Extraordinary room-temperature hydrogen sensing capabilities of porous bulk Pt–TiO$_2$ nanocomposite ceramics

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Abstract

Metal oxide semiconductors (MOSs) are among the most promising materials for sensing hydrogen in distributed use, yet prevalent hydrogen sensors based on porous thick-film MOSs have the standing and serious drawback of demanding high working temperatures. Here we report on the surprising experimental observation of porous bulk Pt–TiO$_2$ nanocomposite ceramics that exhibit ultrahigh hydrogen sensitivities of the order of $10^4$ for 1000 ppm H$_2$ in N$_2$ at room temperature, with fast response and short recovery times of 10 s and 20 s, respectively. We also demonstrate that hydrogen diffuses in the bulk ceramics with an unusually high diffusion coefficient, and a novel hydrogen sensing mechanism rooted in hydrogen chemisorption on TiO$_2$ is established. The central findings help to enrich our understanding of hydrogen interaction with MOSs, and are also expected to be instrumental in developing related technologies with hydrogen as the energy carrier.

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Introduction

Hydrogen is expected to have immense potentials in future fuel cells and hydrogen-powered automobiles, which will unavoidably face mounting safety concerns [1]. Among the several different classes of hydrogen sensors already available on the market, the one based on metal oxide semiconductors (MOSs) is especially attractive for sensing hydrogen in distributed use, as it is relatively compact, durable, and simple in operation [2]. Unfortunately, prevalent commercial MOS hydrogen sensors such as those based on porous thick-film SnO$_2$ all have to work at temperatures (300–700 °C) much higher than room temperature [3], which naturally requires high power consumption, and also results in undesirable high cross-sensitivity and decreased lifetime. Various
nanostructured MOSs with large surface-to-volume ratios have been successfully synthesized in the past decades, which have been found especially promising for photocatalysis and low-temperature gas sensing [4–7]. While low-dimensional nanostructured MOSs can be directly applied for photocatalysis [8,9], for gas sensing nanostructured MOSs have to be connected to electric circuits. For this reason one-dimensional (1D) MOS nanomaterials are relatively suitable and have been fabricated as MOS hydrogen sensors with impressive low-temperature hydrogen sensing capabilities [10,11]. Nevertheless, such materials still encounter the standing shortcomings of difficulties in forming low-resistance contacts, low mechanical and thermal robustness [12], and strong adsorption of other unwanted gases in surrounding atmosphere [13,14], hindering their potential practical gas-sensing applications. So for gas-sensing, MOSs in bulk forms, such as in porous thick films, are highly preferred in numerous circumstances. It is strange that bulk MOSs have been rarely investigated for room-temperature hydrogen sensing applications up to date, and few systematic investigations have been conducted on room-temperature reactions between hydrogen and MOSs, either. A clear mechanistic understanding for room-temperature hydrogen sensing of MOSs is thus still lacking, in many cases with mutually contradictory assumptions [2,6,15].

Herein, we present some striking findings on room-temperature hydrogen sensing capabilities of bulk MOSs. We show that a porous bulk Pt–TiO2 nanocomposite ceramic material, readily fabricated from TiO2 and Pt nanoparticles through pressing and sintering, exhibits extraordinary room-temperature hydrogen sensitivities of the order of 104 for 1000 ppm H2 in N2, with fast response and short recovery times of 10 s and 20 s, respectively. We further reveal a fast diffusion of hydrogen at room temperature in the porous bulk ceramics, and propose a hydrogen sensing mechanism rooted in chemisorption of hydrogen on TiO2. These central findings help to enrich our understanding of hydrogen interaction with MOSs, and are also expected to be instrumental in developing related technologies with hydrogen as the energy carrier.

**Experimental methods**

**Material preparation**

Commercial TiO2 nanoparticles, P25 (ca. 80% anatase and 20% rutile), purchased from the Degussa Co., were used as the starting material. The TiO2 powder was dispersed in deionized water and magnetically stirred. Pt powder (particle sizes of ~10 nm) was added to the suspended system according to a weight ratio of 5:95 for Pt:TiO2. After stirring for 2 h, the system was dried at 110 °C in oven. The dried powder was then pressed into cylindrical pellets (~1.7 mm in thickness and ~12 mm in diameter) by applying about 10 MPa pressure through a hydraulic press. Pellets of pure P25 were also made for comparing purpose.

