

Gas sensing capabilities of TiO₂ porous nanoceramics prepared through premature sintering

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Abstract: Pure and noble metal (Pt, Pd, and Au) doped TiO₂ nanoceramics have been prepared from TiO₂ nanoparticles through traditional pressing and sintering. For those samples sintered at 550 °C, a typical premature sintering occurred, which led to the formation of a highly porous microstructure with a Brunauer–Emmett–Teller (BET) specific surface area of 23 m²/g. At room temperature, only Pt-doped samples showed obvious response to hydrogen, with sensitivities as high as ~500 for 1000 ppm H₂ in N₂; at 300 °C, all samples showed obvious responses to CO, while the responses of noble metal doped samples were much higher than that of the undoped ones. The mechanism for the observed sensing capabilities has been discussed, in which the catalytic effect of Pt for hydrogen is believed responsible for the room-temperature hydrogen sensing capabilities, and the absence of glass frit as commonly used in commercial thick-film metal oxide gas sensors is related to the high sensitivities. It is proposed that much attention should be paid to metal oxide porous nanoceramics in developing gas sensors with high sensitivities and low working temperatures.

Keywords: TiO₂; porous nanoceramics; premature sintering; sensors; hydrogen; CO

1 Introduction

As the electrical conductivity (or electrical conductance) of some metal oxide semiconductors (MOSs), such as SnO₂, TiO₂, and ZnO, varies obviously upon

adsorption/desorption of some gases, these MOSs have been successfully developed as gas sensors with such advantages as simple structures and easy operations [1]. Nowadays, most commercial MOS gas sensors are fabricated in porous thick films, which are relatively compact, durable, and cheap. Unfortunately, those thick-film MOS gas sensors all have such drawbacks as low sensitivities and high working temperatures

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(~500 °C) [2], which have greatly limited their applications due to high power consumption, safety hazards, and decreased lifetime. Nanomaterials have been extensively investigated for developing new gas sensors with high sensitivities and low working temperatures in the past decades. Various MOS nanostructures, including nanotubes [3,4], nanowires [5,6], and nanobelts [7], have been synthesized and explored for preparing such gas sensors. Although their sensitivities have been dramatically increased and their working temperatures have been considerably lowered even down to room temperature, all those sensors have not been commercialized for practical applications up to date due to some shortcomings inherent in low dimensional MOSs, such as low thermal stability and mechanical strength [8,9], strong adsorption of moisture [10], and difficulty in mass production. Recently, Xu *et al.* [11] have developed a novel solvothermal hot-press (SHP) process to prepare highly porous MOS bulk nanomaterials, which they have named as porous nanosolids (PNSs). Such PNSs are believed to possess both high reactivity of nanoparticles and strength of nanoceramics, which would be especially attractive for gas sensing applications. A sensitivity of 19 for 4000 ppm CO at 300 °C has been observed for sensors based on SnO₂ PNSs [12], and Pt-loaded SnO₂ PNSs were even found to show obvious responses to CO at room temperature [13], although their response and recovery time are still needed to be shortened. As a matter of fact, with very large specific surface areas and high surface free energies, nanoparticles in contact can become connected to one another at contact points at relatively low temperatures [14], which is usually known as premature sintering, primarily in the case of sintering materials having a nanostructure, and leads to the formation of a highly porous microstructure with obviously enhanced mechanical strength. Presently, we have taken advantage of premature sintering to prepare several kinds of TiO₂ porous nanoceramics. To our great surprise, some highly impressive gas sensing capabilities have been revealed in these readily-prepared porous nanoceramics, as will be reported in this paper.

