 mol%. However, the response was still 5.2 times higher than that of the pure  $\text{SnO}_2$  sensor.

Fig. 7(a) showed the dynamic response characteristics of sensors based on the 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers to 100 ppm acetone at 200 °C. We could observe from the figure that the sensor exhibited a continuous and intact response-recovery curve with a short response

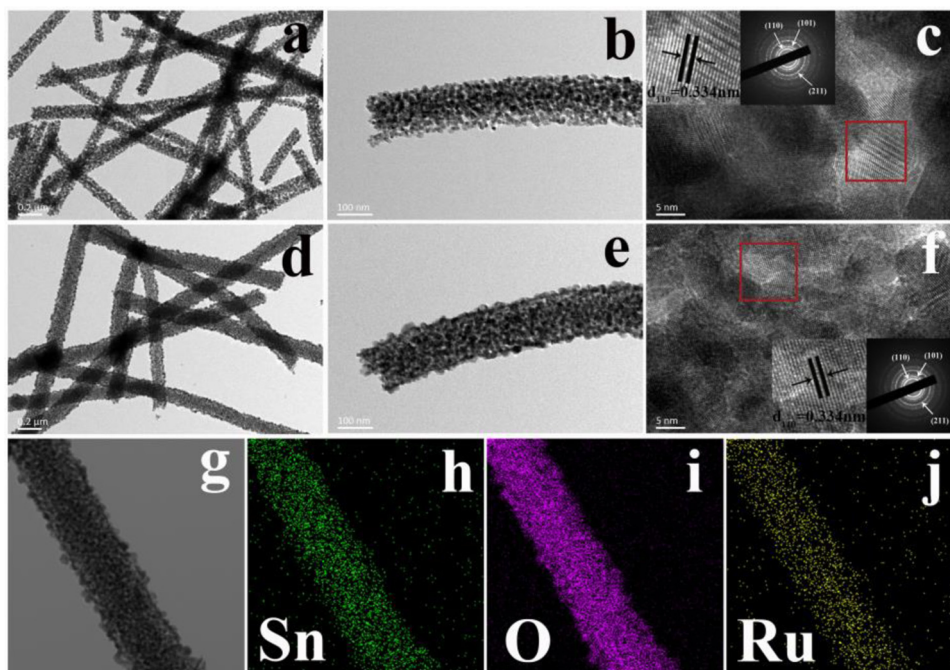


Fig. 5. TEM images of (a–c) pure  $\text{SnO}_2$  nanofibers, (d–f) 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers, and (g–j) EDS elemental mapping images of Sn, O and Ru in 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers.

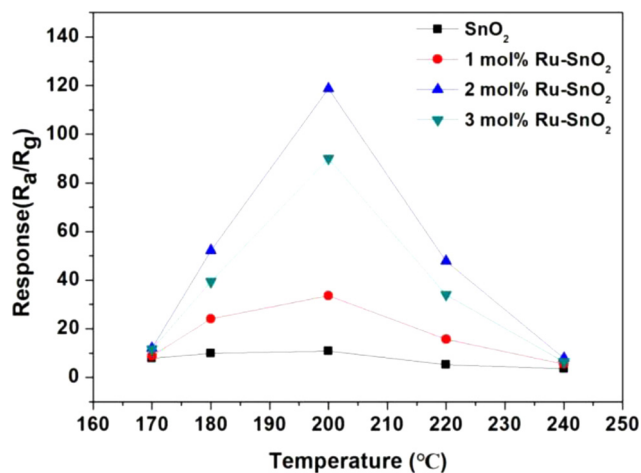


Fig. 6. Response of sensors based on pure and 1, 2, 3 mol% Ru-doped  $\text{SnO}_2$  nanofibers to 100 ppm acetone as a function of the operating temperature.

