A New Highly Selective H_2 Sensor Based on TiO_2/PtO−Pt Dual-Layer Films

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A new highly selective hydrogen sensor based on TiO_2/PtO−Pt dual-layer films has been prepared. At 180−200 °C, the prepared nanostructured sensor exhibits an excellent selectivity and good sensitivity to H_2 in air but is immune to many other kinds of reductive gases such as CO, NH_3, and CH_4. The sensor can give a faithful response to 1% H_2 in air, while the limitation for detecting H_2 in nitrogen is less than 1000 ppm. Influences of operation temperature and humidity on the sensing performance of the sensor were also investigated. The mechanism of the present sensor was attributed to the partial reduction of Ti^{4+} to Ti^{3+} by hydrogen catalyzed by a thin film of surface-oxidized Pt nanoparticles.

Introduction

Intensive studies have been made on gas sensors based on TiO_2 or SnO_2. Gas selectivity is a very important indicator that measures the ability of a sensor to precisely identify a specific gas in a gaseous mixture, which is a necessary characteristic for developing integrated gas sensor arrays. As an important chemical for many industrial processes, hydrogen leaks easily from systems and is one of the most explosive gases. Therefore, a lot of effort has been put into investigating hydrogen sensors and improving their selectivity.[1−12] It has been reported that covering a metal oxide sensor with a layer of organic or silica membrane as a molecular sieve renders the sensor an improved selectivity to hydrogen, but the decorated sensor still gives responses to the other reductive gases.[8−12] Recently, several selective hydrogen sensors have been reported which are insensitive to some reductive gases such as CO and CH_4 at a low concentration.[1,8] However, NH_3 even at a low concentration usually severely interferes with the detection of H_2.[8] On the other hand, selective detection of hydrogen in air is a more difficult task than that in an inert ambience because O_2 in air usually restrains a sensor from detecting H_2 with a high selectivity and sensitivity.

The gas-sensing performance and structure of a Pt/TiO_{2-x} thin film prepared by evaporating a thin layer of Ti covered with a Pt film 6.5 nm in thickness and oxidation treatment at 900 K has been studied.[13,14] The sensor so prepared is capable of detecting reductive gases at 575 K in a vacuum, but did not exhibit obvious selectivity to H_2. The Pt/TiO_{2-x} film in its activated state is composed of metallic platinum and titania with a discontinuous island structure.

In this paper, we report the preparation and properties of a new highly selective sensor for detecting hydrogen in air. The present gas sensor consists of a continuous porous film of surface-oxidized Pt nanoparticles (PtO−Pt) on a glass substrate and a titania thin film covering the PtO−Pt film. The nanostructured dual-layer films are designed to utilize a process of partial reduction of TiO_2 with hydrogen, which is catalyzed by the PtO−Pt porous film, to induce a change in the concentration of charge carriers in the titania film at relatively low temperatures, which may increase the sensing selectivity for H_2 because H_2 as a reductant is more active than other usual reductive gases. Operated at 180−200 °C, the TiO_2/PtO−Pt dual-layer film sensor exhibits a very high selectivity and good sensitivity toward hydrogen in air, which is a remarkable progress compared with the performance of previously reported titania-based hydrogen sensors.[5−8]

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Experimental Section

Materials. Tetraisopropyl orthotitanate ($Ti(OC_3H_7)_4$) and PPh_3 were purchased from Aldrich Chemical Co. Hexahydrated hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 99%) was purchased from Beijing Hongke Chemical Products Co. Organic solvents and other chemicals of AR grade were used as received. H_2, CO, and NH_3 gases with purities higher than 99.99% were supplied by Beijing Analysis Equipment Co.

Preparation of the PtO−Pt Thin Film. A toluene colloidal solution of PPh_3-modified Pt nanoclusters (PPh_3−Pt) with an average Pt particle size of 1.3 nm was prepared as we reported previously.[15] A piece of glass or quartz substrate (10×10 mm^2) was immersed into this colloidal solution and kept there for 2 days, during which a homogeneous self-assembly film of PPh_3−Pt nanoclusters with a thickness of about 100 nm as measured by SEM was formed on the surface of the glass or quartz substrate. The PPh_3−Pt film on the substrate was washed with toluene, dried at 100 °C, and then annealed in air at 400 °C for 30 min to give a porous PtO−Pt film.

