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Article

H_2 Sensor Based on Au/TiO_2 Nanoparticles Synthesized by Flame Spray Pyrolysis

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Abstract. TiO_2 is used extensively as a gas sensing material due to its change in electrical conductivity under analyst gas exposure. Gold (Au) is a good catalyst that promotes chemical reactions by reducing the activation energy between sensing film and particular gas. Unloaded TiO_2 and TiO_2 nanoparticles loaded with 0.25–0.75 at% Au were successfully produced in a single step by Flame spray pyrolysis (FSP) technique. The structure and morphology of as-prepared products have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM). TiO_2 and Au-loaded TiO_2 nanoparticle films were prepared by spin-coating technique. The gas sensing of H_2 was studied at the operating temperatures ranging from 300-350°C in dry air. It was found that the TiO_2 loaded with Au sensing film showed higher response of H_2, with faster response time (within second) than pure TiO_2 sensing film. The response increased and the response time decreased with increasing of H_2 concentration.

Keywords: H_2 , Gas sensor, Au/TiO_2 nanoparticles, flame-made.

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1. Introduction

Noble metals supported on oxides are used in many applications in the paintings, cosmetics, pharmaceuticals, ceramics, electronics, photocatalysts, and sensors. Flame spray synthesis is investigated as a method for one-step synthesis and deposition of porous catalysts onto surfaces and into microreactors [1]. FSP is described in more detail by Mädler et al. (2002) [2]. FSP was successfully used for the preparation of pure TiO_2, Zn/TiO_2 [3], Fe/TiO_2 [4], Au/TiO_2 [5–6], Nb and Cu/TiO_2 [7], Pt/TiO_2 [8], WO_3/TiO_2 [9].

Titanium dioxide is one of the most promising candidates for gas sensor [10–12] due to its cheapness, stability and environmental safety. Titanium dioxide (TiO_2) is an n-type semiconductor material [13] (anatase, E_{bg} = 3.2 eV ; rutile, E_{bg} = 3.0 eV) such that its absorption edge occurs below 400 nm [14]. The sensing properties are based on reactions between semiconductor oxides and gases in the atmosphere. These reactions produce changes in electrical properties of semiconductors, analyte detection is signaled by a change in the electrical conductivity of the sensor film [15–18].

Sensitivity of TiO_2 sensors can be improved by addition of dopants such as Ta, Pt, V_2O_5, Li, La, Co, Cu, Nb, Cu, Cr, Ag, Au [19–28], The most important effect of dopant addition in TiO_2 is increasing the conductivity, slowing down anatase with rutile transformation and reducing grain growth. We emphasize on the gold nanoparticles because gold nanoparticles has earned its reputation as an excellent catalyst in gas sensing performances [28–30].

Hydrogen is expected to replace conventional energy sources and promising potential fuel for buses, cars, and other vehicles. Safety is an important issue when hydrogen is used as fuel in futuristic automobiles, therefore there is need for hydrogen sensor to monitor the fuel leak. An explosive mixture can form if hydrogen leaks into the air from a valve or tank.

2. Experimental

The unloaded TiO_2 and Au-loaded TiO_2 samples were prepared through a flame spray pyrolysis route using titanium isopropoxide and Gold (III) chloride starting materials [31] as starting materials. This solution was added drop wise into a dilute ethanol solution under stirring material. The dopant concentrations in at% fraction of Au were set as 0.25%, 0.5% and 0.75%, respectively. In a typical run, the precursor is fed into a FSP reactor by a syringe pump with a rate of 5 ml/min while 5 l/min O_2 was being dispersed (5/5 flame).The gas flow rates of methane and O_2 supporting flamelet were 1.19, and 2.46 l/min respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle [32].

The phase and crystallinity were analyzed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM). The specific surface area (SSA_{BET}) of the nanoparticles was measured by nitrogen adsorption (BET analysis). The existence of Au was confirmed by Energy dispersive X-ray spectroscopy (EDS).

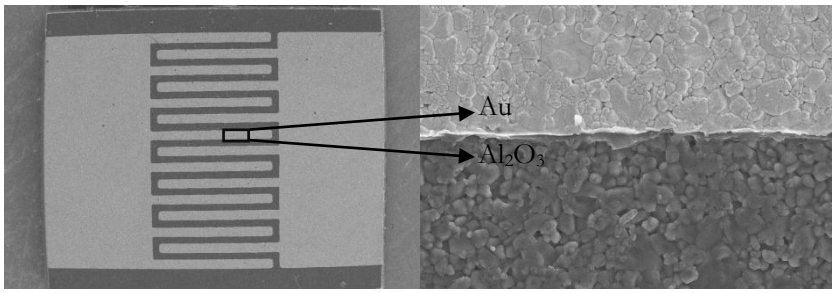

Fig. 1. SEM images were observed with different magnification of Al_2O_3 substrate interdigitated with Au electrodes.