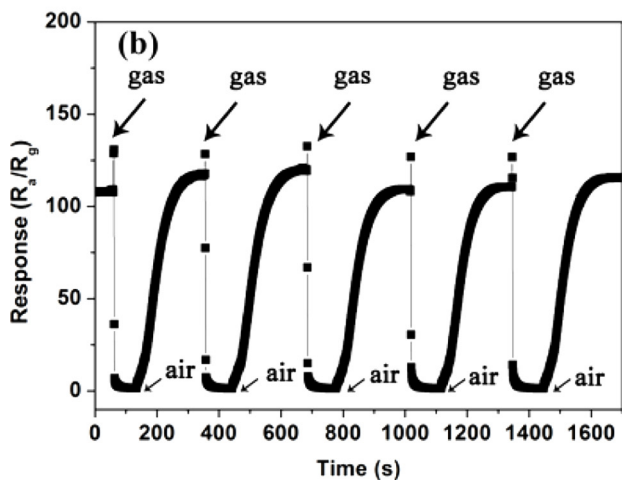
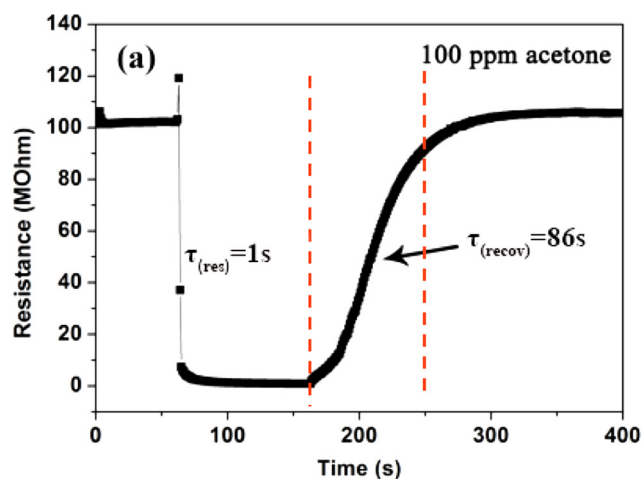


Fig. 7. (a) Response and recovery curves. (b) Five reversible cycles of the response curves with little deviation were shown in Fig. 7(b), which fully illustrated that the sensor exhibited an excellent stability and repeatability.

time of 1 s and recovery time of 86 s. Then, five reversible cycles of the response curves with little deviation were shown in Fig. 7(b), which fully illustrated that the sensor exhibited an excellent stability and repeatability.

The dynamical response-recovery curves of sensors based on pure  $\text{SnO}_2$  and 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers toward different concentration of acetone at 200 °C were shown in Fig. 8(a). We could

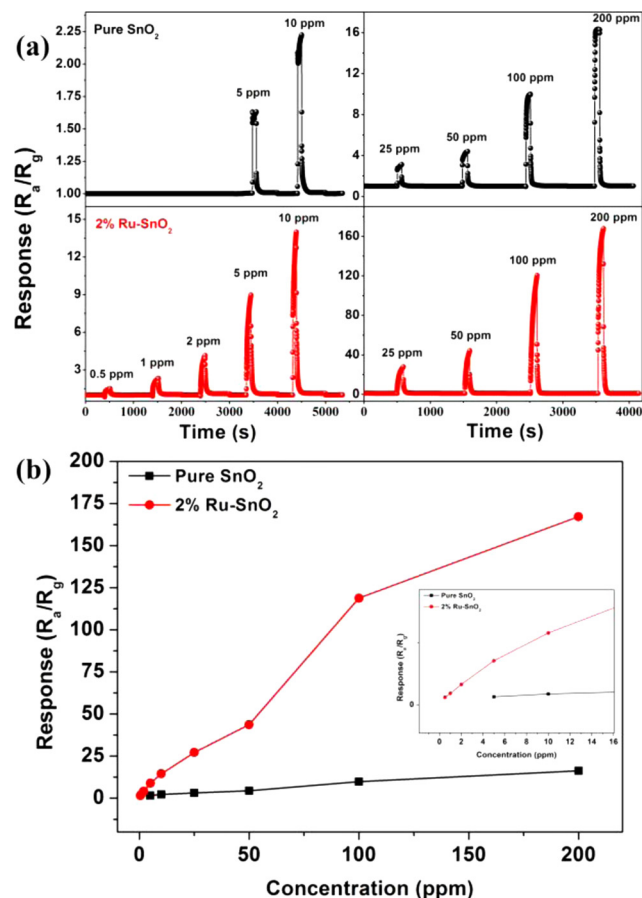


Fig. 8. (a) The dynamic response curves of sensors based on pure  $\text{SnO}_2$  and 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers versus acetone concentration in the range of 0.5–200 ppm at 200 °C (b) is the corresponding linear graph of (a).

