

Sonochemically Prepared SnO₂ Quantum Dots as a Selective and Low Temperature CO Sensor

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Abstract—In this study, a low temperature sensor highly selective to CO in presence of methane is fabricated by using 4 nm SnO₂ quantum dots (QDs) prepared by sonication assisted precipitation. SnCl₄ aqueous solution was precipitated by ammonia under sonication, which continued for 2 h. A part of the sample was then dried and calcined at 400°C for 1.5 h and characterized by XRD and BET. The average particle size and the specific surface area of the SnO₂ QDs as well as their sensing properties were compared with the SnO₂ nano-particles which were prepared by conventional sol-gel method. The BET surface area of sonochemically as-prepared product and the one calcined at 400°C after 1.5 hr are 257 m²/gr and 212 m²/gr respectively while the specific surface area for SnO₂ nano-particles prepared by conventional sol-gel method is about 80m²/gr. XRD spectra revealed pure crystalline phase of SnO₂ is formed for both as-prepared and calcined samples of SnO₂ QDs. However, for the sample prepared by sol-gel method and calcined at 400°C SnO crystals are detected along with those of SnO₂.

Quantum dots of SnO₂ show exceedingly high sensitivity to CO with different concentrations of 100, 300 and 1000 ppm in whole range of temperature (25- 350°C). At 50°C a sensitivity of 27 was obtained for 1000 ppm CO, which increases to a maximum of 147 when the temperature rises to 225°C and then drops off while the maximum sensitivity for the SnO₂ sample prepared by the sol-gel method was obtained at 300°C with the amount of 47.2. At the same time no sensitivity to methane is observed in whole range of temperatures for SnO₂ QDs. The response and recovery times of the sensor sharply decreases with temperature, while the high selectivity to CO does not deteriorate.

Keywords—Sonochemical, SnO₂ QDs, SnO₂ gas sensor.

I. INTRODUCTION

TIN dioxide, a wide band gap semiconductor with high chemical stability and excellent optical and electrical properties, has been widely used for various devices, such as gas sensors. Tin oxide semiconductor sensors are widely used

for detection of various pollutant and combustible gases. The advantages of these sensors are: high sensitivity, simple design, and low weight and cost [1, 2]. Since gas sensing properties of SnO₂ materials are strongly dependant on their size, over the past few years, remarkable progress has been made in the synthesis of nano-structured SnO₂ materials. QDs are nano-materials with the grain size less than 5nm which show unique electrical and catalytic properties due to their ultra-fine grain size. QDs unique properties can be arise from two reasons: The main reason can be attributed to the completely depletion of ultra-fine grains by charge carriers, in addition the increase of the surface-to-bulk ration by decreasing the grain size of the particles play an important role in high reactivity of the particles.

One of the latest technologies used for fabrication of ultra-fine nano-structured materials is utilizing ultrasound radiation which is named: "sonochemistry": Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) [3]. Sonochemical method is widely used to synthesize the nano-structured materials due to its unique properties which are related to acoustic cavitation: the generation, growth and cavitation of micron-sized bubbles in the liquid solutions. As ultrasound passes through a liquid, the expansion cycles exert negative pressure on the liquid, pulling the molecules away from one another. If the ultrasound is sufficiently intense, the expansion cycle can create cavities in the liquid. This will occur when the negative pressure exceeds the local tensile strength of the liquid. Once formed, small gas bubbles irradiated with ultrasound will absorb energy from the sound waves and grow. Once the cavity has overgrown, either at high or low sonic intensities, it can no longer absorb energy as efficiently. Without the energy input the cavity can no longer sustain itself. The surrounding liquid rushes in, and the cavity implodes. The collapse of bubbles thus occurs during the compression cycle. The compression of cavities when they implode in irradiated liquids is so rapid than little heat can escape from the cavity during collapse. The surrounding liquid, however, is still cold and will quickly quench the heated cavity. Thus, one generates a short-lived, localized hot spot in an otherwise cold liquid. Such a hot spot is the source of unique properties which include high temperature of roughly 5000° C (9,000° F), a pressure of about 1000 atmospheres, a lifetime considerably less than a microsecond, and heating and cooling rates above 10 billion° C per second [4,5]. It is proved that strong van der Waals attraction tends to induce irreversible agglomeration as the size of zero- and one

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dimensional nanostructures decreases which can exceedingly retards the diffusion of the target gas toward the surface of the sensor as well as the counter diffusion of the product gases to the ambient atmosphere, which greatly reduces the sensor response speed [6]. Ultrasound irradiation provides ample energy to hinder such agglomeration, though as it is also reported by Nandini Das [7], tension to agglomeration due to the adsorption of humidity is not prohibited. Thus by means of this unique method we can obtain ultra-fine nano-crystalline SnO_2 which can show significant gas sensing properties such as high sensitivity and remarkable reduction in sensing temperatures which makes adding of any dopant unnecessary.

