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

Caochuang Wang$^1$, Pengcheng Li$^1$, Yongming Hu$^2$, Liqun Xu$^3$, Zhen Zhou$^3$ and Wanping Chen$^1$

1 School of Physics and Technology, Wuhan University, Wuhan 430072, China
2 Hubei Key Laboratory of Ferro and Piezoelectric Materials and Devices, Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, China
3 Huaneng Wuhan Power Generation Co., Ltd., Wuhan 431415, China
Email: wpchen@whu.edu.cn

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 °C) [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$_2$PtCl$_6$ solution was dropped slowly into the suspension until the molar number of H$_2$PtCl$_6$ 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 °C 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 °C 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 °C 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 Ka 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$_2$PtCl$_6$ solution is dropped into a suspension of SnO$_2$ nanoparticles and zinc powder:

\[ Pt^{4+} + 2Zn \rightarrow Pt + 2Zn^{2+} \]  

\[ 2H^+ + Zn \rightarrow H_2 + Zn^{2+} \]

In this way, one mole H$_2$PtCl$_6$ 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](image)

**Figure 1.** X-ray Diffraction Patterns Taken for the Surface of Four Sintered Pellets Prepared from Pt-SnO₂ 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 °C for 2 h in air. Some previous studies have clearly shown that the grain-growth of SnO₂ nanoparticles is very limited when the ceramics are sintered at temperatures as high as 1000 °C. 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 °C 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-SnO₂ nano-ceramics with numerous nanoscale pores and with Pt rather uniformly dispersed, which should be highly attractive for gas sensing applications.
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.
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-SnO₂ system than its catalytic effect on H₂.

It is well known that the resistance of SnO₂ 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-SnO₂ composite nano-ceramics with different Pt contents strongly suggests that Pt is able to dramatically promote oxygen chemisorption on SnO₂. With increasing Pt content, more oxygen is chemisorbed on SnO₂ 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 SnO₂ 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-SnO₂ composite nano-ceramics to achieve attractive overall room-temperature hydrogen sensing capability.

4. Conclusions
Pt-SnO₂ nano-mixtures with 0, 0.25, 1 and 2.5 wt% Pt separately were prepared using SnO₂ nanoparticles, zinc powder and H₂PtCl₆ through a replacement reaction. Pt-SnO₂ composite nano-ceramics with Pt nanoparticles well dispersed have been successfully prepared from these Pt-SnO₂ 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 decrease steadily. It is proposed that Pt as a catalyst promotes not only hydrogen chemisorption but also oxygen chemisorption on SnO₂ 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
This work was partially supported by the National Natural Science Foundation of China under Grant 
No. 61274073 and J1210061.

6. References
[1] Rusman N A A and Dahari M 2016 Int. J. Hydrogen Energy 41 12108
[2] Moy R 2003 Science 301 47.
[3] Korotcenkov G 2013 Handbook of Gas Sensor Materials: Properties, Advantages and 
Shortcomings for Applications vol 1 (New York: Springer) p 81
[4] Boon-Brett L, Bousek J, Black G, Moretto P, Castello P and Hubert T 2010 Int. J. Hydrogen 
Energy 35 373.
[5] Hubert T, Boon-Brett L, Black G and Banach U 2011 Sens. Actuators B 157 329
[6] Chen W P, Xiong Y, Li Y S, Cui P, Guo S S, Chen W, Tang Z L, Yan Z J and Zhang Z Y 2016 
Int. J. Hydrogen Energy 41 3307
[7] Li P C, Xiong Z H, Zhu S, Wang M Y, Hu Y M, Gu H S, Wang Y and Chen W P 2017 Int. J. 
Hydrogen Energy 42 30186
[8] Zhu S, Li P C, Wu G T, Li Z Y, Wu P, Hu Y M, Gu H S and Chen W P 2018 Int. J. Hydrogen 
Energy 43 21177
[9] Song C B, Wu G T, Sun B L, Xiong Y, Zhu S, Hu Y M, Gu H S, Wang Y and Chen W P 2017 
Int. J. Hydrogen Energy 42 6420
[10] Xiong Y, Chen W P, Li Z Y, Cui P, Guo S S, Chen W, Tang Z L, Yan Z J and Zhang Z Y 2016 
Nano Res. 9 3528
[11] Wang M Y, Sun B L, Jiang Z Y, Liu Y, Wang X N, Tang Z L, Wang Y and Chen W P 2018 J. 
Nanosci. Nanotechnol. 18 4176
[12] Zhu S, Liu Y, Wu G T, Fei L F, Zhang S H, Hu Y M, Yan Z J, Wang Y, Gu H S and Chen W P 
2019 Sens. Actuators B 285 49
[13] Zhang H, Yang D, Ma X Y, Jiang J Y, Xu J and Que D L 2004 Nanotechnol. 15 622.
[14] Lee J M, Park J, Kim S, Kim S, Lee E and Kim S J 2010 Int. J. Hydrogen Energy 35 12568
[15] Hassan J, Mahdi M, Chin C, Abu-Hassan H and Hassan Z 2013 J. Alloys Compd. 546 107
[16] Heiland G 1988 Chem. Sens. Technol. 1 15