2 Experimental procedure

A commercial photocatalyst Degussa P25, which is

TiO₂ nanoparticles with average particle size of 25 nm, and powders of Pt, Pd, and Au, were used as the starting materials in this work. Three kinds of mixtures, P25 and Pt, P25 and Pd, and P25 and Au, were prepared through mixing P25 and the noble metal powders separately at weight ratio of 95:5. As-received P25 and the mixed powders were pressed into pellets of 12 mm in diameter and 2 mm thick. The pellets were heat-treated in air for 2 h at a series of temperatures, from 250 to 950 °C with a step of 100 °C. For gas sensing measurement, a pair of rectangle Pt electrodes, with a gap of 2 mm between them, was coated on one major surface of each pellet through DC magnetron sputtering.

Gas sensing measurement was conducted in a sealed chamber (~250 mL) with gas inlet and outlet. Two gases, the target gas and N₂ as carrier gas were mixed at some ratios to achieve the designed concentrations and flowed into the chamber through the gas inlet line. The typical flow rate was 400 sccm and the pressure in the chamber was maintained a little higher than one atmospheric pressure. A heating system and a temperature control unit were used to maintain the temperatures needed for the measurement. A DC voltage of 15 V was applied between the electrodes of the pellets and the response of the pellets to the target gas was measured in terms of the changes in the flowing current, which was measured through a digital multimeter (Agilent 34970A) connected to a personal computer and all data acquisitions were carried out automatically through the computer.

X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Bruker D8 advance) using Cu K α radiation. Microstructural analyses were conducted through a scanning electron microscopy (SEM; SIRION, FEI, the Netherlands). Specific surface areas, pore volumes, and pore size distributions of the pellets were estimated through measuring nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2020 V4.01 system.

3 Results and discussion

A detectable decrease in diameter could be observed for the pellets after being heat-treated at temperatures as low as 450 °C, and for the pellets heat-treated at

550 °C, the decrease in diameter reaches ~3.5%, indicating that densification starts at a very low temperature due to the high specific surface of P25. The diameter of the pellets is monotonously decreased with increasing heat-treating temperature up to 850 °C, indicating that densification spans a very wide temperature range. The surface of the pellets is found to become smooth and glossy after being heat-treated at temperatures above 450 °C. These facts suggest that a premature sintering has occurred in those pellets heat-treated at such low temperatures around 550 °C.

In as-received P25, TiO₂ exists in anatase and rutile phases with an approximate ratio of 80:20. The XRD patterns taken for undoped and three kinds of noble metal doped TiO₂ pellets sintered at 550 °C are shown in Fig. 1, from which we can see that the dominant phase in all samples is anatase TiO₂, indicating that the transformation from anatase to rutile is not significant in these pellets when sintered at 550 °C. For the three kinds of noble metal doped pellets, a few weak peaks from the noble metals can be observed in their XRD patterns. So the noble metals exist as a secondary phase in the ceramics, which is reasonable given the stability of the noble metals.

Figure 2 shows a representative micrograph taken on a fractured surface of an undoped TiO₂ sample sintered at 550 °C. A large amount of pores can be clearly seen in the microstructure, which is related to the fact that the densification is far from fulfillment at this temperature and has been analyzed in depth through measuring nitrogen adsorption–desorption isotherms at 77 K, as shown in Fig. 3. An obvious hysteresis can be seen in the adsorption–desorption isotherms, which is a characteristic of Type IV sorption behavior (according to IUPAC classification) and typical for porous metal

oxides with pores of undefined distribution and shape. The specific shape of the hysteresis loop can be further classified as Type H1, which is usually observed for aggregates of grains with relatively uniform size. Determined from the adsorption–desorption isotherms of Fig. 3 by using the Barrett–Joyner–Halenda (BJH) model, the pore size distribution for the TiO₂ nanoceramics is obtained and shown in Fig. 4. Two

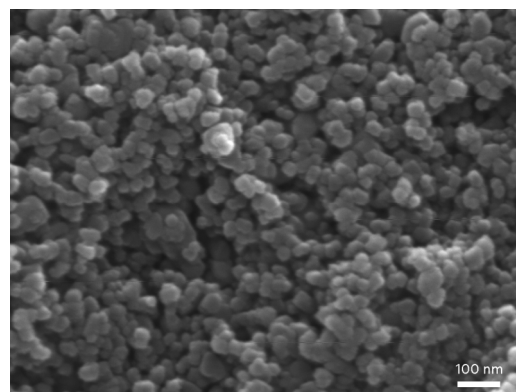


Fig. 2 SEM micrograph taken on a fractured surface of undoped TiO₂ nanoceramics sintered at 550 °C.