Carbon monoxide is one of the most common and dangerous pollutants present in the environment due to emissions from automated vehicles, aircrafts, industrial wastes, etc. Its poisonous effects on human life are well known. Thus a CO gas sensor showing high sensitivity especially at low temperatures is of great importance.

In this study we present a highly sensitive SnO_2 gas sensor which is fabricated through sonochemical route. The sensor shows high selectivity to CO in the presence of methane as well as high sensitivity to this gas at low temperatures (below 100°C) due to their quantum dot effects. Our investigation also demonstrates the evident enhancement in gas sensing properties of SnO_2 nano-particles prepared by sonochemical route in comparison with ones fabricated by conventional sol-gel method in our laboratory.

II. EXPERIMENTAL

SnO_2 QDs were prepared by a sonochemical-assisted precipitation method using 50 cc aqueous solution of SnCl_4 , 0.15 mol/lit. the solution was irradiated for 10 minutes by a high-intensity ultrasonic processor (model- 250UL, Helchier, Germany, 250W; frequency 24 kHz, 6 mm titanium-tip probe), using a direct-immersion ultrasonic horn. A 32% ammonia solution was then added dropwise to the above solution while sonicating, so that the final pH value of the solution was controlled to be in the range of 9-10. The temperature was controlled in range of $70\text{--}80^\circ\text{C}$ during sonication using a water bath. The sonication was continued for 2h so that a milky, transparent and homogeneous solution is obtained. the precipitate was then centrifuged and washed several times with deionized water, to remove chlorine ions, then dried slowly at 70°C . After being dried a part of the sample was calcined at 400°C for 1.5 h.

The sample after calcination was pasted onto the alumina ceramic flat substrates with previously deposited gold contacts with 1.5 mm spacing. After sintering at 400°C for 45min, the samples were ready for gas-sensing tests. At the same time for comparison a paste of SnO_2 nano-powders synthesised by conventional sol-gel method was also applied onto a substrate with the same condition.

The study on the gas-sensing properties of our sample, sensitivity of the sensor to CO with different concentrations of 100,300 and 1000ppm, as well as 5000ppm methane, was measured.

To study the performance of the sensors in the presence of different gases of various compositions, a testing setup in which the gas flow rates were controlled by means of two mass flow controllers (MFC), was used. The sensitivity of the sensors was measured in a flow experimental setup, consisting of a gas manifold, a glass U-tube reactor (holding the sensors) immersed in a molten salt bath for a uniform temperature, and electrical measurement devices interfaced to the computer for continuous monitoring of the sensors' sensitivity. About 10 cm of the reactor, packed with glass beads, was used as a gas pre-heater. Testing gases were mixed with air different flow rates of air to adjust the concentration of the gases passing over the sensors. The temperature of the sensors was varied from 25 to 300°C . Depending upon the operating temperature, sensor's resistance may vary from a few tens of ohms to a few mega ohms. The sensitivity of the sensor is defined as its resistance in air divided by that in the gas, i.e., $R_{\text{air}}/R_{\text{gas}}$.

The BET surface area measurement of the samples was carried out by nitrogen adsorption after degassing of the as-prepared and calcined catalysts at 70 and 300°C respectively for 2 h, using a CHEMBET 3000 apparatus.

The dried and calcined powders were examined using X-ray diffraction (CM 200 FEG TEM Philips- M.E.R.C Philips, PW, 1710 with Cu K α radiation). The average grain sizes of the powders were calculated using Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \alpha} \quad (1)$$

III. RESULT AND DISCUSSION

The XRD pattern of SnO_2 nanoparticles fabricated by sonochemical-assisted method as well as sol-gel method is shown in Fig. 1. Compared to JCPDS (File No. 41-1445) standard pattern, the peaks in Fig. 1a, 1b agreed well with cassitrite structure of SnO_2 crystal, with no additional lines belonging to other phases such as SnO while the trace of SnO phase is detected in the sample prepared by sol-gel method (Fig. 1c).

