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NO₂ Gas sensing properties of hydrothermally prepared platinum doped indium oxide nanoparticles

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Abstract

Gas sensors were fabricated using nanostructured indium oxide (In₂O₃) and platinum doped indium oxide (Pt-In₂O₃) prepared by surfactant assisted hydrothermal method. The optimum working temperature of the sensors was around 165 °C, which is lower than the literature reports. The sensor fabricated using Pt-In₂O₃ exhibited higher response as compared to undoped In₂O₃. Their gas sensing properties investigated with NO₂ gas with 2.5 and 5 ppm revealed that the sensors showed a concentration dependent electrical resistance.

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1. Introduction

Gas sensors based on semiconducting metal oxide (SMO) nanoparticles have attracted continuous attention due to their easy fabrication, low cost and convenient integration with process and monitoring instruments. NO₂ is a toxic gas generated from the combustion of fuels in internal combustion engines and chemical industries, which leads to

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inflammation of lungs, breathing difficulties and emphysema [1-2]. Safety standard by American Conference of Governmental Industrial Hygienists (ACGIH) listed the airborne exposure limit of NO_2 as 3ppm over an 8-hour work shift and as 5 ppm for short term exposure limit. A range of gas sensors based on SMOs, such as SnO_2 , WO_3 , ZnO , In_2O_3 , Fe_2O_3 , NiO , TiO_2 , ZrO_2 , Ga_2O_3 and CuO have been investigated for the detection and quantification of NO_2 gas [3]. Among them, In_2O_3 based SMO sensors exhibit lower resistance, lower optimum operating temperature with faster response and recovery times as compared to other oxides [4]. The gas sensing characteristics of nanostructured SMOs depends on the particle size and morphology of sensing materials [5]. Nanostructured In_2O_3 with various morphologies has been prepared by different methods, such as hydrothermal [6-7], laser ablation [8], electrospinning [9], vapour-liquid-solid (VLS) [10], carbothermal [11] and thermolysis of coordination polymers [12-13]. Doping SMOs with noble metals, such as platinum and palladium further enhances the sensitivity of the gas sensors [5,14]. However, only limited work is found in the literature for the NO_2 sensing properties of Pt- In_2O_3 nanomaterials [14,15]. In the present work, we report the NO_2 sensing characteristics of sensors fabricated using nanostructured In_2O_3 and Pt- In_2O_3 prepared by surfactant assisted hydrothermal method.

2. Experimental

2.1. Preparation of nanostructured In_2O_3 and Pt- In_2O_3

In_2O_3 and Pt- In_2O_3 nanoparticles were prepared by one pot *in-situ* hydrothermal method assisted with ethylene glycol (EG) and cetyltrimethylammonium bromide (CTAB) [16]. Briefly, 0.2804 g of hexamethylenetetramine (HMT, dissolved in 15 mL de-ionised water) was added to 12.5 mL of aqueous solution of indium nitrate (0.08 mol L^{-1}), 2.5 mL of EG and 3.0 g of CTAB under vigorous stirring. The resulting solution was autoclaved at 160°C for 8 h. Indium hydroxide ($\text{In}(\text{OH})_3$), formed as a white precipitate was washed with water, dried at 110°C and sintered at 400°C for 3 h under atmospheric conditions to afford bright yellow In_2O_3 . For the preparation of Pt- In_2O_3 , an aqueous solution of hexachloroplatinic acid (H_2PtCl_6) was added to the hydrothermal mixture before the autoclaving process. The atomic ratio of platinum was kept as 1 % with respect to indium metal and the Pt- In_2O_3 nanoparticles were obtained as grayish yellow powders. The details regarding formation, structural properties, dimension and morphology of both In_2O_3 and Pt- In_2O_3 were discussed elsewhere [16]. The transmission electron microscopic investigation confirmed that both the nanoparticles possessed short rod-like shapes. The lengths of the nanorods were in the range of 5–25 nm with maximum population between 10 and 15 nm and the widths of nanorods were around 5 nm [16].

2.2. Experimental set-up for testing of gas sensors

The home-made sensor consisted of parallel type gold electrodes (dimension of electrodes: $3 \text{ mm} \times 3 \text{ mm}$; gap between the electrodes: $500 \mu\text{m}$) on an alumina substrate mounted over a resistive heater. A homogeneous suspension of respective In_2O_3 and Pt- In_2O_3 nanoparticles was drop casted between each pair of electrodes and annealed at 350°C for 1 hr. The sensor structure was placed in a cylindrical gas cell of volume 7.5 mL and contact wires were taken from the terminals to connect the sensors with the measuring and controlling instruments. The resistance and temperature data were acquired using Agilent 34970A data acquisition unit interfaced with a computer. An Agilent U8001A DC power supply was used as DC power source for the heater and the temperature was controlled with a PID temperature controller unit. Mass flow controllers were used to mix NO_2 gas with carrier gas ($20\% \text{ O}_2/\text{N}_2$) to get the desired NO_2 concentration. Figure 1 depicts the block diagram of gas sensing setup.

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