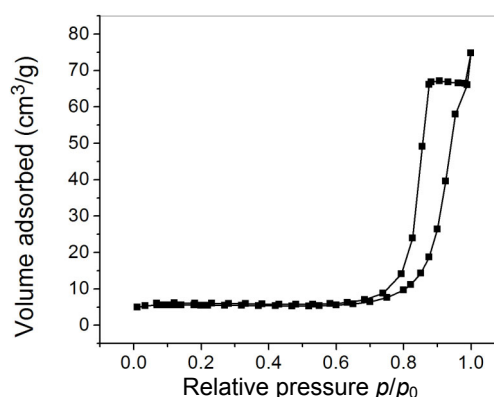


Fig. 3 N₂ adsorption–desorption isotherms measured at 77 K for undoped TiO₂ nanoceramics sintered at 550 °C.

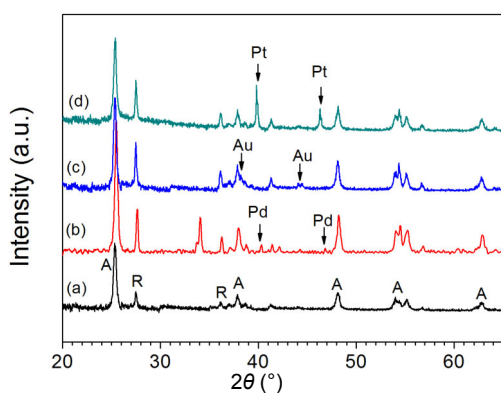


Fig. 1 XRD patterns taken on the surfaces of TiO₂ nanoceramics sintered at 550 °C: (a) undoped, A: anatase, R: rutile; (b) Pd-doped; (c) Au-doped; and (d) Pt-doped.

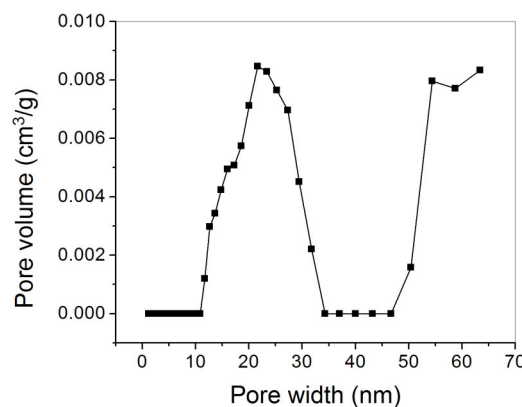


Fig. 4 Pore size distribution for undoped TiO₂ nanoceramics sintered at 550 °C calculated by desorption isotherm.

groups of pores are observed: one is centered around 20 nm and the other one is mostly above 50 nm. So the pores are indeed of much undefined distribution. The Brunauer–Emmett–Teller (BET) specific surface area of the nanoceramics is about 23 m²/g, which is approximately one half of that of as-received P25. So a highly porous microstructure with large specific surface area has been formed in the nanoceramics prepared through premature sintering, which should be attractive for gas sensing applications.