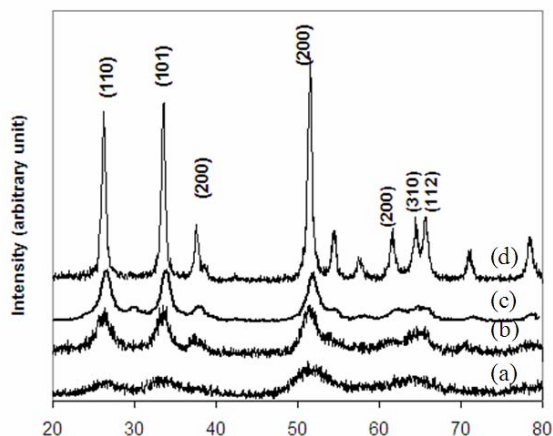


Fig. 1 XRD pattern of SnO_2 nanoparticles fabricated by: (a) Sonochemical method, as prepared sample, (b) sample (a) after calcination at 400°C for 1.5 h. (c) sol-gel, calcined at 400°C for 2h, (d) sample c after calcination at 600°C for 2h.

The broad peaks illustrated in Fig. 1a, 1b indicate the ultra-fine SnO₂ nano-particles obtained using sonochemical method. The sharper peaks in Fig. 1b indicate the growth of the SnO₂ crystals due to the thermal treatments. The XRD diagram of as-prepared SnO₂ (Fig.1) evidently proves the generation of crystalline phase before applying any thermal treatment. In order to enlighten such a phenomenon we should first explain briefly about the regions where sonochemical reactions take place. It has been reported that three different regions are formed in the aqueous sonochemical process: (i) the gas phase within the cavitation bubble, where elevated temperature (several thousand degrees) due to the formation of hot spots and high pressure (hundreds of atmosphere) and high cooling rates ($>10^{10}$ K/s) are produced; (ii) the interfacial zone between the bubble and the bulk solution where the temperature is lower than that inside the bubble but still high enough for a sonochemical reaction; and (iii) the bulk solution at ambient temperature where reaction still takes place [8]. Generally sonochemical reactions of volatile precursors occur in the gas phase inside the cavitation bubbles while the collapsing of such bubbles occur in a very short time (less than a nanosecond) and because of the high cooling rates which are obtained during the collapse of the bubbles there is no enough time for the formation of crystalline phase while such ample time is provided in the interface region where the sonochemical reactions of nonvolatile precursors occur. Of the aforementioned three regions, we prefer the interfacial zone as the region where the crystallization occurred mainly because of the low vapor pressure of the reactants. The XRD pattern of our as-prepared SnO₂ sample (Fig. 1a) in which the cassitrite crystalline peaks are obvious also confirms our anticipated reaction region.

The BET surface area and particle size of SnO₂ samples fabricated by both sonochemical-assisted and sol-gel methods and the average particle diameters corresponding to these surface areas as well as those calculated by using Scherrer's equation based on the peak broad analysis at the (110) peak, are presented in Table I.

TABLE I
THE XRD AND BET SURFACE AREA (S) AND THE CORRESPONDING GRAIN SIZE (D)

Sample	BET		XRD
	S (m ² /g)	d (nm)	d (nm)
as-prepared SnO ₂	257.2	3.38	2.21
Sample a calcined at 400°C, 1.5 h	212.4	4.09	3.51
Sol-gel, Calcined at 400°C	80.14	10.85	6.12
Sol-gel, Calcined at 600°C	64.89	13.4	9.2

As is depicted in Table I, using sonochemical method leads to a significant increase of surface area and consequently a

remarkable decrease in particle size of the catalyst. In addition there is some how dramatic difference between the BET and XRD surface area of the samples fabricated by sol-gel method which is attributed to the agglomeration of particles, however this tension to agglomeration is hindered using sonochemical method. This different is more dramatic while comparing the BET surface area and the corresponding particle size of the samples prepared by sonochemical and sol-gel method. The ultrasonic radiation provides ample energy to break the gel-clusters created in solution during synthesis of nano-structured materials by means of conventional synthesis methods) and as the result hinders the agglomeration of particles in product.

The sensitivity of sonochemically prepared SnO₂ as well as SnO₂ sample prepared by sol-gel method to CO with different concentrations at temperature range of 25-300°C is illustrated in Fig. 2.