These pellets were then heated in air for 2 h at a series of temperatures, from 250 to 950 °C with a step of 100 °C. Due to the large specific surface area of the nanoparticles, a sintering-induced decrease in diameter was detected when the pellets were treated at temperatures as low as 450 °C. Through DC magnetron sputtering, a pair of rectangular Pt electrodes were coated on the major surfaces of those pellets intended for hydrogen-sensing measurement.

**Hydrogen sensing measurement**

During the sensing measurements, a pellet was placed in a sealed chamber (of volume ~350 ml) with a gas inlet and outlet. In the response process, N2 was used as the carrier gas, and H2 was mixed with N2 in appropriate ratios to realize desirable hydrogen concentrations. In the recovery process, air gas was pumped into the chamber. The total gas flow rate was kept at about 300 ml/min. A 15 V DC voltage was applied between the two electrodes and the electric current was measured to calculate the real-time resistance response of the sensor to hydrogen. All the data acquisition was carried out automatically through a computer.

**Results and discussion**

The transition from anatase to rutile was observed in the pellets heat-treated at and above 650 °C, while such transition was not observed in those pellets heat-treated at and below 550 °C [16]. We have thus chosen 550 °C as the sintering temperature for those pellets used in further hydrogen-sensing investigation, at which there was a 3.5% decrease in diameter after sintering. Fig. 1a shows a schematic of a sensor and a scanning electron microscopy (SEM) image of the Pt–TiO2 ceramics sintered at 550 °C. TiO2 grains are ~30 nm in diameter and numerous nanosized pores are present. According to energy dispersive spectroscopy (EDS) analysis, the Pt clusters mostly exist as aggregates of a few micrometers in size and ~10 μm apart from one another, with a typical aggregate partially revealed in the bottom-right corner of Fig. 1a. Obviously, porous bulk Pt–TiO2 nanocomposite ceramics have thus been prepared through convenient pressing and sintering.

The sintered pellets of pure P25 show no detectable response to hydrogen at room temperature. In contrast, Pt–TiO2 nanocomposite ceramics exhibit surprising and extraordinarily strong room-temperature hydrogen sensing behaviors as shown in Fig. 1b. Upon exposure to 1000 ppm H2 in N2, the resistance of the ceramics quickly decreases by a factor of over 6000 at room temperature, indicating a sensitivity of over 6000 in terms of R/Rg (where Rg and Rs are the electrical resistances of the sensor in clean air and in the measuring gas, respectively). Previously, such high hydrogen sensitivities at room temperature could only be achieved using much less robust MOS nanostructures, such as networks of Pd-decorated SnO2 nanowires [10]. Considering that prevalent commercial SnO2 thick-film hydrogen sensors have to work at elevated temperatures, the ultrahigh room-temperature sensitivities of the Pt–TiO2 ceramics demonstrated here represent a breakthrough discovery in bulk MOS-based hydrogen sensing.

Another vitally important characteristic of a sensor is its response and recovery times. As shown in Fig. 1b, the ceramics exhibit a 90% response time of ~10 s and a
comparatively short 90% recovery time of ~20 s. In contrast, the 1D/quasi-1D nanostructure-based sensors that exhibit fast response will often encounter the common drawback of too slow room-temperature recovery [17,18]. Furthermore, the overall response and recovery behaviors shown in Fig. 1b have little variations in five successive sensing cycles, indicating high repeatability in hydrogen sensing.

The ceramics also show excellent sensing capability over a large range of hydrogen concentrations. As shown in Fig. 1c and d, the sensitivity decreases with decreasing hydrogen concentration, as expected; yet even at 30 ppm H2 in N2, the sensitivity is still ~200. This is still an extraordinarily high sensitivity at such a low hydrogen concentration.

Aside from ultrahigh sensitivities, the Pt–TiO2 composite ceramics also possess high hydrogen sensing selectivity, shown by the lack of any visible responses upon in-gassing of CO and NO2 at room temperature. This high selectivity is tied to the drastically different catalytic reactions of the Pt aggregates with H2, CO, and NO2 [11].

