Preparation and Gas Sensitivity of Two-Dimensional Tungsten Oxide Supported High Density Gold Nanoparticles

Fei Hui, Yanhui Chen, Quan Zhou, Chunhui Wang, Meng Qi, Wei Li, Luyan Yang and Ang Li*

Institute of Microstructure and Properties of Advanced Materials, Beijing University of Technology, Beijing, 100124
Email: ang.li@bjut.edu.cn

Abstract. Nano-noble metal materials loaded metal oxide greatly reduce application costs, improve catalytic performance and sensing efficiency compared with oxide substrates. A simple and efficient load method plays an important role in promoting its commercialization. Nano-tungsten oxide is a kind of excellent gas sensing materials and it had been widely used. Noble metal loading can form abundant active centers on the surface of tungsten oxide and become an effective way to improve its gas detecting performance. The complexity and high cost of the loading methods hinder the its application and commercialization on supported catalysts. In this paper, Au/WO$_2$$_6$ composites with high loading rate were prepared on layered tungsten oxide nano-flakes by a simple and low-cost method. The gas sensitivity of WO$_2$$_6$ to ethanol and formaldehyde without Au and with Au were tested. The results show that the loading rate is the highest after reaction for 24 hours. The gas sensitivity of Au loaded WO$_2$$_6$ is significantly improved. The sensitive mechanism on Au/ WO$_2$$_6$ composite were discussed in our work.

1. Introduction
Tungsten oxide is an excellent gas sensitive material and photocatalytic material, which has been widely used in semiconductor gas sensing, photocatalysis, electrode materials, photoelectric devices and other fields.[1] When tungsten oxide is used as gas sensitive material, harmful gases such as NO$_x$, H$_2$S, H$_2$, C$_2$H$_5$OH can be detected.[2] However tungsten oxides have many drawbacks as a typical metal semiconductor oxide, such as single structure, low gas sensitivity, poor gas selectivity, low photocatalytic efficiency and so on, which limit the application of tungsten oxide as gas sensitive material and photocatalyst.[3] The method of noble metal loading can form abundant active centers on the surface of tungsten oxide semiconductor, which will be conducive to the selective adsorption of detected gases, and greatly improve the selectivity and sensitivity of treated gases.[4] At the same time, the increase of active sites also provides the initial reaction sites for energy absorption and conversion in photoelectric catalysis process, and increases the reaction channels.[5] Therefore, it is feasible to improve the catalytic performance and gas sensitivity of tungsten oxide supported by noble metals, and it is the preferred scheme to realize large-scale industrial production at low cost.[6] In recent years, the research of tungsten oxide supported noble metals as gas sensitive materials and photocatalytic materials has become more and more extensive, and the types of noble metals have been extended to Au, Ag, Pt and so on.[7] For example, Xiang and others prepared gas-sensing materials by loading Au nanoparticles into WO$_3$ nanotubes, and tested their sensitivity to various gases, such as H$_2$, CO, CH$_4$, etc.[4]
By comparing the gas sensitivity of Au/WO$_3$ with that of ZnO$_2$, they found that Au/WO$_3$ had better gas sensitivity; Tama’s et al found that Au/WO$_3$ had excellent catalytic performance for CO oxidation at low temperature.[8]

There are many preparation methods of Au nanoparticles supported on tungsten oxide, such as impregnation method, ion exchange method, chemical vapor deposition method, coprecipitation method.[9] Among them, the impregnation method is to immerse the carrier in the solution containing Au active components (such as AuCl$_3$, HAuCl$_3$·H$_2$O), evaporate the solvent and finally reduce Au in hydrogen atmosphere, thus forming the supported Au/WO$_3$ complex.[10] However, the particle size of Au obtained by this method is larger, the average particle size is more than 20 nm, and the Au particles are aggregated in large quantities.[11] Ion exchange method is to combine the aqueous solution of HAuCl$_4$ with HY (or HY). NaY zeolite is co-heated with zeolite to replace H or Na$^+$ on the surface or inside of the carrier, and then activated by roasting and reduction to prepare Y-zeolite as gold catalyst. This method is also not suitable for tungsten oxide supported Au.[12] Chemical vapor deposition (CVD) is to transfer vapor of volatile organic gold compounds to metal oxides with high specific surface area. The average particle size of Au prepared by this method is small (about 2 nm), but its chemical process is complicated, the preparation conditions are strict, and the cost is high.[13] The coprecipitation method is to add HAuCl$_4$ solution and metal nitrate solution of corresponding carrier oxides into the aqueous solution of alkaline precipitator, at the same time. Two kinds of co-precipitates of hydroxides were obtained, and Au/WO$_3$ composite was obtained by filtration, washing, drying and roasting. The particle size of Au obtained by this method was also larger (20-50 nm). [14] In addition to the above commonly used preparation methods, laser assisted deposition, spray pyrolysis and microwave method are also used.[15] However, these methods are seldom used in practical industrial applications due to their high cost. Therefore, a simple and low-cost load method has become a prerequisite for industrialization.

