Effects of Pt Content on Room-Temperature Hydrogen Sensing Characteristics of Pt-SnO$_2$ Nano-Composite Ceramics

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Abstract. A series of Pt-SnO$_2$ nano-mixtures with 0, 0.25, 1 and 2.5 wt% Pt separately were prepared using SnO$_2$ nanoparticles and H$_2$PtCl$_6$. Through pressing and sintering, Pt-SnO$_2$ nano-composite ceramics with Pt nanoparticles well dispersed have been successfully prepared from the nano-mixtures. Their resistance is found to increase monotonously and greatly with increasing Pt content, which is increased by three orders of magnitude when Pt is increased from 0 to 2.5 wt%. All those samples with a Pt content show distinct responses to hydrogen at room temperature, while their hydrogen sensitivity and their recovery time both decease dramatically with increasing Pt content. These results strongly suggest that Pt as a catalyst promotes oxygen chemisorption on SnO$_2$ and the reaction between hydrogen and oxygen at room temperature. Pt thus has catalytic effects on both hydrogen and oxygen, which leads to quite complicated effects of Pt content on the room-temperature hydrogen sensing behaviors of semiconducting metal oxides.

1. Introduction

As a clean and renewable energy carrier, hydrogen has been receiving more and more attention and being applied in more and more automobiles in recent years [1]. However, hydrogen is very dangerous because it is odorless, colorless, and explosive in air over a large concentration range of 4%-75%. The rapidly increasing quantity of hydrogen automobiles has caused much concern over hydrogen safety [2]. Nowadays, all commercial hydrogen sensors are not quite satisfactory for hydrogen automobiles in one way or another. For example, commercial hydrogen sensors based-on SnO$_2$ thick films are generally considered most suitable for hydrogen automobiles due to their low cost, high stability in harsh environment and simplicity of fabrication and use [3]. Unfortunately, they have to work at elevated temperatures (around 400 ℃) [4], which brings additional security risks and increases energy consumption [5]. Extensive investigations have been conducted to develop semiconducting metal oxide (MOX) hydrogen sensors that can work at room temperature.

In the past few years, several Pt-MOX composite ceramics have been surprisingly found to possess extraordinary room-temperature hydrogen sensing capabilities [6-10]. As bulk materials, they are promising to be applied as room-temperature MOX hydrogen sensors and should be studied systematically. Generally speaking, Pt in the composites is believed to decompose hydrogen molecules into hydrogen atoms, which are chemisorbed on MOXs at room temperature and result in the observed room-temperature hydrogen sensing capabilities. According to a recent investigation, for Pd-SnO$_2$ composite ceramics [11], there exists an intriguing interaction between Pd and SnO$_2$ at high

temperatures, whose product of Pd^{4+} leads to an unexpected room-temperature CO sensing capability for the composite [12]. Presently, we have conducted a study on the effects of Pt content on room-temperature hydrogen sensing characteristics of Pt-SnO_2 nano-composite ceramics, which first reveals that Pt has a catalytic effect on oxygen other than hydrogen chemisorption on SnO_2 for Pt-SnO_2 system. The results reported in this paper should be important not only for mechanism study but also for further property improvement of room-temperature MOX hydrogen sensors.

2. Experimental Methods

2.1. Materials Preparation
SnO_2 nanoparticles (70 nm) and zinc powder were dispersed in deionized water at a series of ratios and magnetically stirred. For every suspension, 0.1 M H_2PtCl_6 solution was dropped slowly into the suspension until the molar number of H_2PtCl_6 reached to one third of that of the zinc powder in the suspension. After 4h of stirring, the suspensions were centrifuged and dried in oven at 110 ℃ for 12 h. The dried powders were pressed into cylindrical pellets (~10 mm in diameter and ~1.5 mm thick) at 2 MPa through a hydraulic press with deionized water added as binder. The pellets were sintered in air at 1000 ℃ for 2h, and a pair of rectangular Au electrodes was coated on a major surface of sintered pellets through DC magnetron sputtering for gas sensing measurement.

2.2. H_2 Sensing Measurement
A commercial gas sensing measurement system (GRMS-215, Partulab Com., Wuhan, China) was used in this study. Samples were placed in a sealed quartz chamber (about 350 mL), which has four gas entrances and a gas outlet to change internal atmosphere. In the response process, specific atmospheres were introduced through mixing O_2, N_2, and 5% H_2 in N_2 at some designed ratios. The total gas flow rate was 300 mL/min. In the recovery process, air was pumped into the chamber at a rate of 1000 mL/min. Through a Keithley 2400 Source/Meter, a DC voltage of 10 V was applied between the Au electrodes of the samples and the flown electric current was recorded. The room temperature was kept at 25 ℃ and the relative humidity (RH) in air was measured.