Al_2O_3 substrates interdigitated with Au electrodes were used as a sensor substrates presented in Fig. 1. The alumina substrate had a dimension of 0.4 cm × 0.55 cm × 0.04 cm. Interdigitated width, interdigitated spacing and area of the electrode were 100 μm, 100 μm and 0.24 cm × 0.4 cm, respectively. An appropriate quantity of 0.28 ml homogeneous mixed solution was prepared by mixing nanoparticles into an organic paste composed of ethyl cellulose (Fluka, 30–60 mPa.s) as the temporary binder and terpineol (Aldrich,

90%) which acted as a vehicle binder and a solvent, respectively. The resulting paste was spin-coated on Al_2O_3 substrates (Semiconductor Wafer, Inc, 96%) with interdigitated Au electrodes. The electrode pattern was made by DC sputtering of 50 nm-thick Cr and 200 nm-thick Au layers and lift-off process. The sensing films were subsequently annealed at 400°C for 2h with heating rate of 2 °C/min for binder removal. The particle size was found to be slightly changed after annealing at 400°C [33].

The sensor characteristics of sensing films were characterized towards the high concentration of H_2 gas. The flow through technique was used to test the gas-sensing properties of sensing films. A constant flux of synthetic air of 2 L/min as gas carrier was flown to mix with the desired concentration of pollutants dispersed in synthetic air. All measurements were conducted in a temperature-stabilized sealed chamber at 20°C in dry air. The gas flow rates were precisely manipulated using a computer controlled multi-channel mass flow controller. The external NiCr heater was heated by a regulated DC power supply to different operating temperatures. The operating temperature was varied from 250–350°C but the sensing test in this work was performed at 300°C and 350°C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 10 V DC bias and current measurement through a picoammeter. The sensor was exposed to a gas sample for ~5 minutes for each gas concentration testing and then the air flux was restored for 15 min. The H_2 concentration was varied from 200 to 1% in volume percentage of concentration [34].

3. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of flame-spray-made pure TiO_2 and 0.25–0.75 at% Au/TiO_2 nanopowders. All samples were highly crystalline, and all peaks can be confirmed to be the anatase ((101), (004), (200), (105), (211) and (204)) and Rutile ((110), (101), (111), (211) and (301)) phase of TiO_2, which matched well with the JCPDS file No. 00-021-1272 and JCPDS file No.04-008-8142 respectively. Au peaks ((111), (200), (311) and (220)) were found in these patterns (JCPDS file No. 04-0784) [35]. It can be assumed that the amount of Au concentration was very low, which affected the appearance of the Au peaks.

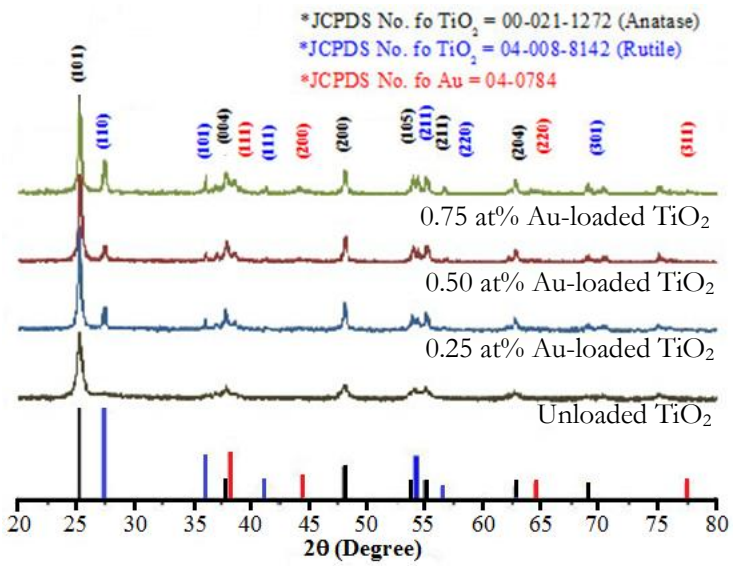

Fig. 2. XRD patterns of the investigated unloaded TiO_2 and Au-loaded TiO_2 samples.