Precious metals (Pt, Pd, Au, Ag) are the most common metal catalysts used to improve gas sensing properties of semiconductor gas sensors.[16] Catalytic reactions on the surface of semiconductors form the acceptors of semiconductor gas sensors. Metals with catalytic activity are used as assistants to improve the selectivity and sensitivity of sensors and shorten the response recovery time.[17] The related work has been extensively studied. At present, there are two mechanisms to explain the role of metal doping in improving the sensitivity of sensors. One is chemical sensitivity, the other is electronic sensitivity.[18] The mechanism of Au in enhancing the sensitivity of semiconductor gas is electronic sensitivity.[19] In terms of electronic mechanism, the reaction with target gas molecule occurs on the surface of the dopant rather than the substrate. In this process, the change of the charge of the dopant results in the change of the surface potential energy, which leads to the change of the metal oxide resistance. In addition, Au doping provides more active centers for active catalysts, which plays an important role in improving the sensitivity of the matrix.[20]

In this paper, a simple and cheap deposition method for preparing WO$_{2.6}$-loaded Au nanoparticles is reported. Two-dimensional matrix material as WO$_{2.6}$ nanoparticles with more active sites were used in our work in order to improve reaction activity. The method is simple and the obtained nano-Au particles have small particle size and high loading rate. This method can be extended to similar noble metal supported metal oxide systems and provide a basis for industrial production. The gas sensitivity of the prepared Au/WO$_{2.6}$ composite to ethanol and formaldehyde were tested and gas sensitivity of the WO$_{2.6}$ gas sensor loaded with Au behave better behaviors than that pure WO$_{2.6}$ without Au. The improved sensitivity mechanism of Au/WO$_{2.6}$ was discussed.

2. Experimental Section

2.1. Reagents and Instruments
H AuCl$_4$·4H$_2$O, sodium borohydride (NaHB$_4$) and potassium carbonate (K$_2$CO$_3$) all came from Beijing chemical reagent co., LTD. WO$_{2.6}$ tungsten trioxide powder came from zhiti nano technology co., LTD.
Transmission electron microscope (TEM): FEI Titan-TEM, X-ray diffractometer (XRD): D8-ADVANCEX, BRUKER, Germany; Gas Sensitive Tester: WS-30A, Zhengzhou Weisheng Technology Co., LTD.

2.2. Preparation of Au NP@WO$_{2.6}$
Sodium borohydride reduction method: 40 mL of deionized water were added to 0.6 mL of HAuCl$_4$ with a mass fraction of 1%, and then 0.2 mL of potassium carbonate solution with a concentration of 0.2 mol/L were added. Continuously stir and add 0.5 mL-2 mL of freshly prepared sodium borohydride solution until the color changes from blue-purple to orange-red. 20 mg WO$_{2.6}$ nanometer powders were added to nano-Au sol of different volumes (3~15ml), and then the mixture was ultrasound for 1 h and were stirred for 1~48h respectively. Following drying process were carried out in an oven at 80°C for 24 h and then they were sintered at different temperature from 200~800°C. The final products were then washed for 5 times with ethanol and deionized water.

2.3. Gas-Sensing Properties Research
Pure WO$_{2.6}$ nanoparticles or Au/WO$_{2.6}$ composites were mixed with antimony and appropriate amount of ethanol in agate mortar. After grinding and forming a paste evenly, the surface layer of ceramic tube containing Pt electrode and Ni-Cr heater coil is dripped to form a gas-sensitive sensor element (Figure 1). Sensor components were aged for 2 days at 200°C. The WS-30A gas sensitivity tester was used in the gas sensitivity test experiment. The gas sensor to be tested is installed in an 18 L air chamber. Ethanol and formaldehyde were used to test the gas sensitivity of samples at room temperature. The test gas is introduced into the test chamber through a syringe, and the discharge of the test gas is realized by opening the gas hood. The gas-sensitive test circuit is shown in Figure 1. Resistance of gas sensitive sensor components in air ($R_a$) and test gas ($R_g$) were recorded respectively.