observe that the responses to acetone of the two sensors enhanced while we increased the concentrations of the acetone gas. In addition, it was obviously that the response of the sensor based on 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers was greatly higher than that of the pure  $\text{SnO}_2$  nanofibers. Fig. 8(b) showed the corresponding linear graph of Fig. 8(a). The responses of sensor based on pure  $\text{SnO}_2$  nanofibers were 1.6, 2.2, 3.1, 4.4, 9.9, 16.3 to 5, 10, 25, 50, 100, 200 ppm acetone, while the responses of sensor based on 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers were 8.9, 14.5, 27.1, 43.7, 118.8, 167.2 to 5, 10, 25, 50, 100, 200 ppm acetone, respectively. In addition, the minimum acetone detection limit of the sensor based on 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers was measured as 0.5 ppm, while the minimum acetone detection limit of the pure one was measured as 5 ppm. It is worth noting that the response of the sensor based on 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers did not tend to be saturated when the acetone concentrations were raised to 200 ppm, which indicated that the sensor was suitable for a wide range of acetone detection. Therefore, the results proved that the sensor based on 2 mol % Ru-doped  $\text{SnO}_2$  nanofibers exhibited not only a good response-recovery properties, but also a wide detection range.

Subsequently, the gas responses of sensors based on pure  $\text{SnO}_2$  and 2 mol% Ru-doped  $\text{SnO}_2$  nanofibers to 100 ppm of seven VOCs at 200°C were tested. The test VOCs were ethanol ( $\text{C}_2\text{H}_6\text{O}$ ), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), methanol ( $\text{CH}_4\text{O}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), toluene ( $\text{C}_7\text{H}_8$ ), benzene ( $\text{C}_6\text{H}_6$ ) and xylene ( $\text{C}_8\text{H}_{10}$ ). As shown in Fig. 9, the sensor based on 2 mol% Ru-doped  $\text{SnO}_2$  samples exhibited enhanced response for each test gas compared with the pure  $\text{SnO}_2$ . Additionally, the response of the sensor based on 2 mol% Ru-doped nanofibers to acetone were visibly higher than other gases, having a response of 118.8–100 ppm acetone, which was 12 times higher than pure  $\text{SnO}_2$  at 200 °C. Meanwhile, the

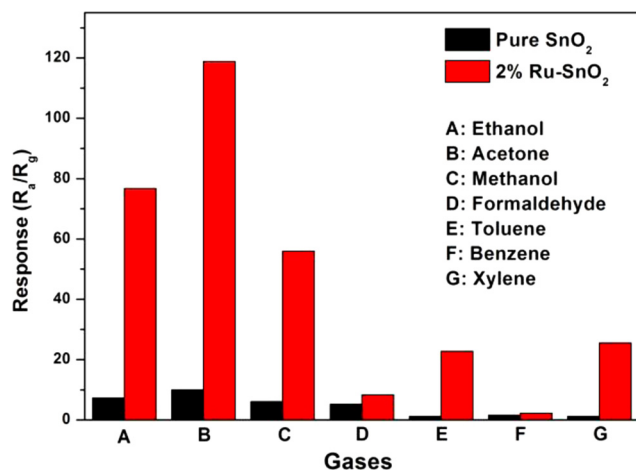


Fig. 9. Gas responses of sensors based on pure SnO<sub>2</sub> and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers to 100 ppm various target gases at 200°C.

responses to 100 ppm ethanol ( $R_a/R_g = 76.7$ ), methanol ( $R_a/R_g = 55.9$ ), formaldehyde ( $R_a/R_g = 8.28$ ), toluene ( $R_a/R_g = 22.8$ ), benzene ( $R_a/R_g = 2.2$ ) and xylene ( $R_a/R_g = 25.5$ ) at 200 °C were also enhanced by Ru doping. So, it was indicated that the sensors based on Ru-doped SnO<sub>2</sub> nanofibers could detect acetone, selectively.

### 3.3. Mechanism of the enhanced gas sensing performance

In consideration of the fact that the gas sensing properties of gas sensor are greatly influenced by the carrier concentration and the chemisorbed oxygen species on the surface of the sensing materials, we investigated the electrical conductivity and the distribution of chemisorbed oxygen species of the pure and Ru-doped SnO<sub>2</sub> nanofibers [39]. First, we examined the electrical conductivity of pure and Ru-doped SnO<sub>2</sub> samples in air ( $R_a$ ), the results showed that the resistances of the sensors increased after Ru doping. The resistance of sensor based on pure SnO<sub>2</sub> was 0.05 MΩ at 200 °C while the resistance of sensor based on 2 mol% Ru-doped SnO<sub>2</sub> was 102.2 MΩ at the same temperature. The increase of  $R_a$  after Ru doping might be due to the decrease of the grain size of SnO<sub>2</sub>. From the results of FESEM and XRD, we knew that Ru doping could effectively inhibit the grain growth of SnO<sub>2</sub>. It was reported that the resistance of the oxide semiconductor would increase when the grain size decrease, meanwhile resulting in an improvement of the gas sensing properties of the gas sensor [41]. In addition, Fig. 10