All samples were first examined with regards to their gas sensing capabilities at room temperature, and they are found to show no detectable responses to CO or NO₂ at room temperature. As for hydrogen, while undoped, Pd-doped, or Au-doped TiO₂ nanoceramics display no noticeable responses to it at room temperature, Pt-doped TiO₂ nanoceramics are found to exhibit surprisingly high responses to it at room temperature, as shown in Fig. 5. Upon exposure to 1000 ppm H₂ in N₂, the resistance is decreased by a factor of 500 with a 90% response time of 10 s, and upon air, the resistance is completely recovered with a 90% recovery time of 20 s. Namely, the nanoceramics show a room-temperature sensitivity of 500 for 1000 ppm H₂ in N₂, which is a very high hydrogen sensitivity for bulk materials [2]. Figure 6 shows the responses of the Pt-doped TiO₂ nanoceramics to 1000 ppm H₂ in N₂ and air at room temperature, respectively, in three continuous cycles, from which a relatively good repeatability can be observed in these cycles.

For n-type metal oxide semiconductors, it is generally believed that their exposed surfaces adsorb the oxygen molecules from the ambient gas components, which capture electrons from the conduction band and

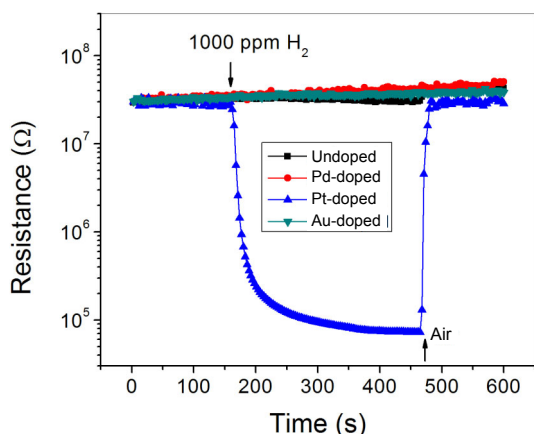


Fig. 5 Room-temperature responses to 1000 ppm H₂ of sensors based on undoped, Pd-doped, Pt-doped, and Au-doped TiO₂ nanoceramics sintered at 550 °C.

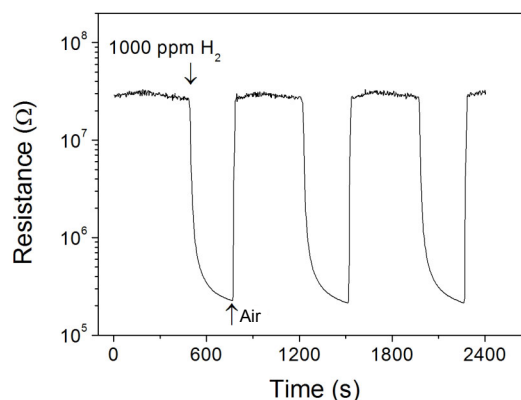


Fig. 6 Room-temperature responses of Pt-doped TiO₂ nanoceramics sintered at 550 °C to 1000 ppm H₂ and air, respectively.

result in the formation of depletion layers beneath the surfaces [15], where the carrier concentration is decreased and consequently the resistance of the semiconductors is increased. When exposed to reducing gases, including H₂, the gases will react with the adsorbed oxygen molecules and release the trapped electrons back to the conduction band. This leads to an increasing carrier concentration and the resistance of the semiconductors is thus decreased [16]. It is well known that Pt has a catalytic effect for hydrogen, namely dissociates hydrogen molecules into hydrogen atoms [17], which are highly reactive even at room temperature [18]. So the observed room-temperature hydrogen sensitivity for Pt-doped TiO₂ nanoceramics can be well explained: hydrogen molecules are first split into hydrogen atoms by Pt, and then react with oxygen molecules adsorbed on TiO₂ at room temperature, and the resistance of TiO₂ is thus decreased. However, Pd is also known to have a catalytic effect for hydrogen and is often used for achieving room-temperature hydrogen sensors [19]; it is strange that Pd-doped TiO₂ nanoceramics are found to show no detectable responses to hydrogen at room temperature and form a sharp contrast with Pt-doped TiO₂ nanoceramics in this study.