So far we have demonstrated that those Pt–TiO2 composite ceramic materials are ideal for hydrogen sensing in many important aspects, including the readily accessible and stable bulk form, ultrahigh room-temperature sensitivities, fast response and short recovery times, high repeatability, and high gas selectivity. Next we turn our attention to the likely underlying room-temperature hydrogen sensing mechanisms, which for bulk ceramic materials have so far been largely overlooked. We first designed a special experiment to study the diffusion of hydrogen in the bulk Pt–TiO2 ceramics, in which a pair of Pt electrodes were coated on the two opposite major surfaces of a sufficiently thick (~1.7 mm) sintered pellet, with its side surface sealed by epoxy as illustrated in Fig. 2a. This configuration was adopted to avoid possible formation of a short circuit on the surface layer between the electrodes, to ensure that the electrical resistance change must reflect the evolution of the bulk property during hydrogen sensing. A representative hydrogen absorption and sensing curve is shown in Fig. 2b. Compared with the results shown in Fig. 1b, this configuration again yields ultrahigh sensitivity, but its response to hydrogen clearly indicates multiple electronic/ionic processes, reflected by the two stages with distinctly different slopes. As the decrease in resistance is primarily related to some hydrogen-induced reactions, the ultrahigh sensitivity demonstrates that a low-resistance path has been established along the thickness direction of the pellet when exposed to hydrogen, indicating that hydrogen is accessible to the very interior of the pellet at room temperature.

The slope of the first response stage is much lower than that of the second stage, and the much faster second stage resembles well the monotonous behavior shown in the first configuration (see Fig. 1). So the first stage should correspond to the hydrogen diffusion process over the relatively long distance along the thickness direction of the sample in the
second configuration. The time when the measured resistance begins to decrease upon hydrogen exposure is taken as $t = 0$. During hydrogen diffusion along the thickness ($\sim 1.7$ mm) direction of the pellet, hydrogenated layers grow from each of the two major surfaces inwards. Since the presence of hydrogen leads to a dramatic decrease in the resistivity of TiO$_2$, the measured resistance in the first stage of response in Fig. 2 is dominated by that of the central un-reacted layer, which is proportional to the thickness of (1.7 – $x$). At any given time $t$, when the measured resistance is $R$, the corresponding $x$ value is calculated according to $R/R_0 = \frac{1.7 - 2x}{1.7}$, where $R_0$ is the resistance measured in air. The diffusion coefficient $D$ is then calculated using the formula of diffusion length $x = 2\sqrt{D t}$, as shown in Fig. 3. The transition from the first to the second stage corresponds to the effective merging of the two reaction fronts around the center of the pellet. Based on this picture, we estimate the effective room-temperature diffusion coefficient of hydrogen in the ceramics to be $4.2 \times 10^{-5}$ cm$^2$/s, which is rather high for typical bulk diffusion processes in oxide materials and should be responsible for the observed fast response and short recovery times of the bulk materials. As a matter of fact, for pure P25 pellets sintered at 550 °C, the presence of numerous cylindrical mesopores has been revealed, and the Brunauer–Emmett–Teller (BET) specific surface area of the ceramics is calculated to be around 23 m$^2$/g [16]. Such a BET specific surface area is close to one half of that of as-received P25. So the bulk ceramics prepared from TiO$_2$ nanoparticles through convenient pressing and sintering is highly porous with cylindrical mesopores, which are ideal for gas-sensing applications via molecular diffusion and explain the observed high bulk diffusion coefficient of hydrogen as detailed above.

Given that the sensitivities of those commercial hydrogen sensors based-on thick-film MOSs have remained relatively low up to date, it seems a little surprising that such ultrahigh hydrogen sensitivities can be readily obtained for Pt–TiO$_2$ nanocomposite ceramics in this study. Commercial MOS thick-film hydrogen sensors are usually fabricated through drop-coating, tape-casting or screen-printing, in which thick-films are formed from pastes of active material, namely MOSs, a low softening temperature glass frit, and organic carrier [2]. In a subsequent firing, organic carrier is burnt out while glass frit forms a suitable matrix for the active material. As the glass is inert to target gas, it will seriously decrease the overall sensitivities of thick-films to the target gas due to a series connection between glass frit and MOSs. In this study, glass is not present and the distance between the two electrodes can be connected continuously with TiO$_2$ nanograins whose resistance is sensitive to hydrogen. Compared with commercial thick-film MOSs hydrogen sensors, the nanoceramics in this study not only have relatively high specific surface area as discussed above, the negative influence of glass on the sensitivities have also been avoided. So ultrahigh hydrogen sensitivities at room temperature have been observed for them.

