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Non-aqueous synthesis of In_2O_3 nanoparticles and its NO_2 gas sensing properties

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Abstract

An indium trioxide (In_2O_3) nanoparticle based conductometric sensor has been fabricated and tested towards NO_2 gas. Novel chemical synthesis method was developed, in which benzylamine was mixed with indium acetate to form $In(OH)_3$ as a precursor to form In_2O_3. Micro-characterization results revealed that the average size of the In_2O_3 nanoparticles is 8 nm and the particles have a cubic crystalline phase. Sensors exhibited very high sensitivities towards NO_2 at an operating temperature of 150°C. Fast response and recovery with good repeatability along with stable baseline were observed.

Key words: Indium oxide, solvothermal, nanoparticles, NO_2 sensing

Introduction

Reliable gas sensors are required to monitor NO_x contents in air to maintain health and safety standards. The environment is being polluted due to NO_x emissions from different industrial activities. Therefore, the demand for reliable and inexpensive NO_2 sensors operating in wide concentration range is extremely high. Nanostructured In_2O_3 is a very promising material for NO_2 sensing [1-4]. They provide enhanced surface-to-volume ratios which consequently increases interaction of analytes with the surface of the nanoparticles.

There are many techniques to form In_2O_3 nanoparticles such as chemical vapor deposition (CVD), aerosol-assisted evaporation and hydrothermal synthesis [5-7]. Out of them, non-aqueous synthesis has been a popular technique to form nanoparticles [8]. However, In_2O_3 nanoparticles obtained from the aminolysis reaction between indium acetate ($In(OAc)_3$) and benzylamine ($PhCH_2NH_2$) at 180 °C have not been reported in literature. Other non-aqueous techniques employing different solvents require higher temperature (220 °C) and extensive periods of heating (2 days) [8, 9].

Experimental

(a) Synthesis of In_2O_3:

All the chemical reagents employed are of analytical grade and used without further purification. In this work, In_2O_3 nanoparticles were synthesized through the aminolysis reaction of indium acetate in the presence of benzylamine in one pot. We suggest that the substitution reaction took place between the acetate group of $In(OAc)_3$ and the NH_2 group of benzylamine, forming $In(OH)_3$. The intermediate $In(OH)_3$ was immediately transformed into In_2O_3 at the reaction temperature. After reaction, white In_2O_3 powder was separated through centrifugation, rinsed by ethanol, and dried in a vacuum oven at 90 °C for 12 h. The suggested aminolysis mechanism is shown in Fig 1.

In_2O_3 nanoparticles were characterized using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) techniques.

(b) Sensor fabrication and gas testing

The sensors were fabricated after spin coating of In_2O_3 nanoparticles onto an alumina substrate with pre-patterned interdigitated transducer (IDT). The sensor was annealed for 12 hours at 400 °C with a ramp up/down of 2 °C/min. Annealing was performed to enhance the crystal structure of In_2O_3 nanoparticles as well as to eliminate all organic residue/contamination. Once completed, the gold wires were attached to the sensor with silver epoxy and left to dry on hot plate at 100 °C for 15 mins. The sensor was then mounted into a custom made gas chamber set-up connected to computer controlled mass flow controllers (MFCs) and data acquisition system.

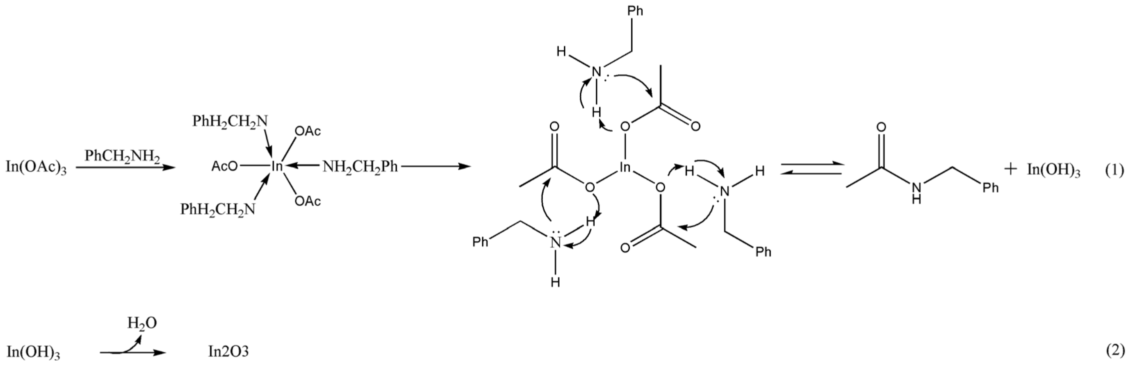

Fig. 1 Reaction between indium acetate and benzylamine.

