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Ethanol sensing behaviour of sol–gel dip-coated TiO_2 thin films

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ABSTRACT

The TiO_2 nanoparticles were synthesized by sol–gel method initiating titanium isopropoxide–propanol mixture as a precursor solution. The obtained TiO_2 nanoparticles were then deposited onto the glass substrate using dip-coating method under optimized conditions. The ethanol sensing behaviour of the prepared TiO_2 thin film was studied by chemiresistive method at room temperature (~30 °C). The nanoparticle of TiO_2 as thin film formed exhibited good sensing response of 535% with response–recovery times of 5 s and 52 s, respectively, in the presence of 50 ppm of ethanol vapour. The effect of electrical resistance hysteresis was also discussed to emphasize the reversible nature of the TiO_2 film.

1. Introduction

Ethanol is widely used in perfumes, explosives and in automotive fuel industry [1]. The Occupational Safety Health and Administration (OSHA) established the maximum recommended exposure level of ethanol to be 1000 ppm [2]. Exposure to ethanol vapour results in health problems such as headache, drowsiness, irritation of eyes, liver damage and difficulty in breathing [2]. In recent years, semiconductor metal oxides have been recognized for their potential uses in fabricating electronic, optoelectronic, electromechanical and electrochemical devices because of their overwhelming electrical, optical, mechanical and thermal properties. In particular, semiconductor metal oxide thin-film-based gas sensors have attracted attention because of their ability to modify their electrical conductivity in the presence of toxic gases and vapours. The main drawback of the semiconductor based sensor is its high operating temperature which leads to large power consumption, decreases in sensor life and complicated heater design [3]. Therefore, the principle requirements for a good chemical sensor are cost effectiveness, high reactivity towards the target gas/vapour, high sensing response, fast response time, short recovery time, good reversibility, long-term stability, selective detection and low-temperature operation. The above-mentioned requirements can be met by developing a nanostructured sensing material, which provides a larger surface area, stronger self-catalytic nature and chemical-environment-dependent electrical properties.

Titanium dioxide (TiO_2) is an n-type wide-band-gap metal oxide semiconductor having wide range of applications, from pigments to sunscreen, photovoltaic to antimicrobial coatings. TiO_2 nanoparticles can be synthesized by various chemical methods, such as the chloride process [4], sulfate process [4], impregnation [5], co-precipitation [6], direct oxidation of $TiCl_4$ [7], hydrothermal method [8] and sol–gel processing [9]. Among these methods, sol–gel processing is more advantageous than the others owing to its simple and ease in synthesizing different nanostructures.

Different nanostructured TiO_2 materials have been widely used for various oxidizing or reductive gas/vapour detection. Lin et al. [10] reported the use of TiO_2 nanotubes as a room-temperature formaldehyde sensor. Moon et al. [11] demonstrated nanocrystalline Pd-doped TiO_2 nanofibres as a NO_2 sensor operating at 180 °C. Radecka et al. [12] demonstrated a flame-spray-deposited Cr-doped TiO_2 nanopowder as a hydrogen sensor operating at 400 °C. Garzella et al. [13] reported sol–gel-deposited TiO_2 thin films as ethanol sensors operating at 500 °C. The present work reports on room temperature ethanol sensing properties of sol–gel dip-coated TiO_2 thin films prepared on glass substrate. Various sensing performance such as response–recovery time, detection limit, hysteresis, selectivity, stability and reproducibility were analyzed and reported.

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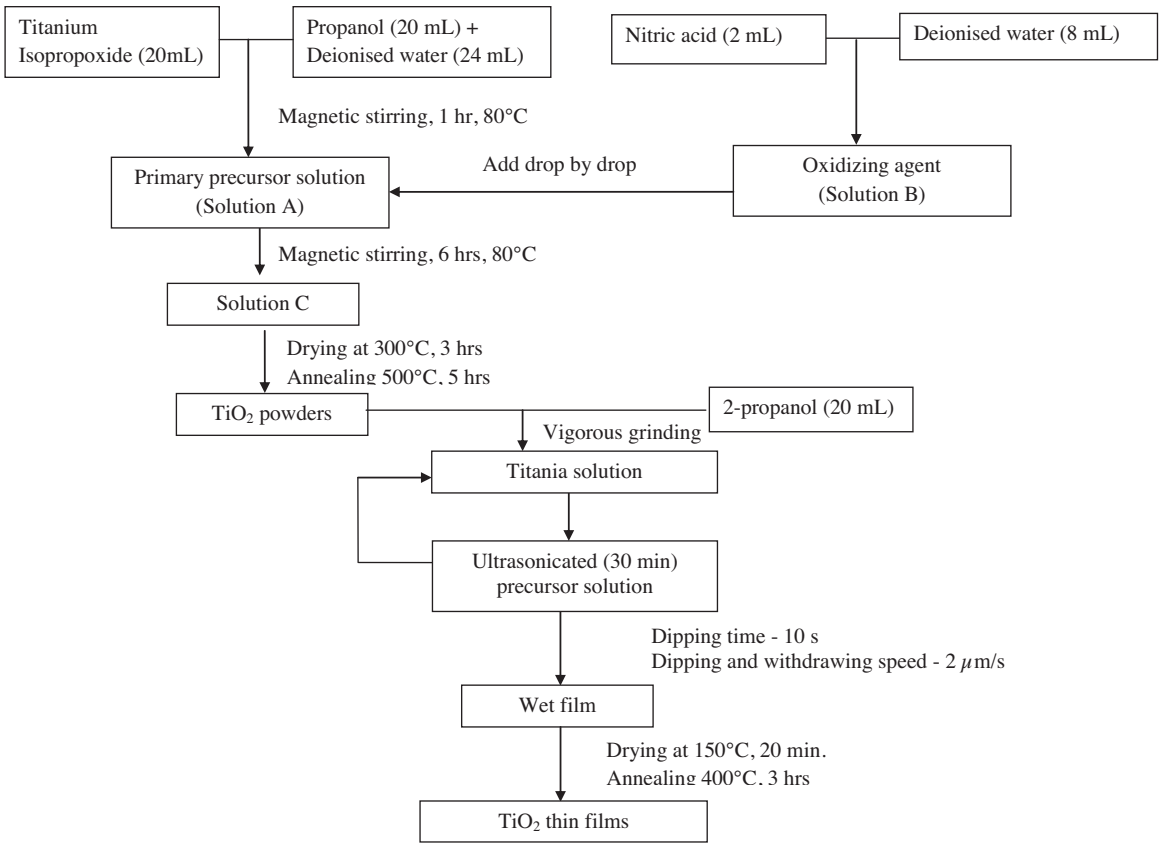