2.3. Materials Characterization
X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (BRUKER AXS D8 ADVANCE) using Cu $K\alpha$ radiation. Microstructural analyses were performed through a scanning electron microscopy (SIRION TMP). Energy dispersive spectroscopy (EDS) analyses were recorded through OXFORD Aztec 250 instrument.

3. Results and Discussion

3.1. Phase and Microstructural Analyses
The following reactions occur when a H_2PtCl_6 solution is dropped into a suspension of SnO_2 nanoparticles and zinc powder:

$$Pt^{4+} + 2Zn \rightarrow Pt + 2Zn^{2+} \tag{1}$$

$$2H^+ + Zn \rightarrow H_2 + Zn^{2+} \tag{2}$$

In this way, one mole H_2PtCl_6 reacts with three mole Zn and metallic Pt is deposited on SnO_2 nanoparticles. This method has been widely used to prepare nano-mixtures of noble metals (e.g. Pd, Pt) and MOXs, where the noble metals are usually a few nanometers in size [13, 14]. In this study, we have prepared a series of nano-mixtures of Pt-SnO_2, whose Pt content was 0, 0.25, 1 and 2.5 wt%, separately.

Figure 1 shows the X-ray diffraction patterns taken for the surface of four sintered pellets prepared from this series of Pt-SnO_2 nano-mixtures. For all samples, all strong peaks are from rutile SnO_2. For the samples of 1 and 2.5 wt% Pt, two small peaks from Pt can be observed. It indicates that the Sintered pellets we obtained are composites of SnO_2 and Pt, though the peaks of Pt cannot be seen for

the pellet of 0.25 wt% Pt due to its low Pt content. As a matter of fact, Pt is well known for its high stability at high temperatures.
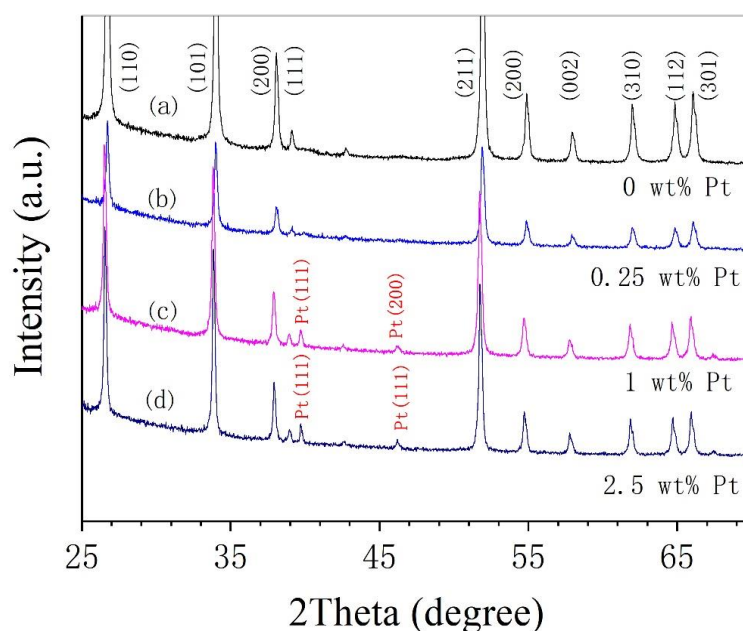

Figure 1. X-ray Diffraction Patterns Taken for the Surface of Four Sintered Pellets Prepared from Pt-SnO_2 Nano-Mixtures with 0, 0.25, 1 and 2.5 wt% Pt, Separately

As for microstructure, the four kinds of sintered pellets are very similar. Figure 2 shows an SEM micrograph with EDS analyses for a sample of 2.5 wt% Pt sintered at 1000 ℃ for 2 h in air. Some previous studies have clearly shown that the grain-growth of SnO_2 nanoparticles is very limited when the ceramics are sintered at temperatures as high as 1000 ℃. Most grains in this micrograph are also around 100 nm in size and the microstructure appears relatively dense for a low magnification. It should be pointed out, however, that there was actually no shrinkage in diameter after the pellets were sintered at 1000 ℃ and numerous nanoscale pores can be observed in the microstructure for high magnifications. The EDS analyses clearly show that Pt is rather uniformly dispersed. Due to their small size, however, Pt nanoparticles cannot be directly observed in the SEM micrograph. Obviously, through a very simple and convenient process, we have obtained Pt-SnO_2 nano-ceramics with numerous nanoscale pores and with Pt rather uniformly dispersed, which should be highly attractive for gas sensing applications.