![Figure 1. (a) Ceramic tube (b) Ni-Cr heater (c) senser pedestal (d) Gas sensing test electric circuit](image)

3. Results and Discussion

3.1. Preparation and Characterization of Au Nanoparticles
Gold nanoparticles were prepared by sol-gel method. The results showed that the amount of NaHB$_4$ added ranged from 0.5ml to 2ml, and the size of the gold particles generated was similar. Figure 2 shows the TEM image and particle size distribution of the Au sol obtained by adding 2ml of NaHB$_4$ as the reductant. The gold particles present multiple twins, with particle size distribution of 2~10 nm and average particle size of 4 nm.
3.2. Effect of Stirring Time on Loading Efficiency on Au/WO$_{2.6}$ Composites

The loading rate of Au onto the WO$_{2.6}$ nanoparticles will change with stirring time as shown in typical TEM images in Figure 3 with the Au dose of 5 ml. It can be seen from the figures that the stirring time is an important factor affecting the load rate of Au. Longer the stirring time promoted more Au particles onto the WO$_{2.6}$ nanosheets within 24 h. Prolonged reaction time longer than 24 h will not increase the load rate of Au onto the WO$_{2.6}$ nanosheets.

Figure 3. TEM image of WO$_{2.6}$ loaded Au particles at different stirring times
(a) 1h (b) 5h (c) 10h (d) 24h

3.3. Effect of Sintering Temperature on Morphologies and Load Rate

The sintering temperatures will also change morphologies of the final products. Typical TEM images on product of the load after sintering in the atmospheric environment is 200°C, 400°C, 600°C, 800°C with the content of Au is 5 ml and stirring for 24 h were shown in Figure 4. Products sintered temperature under 200 °C and 400 °C of Au/WO$_{2.6}$ have similar morphologies with original WO$_{2.6}$ nanoparticles. Morphologies of WO$_{2.6}$ nanoparticles under sintered 600°C changed to near spherical shape. Morphologies of WO$_{2.6}$ substrates, however, changed completely to spherical nanoparticles with few nanometers scales.

Figure 4. TEM image of WO$_{2.6}$ supported Au particles at different sintering temperatures
(a)200°C (b) 400°C (c) 600°C (d) 800°C

An XRD results in Figure 5 give detail structural information on Au/WO$_{2.6}$ composite products sintered under different temperatures. The XRD diffraction peaks of products sintered under 200 °C and 400 °C can be signed to monoclinic WO$_3$ phase with standard JCPDS card NO. 71-2450. Au nanoparticles belong to cubic phase (JCPDS NO.65-2870). The XRD diffraction
peaks of products sintered under 600°C and 800°C can be assigned to orthogonal WO₃ with standard JCPDS card No. 41-0371 which has lattice parameters of a=0.73nm, b=0.75nm, c=0.39nm. The Au nanoparticles remain cubic phase structure under sintered 600 °C and 800 °C. Phase transition of substrate tungsten oxide happens at 600 °C and above and sintered load products below 400°C have no obvious phase transition and wouldn’t change the crystal phase structure of the substrate.

![Figure 5. XRD spectra of WO₂.₆ supported Au particles at different sintering temperatures](image)

3.4. Gas-Sensing Properties of the Sensor
Gas sensitivity on pure WO₂.₆ and Au/WO₂.₆ composites powders were then tested in order to see their gas sensitive properties. Figure 6a shows the sensitivity of undoped and Au-loaded samples to ethanol of different concentrations (25~400 ppm) at 280°C. It can be seen that the sensitivity of Au-loaded samples is higher than that of unloaded samples. The sensitivity of samples increases with the increase of ethanol concentration in the range of 25~400 ppm of ethanol concentration. The sensitivity of the WO₂.₆ element loaded with Au is higher than that of the non-loaded WO₂.₆ substrates at different concentrations, especially at high concentrations which further shows highly improved sensitivity of the Au/WO₂.₆ composites. Sensitivity of WO₂.₆ element loaded with Au to ethanol vapor varies in the range of 3~6.5 within the range of 25 ppm~400 ppm while the sensitivity of non-loaded WO₂.₆ element varies in the range of 1.5~4.5. Similarly, Fig. 6b shows the sensitivity of unloaded and loaded Au samples to formaldehyde with different concentrations (25~200 ppm) at 280 C. From the figure, we can see that the sensitivity of the samples loaded with Au is higher than that of the samples without Au, and the sensitivity of the samples increases with the increase of the concentration of formaldehyde in the range of 25-200 ppm. The sensitivity of WO₂.₆ element loaded with Au to formaldehyde vapor varies from 1.35 to 2.05 in the range of 25 ppm~200 ppm and from 1 to 1.35 in the range of non-loaded WO₂.₆ composite.