An average BET equivalent particle diameter (d_{BET}) was calculated using the average density of unloaded TiO_2 and Au-loaded TiO_2 as shown in Table 1. The accurate particle size and morphology of unloaded TiO_2 dispersion were confirmed by HR-TEM images.

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Table 1. The specific surface area (SSA_{BET}) and d_{BET} of unloaded TiO_2 and Au-loaded TiO_2 nanoparticles.

Samples	Specific surface area, SSA (m^2/g)	d_{BET}(nm)
Unloaded TiO_2	154.2	10.1
0.25 at% Au-loaded TiO_2	81.0	19.1
0.50 at% Au-loaded TiO_2	81.4	18.7
0.75 at% Au-loaded TiO_2	87.9	16.9

HR-TEM images of unloaded TiO_2 and 0.25, 0.50, 0.75 at% Au-loaded TiO_2 nanoparticles are shown in Fig. 3. It can be seen that Au nanoparticles seen as darker spots are deposited on larger TiO_2 nanoparticles. The crystallite sizes of spherical particles were found to be in the range of 10–20 nm. The existence of Au nanoparticles was shown as EDSs spectra in the insets.

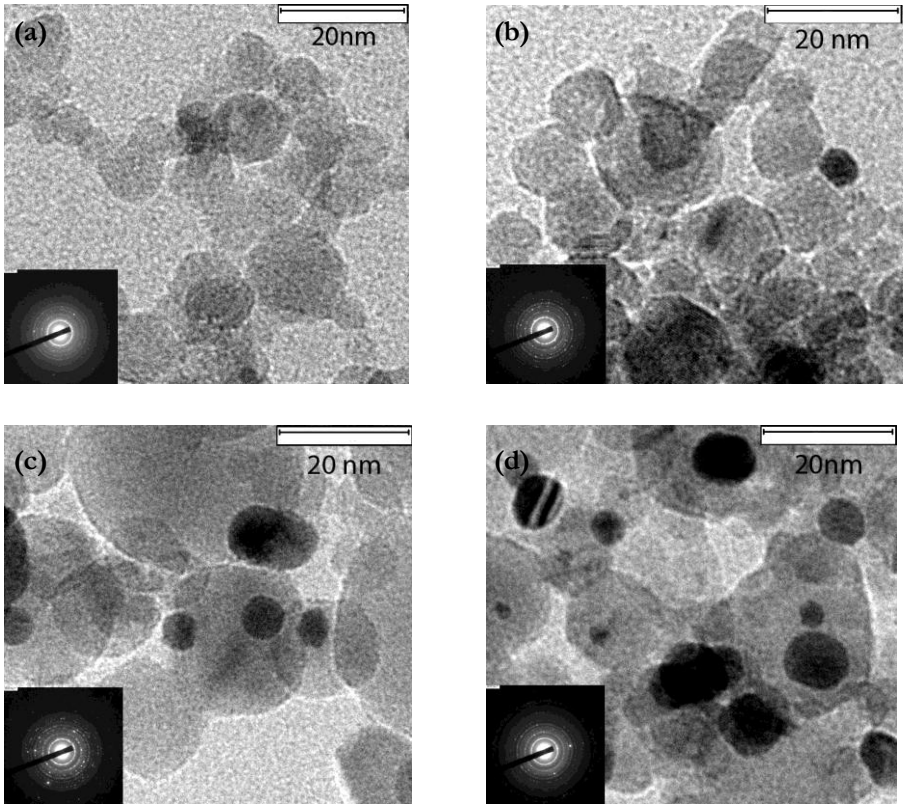

Fig. 3. HR-TEM bright-fields image of highly crystalline flame-made of (a) unloaded TiO_2, (b) 0.25at% Au-loaded TiO_2, (c) 0.50 at% Au-loaded TiO_2 and (d) 0.75 at% Au-loaded TiO_2 nanoparticles. Insets show the EDS spectra of all samples.

The surface morphology image and EDS spectrum of elements for 0.75 at% Au-loaded TiO_2 nanoparticles are shown in Fig. 4. It can be seen that the film surface is highly porous and contains high-density nanoparticles with diameters smaller than 50 nm. The EDS spectrum in the inset of Fig. 4 clearly shows elemental signals corresponding to Ti, O and Au. The EDS data confirms the existence of Au and the Au content in this region is found to be 0.73 at%, which is in good agreement with the intended concentration.