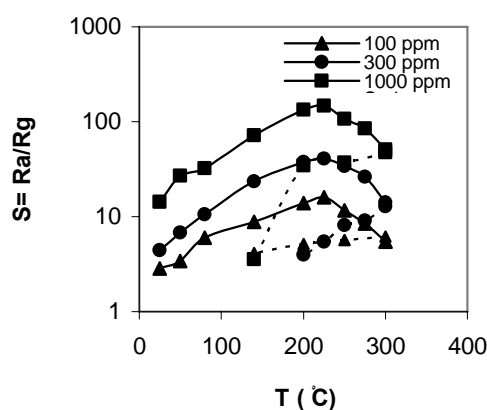


Fig. 2 Sensitivity of SnO₂ QDs prepared by sonochemical method (solid line) and SnO₂ nanoparticles prepared by sol-gel method (dashed line) to various concentration of CO at different temperatures

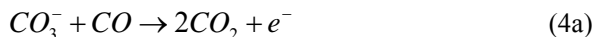
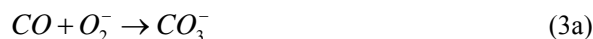
Fig. 3 shows that at the same concentration of CO gas, the sensitivity of the SnO₂ gas-sensor prepared using sonochemical route is about 3 times higher than that of conventional sol-gel ones. The most enthusiastic point revealed by Fig.3 is that our QD SnO₂ fabricated by sonochemical method shows high sensitivity to CO in the temperatures lower than 100°C which is a good approach to fabrication of a low temperature gas-sensor without using any dopant. Generally there are two models to describe gas-sensing properties of nano-materials: grain model and neck model. It has been established that the grain size and the width of the necks are the main parameters that control gas-sensing properties in metal oxide films as well. Usually it is displayed through the so-called "dimension effect" e.g., a comparison of the grains size (d) or necks width (X) with the Debye length (L_D):

$$L_D = \sqrt{\frac{\epsilon k T}{2 \pi e^2 N}} \quad (2)$$

Where k is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric constant of the material, and N is the concentration of charge carriers. It is clear that the width of the necks determines the height of the potential barrier for current carriers, while the length of the necks determines the depletion-layer width of the potential barrier. It is necessary to note that the increase of the necks length increases the role of necks in the limitation of metal oxide conductivity, and correspondingly in gas-sensing effects. The grain size would determine the depth of valley on the potential distribution within grains [9]. It is necessary to note that the applicability of "grains" or "necks" models depends strongly on the technological routes used for metal oxides synthesis or deposition and sintering conditions. Usually the appearance of necks is a result of high temperature annealing ($T > 700\text{--}800^\circ\text{C}$) [10]. In our experiments the annealing temperature is 400°C in which we can assume that the formation of necks between grains are very short or are absent. It means that for description of gas-sensing properties of our sensors we can use the "grains" model. According to this model, between grains there are Schottky type contacts with the height of potential barrier depending on the surrounding atmosphere. In the frame of such approach the grain boundary space charge or band bending on inter-grain interfaces are the main parameters controlling the conductivity of nanocrystalline metal oxides. In this model it is assumed that the grains with size smaller than few nanometers are completely depleted by charge carriers. It was demonstrated that, when the grain size becomes comparable to twice the Debye length, a space-charge region can develop in the whole crystallite. This case is the most desirable, since it allows achievement of maximum sensor response [11, 12]. Thus because the Debye size of SnO_2 is $L_D=3\text{nm}$ at 250°C our sonochemically prepared QDs with the particle size near to this value show high sensitivity even at low temperatures. Besides, the surface reactivity of particles is known to rapidly increase with the increase of the surface-to-bulk ratio because the strong curvature of the particle surface generates a larger density of defects, which are the most reactive surface sites. This high reactivity has largely been taken advantage in catalysis, where ultra-fine particles have been used for decades. When properly processed during the fabrication of chemical semiconductors sensors, these nanoparticles are sufficiently reactive to make the use of catalytic additives (such as Pt or Pd) unnecessary and to decrease the working temperature of the sensors without any loss of sensitivity [13].

It can be observed that the sensitivity of SnO_2 increases by increasing the temperature reaches a maximum and then drops off. The maximum amount of Sensitivity to CO for sonochemically prepared nano-crystalline SnO_2 and those prepared by sol-gel method are 147 and 47 respectively. The surface oxygen species have been evidenced with spectroscopic techniques on the surface of SnO_2 : at lower temperature ($<200^\circ\text{C}$) oxygen adsorbs on SnO_2 non-dissociatively in a molecular form (either neutral $\text{O}_{2(\text{ads})}$ or charged $\text{O}_{2(\text{ads})}^-$) and at higher temperatures it dissociates into atomic oxygen (either neutral $\text{O}_{(\text{ads})}$ or charged $\text{O}_{(\text{ads})}^-$) [12,13]. Koziej. Et al [14] introduces these two mechanisms for explaining their results at different temperatures:

At lower temperatures:



At higher temperatures:



These mechanisms perfectly explain the reasons of occurrence a maximum in SnO_2 samples.