For hydrogen interaction and sensing of MOSs at elevated temperatures, the most widely accepted mechanism involves the chemisorption of oxygen on MOSs [2], which leads to the formation of electron depleted layers beneath the surface of MOSs. When hydrogen, and other reducing gases as well, reacts with such chemisorbed oxygen, the thickness of the depleted layers will decrease, and the resistance of the MOSs will decrease accordingly. To verify whether this prevailing mechanism is valid for the room-temperature hydrogen absorption and sensing behaviors observed in this study, we have conducted some special measurements as shown in Fig. 4. The ceramics display relatively high and steady conductivity in a mixed atmosphere of 1000 ppm H$_2$ in N$_2$. When the hydrogen flow was stopped, the surrounding atmosphere was changed to N$_2$ and the resistance was found to increase slowly in N$_2$. And when the atmosphere of 1000 ppm H$_2$ in N$_2$ was restored, the initial high conductivity corresponding to the mixed atmosphere was promptly restored. As O$_2$ was absent in this process, the drastic increase/decrease in the resistance could hardly be explained in terms of oxygen

![Diagram](image-url)
chemisorption. As a matter of fact, many studies have shown that for oxygen chemisorption on MOSs, the leading oxygen species is $\text{O}^-$ which starts to be dominant at temperatures above 150–220 °C [19,20]. So for the room-temperature hydrogen absorption and sensing behaviors observed in this study, a mechanism rooted in hydrogen chemisorption on TiO$_2$ is highly favored: First, molecular hydrogen can easily penetrate into the bulk of the porous ceramic materials. Subsequently, the Pt aggregates in the ceramics are effective in decomposing the incoming molecular hydrogen [21]. In the third step, such decomposed hydrogen atoms can efficiently migrate into the surfaces or Pt–TiO$_2$ interfaces of the TiO$_2$ nanoparticles via a spill-over process [22,23]. Lastly and most crucially, the hydrogen atoms become chemisorbed on TiO$_2$ nanoparticles with their electrons denoted [24]. Expressing a molecular hydrogen as $\text{H}_2(g)$, and a chemisorbed hydrogen ion on TiO$_2$ as $\text{H}^+$, the overall reaction in the response stage can be described as:

$$\text{H}_2(g) \xrightarrow{\text{Pt-TiO}_2} 2\text{H}^+ + 2e^{-}. \quad (1)$$

where $e^-$ represents a released electron contributing to the conductivity.

To further understand hydrogen chemisorption on the TiO$_2$ porous ceramics, we have also tried to produce such hydrogen chemisorption in an electrochemical way [25], in which a sintered P25 pellet was used as the cathode to electrolyze water in a NaOH solution. To our surprise, the chemisorbed hydrogen was found to be so reactive that such hydrogen atoms effectively reduce Cu$^{2+}$ in aqueous solutions to Cu$_2$O deposited on TiO$_2$ at room temperature, as shown in Fig. 5. With such a high reactivity, the increase/decrease in resistance in Fig. 4 now can be satisfactorily understood: In N$_2$, chemisorbed hydrogen atoms will combine with one another and leave from TiO$_2$ in the form of molecules, resulting in the relatively slow resistance increase; when the surrounding atmosphere is in air, chemisorbed hydrogen will react with oxygen more intensively [26], leading to the fast recovery.

Conclusion

We have achieved some novel and surprising findings on the room-temperature hydrogen absorption and sensing behaviors of properly functionalized bulk porous Pt–TiO$_2$ nanocomposite ceramics. Intriguing aspects included fast effective hydrogen diffusivity, ultrahigh hydrogen sensitivity, fast response and short recovery times, and high gas selectivity. Collectively, these results point to a novel hydrogen sensing mechanism rooted in hydrogen chemisorption on TiO$_2$. These findings help to enrich our microscopic understanding of room-temperature hydrogen interactions with different MOSs, and should also have important application potentials in various technological developments with hydrogen as the energy carrier in view of the stability, readiness for mass production, and suitability in everyday-life circumstances inherent with bulk MOSs.

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