Size-Dependent H₂ Sensing Over Supported Pt Nanoparticles

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Catalyst size affects the overall kinetics and mechanism of almost all heterogeneous chemical reactions. Since the functional sensing materials in resistive chemical sensors are practically the very same nanomaterials as the catalysts in heterogeneous chemistry, a plausible question arises: Is there any effect of the catalyst size on the sensor properties? Our study attempts to give an insight into the problem by analyzing the response and sensitivity of resistive H₂ sensors based on WO₃ nanowire supported Pt nanoparticles having size of 1.5 ± 0.4 nm, 6.2 ± 0.8 nm, 3.7 ± 0.5 nm and 8.3 ± 1.3 nm. The results show that Pt nanoparticles of larger size are more active in H₂ sensing than their smaller counterparts and indicate that the detection mechanism is more complex than just considering the number of surface atoms of the catalyst.

Keywords: Gas Sensor, WO₃ Nanowires, Pt Nanoparticles, H₂ Sensing.

1. INTRODUCTION

Tungsten oxide nanostructures are well-known for their excellent sensitivity towards hydrogen,^{1–3} due to the fact that oxygen defects are generated throughout their partial reduction by hydrogen thus increasing electrical conductance. When using oxygen or air as carrier gas, WO₃ is able to recover after each H₂ pulse; however, in inert atmosphere, oxidation cannot occur making such sensors sensitive but not completely reversible. Both response and sensitivity can be remarkably intensified by the introduction of metals, such as Pt or Pd, as dissociation of hydrogen thereby reduction of the support is facilitated on their surfaces. Since both Pt and Pd can also promote oxidation, an enhanced sensor recovery is expected (i.e., insertion of oxygen in the vacancies at the anionic sites of the support).

Over the past several years, different forms of WO₃ sensitized by the addition of platinum have been extensively studied for hydrogen detection.^{4–7} Nevertheless, studies

examining the influence of size and morphology of metal nanoparticles on the sensorial properties is lacking in the field. It is interesting, since the catalyst size-effect on the catalytic activity, yield or selectivity in surface chemical processes were discussed by several groups for Pt supported on WO₃.^{8–11} Moreover, both in electrocatalytic oxygen reduction reaction (ORR),¹² and photocatalytic hydrogen evolution¹³ the size of Pt nanoparticles seems to play a role. Since in catalytic processes applying similar materials having differences only in the size and dispersion of the metal particles showed significant influence on the reaction rate, thus such features and their effect are studied here as expected to play an important role in gas sensing as well.

In particular, we investigate the performance of Taguchi-type gas sensors based on platinum nanoparticles with finely tuned sizes, 1.5 ± 0.4 nm, 6.2 ± 0.8 nm, 3.7 ± 0.5 nm and 8.3 ± 1.3 nm, supported on hydrothermally synthesized WO₃ nanowires in hydrogen sensing. Using these samples, we are able to compare response and sensitivity quantitatively as a function of particle size. Insight gained through

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this study will facilitate the development of design principles for materials to be used in gas sensors.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Tungsten-Trioxide Nanowires (WO₃ NW)

Tungsten trioxide nanowires were prepared by the hydrothermal process reported before.¹⁴ First sodium tungstate (2.5 g) and sodium sulfate (3.0 g) were dissolved in distilled water (80 mL) then sulphuric acid (3 M) was added dropwise to set the pH of the clear solution to 1.5. After 10 min of stirring, the mixture was transferred into a Teflon-lined stainless steel autoclave and was kept at 180 °C for 48 h. The product was collected by centrifugation, washed with distilled water and ethanol and finally dried in air at 60 °C.

2.2. Preparation of Pt Nanoparticles

For 1.5 nm sized Pt nanoparticles, first 29 mg PtCl₄ were dissolved in 2.5 mL ethylene glycol and was mixed 2.5 mL of 0.5 M NaOH in ethylene glycol in a three-necked round bottom flask. After 30 minutes of sonication, the flask was purged with atmospheric pressure argon gas in cycles to get rid of oxygen and water. After three purging cycles, the flask was immersed into an oil bath heated to 160 °C; both the reaction mixture and the oil bath were vigorously stirred. After 180 minutes, the flask was cooled down to room temperature and the pH of the suspension was neutralized by adding 2 M aqueous HCl solution. After neutralization, 40 mg polyvinylpyrrolidone (PVP, MW = 40,000) dissolved in 2 mL ethanol was mixed in, then the product was collected by centrifugation. The nanoparticles were washed with hexane and were redispersed in ethanol for at least 2–3 centrifugation cycles, and the as received product was redispersed and kept in ethanol.