Fabrication of the Sensor. A colloidal solution of titanium oxide was prepared by hydrolyzing $Ti(OC_3H_7)_4$ in an aqueous solution of HNO_3 (0.1mol/L).[16] Nanoparticles of titanium oxide in the obtained colloidal solution have a mean diameter of 4.1 nm with a size distribution from 3.4 to 5.4 nm as determined by TEM measurements.[17] The colloidal solution (0.5 mL) was dropped onto the PtO−Pt film and spun at 1500 rpm for 20 s to form a titanium oxide film on the PtO−Pt film. After being dried in air at 100 °C, the films on the substrate were annealed at 400 °C for 30 min to finish the preparation of a dual-layer film sensor.

Characterization of the Thin Films. Microstructures of the prepared films were studied with a transmission electron microscope (JEM-200CX) and a field emission scanning electron microscope (JSM-6700F). XPS analyses of the prepared films were carried out on a VG ESCA LAB-5 (VG Co.) spectrometer. An Al Kα X-ray source was used and the anode operated at 9 kV and 18.5 mA. The pass energy of the analyzer was fixed at 50 eV. The vacuum of the analysis chamber was about 10^{-7} Pa, and all spectra were measured at a constant analyzer energy mode. The binding energies were calibrated with reference to that of C 1s at 284.8 eV for adventitious hydrocarbon contamination.

Gas Sensitivity Measurements. After two gold wires were attached as electrodes with Ag paste on the surface of a titania film with a distance of 5 mm, the electric current passing through the sensor in different ambiences was measured at demanded temperatures using an electrochemical analyzer at a dc bias of 10 V. The compositions of the sample gases were controlled by mass flow meters. In this work, gas sensitivity is defined as $S = (R_0 - R)/R_0$, where R_0 and R are the measured resistances in air and in the sample gases, respectively.

Results and Discussion

Structure of the Dual-Layer Sensor. To investigate the microstructure of the self-assembly PPh_3−Pt film and the annealed film by TEM, a NaCl crystal substrate instead of a glass substrate was used in the preparation of a PPh_3−Pt thin film using the method described in the Experimental Section. After NaCl was dissolved in water, a piece of the film was transferred onto a TEM grid. Figure 1 shows the TEM photograph of a self-assembly PPh_3−Pt thin film. Pt nanoparticles in the film have an average particle size of 1.3 nm that is the same as the average particle size of Pt nanoparticles in the colloidal solution. The average distance between the close-stacked Pt nanoparticles in the film is less than 1 nm. Large metal aggregations formed by directly contacting the Pt nanocores cannot be observed. XPS measurements revealed that the P species in the PPh_3−Pt film has a P 2p binding energy of 131.4 eV, which is only a little higher than that of PPh_3 (131.0 eV), implying that the Pt nanoparticles are still surrounded by PPh_3 molecules. After the PPh_3−Pt film was heated in air at 400 °C for 0.5 h, PPh_3 in the film decomposed and the PPh_3−Pt film was transformed into a conductive and light-transparent film. Pt particles with a size up to 10 nm formed by the aggregation of the small Pt nanoparticles during the heat treatment can be clearly observed in the TEM photograph of the annealed film (Figure 2a). The electron diffraction pattern of the annealed film (Figure 2b) shows the sharp diffraction points with *d* spacings of 0.226, 0.196, 0.137, and 0.116 nm, respectively, which can be indexed as (111), (200), (220), and (311) reflections of fcc Pt. Diffraction signals from the platinum oxide crystal cannot be observed in the electron diffraction pattern.

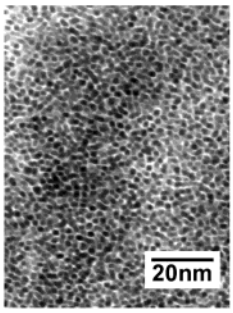

Figure 1. TEM micrograph of a self-assembly thin film of PPh_3−Pt nanoclusters.

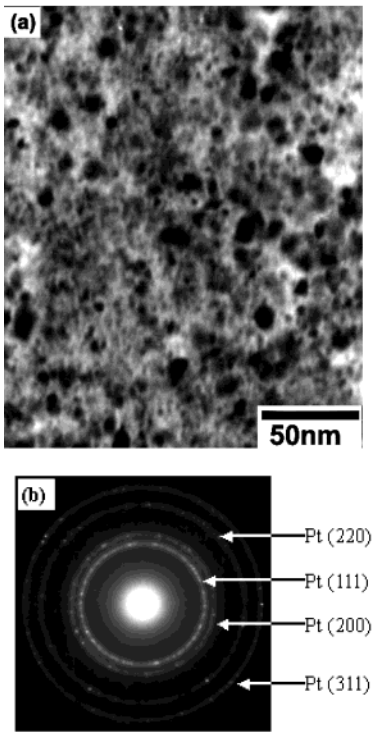

Figure 2. TEM micrograph (a) and electron diffraction pattern (b) of a PtO−Pt film annealed in air at 400 °C for 0.5 h.