The sensitivity of SnO_2 QDs prepared by sonochemical-assisted precipitation method to 5000ppm methane and 1000ppm CO is depicted in Fig. 3 as well. In order to filter all impurities and making sure of the existence of pure methane, Methane is filtered by Au catalytic filter before being used in gas-sensing tests.

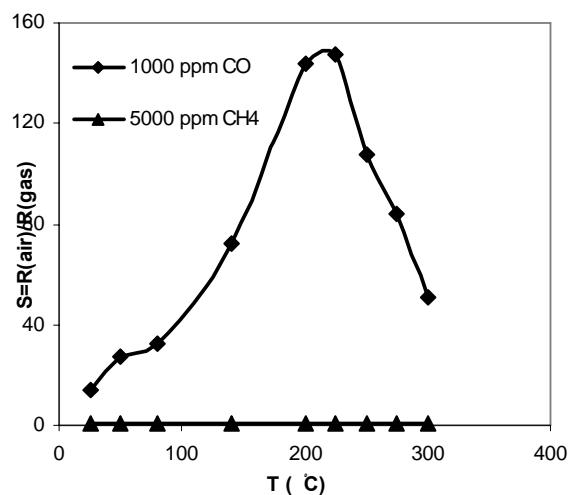


Fig. 3 Sensitivity of SnO_2 QDs to 1000 ppm CO and 5000 ppm methane at different temperatures

As is clearly illustrated in Fig. 3, our QD SnO_2 has significantly high sensitivity to CO in whole temperature range of $25\text{--}300^\circ\text{C}$ while at the same time it shows no sensitivity to methane. It can be concluded that the sensor is highly selective to CO and ethanol in the presence of methane which is an important achievement. Earlier it was observed by Seok-Kyun Song, Et al [1], that undoped SnO_2 nanoparticles show no sensitivity to methane below 400°C . Our observation shows that our QD SnO_2 gas-sensor shows similar behavior.

The recovery and response times of our SnO_2 QD gas sensor to 300 ppm CO at 80 and 225°C are illustrated in Fig. 5. The diagram is drawn according to data which are extracted from the response curve recorded by the recorder. The resistances are normalized to their final stable values.

A rather long 90% response and recovery of about 1 and

1.8 min, respectively, are observed for the sensor at 225°C which are much shorter than those at 80°C. The less time of response to higher temperature is likely due to the desorption of oxygen species. Another cause can be the high reactions rate at the elevated temperature, so the reaction mainly on the surface of sensor, reducing the gas concentration in the bulk and therefore diminishing the response [15].

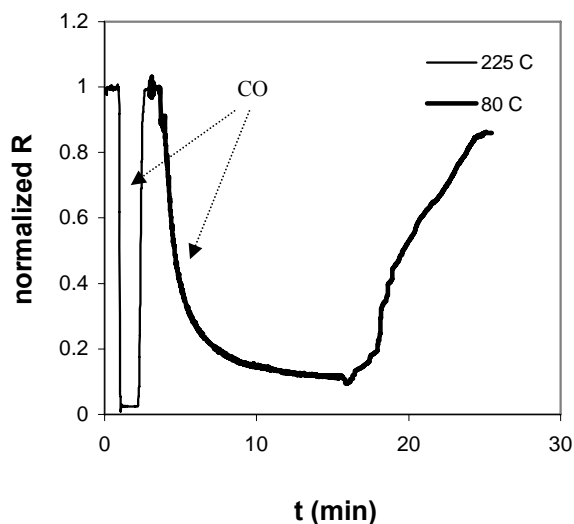


Fig. 4 Recovery and response times of SnO₂ QDs to 1000 ppm CO at 225 and 80°C. Sensor response to 1000

IV. CONCLUSION

We now introduced a new low temperature SnO₂ CO gas-sensor fabricated by unique sonochemical method. Being responsible for the dramatic reduction of SnO₂ particle size, the mechanism is called "acoustic cavitation" which includes the generation, growth and the collapse of micron-size bubbles in the precursor solution. SnO₂ QDs show significantly high sensitivity to CO in whole temperature range of 25-300°C which is 3 times higher than that of conventionally fabricated sensors in sol-gel method. The dramatic increase in sensitivity especially low temperature sensitivity of SnO₂ QDs is attributed to "dimension effects" which can be described by "grain model". Our investigations could also present a highly selective SnO₂ gas-sensor to CO in the presence of methane. We also illustrated the recovery and response time of the SnO₂ QD gas-sensor in both low and high temperatures (225, 80°C). The decrease of response to higher temperature is likely due to the adsorption of oxygen species and the high reactions rate at the elevated temperature, so the reaction mainly on the surface of sensor, reducing the gas concentration in the bulk and therefore diminishing the response.

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