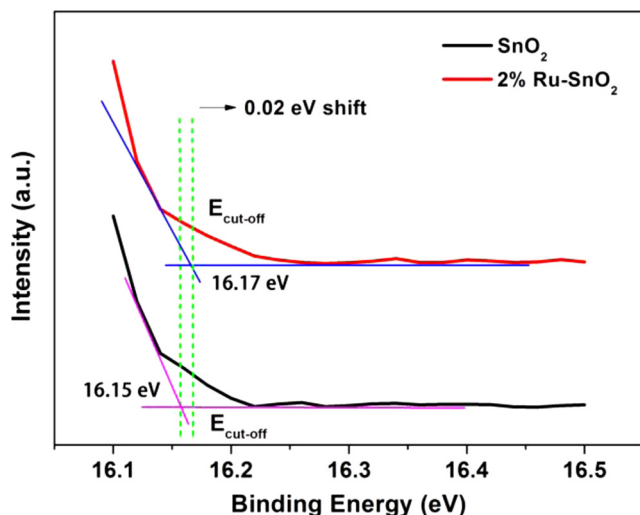


Fig. 10. UPS spectras of pure and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers.

showed the UPS results of pure SnO<sub>2</sub> and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers. The curves of the cut-off edges of the two samples were given by the results and according to the equation that  $\phi = h\nu - E_{cut-off}$ , we calculated the work function ( $\phi$ ) of 2 mol% Ru-doped SnO<sub>2</sub> (21.22–16.17 eV = 5.05 eV) is smaller than that of pure SnO<sub>2</sub> (21.22–16.15 eV = 5.07 eV). Since the work function of oxide semiconductor nanomaterials was less than the electron affinity potential of oxygen, the oxygen molecules could grab electrons from the conduction band and increase the resistance of oxide semiconductor nanomaterials. The smaller work function of oxide semiconductor meant that more electrons could participate in the transfer, which led to further increase of the resistance [40]. Additionally, the lower electron concentration of the Ru-doped SnO<sub>2</sub> nanofibers could be equivalent to the larger Debye length than that of pure SnO<sub>2</sub> nanofibers. According to the space charge model of n-type oxide semiconductor based gas sensors, when the grain size of the sensing materials was below or equal to twice of the Debye length, the space charge layer of the grain surface completely exhausted, which could improve the gas sensing properties of the sensing materials, significantly [41].

To further investigate the cause of the improvement in gas sensing properties of Ru-doped SnO<sub>2</sub> nanofibers, XPS analysis were performed. The high-resolution spectras of Sn 3d were shown in Fig. 11(a). The peaks occurred at 486.58 and 495.03 eV, which were assigned to Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> corresponded to oxidation state +4 of tin atoms [42]. The binding energies of the Sn 3d<sub>5/2</sub> peaks of 2 mol% Ru-doped SnO<sub>2</sub> samples (486.68 eV) were 0.1 eV higher than that of pure SnO<sub>2</sub> (486.58 eV). The peaks shift to high binding energy were caused by the loss of electrons in SnO<sub>2</sub> after Ru doping, confirming the incorporation of Ru into the SnO<sub>2</sub> lattice. Fig. 11(b) showed the spectras of Ru 3p of 2 mol% Ru-doped SnO<sub>2</sub> and pure SnO<sub>2</sub> samples. Compared with pure SnO<sub>2</sub>, the Ru related peaks of 2 mol% Ru-doped SnO<sub>2</sub> was certainly detected while it was not detected in pure SnO<sub>2</sub>. The peak of Ru 3p<sub>3/2</sub> was occurred at 463.2 eV, corresponding to oxidation state +4 of Ru atoms. In addition, Fig. 11(c)–(d) were the spectras of O 1s of pure SnO<sub>2</sub> and 2 mol% Ru-doped SnO<sub>2</sub>. From the figure we could observe the O 1s peaks were asymmetric and could be decomposed into three different components, which occurred at  $529.5 \pm 0.4$  eV,  $531.2 \pm 0.6$  eV, and  $532.5 \pm 0.2$  eV, corresponding to lattice oxygen ( $O_L$ ), oxygen vacancy ( $O_V$ ), and chemisorbed oxygen species ( $O_C$ ), respectively [43]. Furthermore, the percentages of  $O_L$ ,  $O_V$ , and  $O_C$  components were 44.02, 21.32, and 34.66% in the pure SnO<sub>2</sub>, while they were 14.90, 58.77, and 26.33% in the 2 mol% Ru-doped SnO<sub>2</sub>. Obviously, the  $O_V$  and  $O_C$  were greatly increased after the incorporation of Ru element to SnO<sub>2</sub>. At present, the widely accepted sensing mechanism of oxide semiconductor gas sensors was the change of carrier concentration caused by the oxidation reduction reactions between the chemisorbed oxygen on the surface of the sensing materials and the target gas. The increase of  $O_V$  component could provide more active sites for the oxidation reduction reactions on the surface of the sensing materials. Whereas, the increase of  $O_C$  component meant that more chemisorbed oxygen species could participate in the oxidation reduction reactions on the surface of the SnO<sub>2</sub> nanomaterials and thus resulted in a larger response in the gas sensing properties of sensing materials.