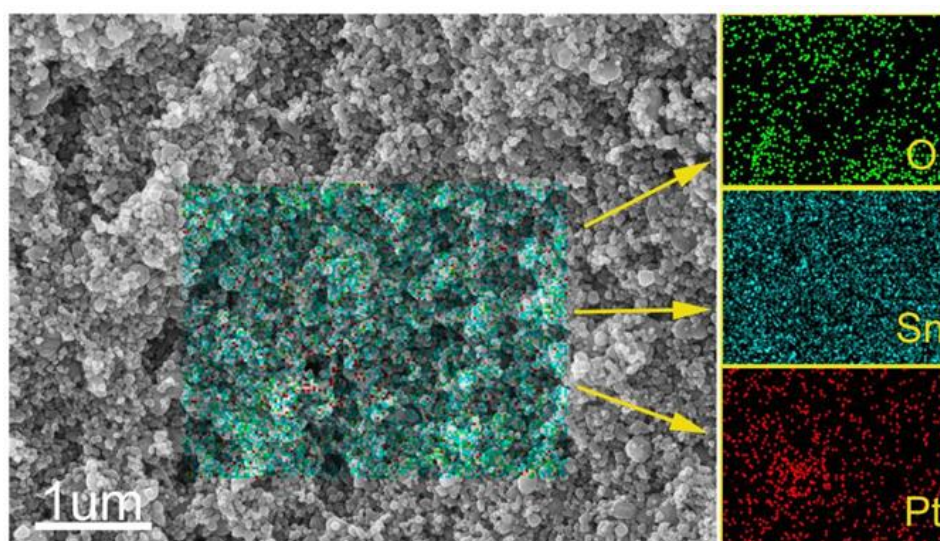**Figure 2.** SEM Micrograph with EDS Analyses for a Pt-SnO$_2$ Nano-Ceramic Sample of 2.5 wt% Pt Sintered at 1000 ℃ for 2 h in Air

3.2. Room-temperature Hydrogen Sensing Characteristics

Extraordinary room-temperature hydrogen sensing capability has been reported for Pt-SnO$_2$ composite nano-ceramics in some previous researches [8,10]. In accordance with these researches, these three kinds of samples with 0.25, 1 and 2.5 wt% Pt separately prepared in this study all respond dramatically to hydrogen at room temperature, while the samples with no Pt exhibit no response to hydrogen at room temperature, as shown in figure 3. It has been proposed that Pt as a catalyst splits hydrogen molecules into atoms, which are chemisorbed on SnO$_2$ and decrease the resistance of SnO$_2$ at room temperature. Obviously, the interaction between hydrogen and Pt plays a vital role in the observed room-temperature hydrogen sensing capability.
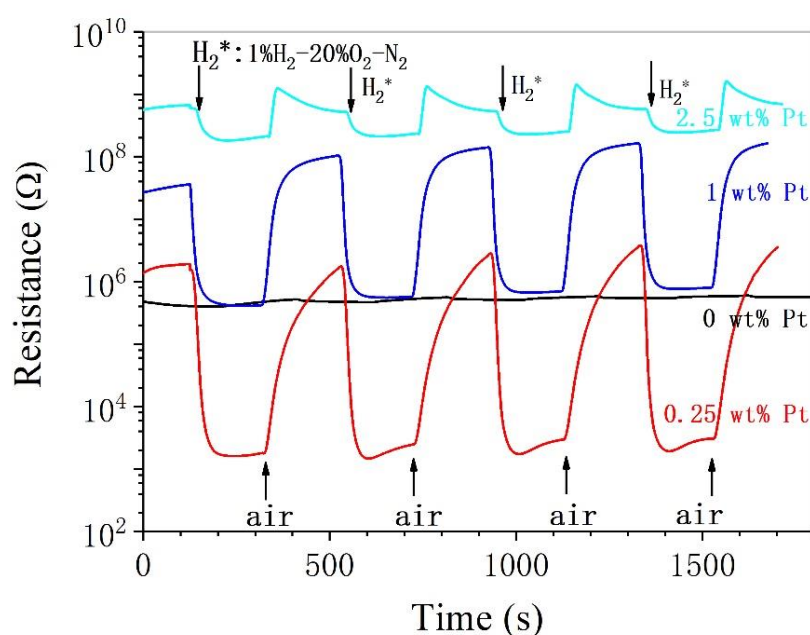