To synthesize 3.7 nm Pt nanoparticles, 0.025 g H₂PtCl₆ and 110 mg polyvinylpyrrolidone (PVP, MW = 40,000) were dissolved in 5 mL ethylene glycol, and were sonicated for 30 minutes to get a homogenous solution. The solution was purged with argon several times then the flask was immersed into an oil bath heated to 160 °C under vigorous stirring. After 60 minutes the suspension was cooled down to room temperature and the product was precipitated by adding acetone and collected by centrifugation. Platinum nanoparticles were washed with hexane and were redispersed in ethanol for at least 2–3 centrifugation cycles, and then the as received product was redispersed in ethanol for storage.

Pt nanoparticles with a diameter of 6.2 nm were synthesized dissolving 0.041 g H₂PtCl₄ and 20 mg polyvinylpyrrolidone (PVP, MW = 40,000) in 5 mL ethylene glycol, followed by ultrasonication for 30 minutes till a homogenous solution was formed. A three-necked round bottom flask was purged three times with argon before it was immersed into an oil bath heated to 200 °C under

vigorous stirring. The as-prepared solution was stirred and kept at this temperature for 120 minutes then it was let to cool down to room temperature. The suspension was precipitated by adding acetone and collected by centrifuging the mixture. The nanoparticles were washed with hexane and redispersed in ethanol for at least 2–3 centrifuging cycles, and the as received product was redispersed and kept in ethanol.

For 8.3 nm Pt nanoparticles, 40 mg H₂PtCl₆ and 40 mg polyvinylpyrrolidone (PVP, MW = 40,000) dissolved in 2.5 mL ethylene glycol and 2.5 mL of 0.075 M NaOH in ethylene-glycol were mixed in a three-necked round bottom flask. After 30 minutes of sonication and three purging cycles using argon, the flask was immersed into a stirred oil bath heated to 160 °C under. The solution was stirred at the afore-mentioned temperature for 180 minutes then it was cooled down to room temperature. The pH of the suspension was neutralized using 2 M of HCl (aq.) solution, followed the precipitation and collection of the product by the addition of acetone and centrifugation. Platinum nanoparticles were washed with hexane and redispersed in ethanol for at least 2–3 centrifuging cycles, and the product was redispersed in ethanol.

2.3. Preparation of Pt@WO₃ NW Suspensions for ICP and Gas Sensing Measurements

First, 50 mg WO₃ NW was suspended in 10 mL of ethanol and was sonicated for 30 minutes. Then 0.5 mg of Pt nanoparticle suspension was added to the dispersion of support material and was sonicated for 4 hours.

2.4. Characterization Methods

The morphology of the nanowires was characterized by scanning (SEM; Hitachi S-4700) as well as transmission electron microscopy (TEM, Fei Technai G2 20 X Twin). For SEM investigation, samples were spread on the surface of a piece of carbon tape attached to an aluminum sample holder. For TEM measurements, samples were sonicated in ethanol before being dropped on a copper mounted holey carbon film and dried. For the particle size distributions of the size-controlled Pt nanoparticles a few hundreds of particles were measured on the TEM images using ImageJ software.

Powder X-ray diffraction (XRD) patterns were obtained from powder samples mounted on silicon slides using a Rigaku Miniflex II XRD instrument operating with Cu K α radiation (λ = 1.5406 Å).

Pt content of the Pt@WO₃ NW dispersions was determined using an Agilent 7700x type ICP-MS.¹⁵

2.5. Gas Sensor Measurements

For gas sensor measurements, polycrystalline Al₂O₃ substrates having screen-printed thick film electrodes of Pt with a distance of 200 μ m were used. In order to control

the spreading of the deposited material a piece of Kapton tape with a hole of 2 mm diameter, made using a puncher, was mounted on the chip. The chip was placed on a hot plate set at 40 °C and 8 droplets of 2 μ L of Pt@WO₃ NW dispersions was drop casted into the hole. Using this method, the concentration of the sensing material, Pt@WO₃ NW, on each chip was the same, namely 0.026 mg/mm². After the material dried in the hole, the Kapton tape was removed.