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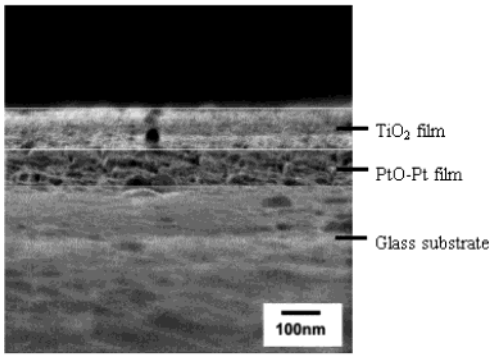

Figure 3. HRSEM photograph of the cross-section of the TiO_2/PtO−Pt dual-layer films supported on a glass substrate.

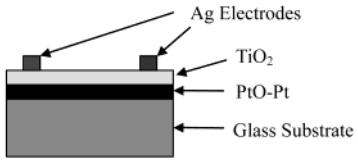

Figure 4. Scheme of the cross-section of a prepared dual-layer sensor.

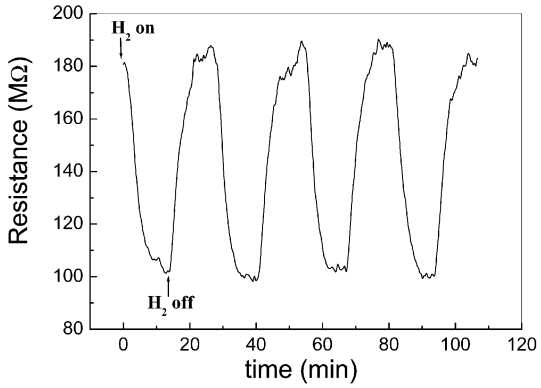

Figure 5. Sensing resistance vs time for exposures of air containing 2.0% hydrogen. The operating temperature is 200 °C.

However, XPS measurements revealed that the Pt $4f_{7/2}$ binding energy of the Pt species in the annealed film has a value of 72.4 eV that is 1.5 eV higher than that of metallic Pt (70.9 eV) but is lower than that of PtO (73.8 eV) by 1.4 eV. From the TEM and XPS experiment results, it can be concluded that the annealed metal film is composed of Pt nanoparticles covered with a thin layer of platinum oxide.

Figures 3 and 4 show an SEM photograph and a scheme of the cross-section of the prepared TiO_2/PtO−Pt dual-layer sensor, respectively. From Figure 3, it can be seen that the titania and PtO−Pt films are 110 and 100 nm in thickness, respectively. Holes with diameters of several tens of nanometers can be clearly observed in the PtO−Pt film, whereas the tiny holes in the titania film cannot be observed in the SEM micrograph since the resolution of SEM is not high enough.

Performance of the Prepared Gas Sensor. Figure 5 shows the response ability to H_2 in air of the prepared TiO_2/PtO−Pt dual-layer sensor. When an air flow containing 2.0% H_2 was introduced into the system at 200 °C, the measured resistance of the dual-layer sensor decreased from about 180 to 100 MΩ, whereas after the hydrogen gas was turned off, the resistance reverted to

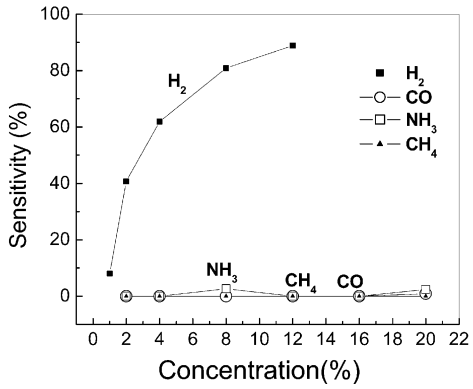

Figure 6. Gas sensitivities of the TiO_2/PtO−Pt dual-layer sensor to H_2, NH_3, CO, and CH_4 in air.