Results and discussion

The XRD spectrum of In_2O_3 nanoparticles is shown in Fig. 2. The XRD data reveal that the In_2O_3 nanoparticles contain cubic phase (ICDD 06-0416). The diffraction peaks show good crystalline films and match very well with ideal lattice constants.

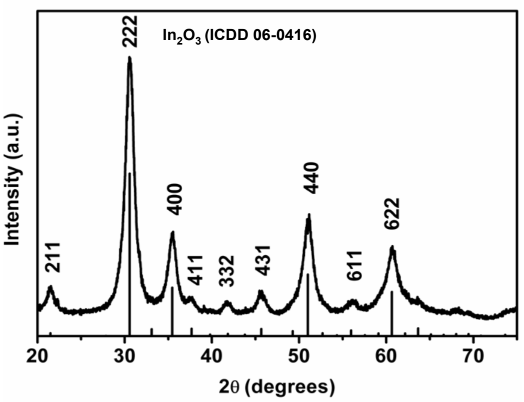

Fig. 2: XRD spectrum of In_2O_3 nano-particles.

The FE-SEM image (Fig. 3) magnifies the In_2O_3 nanoparticles. Further imaging towards the nanoparticles employing TEM microscope reveals the approximate particle size and the distribution of In_2O_3 (Fig. 4 (a) and (b)). The size distribution analysis shows that the average size of the particles is around 8 nm. The selected-area electron diffraction (SAED) pattern is shown in Fig. 5, further confirming the crystal structure of In_2O_3 nanoparticles.

It was found that the lattice spacing of 0.29 nm between the adjacent fringes (Fig. 6) corresponds to the d-spacing of the (222) planes in cubic In_2O_3.

Dynamic response of the developed sensor towards NO_2 at 150 °C is given in Fig. 7. The sensor response (S) toward NO_2 was calculated according to the equation, $S = R_{gas}/R_{air}$, where R_{air} and R_{gas} are the sensor resistances in air and in the presence of NO_2, respectively. The sensor has a high response of ~23 and ~897 towards the lowest and the highest examined concentration of NO_2 (500 ppb and 10 ppm), respectively. The measured response and recovery towards NO_2 with concentration of 500 ppb is 16 and 24 s, respectively.

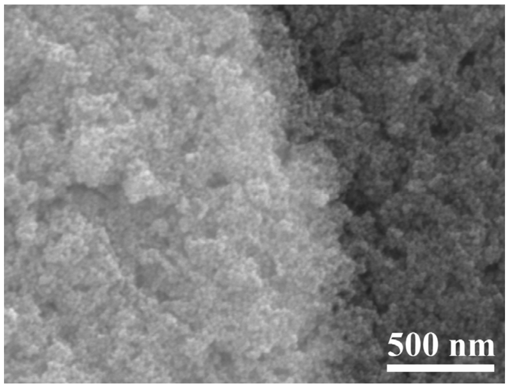

Fig. 3: FE-SEM image of In_2O_3 nanoparticles on the conductometric transducer.

The electrical characterization of the sensor showed that the response has increased tremendously compared to other nanostructured In_2O_3. It is well known that when an n-type semiconductor metal oxide is exposed to air, oxygen molecules can adsorb on the surface of the particles and form O^{2-}, O_2^{2-}, O_2^- ions by capturing electrons from the conductance band, which in turn produces an electron-depleted space-charge layer in the surface region. As the dimensions of the nanoparticles are sufficiently reduced, they can be completely depleted and the response to gases increases. [10, 11]. Figure 8 shows the correlation between the sensor response and the NO_2 gas concentration (500 ppb – 10 ppm) at the optimized operating temperature of 150 °C. The plot shows a perfectly linear characteristic indicating that the sensor may be able to detect higher NO_2 concentrations with enhanced sensitivities. Therefore, the In_2O_3 nanoparticles would be promising candidates for fabrication of high performance gas sensors.