As all samples show no detectable responses to CO at room temperature, their sensing capabilities to CO were further studied at elevated temperatures. All samples exhibit no detectable responses to CO until 200 °C, while noble metal doped samples begin to exhibit some weak responses at about 220 °C. At 250 °C, they already display very strong responses to CO. Figure 7 presents the responses of undoped and doped TiO₂ nanoceramics to 700 ppm CO at 300 °C. The resistance of the sensor based on undoped TiO₂

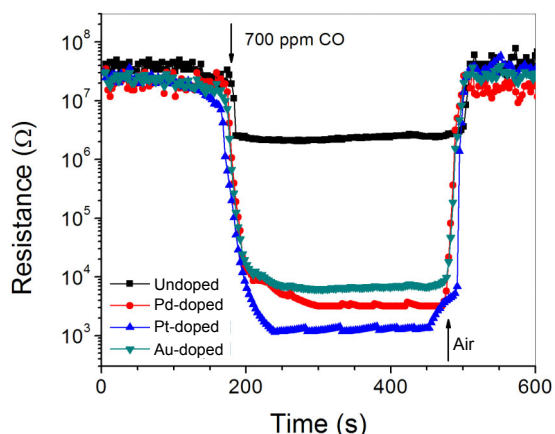


Fig. 7 Responses to 700 ppm CO at 300 °C of sensors based on undoped, Pt-doped, Au-doped, and Pd-doped TiO₂ nanoceramics sintered at 550 °C.

nanoceramics is decreased by a factor of 20 upon exposure to 700 ppm CO at 300 °C, namely the sensor has a sensitivity of 20 for 700 ppm CO at 300 °C, which is quite similar to that reported by Yu *et al.* for SnO₂ nanoporous solids. So these two kinds of metal oxide bulks are quite similar in their sensing capabilities for CO, though they are prepared quite differently. On the other hand, the resistance of the three kinds of noble metal doped TiO₂ is decreased much more greatly upon exposure to 700 ppm CO at 300 °C, among which the sensor based on Pt-doped TiO₂ nanoceramics shows the highest sensitivity, over 30000 for 700 ppm CO at 300 °C. Obviously, noble metal doping is very effective in achieving such high CO sensitivities, though the responses are not quite stable at this temperature.

It should be pointed out that the hydrogen sensitivities of Pt-doped TiO₂ nanoceramics and the CO sensitivities of noble metal (Pt, Pd, and Au) doped TiO₂ nanoceramics revealed in this study are unusually high when compared with those of commercial gas sensors based on thick-film MOSs [2]. Thick-film MOS gas sensors are actually composed of MOSs as the active material and glass frit that forms a suitable matrix for MOSs. As an inert material to the target gas, glass frit will seriously decrease the overall sensitivities of thick films to target gas due to a series of connection between glass frit and MOSs. While in TiO₂ nanoceramics in this study, the distance between the two electrodes are connected continuously with active material, it is reasonable that surprisingly high gas sensitivities have been observed for the nanoceramics. Such ultrahigh gas sensitivities revealed

in this study clearly demonstrate the great potentials of MOSs in achieving high gas sensitivities once the interference from glass frit is avoided, which deserves much more attention in pursuing high-performance gas sensors.

4 Conclusions

Pure and noble metal (Pt, Pd, and Au) doped TiO₂ porous nanoceramics have been successfully prepared from TiO₂ nanoparticles through premature sintering, with a BET specific surface area of 23 m²/g for those sintered at 550 °C. Pt-doped samples were found to show room-temperature sensitivities as high as ~500 for 1000 ppm H₂ in N₂; all three kinds of noble metal doped samples were found to show sensitivities above 10³ for 700 ppm CO in N₂ at 300 °C. The catalytic effect of Pt for hydrogen should play a vital role in the observed room-temperature hydrogen sensing capabilities, while the high sensitivities should have resulted from avoiding the use of glass frit. MOS porous nanoceramics prepared from their nanoparticles through premature sintering are promising for developing high-performance bulk gas sensors.

Acknowledgements

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