Gas response measurements were performed in a Linkam THMS600 heating and freezing stage connected to a Keithley 2636A sourcemeter. Pre-mixing and flow rate of hydrogen and the carrier gases were controlled by mass flow controllers MKS Instruments 1179A Mass-Flo® (flow rate range of 1–1000 sccm) connected to a computer. Hydrogen (1% H₂, 99% N₂), synthetic air 5.0 (79% N₂, 21% O₂) and Argon 6.0 were purchased from AGA. At first, the chip was heated to 150 °C and after stabilization; it was exposed to six different concentration of hydrogen impulses from 20 to 1000 ppm. The response of the sensors was measured at 200 and 250 °C in the same manner.

3. RESULTS AND DISCUSSION

Tungsten trioxide nanowires were prepared in acidic aqueous media using sodium tungstate as precursor by a hydrothermal process at elevated temperature. As a result, bundles of nanowires were formed throughout the 48-hour synthesis (Fig. 1(b)) revealed by SEM analysis. Further electron microscopic investigations showed nanowires with diameter and length of 100–500 nm and 1–7 μ m (Fig. 1(a)), respectively. On the X-ray diffraction (XRD) pattern Figure 1(c). Each and every diffraction peaks can be assigned to hexagonal tungsten (VI) oxide with the evidence of no impurities are present.

Pt nanoparticles were prepared by polyol method using PtCl₄ and H₂PtCl₄ as precursors and PVP as capping agent in ethylene glycol media. The synthesis resulted in spherical particles with relatively narrow size distribution of 1.5 $\pm$ 0.4 nm, 3.7 $\pm$ 0.5 nm, 6.2 $\pm$ 0.8 nm and 8.3 $\pm$ 1.3 nm (Figs. 2(a–h)) revealed using TEM analysis.

Figures 3(a)–(d) show typical TEM images for the four nanoparticles of different sizes on the WO₃ nanowire surface. On the one hand, it is clear from the images that

nanoparticles bigger than approx. 4 nm are well dispersed on the surface, but on the other hand, slight aggregation can be observed in the case of the smallest nanoparticles (Fig. 3(a)).

Both pristine and Pt decorated WO₃ nanowires show decreased resistance when exposed to pulses of H₂ both in air and argon carrier gas, which is in good agreement with our results in previous studies reporting gas sensing with various forms of WO₃ nanomaterials (anodic oxide, nanoparticles and nanowires).^{1–3} The decreased sensor resistance (or increased conductance) of Taguchi-type devices upon reductive analytes such as H₂ in our experiments is a signature of *n*-type semiconducting behavior. It is clear from our measurements, that Pt can sensitize the device significantly allowing for reliable detection of H₂ in the lowest applied gas concentration (20 ppm) even at low temperature (150 °C).

The major difference between air and argon buffered H₂ sensing is the recovery of the devices between subsequent H₂ pulses. In the case of air carrier, the sensor resistance returns back to its normal background value, whereas in argon, we observe poor recovery, which can be reasonably explained by the conduction and sensing mechanisms of semiconducting oxide based materials. Since the conduction of oxides is mostly governed by the drift of O-defects, the more defects created, we shall observe increased conductance of the material. As H₂ can effectively reduce the surface of WO₃ thus creating O-defects in the lattice and thus conductivity is increased. After the H₂ pulse, in air, the O-vacancies are filled again and the sensor recovers. On the other hand, in Ar, we expect and observe a better reduction of WO₃ and thus even higher increase of the sensor conductance as compared to air buffer. However, after the H₂ pulse, the surrounding Ar is not oxidizing back the lattice and thus the original lattice chemistry and conductivity cannot be restored resulting in the poor recovery of the sensors.

While the raw measurement data plotted in the panels of Figure 4 enables a good mechanistic analysis of general sensor behavior concerning temperature and gas composition (concentration and carrier chemistry), any direct assessment of Pt nanoparticle size dependent sensor response is very limited for two reasons. Firstly, the metal loading of the WO₃/Pt composites is different in the used

Figure 1. Characterization of WO₃ NW. TEM (a) and SEM (b) images of the WO₃ nanowires; XRD pattern of WO₃ NW (c).