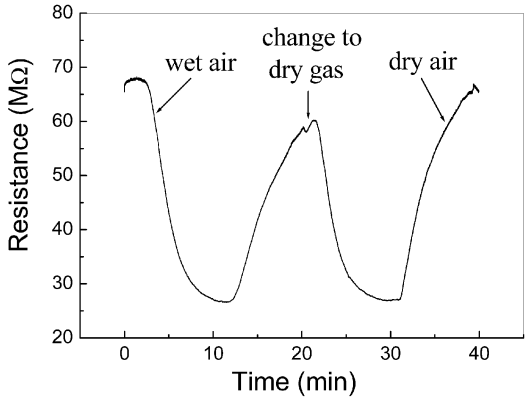

Figure 7. Sensitivity to 4.0% H_2 in dry and wet air at 200 °C. The thickness of the titania film is about 50 nm.

the initial value as shown in Figure 5. This response cycle can be repeated faithfully again and again. The sensing process of the prepared hydrogen sensor is therefore reversible and repeatable.

Sensitivities of the dual-layer sensor to different reductive gases at 200 °C are shown in Figure 6. It can be observed from Figure 6 that the sensing sensitivities toward CO, NH_3, and CH_4 are quite low and independent of the gas concentrations. In contrast, the sensor is quite sensitive to H_2, and the sensitivity to hydrogen strongly depends on the hydrogen concentration in air, indicating that the sensor has a very high selectivity to hydrogen in air, and is capable of semiquantitatively measuring the concentration of H_2 in air within a range from 1% to 10%. When the sensor is operated in N_2 ambience, the detecting limitation for H_2 is less than 1000 ppm. It should be mentioned that, using a usual Pt metal film instead of the nanostructured platinum film, we could not prepare a dual-layer sensor due to the failure of preparing a TiO_2 thin film without cracks on the Pt metal film, which caused a direct contact between the Ag electrodes and the Pt film.

The influence of humidity on the sensing properties of the present sensor was investigated by comparing the response abilities of a prepared dual-layer sensor to H_2 in dry air and wet air obtained by passing an air flow through water in a vessel at room temperature. The influence of humidity on the sensing process is negligible at this condition as shown in Figure 7.

Figure 8 shows the temperature influence on the sensitivities to different reductive gases. The sensitivity to hydrogen increases with operating temperature up

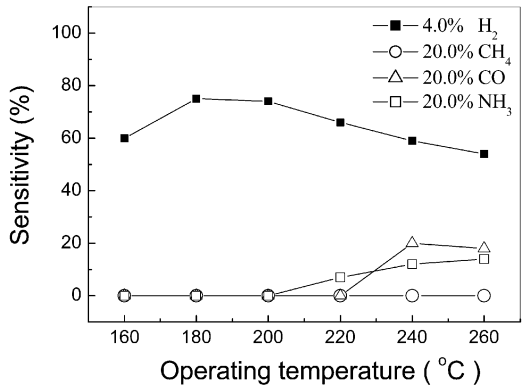

Figure 8. Influences of the operating temperature on the sensitivities to different reductive gases in air.

to 180 °C; however, when the temperature is higher than 200 °C, the sensitivity decreases gradually with increasing operating temperature. Responses to NH_3, CO, and CH_4 in air cannot be observed at temperatures lower than 200 °C; however, when the operating temperature is increased to 240 °C, responses to NH_3 and CO with a sensitivity of about 20% can be observed. Therefore, the optimum operating temperature of the present sensor for detecting H_2 with a high selectivity is in the range from 180 to 200 °C. The working temperature of the prepared sensor is much lower than that of hydrogen sensors based on TiO_2 reported previously,[5,7] although it is higher than that of a hydrogen sensor made from Pd mesowires.[1] It should be mentioned that, in many real applications, a previous heat treatment at a temperature above 200 °C is necessary for removing adsorbed contaminants. Therefore, the stability to heat is also an important factor for a reliable sensor. For the present dual-layer sensor, a previous heat treatment at 400 °C in air does not influence its sensing properties, suggesting an excellent stability to heat.

The present H_2 sensor exhibits satisfactory selectivity, sensitivity, and stability. However, it seems that further attempts are needed to improve the response speed several to 10 times before the sensor can be put into real application. We believe that embedding suitable catalysts in the layer of TiO_2 or optimizing the structure of the new type of sensors may improve the response speed remarkably.