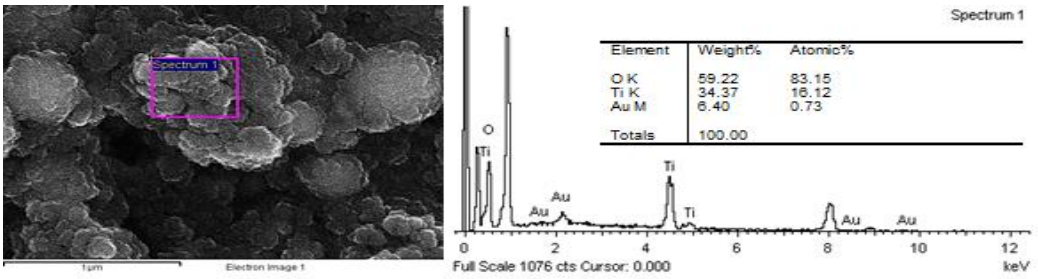

Fig. 4. SEM image of the flame-made (5/5) 0.75 at% Au-loaded TiO_2 nanoparticles and EDS spectrum for the region indicated in the cropped region.

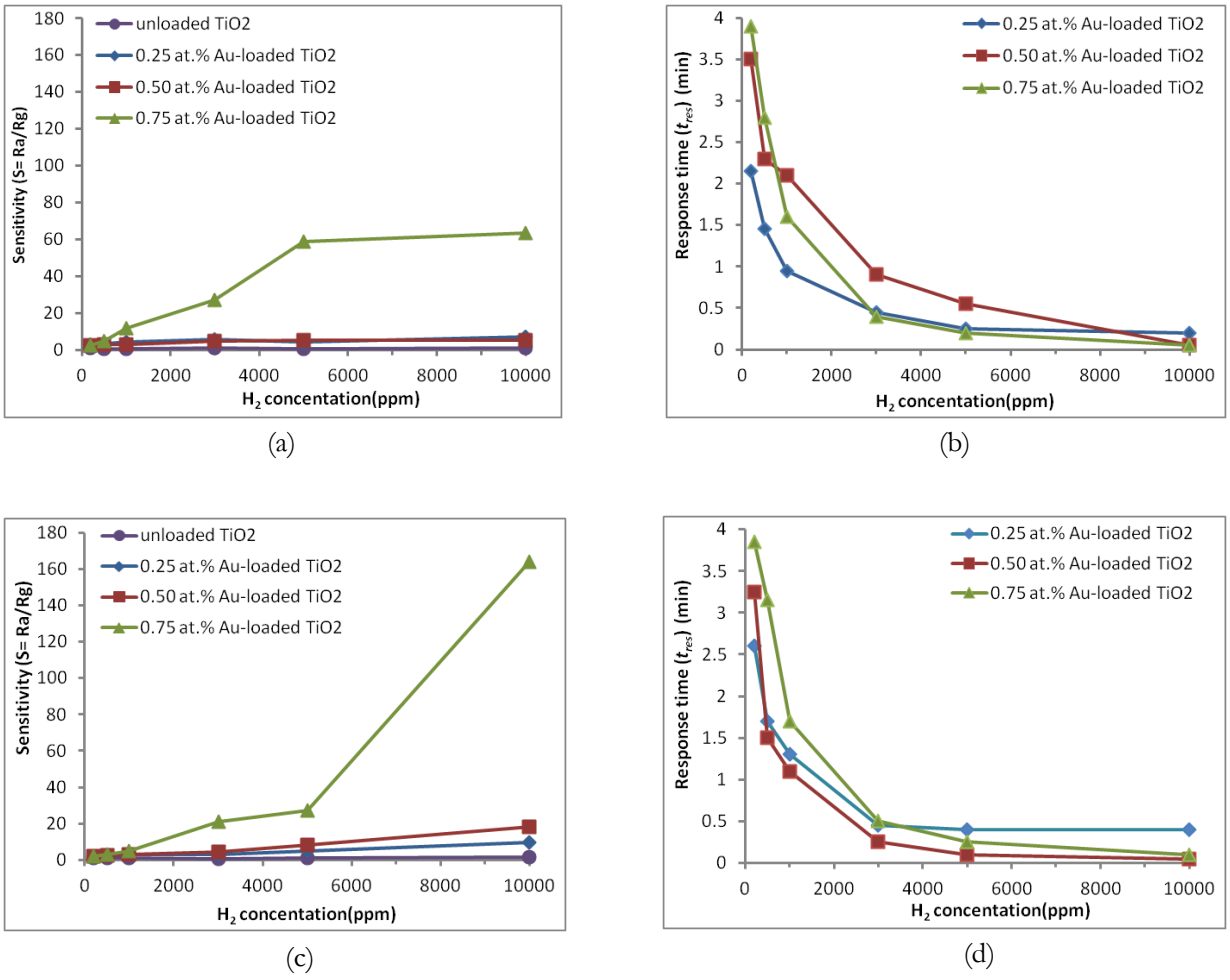

Fig. 5. Sensing performance of sensitivity and corresponding response times of unloaded TiO_2 sensors and loaded with 0.25, 0.50, 0.75 at% sensors as a function of H_2 concentration in dry air at (a-b) 300°C and (c-d) 350°C. The sensitivity increased and the response times decreased with increasing H_2 concentration.

In this study, the gas sensing properties of unloaded TiO_2 and Au-loaded TiO_2 sensing films are characterized in terms of response, response time and recovery time as a function of operating temperature, gas concentration and Au loading. The gas-sensing response, S, is defined as:

$$S = R_a/R_g \text{ (for reducing gas)}$$

where R_a is the resistance in dry air, and R_g is the resistance under a reducing gas. The response time, T_{res} is defined as the time required to reach 90% of the steady response signal. The recovery times, T_{rec} denotes the time needed to recover 90% of the original baseline resistance.

The sensitivity and response time of the thin films of unloaded TiO_2 and Au-loaded TiO_2 nanoparticles as a function of H_2 concentration between 0.02 and 1 vol.% of concentration at 300 and 350°C are shown in Fig. 5. The sensitivity increased considerably by Au-loaded TiO_2 nanoparticles with 0.75 at% Au from 63.8 at 300°C to 164 at 350°C [show in Figures 5(a,c)]. Therefore, doping the TiO_2 nanoparticles with 0.75 at% Au sensor at 350°C had better sensitivity than 300°C. In Fig. 5 it can be seen that the sensitivity increased considerably by Au-loaded TiO_2 nanoparticles with 0.75 at% Au. The sensitivity of 164 and response time of 0.1 min were obtained at 1 vol.