![Figure 6. Concentration-sensitivity curves of unloaded Au and loaded Au WO₂.₆ gas sensors for (a) ethanol and (b) formaldehyde](image)

The response recovery curves of unloaded Au and loaded Au WO₂.₆ components were
tested in ethanol atmosphere with ambient temperature of 10–20°C with ambient humidity of 30%–40% and working temperature of 280°C and gas concentration of 100 ppm. The results are shown in Figure 7. It can be seen that the gas sensor has a good response to ethanol vapor and increase ethanol vapor amount induced increased gas diffusion. The response time and recovery time of the WO2.6 element loaded with Au to ethanol vapor are shorter than those of the WO2.6 substrates. The response time of WO2.6 element loaded with Au to ethanol vapor is about 18s at 100ppm, and that of WO2.6 element unloaded with Au is about 23s at 100ppm. After separation from the test gas, the resistance of the element increases and the load voltage decreases. The recovery time of WO2.6 element loaded with Au to ethanol vapor is about 20s at 100ppm, and the recovery performance is better and the recovery time is shorter than that of WO2.6 without Au. The gas selectivity of WO2.6 gas sensor were also investigated and it shown that the sensitivity of both WO2.6 and Au/ WO2.6 composite to ethanol vapor at various concentrations (25ppm–200ppm) were higher than that to formaldehyde vapor. These results indicated that Au/WO2.6 composite are highly selective to ethanol vapor.

![Figure 7. Response time and recovery time curves of unloaded Au and loaded Au WO2.6 gas sensors to (a) ethanol and (b) formaldehyde](image)

3.5. Sensing Mechanisms of Au-loaded WO3

Oxygen deficient WO2.6 is typical of n-type semiconductor and it belong to principle of gas sensitive surface control model. the change of the resistance depends on the surface of the amount and type of chemical absorption of oxygen. Inherent conductivity increases with the increase of temperature in terms of n-type semiconductor oxide. The adsorption of oxygen can be attribute to capture the oxide electronic into oxygen ion (O−, O2−, O3−). The conductance of the oxide decreases with the decrease of temperature. The process can be represented by the following reaction:

\[ \text{O}_2^\text{(gas)} \rightarrow \text{O}_2^\text{(ads)} \]  
\[ \text{O}_2^\text{(ads)} + e^- \rightarrow \text{O}_2^- \text{(ads)} \]  
\[ \text{O}_2^- \text{(ads)} + e^- \rightarrow 2 \text{O}^- \text{(ads)} \]  
\[ \text{O}^- \text{(ads)} + e^- \rightarrow \text{O}^{3-} \text{(ads)} \]  

When the sample is exposed to the reductive ethanol gas, the ethanol molecule can not only capture the electrons from the conduction band of WO2.6, but also chemically adsorb with the oxygen species on the surface of WO2.6. Surface electron energy of ethanol is more negative than that of oxygen and it leads to an increase in electron depletion layers and potential barriers. The electron depletion layers then lead to an increase in the electrical resistance of the sensors which leak into the ethanol atmosphere. Sensitivity response increases according to the sensitivity definition of \( S = \frac{R_{g}}{R_a} \). We proposed the C2H5OH reaction kinetics in Figure 8. When WO3 are exposed to air, oxygen molecules will be adsorbed on the surface especially on steps of the sheet-like particles. Oxygen ions can be formed by capturing electrons from the conduction band. In step 2, when the sensor is exposed to C2H5OH, C2H5OH molecules on the gold surface are dissociated into H atoms which corresponding to step 3. In step 4, C2H5OH atoms dissociated by Au particles are
transferred to the WO$_3$ surface and interact with reabsorbed oxygen ions. Therefore, oxidation of C$_2$H$_5$OH gold nanocrystals leads to electron transfer in the semiconductor WO$_{2.6}$ and changes in resistance of the sensing material. The decrease in interfacial resistance confirms that the sensitivity of the hydrogen sensor is much better than that of pure WO$_3$. Improved sensitivity of load composites can be attribute to that adsorbed Au provided more paths for electron transfer than unloaded WO$_{2.6}$ substrates.