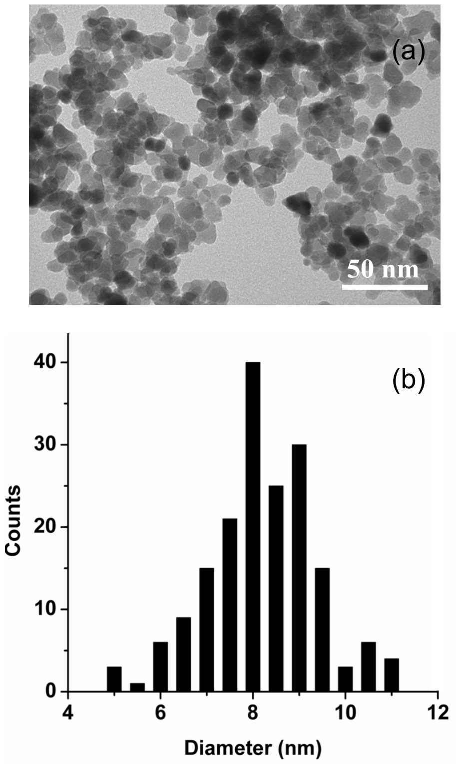

Fig. 4: (a) TEM image of the prepared In_2O_3 nanoparticles and (b) corresponding particle size distribution measured from more than 100 particles.

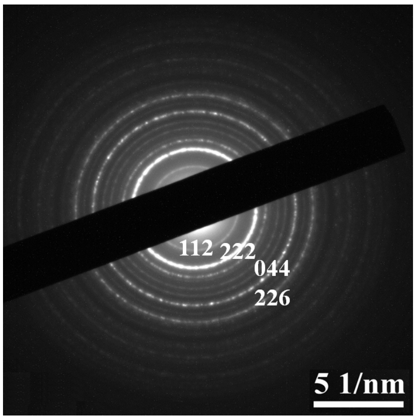

Fig. 5: SAED pattern indicating of In_2O_3 nanoparticles.

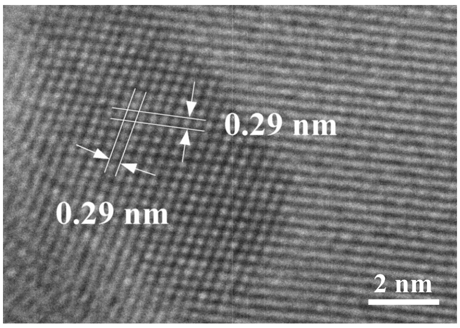

Fig. 6: HRTEM image featuring the lattice spacing of the In_2O_3

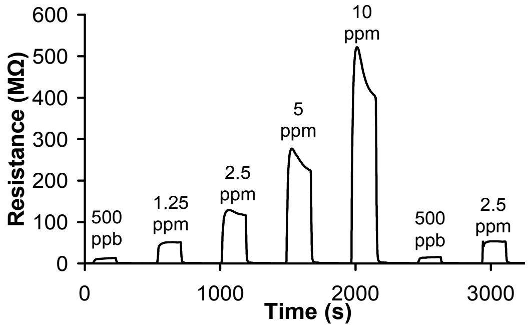

Fig. 7: Dynamic response of the In_2O_3 based sensor towards NO_2 at 150 °C.

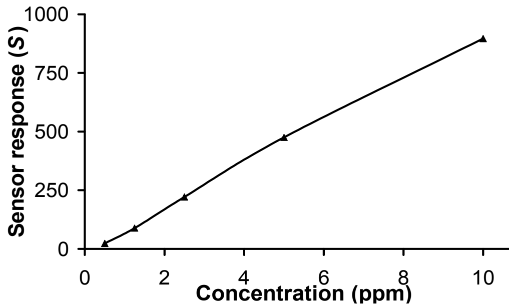

Fig. 8: Sensor response versus NO_2 gas concentration at 150 °C.

Conclusions

The In_2O_3 nanoparticles were successfully synthesized from non-aqueous solutions of indium acetate and benzylamine through the aminolysis mechanism. The nanoparticles were later successfully employed as sensitive layers for the development of novel conductometric NO_2 sensor. The developed device shows excellent sensing performance towards NO_2 at ppb levels at an operating temperature of 150 °C. Fast response and recovery with good repeatability along with stable baseline were observed.

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