Fig. 1. Experimental process used to prepare the TiO_2 thin films.

2. Materials and methods

2.1. Sensing element preparation and characterization

Fig. 1 depicts the outline of TiO_2 thin film preparation. First, the titanium dioxide (TiO_2) nanoparticles were synthesized by hydrolysis process which was reported earlier [14] through a sol–gel method using titanium isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, 97% Sigma Aldrich) and 2-propanol (C_3H_8O, Merck) as precursors with deionized water as solvent. Briefly, the titanium isopropoxide of 20 mL was dissolved in a mixture of 2-propanol (20 mL) and deionized water (24 mL). This mixture (solution A) was then heated at 80 °C under continuous stirring for 1 h. Then a solution of oxidizing agent was prepared by dissolving 2 mL of nitric acid in 8 mL of deionized water under constant stirring (solution B). Then the solution B is added drop by drop to solution A under constant stirring at 80 °C, obtained solution C. The resultant solution C was subjected to stirring for 6 h at 80 °C and then drying at 300 °C for 3 h in ambient condition to obtain TiO_2 nano powders. The prepared powders was then annealed at 500 °C for 5 h and allowed to cool to room temperature slowly. To prepare TiO_2 nanoparticles as thin film on glass substrate, a precursor solution was prepared by mixing 20 mL of 2-propanol and 2 g of prepared TiO_2 nano powders. A glass substrate was dipped in the precursor solution and withdrawn slowly to obtain thin film of TiO_2 using computer controlled dip coating unit (HOLMARC, HO-TH-01). The optimized condition for obtaining well adherent and uniform distribution of TiO_2 nanoparticle over the substrate was given in Fig. 1. The particle size and distribution was observed using a Transmission Electron Microscopy (TEM, JEOL, JEM 2100, Japan) operating at 200 kV. The phase and crystal structure of the TiO_2 thin film were investigated using X-Ray Diffraction unit (XRD, Bruker D8, Focus, Germany) with Cu $K\alpha_1$ (1.5406 Å) X-ray. The thickness of the film was obtained from stylus profilometer (Mitutoyo SJ 301). The surface morphology and elemental identification were obtained using Field-Emission Scanning Electron Microscopy (FE-SEM, JEOL-6701F, Japan) coupled with Energy Dispersive Spectroscopy (EDS). For vapour sensing studies, the liquid ethanol (98% Purity, Merck, India) was purchased and utilized as such without further purification.

2.2. Senor fabrication and ethanol vapour sensing studies

The ethanol-vapour-sensing characteristics of TiO_2 film was examined using a home-built testing chamber with a capacity of 1.5 L. Prior to sensing studies, the film was conditioned by heating at 300 °C for 24 h to remove pre-adsorbed water and organic molecules. Electrical contacts were developed over a film surface area of 12 mm × 10 mm using thin copper wire and highly conducting silver paste.

The sensing film was placed inside the testing chamber using sample holder. Changes in the electrical resistance of the film during the process of injection and venting of ethanol vapour were monitored using LabVIEW controlled data acquisition system (DAQs). The stable resistance of the TiO_2 film in dry air atmosphere was taken as baseline resistance (R_o) and is 0.71 GΩ. The calibrated volume of ethanol solution was introduced into the test chamber and the concentration of the generated vapour was obtained using the following relation (1)

$$C\,(\text{ppm}) = \frac{\delta \times V_\Gamma \times R \times T}{M \times P_b \times V_b} \times 10^6 \quad (1)$$

where C is the concentration of liquid ethanol (ppm), δ is the density of ethanol (g/mL), V_Γ is a injected ethanol volume (μL), R is the universal gas constant (8.3145 J/mol K), T is the absolute