**Figure 8.** Mechanism of reaction between C$_2$H$_5$OH and Au@WO$_3$

4. **Conclusion**

In this paper, a simple and universally applicable preparation method of WO$_{2.6}$ powder-loaded Au nanoparticles was reported. Effects of the amount of Au sol, stirring time and calcination temperature on the load rate of WO$_{2.6}$ powdery Au nanoparticles. TEM, HRTEM were used to analyze the loading mechanism of Au nanoparticles on WO$_{2.6}$ powders. The mixing time of 24 h, calcination temperature is 400°C, WO$_{2.6}$ powder load the highest rate of Au nanoparticles. The calcination temperature higher than 600°C will change the morphology and structure of WO$_{2.6}$ substrate change. The gas sensitivity of the prepared Au/WO$_{2.6}$ to ethanol and formaldehyde were also studied. The WO$_{2.6}$ gas-sensitive of Au/WO$_{2.6}$ composites was more sensitive to ethanol and formaldehyde than the WO$_{2.6}$ substrates. WO$_{2.6}$ is more selective to ethanol than to formaldehyde. Improved sensitivity of load composites can be attribute to that adsorbed Au provided more paths for electron transfer than unloaded WO$_{2.6}$ substrates.

5. **Acknowledgment.**

This work was supported Natural Science Foundation of China in grants (No.51872008) and Beijing Natural Science Foundation (No. Z180014) and “111” project under the grand of DB18015.

6. **References**

[1] Nkosi, B., N.J. Coville and G.J. Hutchings 1998 *ChemInform* **19** 25  
[2] Kabcum S., Kotchasak N., Chanee D., Tuantranont A., Wisitsoraat A., Phanichphant S. and Liewhiran C 2017 *Sensors & Actuators B Chemical* **25** 523  
[3] Shufen W, Weiren F, Zichuan L, Aibing Y and Xuchuan J 2018 *J. Mater. Chem. C* **6** 191  
[4] Xiang Q, Meng G F, Zhao H B, Zhang Y, Li H, Ma W J. and Xu J Q 2013 *Journal of Physical Chemistry C* **114** 2049  
[5] Liu X, M H Liu, Y C Luo, C Y Mou, SD Lin., H Cheng, JM Chen, J F Lee and TS Lin 2014 *Journal of the American Chemical Society* **134** 10251  
[6] Yin L, Deliang C, Bingbing F, Hongxia L, Hailong W, Daoyuan Y, Guosheng S and Rui Z 2013 *Materials Chemistry and Physics* **143** 461  
[7] Korotcenkov G., V Brinzari, and B.K. Cho 2016 *Microchimica Acta* **183** 1033  
[8] Grisel, R.J.H.,  Weststrate, C. J. and Goossens A Catalysis Today 2002 72 123  
[9] Cong S, F Geng and Z Zhao 2016 *Advanced Materials* **28** 10518  
[10] Ahmadi M., R. Younesi and M.J.-F. Guinel 2014 *Journal of Materials Research* **29** 1424  
[11] Zanella, R., Giorgio Suzanne, Henry Claude R. anf Louis, Catherine 2002 *J.phys.chem.b* **106** 7634  
[12] Amaniampong, P.N, Kaixi Li, Xinli Jia, Bo Wang, Armando, Borgna and Yanhui Yang
2014 Chemcatchem 6 2105

[13] Vuong, N.M, D. Kim, and H. Kim 2015 Sci Rep 5 11040

[14] Jaafar, N.A, L.J. Minggu and M.B. Kassim 2015 Iet International Conference on Clean Energy and Technology

[15] Anisimov, O.V., Gaman, V. I., Maksimova, N. K., Najden, Yu. P., Novikov, V. A., Sevastyanov, E. Yu., Rudov, F. V. and Chernikov, E. V. 2010 Semiconductors 44 366

[16] Yin L, Deliang C, Bingbing F, Hongxia L, Hailong W, Daoyuan Y, Guosheng S and Rui Z 2013 Materials Chemistry and Physics 143 461

[17] Kim, S., Park Sung Hoon, Park Suyoung , Lee Chongmu 2015 Sensors & Actuators B Chemical 209 180

[18] Li, F, Sijia G, Jingli S, Liang S, Dongming S, Bin W, Yu C and Shengping R 2017 Sensors & Actuators B Chemical 238 364

[19] Xue, D. and Z. Zhang 2018 Functional Materials Letters

[20] Yanbai S, Hongshan B, Tingting L, Xiangxi Z, Xiangxiang C, Anfeng F and Dezhou W 2018 Applied Surface Science 434