Figure 2. TEM images (a–d) and size distribution (e–h) of the prepared Pt nanoparticles.

samples (0.35, 0.08, 0.09 and 0.61 wt.% in WO₃/Pt (2 nm), WO₃/Pt (4 nm), WO₃/Pt (6 nm) and WO₃/Pt (8 nm), respectively). Secondly, the dispersion, i.e., the number of surface atoms in reference to the total number of atoms in the Pt nanoparticles are also different because of the different particle sizes: 0.53 , 0.28 , 0.17 and 0.13 as calculated for the Pt nanoparticles of averaged size of 1.5 ± 0.4 nm, 6.2 ± 0.8 nm, 3.7 ± 0.5 nm and 8.3 ± 1.3 nm, respectively. In order to make the results comparable thus we normalize our raw data with these factors and instead of the magnitude of resistance, we plot the corresponding normalized sensor sensitivity curves¹⁶ as displayed in Figure 5.

After normalization of the raw sensor data with the Pt dispersion and concentration values and plotting the normalized sensitivity curves, we can compare and deduce the Pt nanoparticle size dependent sensing behavior of our materials. We find that the normalized sensitivity values

of the sensors are different and show an interesting trend. Namely, the sensors made of the larger Pt nanoparticles (6 and 8 nm nominal size) are more sensitive to H₂ than the ones with the smaller nanoparticles (2 and 4 nm) suggesting that the surface atoms of larger nanoparticles are more reactive than the ones on smaller nanoparticles. The result is surprising by considering that in heterogeneous catalysis, usually the turn-over-frequency (reaction rate normalized to the number of surface atoms) of hydrogenation reactions are structure insensitive,¹⁷ and indicates that in H₂ sensing it is not only the surface that plays role but probably also the bulk of the catalyst nanoparticle.

Figure 3. Pt nanoparticles of different sizes, 2 nm (a), 4 nm (b), 6 nm (c), and 8 nm (d) supported on WO₃ nanowires.

Figure 4. Sensor resistance measured in two-probe setup on pristine and four different types of Pt nanoparticle decorated WO₃ nanowires at 150, 200 and 250 °C in 20, 50, 100, 200, 500 and 1000 ppm H₂ in (a) air and (b) argon carrier gas.

Figure 5. Sensor sensitivity normalized with Pt nanoparticle dispersion and concentration in the WO₃/Pt nanocomposites measured at 150, 200 and 250 °C.

Note: The lines (B-spline) connecting the discrete data points are only to guide the eye.

This assumption may be reasonable by considering that Pt can dissolve some hydrogen at the applied sensor temperatures.¹⁸ Further, one shall also consider the energy of surface atoms, which depends on the particle size viz. the relative number of lower coordination (i.e., atoms in corner and edge positions), is larger on surfaces of smaller nanoparticles.¹⁹ In addition, the energy density of Pt(111), Pt(110) and Pt(100) facets are different,²⁰ so any alteration of their areal ratio (which happens by changing the particle size) one may expect also changes in the overall surface energy densities in nanoparticles of different size and thus lead to size dependent catalytic activities or sensor response.

4. CONCLUSIONS

We have used Pt nanoparticles with four different sizes, all smaller than 10 nm, supported on WO₃ nanowires in order to compare their performance in hydrogen sensing. According to the measured electrical response of Taguchi-type resistive sensors at various temperatures and gas concentrations, the larger Pt nanoparticles are more active in the partial reduction of WO₃ lattice upon H₂ exposure than their smaller catalyst counterparts. Our study indicates, that apart from the chemistry of sensing materials, their microstructure also plays a significant role, which gives a further freedom to develop and optimize sensor devices in the future.

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16. Sensor sensitivity is defined here as the relative change of sensor conductance in reference to analyte concentration i.e., $(CH_2 - C_{\text{carrier}})/(C_{\text{carrier}} \cdot [H_2])$, where CH_2 is the conductivity measured upon a H₂ pulse, carrier is the background conductivity in the carrier gas just before applying the H₂ pulse, and $[H_2]$ is the analyte concentration. The normalized sensor sensitivity is obtained by dividing the calculated sensor sensitivities with the corresponding Pt dispersion and concentration values.
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