Flexible hydrogen sensor based on Pd/TiO$_2$ nanofilm with fast response

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Abstract. Flexible hydrogen sensors based on palladium (Pd) and titanium dioxide (TiO$_2$) nanofilm on poly(dimethylsiloxane) (PDMS) substrate have been demonstrated. We have prepared PDMS using anodic aluminum oxide template and researched the performance of Pd/TiO$_2$ nanofilm based hydrogen sensors with different thickness of TiO$_2$. The sensor with 6nm thickness of TiO$_2$ has demonstrated the best performance with a response/recovery time of 1.6 s/6 s at 0.2% hydrogen concentration, respectively.

1. Introduction
Clean energy has become a global hot topic due to the increasing environmental pollution, non-renewability of fossil fuels and greenhouse effect. Hydrogen (H$_2$) is good clean energy for its renewable and abundant energy with zero pollutant emission [1]. However, its inflammability above a concentration of 4% restricts the extensive utilization of H$_2$ energy, which motivates a lot of researches on the high performance H$_2$ sensors. In recent years, researchers have focused on the new types of hydrogen sensors such as semiconductors, thermoelectric, optics and so on [2]. Especially, metal palladium (Pd) plays an important role in hydrogen sensors due to its special ability of absorbing hydrogen gas at a normal temperature and pressure. Our group have been working on high efficient Pd based hydrogen sensors [3-7]. We tried to use anodic aluminum oxide (AAO) as a substrate to prepare Pd film with porous nano-network structure, which shows good hydrogen detection performance partly due to the increased specific surface area [5,6]. Meanwhile, flexible H$_2$ gas sensors have attracted general attention because of their light-weight, good mechanical property, various applications and so on [8-12]. Lim et al reported a flexible H$_2$ sensor using Pd nanotubes with large surface area and well-interconnected structure exhibiting extremely high sensitivity [8]. Krško et al reported TiO$_2$ thin film based flexible H$_2$ sensor, which demonstrated a response ($R_0/R_{H2}$) of about 10$^4$ for 1% H$_2$ concentration and a capability of sensing H$_2$ concentration of 30 ppm [9].

Poly(dimethylsiloxane) (PDMS) was chosen as an elastomeric substrate for H$_2$ sensors because of its compatibility with Pd, chemical inertness to H$_2$, and mechanical flexibility. In this work, we have fabricated flexible H$_2$ sensors based on Pd/TiO$_2$ nanofilm using PDMS substrate and researched the relationship between the thickness of TiO$_2$ and the performance of hydrogen sensors at room temperature. The sensor with 6nm thick TiO$_2$ achieves a fast response/recovery time of 1.6 s/6 s at 0.2% hydrogen concentration, respectively.

2. Material and methods
AAO template was fabricated using aluminum plate by a two-step anodic oxidation method [5].
Flexible PDMS substrates were prepared by spin coating PDMS monomer mixed with curing agent at a ratio of 10:1 at 300 rpm on AAO. PDMS film on the AAO surface was peeled off after the sample was placed in a baking oven at 75°C for 2 hours. The thickness of PDMS flexible film is about 1.04 mm. TiO$_2$ was prepared on PDMS via spray pyrolysis using a precursor solution of titanium diisopropoxide bis(acetylacetonate) in ethanol with a volume ratio of 1:39 on heating stage with a temperature of 300°C. The thickness of TiO$_2$ was determined by the volume of precursor solution. Then TiO$_2$ films were in situ annealed on heating stage at 300°C for 60 min. We deposited Pd film with a thickness of 30 nm by DC magnetron sputtering at a deposition rate of 1.5 Å/s on the surface of TiO$_2$. Finally a couple of electrodes of 150 nm Ag was prepared on Pd film through E-beam evaporation. Figure 1 shows the schematic fabrication procedure of Pd/TiO$_2$ nanofilm hydrogen sensor. We chose the thickness of TiO$_2$ as 6, 10 and 12 nm, respectively.

![Figure 1. Schematic fabrication procedure of Pd/TiO$_2$ nanofilm hydrogen sensor.](image)

**3. Result and discussion**

The samples were exposed to a wide range H$_2$ concentrations at room temperature from 0.2% to 1.8% in dry synthetic air for investigating sensing properties. Figure 2 shows the real-time resistance change of the samples at various H$_2$ concentrations. From figure 2, we can see the resistances of three samples decreased under H$_2$ atmosphere and reversed quickly under synthetic air atmosphere, which demonstrates that Pd/TiO$_2$ nanofilm in our work would be discontinuous and work on the “break junction” effect. Meanwhile, the baseline resistances of samples decreased with increasing the thickness of TiO$_2$ observed in figure 2. The decrease of resistance would be due to the enhanced thickness of Pd/TiO$_2$ nanofilm and the improved electrical conductivity.