Figure 3. Room-temperature Response to 1.0% H$_2$-20% O$_2$-N$_2$ and Recovery in Air of 41% RH for Four Pt-SnO$_2$ Nano-Ceramic Samples with 0, 0.25, 1 and 2.5 wt% Pt, Separately
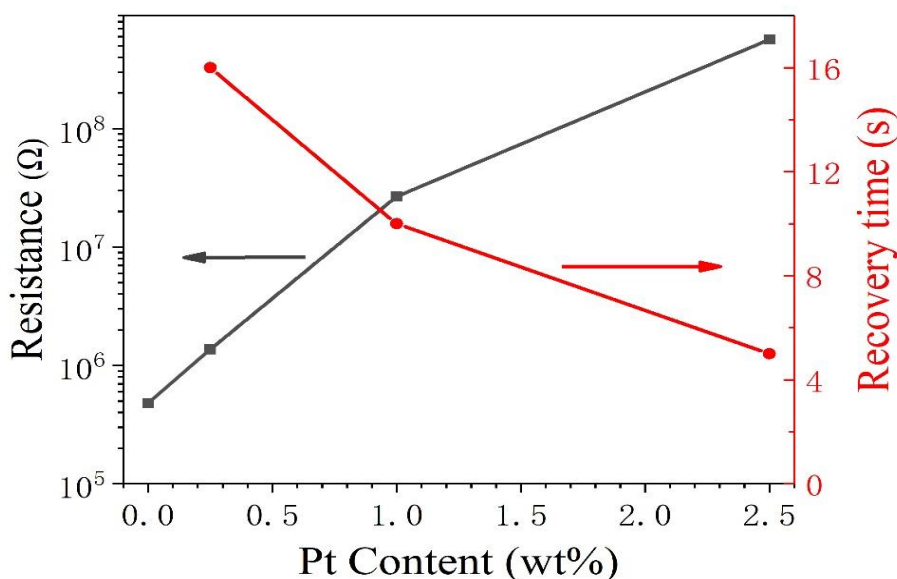
Figure 4. Resistance Dependence on Pt Content for Pt-SnO$_2$ Nano-Composite Ceramics with 0, 0.25, 1 and 2.5 wt% Pt Separately; Recovery Time Dependence on Pt Content for Pt-SnO$_2$ Nano-Composite Ceramics with 0.25, 1 and 2.5 wt% Pt Separately

It is interesting to further compare these four kinds of ceramics with different Pt contents. First of all, it can be clearly seen that their resistance in air increases steadily with increasing Pt content, as shown in figure 4. The resistance of the samples with 2.5 wt% Pt is three orders of magnitude larger than that of the samples with no Pt. Secondly, though Pt is the key to the observed room-temperature hydrogen sensing capability, the hydrogen sensitivity decreases with increasing Pt content among those three kinds of samples with 0.25, 1 and 2.5 wt% Pt separately. Thirdly, the recovery time in air decreases obviously with increasing Pt content among those three kinds of samples with a Pt content, as shown in figure 4. All these results demonstrate that Pt has more complicated effects on room-temperature hydrogen sensing behaviour of Pt-SnO$_2$ system than its catalytic effect on H$_2$.

It is well known that the resistance of SnO$_2$ is greatly increased by oxygen chemisorption, by which an electron-depleted layer is formed and the concentration of free electrons is decreased [15,16]. The great difference in resistance among Pt-SnO$_2$ composite nano-ceramics with different Pt contents strongly suggests that Pt is able to dramatically promote oxygen chemisorption on SnO$_2$. With increasing Pt content, more oxygen is chemisorbed on SnO$_2$ in a more rapid speed, so the resistance is increased and the recovery time in air is decreased. Moreover, Pt must also be able to promote the reaction between oxygen and hydrogen. So with increasing Pt content, less hydrogen is chemisorbed on SnO$_2$ and the hydrogen sensitivity is decreased. Both hydrogen sensitivity and recovery speed are important for hydrogen sensing, it is thus important to optimize the Pt content for Pt-SnO$_2$ composite nano-ceramics to achieve attractive overall room-temperature hydrogen sensing capability.

4. Conclusions

Pt-SnO$_2$ nano-mixtures with 0, 0.25, 1 and 2.5 wt% Pt separately were prepared using SnO$_2$ nanoparticles, zinc powder and H$_2$PtCl$_6$ through a replacement reaction. Pt-SnO$_2$ composite nano-ceramics with Pt nanoparticles well dispersed have been successfully prepared from these Pt-SnO$_2$ nano-mixtures. The resistance increases monotonously and greatly with increasing Pt content for all samples. And for those samples with a Pt content, obvious room-temperature hydrogen sensing behaviors are observed, which depend dramatically on the Pt content. With increasing Pt content, both their hydrogen sensitivity and their recovery time in air decease steadily. It is proposed that Pt as a catalyst promotes not only hydrogen chemisorption but also oxygen chemisorption on SnO$_2$ and also

the reaction between hydrogen and oxygen. Pt thus has rather complicated effects on the room-temperature hydrogen sensing behaviors of MOXs and its content must be optimized to obtain overall attractive room-temperature hydrogen sensing capacity for MOXs.

5. Acknowledgments

6. References

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