## 4. Conclusion

In summary, pure and 1–3 mol% Ru-doped SnO<sub>2</sub> nanofibers were synthesized through a simple electrospinning technique, combined with calcination treatment. In gas sensing applications, a systematic and comprehensive test was performed. The results indicated that the 2 mol % Ru-doped SnO<sub>2</sub> nanofibers showed greatly enhanced gas sensing performance, specially exhibiting an excellent sensibility to acetone gas. At last, according to the results of XPS and UPS, we analyzed the changes of the electron concentration and distribution of oxygen component caused by the incorporation of Ru<sup>4+</sup> into SnO<sub>2</sub> nanocrystals played an important role in increase of gas sensing performance. Thus,

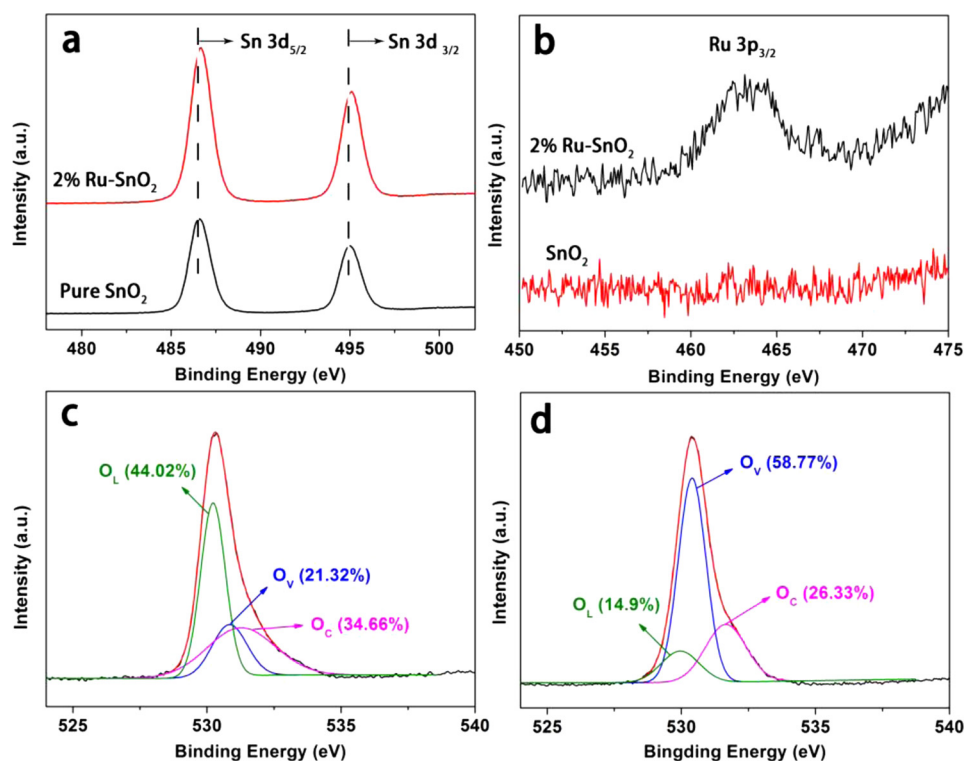


Fig. 11. XPS spectra of SnO<sub>2</sub> nanofibers and Ru-doped SnO<sub>2</sub> nanofibers. (a) Sn 3d for pure and 2 mol% Ru-doped SnO<sub>2</sub>, (b) Ru 3p for Ru-doped samples, (c–d) O 1s XPS spectra of the pure and 2 mol% Ru-doped SnO<sub>2</sub> nanofibers.

the doping of Ru<sup>4+</sup> into SnO<sub>2</sub> nanofibers should be a promising strategy for designing and fabricating high performance acetone gas sensor.

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