![Figure 2. Sensing curve of three samples with different thickness of TiO$_2$ measured under different hydrogen concentrations. (a) 6nm TiO$_2$, (b) 10nm TiO$_2$, and (c) 12nm TiO$_2$.](image)

In order to systematically evaluate the sensing performance, the steady-state response (R) of the sensors was defined as $R = R_0 - R_{H2}/R_0$, where $R_0$ and $R_{H2}$ represents the sensor resistance in pure air and hydrogen gas, respectively. Figure 3 shows the response of hydrogen sensor samples at different hydrogen concentration. From figure 3, the relationship between the response and the square root of H$_2$ partial pressure is not linear for three samples. As we all know, for most resistive Pd-based H$_2$ sensors, the relationship between the resistance change and the square root of H$_2$ partial pressure is approximately linear [13]. Therefore we can further conclude that the Pd/TiO$_2$ nanofilm on PDMS
film works as the “break junctions”. Meanwhile, the numerical value of sensitivity demonstrates the dominating role of Pd in the sensing response of Pd/TiO$_2$ nanofilm and the sensor with 6 nm TiO$_2$ has the optimal sensitivity compared with other samples.

![Figure 3. The steady-state response of hydrogen sensor samples at different hydrogen concentration.](image-url)

![Figure 4. Response and recovery times of three samples with different thickness of TiO$_2$. (a) Response time, (b) Recovery time.](image-url)

The response and recovery times for three samples were shown in figure 4. At room temperature, the sample with 6 nm TiO$_2$ has stable response and recovery at both low and high H$_2$ concentration. However, for the samples with 10 nm and 12 nm TiO$_2$, we could not get the response/recovery times at H$_2$ concentration of 0.2% and 0.4% for the unsteady bringing noise. The response times increased nearly in the linear range of H$_2$ detection at concentrations from 0.2% to 1.8%. Complete recovery was observed for three samples and recovery times were less than 13s at H$_2$ concentration range. Besides, we can see the hydrogen sensor with 6 nm TiO$_2$ shows fastest response in three samples. Especially, the response time and recovery time are respectively 1.6 s/6 s at H$_2$ concentration of 0.2% for the sample with 6 nm TiO$_2$, which are faster than those of the flexible hydrogen sensors based Pd reported
before [11,14].

In order to investigate the enhanced performance of H\textsubscript{2} sensors with TiO\textsubscript{2} layer, the schematic H\textsubscript{2} sensing mechanism for Pd/TiO\textsubscript{2} nanofilm was described in figure 5. With the PDMS prepared by AAO as the substrate, Pd/TiO\textsubscript{2} nanofilm has large specific surface area and “break junctions” of nano-sized Pd particles were formed in nanofilm. Isolated nano-sized Pd particles adsorb hydrogen and form Pd hydride, which leads to a rapid volume expansion of Pd. When some particles touch in the process of expansion, new conducting pathways are formed and the electrical resistance of film is decreased. For TiO\textsubscript{2} particles, dissociatively formed H atoms in Pd will react with the adsorbed oxygen and inject electrons into the TiO\textsubscript{2} layer, which results in the resistance decrease further. With the exist of TiO\textsubscript{2}, the hydrogen dissolution in Pd/TiO\textsubscript{2} nanofilm will be strengthened with the large concentration difference of H atoms at the surface and interior of Pd/TiO\textsubscript{2} nanofilm, shown in figure 5. With the increase of TiO\textsubscript{2} thickness, it would decrease the specific surface area of Pd/TiO\textsubscript{2} nanofilm and result in low hydrogen adsorption and solubility [15].

![Diagram](image_url)

**Figure 5.** Schematic H\textsubscript{2} sensing mechanism for Pd/TiO\textsubscript{2} nanofilm.

4. Conclusion

In conclusion, flexible hydrogen sensors based on Pd/TiO\textsubscript{2} nanofilm with fast response were fabricated on PDMS by controllable thickness of TiO\textsubscript{2}. We used AAO template to regulate the surface morphology of PDMS. We researched the sensor performance and the decreased resistance under hydrogen gas has demonstrated that Pd/TiO\textsubscript{2} nanofilm sensors work on “break junction” effect. The sensor with 6 nm thickness of TiO\textsubscript{2} achieves a fast response/recovery time of 1.6 s/6 s at 0.2% hydrogen concentration, respectively. The fast response of the sensor is mainly due to large specific surface area of Pd/TiO\textsubscript{2} nanofilm and enhanced dissolution of hydrogen into Pd with the help of TiO\textsubscript{2}.

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