% of H_2 concentration for the Au-loaded TiO_2 nanoparticles with 0.75 at% Au. Thus, in this study 0.75 at% Au/TiO_2 showed good sensitivity for H_2 gas as compared to the other literatures. In the present study the sensitivity, however decreased considerably by unloaded TiO_2 and Au-loaded TiO_2 nanoparticles with 0.25 and 0.50 at% Au. The gas-sensing sensitivity, S is defined as the ratio R_a/R_g, where R_a is the resistance in dry air, and R_g is the resistance in test gas. The response time, T_{res} is defined as the time required until 90% of the response signal is reached. The recovery times, T_{rec} denotes the time needed until 90% of the original baseline signal is recovered.

4. Conclusions

Highly crystalline unloaded TiO_2 and 0.25–0.75 at% Au-loaded TiO_2 nanoparticles were prepared by Flame spray pyrolysis. The XRD characterizations showed that unloaded TiO_2, Au-loaded TiO_2 nanoparticles and their corresponding sensing films were highly crystalline with an anatase phase of unloaded TiO_2 and anatase with rutile phase of Au-loaded TiO_2. HR-TEM images showed the nanoparticles having clear spherical morphology. The crystallite sizes of spherical unloaded TiO_2 and 0.25–0.75 at% Au-loaded TiO_2 were found to be ranging from 10 to 20 nm. For Au-loaded TiO_2 powder, small spherical Au nanoparticles were found to disperse over the surface of TiO_2 matrix and the presence of Au element was confirmed by EDS analysis. From BET measurement, SSA_{BET} increased and d_{BET} decreased with increasing Au concentration from 0 to 0.75 at%. TiO_2 nanoparticles loaded with 0.50 at% Au shows good H_2 sensitivity at operating temperature of 300–350°C. The H_2 sensing behaviors were found to improve with Au content of 0.75 at% but deteriorated at lower Au concentration. The sensitivity for 1vol.% of H_2 concentration was 164 for 0.75 at% Au-loaded TiO_2 and at 350°C. The response and recovery times were generally well within 0.1 min in the regime of high sensitivity. Thus, TiO_2 nanoparticles loaded with 0.75 at% Au shows good H_2 sensitivity at operating temperature of 350°C. This present study showed FSP method can control the morphology, sizes, and Au-loaded TiO_2 of nanopowders using the appropriate precursor and flame conditions. The effect of Au Au-loaded TiO_2 improved H_2 sensing behavior in terms of sensitivity, shorter response and recovery times.

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