Sensing Mechanism of the TiO_2/PtO−Pt Dual-Layer Films. The resistance of the PtO−Pt film is much lower than that of the titania film. At 200 °C, the measured surface resistance of the PtO−Pt film is 1.4 MΩ, whereas the surface resistance of a titania film directly coated on a glass substrate measured by the same method is about 310 MΩ at 200 °C in air containing 4% H_2. The sensor resistance in the same condition is less than 100 MΩ, implying that the measured electric current passes through the sensor in a way perpendicular to the surface of the sensor. To confirm this speculation, we interrupt the conductive path in the PtO−Pt film by making an insulated space of about 0.1 mm width between the electrodes before coating the titania film on the PtO−Pt film. In this case, the measured sensor resistance is increased 10 times, proving that the conductive path of the TiO_2/PtO−Pt sensor, during its operation, is double the thickness of the titania film.

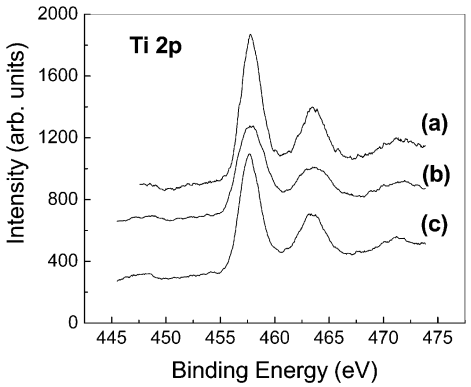

Figure 9. Ti 2p XPS spectra of the sensor treated at different conditions: (a) untreated; (b) treated at 200 °C in air containing 10.0% hydrogen for 10 min; (c) reoxidized in air at 200 °C for 10 min.

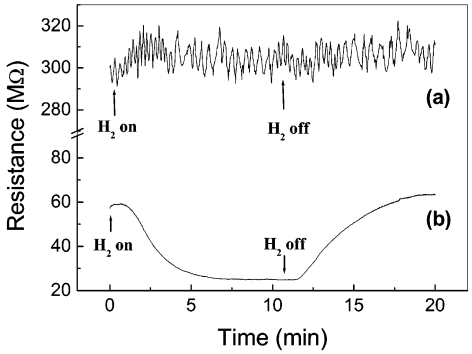

Figure 10. Sensitivity of TiO_2 (a) and TiO_2/PtO−Pt (b) films to 4.0% hydrogen in air at 200 °C.

The sensing mechanism of the present TiO_2/PtO−Pt sensor can be attributed to a partial reduction of Ti^{4+} in the titania film to Ti^{3+} by hydrogen in the presence of the PtO−Pt thin film as a catalyst at 200 °C as we designed. Direct evidence for this mechanism was found from XPS measurements on the sensor before and after heating at 200 °C in air containing 10% H_2 (Figure 9). After being treated with air containing hydrogen at 200 °C for 10 min, the full width at half-maximum (fwhm) of the Ti $2p_{3/2}$ peak centered at 457.8 eV increased from 1.7 to 2.2 eV, indicating the creation of Ti^{3+} ions and formation of surface oxygen vacancies in the film of titania nanoparticles.[18,19] The fwhm value of the Ti $2p_{3/2}$ peak reverted to 1.7 eV after reoxidation in air at 200 °C for 10 min, suggesting that the formed surface oxygen vacancies by the reduction of H_2 in the film of titania nanoparticles had been exhausted. In a real detection process, the sensor resistance is determined by an equilibrium between the formation and elimination of the charger carriers.

Figure 10 shows the responses to H_2 (4%) in air of a titania film and the TiO_2/PtO−Pt film at 200 °C. The TiO_2/PtO−Pt film exhibited a quite good sensitivity, and in contrast, the titania film did not show any observable response, indicating that the PtO−Pt film has a catalytic function for the partial reduction of the covered titania film.

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The mechanism proposed above can well explain the effects of temperature and ambiences on the sensing properties of the prepared TiO_2/PtO−Pt sensor and is helpful for improving the response speed of the new type of sensors in a further study.

Conclusion

A hydrogen sensor composed of dual-layer films of titania and PtO−Pt nanoparticles was prepared for the first time, and exhibits a high selectivity and good sensitivity to hydrogen in air. The sensor can be used to semiquantitatively measure the concentration of H_2 in air within a range from 1% to 10% but does not respond to CO, NH_3, and CH_4. The optimum working temperature for detecting H_2 with an excellent selectivity is in the range from 180 to 200 °C. XPS studies on the prepared sensor proved that the partial reduction of Ti^{4+} to Ti^{3+} and formation of surface oxygen vacancies in the film of titania nanoparticles is an important factor in the sensing mechanism. The PtO−Pt porous film prepared by annealing the self-assembly film of PPh_3–Pt nanoclusters plays the roles of an inserted electrode and a catalyst for the partial reduction of the titania film.

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