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Enhanced ethanol sensing performance of Fe: TiO_2 nanowires and their mechanism of sensing at room temperature

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Abstract

TiO_2 and Fe-doped TiO_2 nanowires were synthesized by spray pyrolysis technique to study their gas sensing properties towards ethanol. Charge transfer from metal dopant to TiO_2, and modification of TiO_2 with Fe doping was investigated for their ability to enhance gas sensing activity. The X-ray diffraction results indicate that the Fe dopant was substitutionally incorporated by replacing Ti^{4+} cations. Fourier transform infrared spectral analysis confirmed the presence of brookite TiO_2. The UV–visible spectra showed the increase in absorption with Fe doping when compared with undoped TiO_2 film, and optical band gap decreased slightly with Fe doping. SEM images revealed the presence of one dimensional structure of straight nanowires for undoped TiO_2 and curved nanowires for Fe doped TiO_2 films. To understand the enhancement of sensing performance of TiO_2 film with Fe doping, the gas sensing mechanism of the film towards Ethanol at room temperature was studied and discussed.

Keywords: TiO_2 films; Spray pyrolysis; XRD; UV; Ethanol sensing

1. Introduction

Ethanol vapor sensing finds large application in the field of food processing, biomedical, chemical industry, and breath analysis. For these applications, it is essential to provide high sensitivity, high selectivity, high stability, low working temperature, and short response and recovery times. Therefore, a great deal of research has been focused on the development of functional materials for high-performance of ethanol vapor sensing. In the past decades, semiconductors were widely used for gas sensing application, in that metal oxide semiconductors were extensively used because of their significant change in resistance upon exposure of gases to trace concentration of particular gas. Metal oxide semiconductors like ZnO, WO_3, SnO_2, TiO_2 and V_2O_5 were used as gas sensors. Among them, TiO_2 has been investigated extensively for gas sensing due to its higher surface reactivity to gases [1]. In order to enhance the gas sensitivity of TiO_2, nanostructures such as nanoparticles (0D) [2], nanowires (1D) [3], nanotubes (1D) [4], nanosheets (2D) [5] and hierarchical nanostructures (3D) [6], with high surface area were synthesized [7]. TiO_2 nanowires were fabricated to improve gas sensing characteristics on a large scale, as nanowires being one dimensional, nanostructure with uniform morphology and a large surface area with controllable less agglomeration have potential applications. However, there are many disadvantages of TiO_2 being used as gas sensors, due to high working temperatures, longer response, recovery time, and lower sensitivity. Recently, many methods were investigated with the focus of improving the gas sensing performance of TiO_2 nanowires. Doping with components such as Au, Pt, Pb, and Ag is known to be effective, because active sites can be produced for particular gas species by doping. However, these sensitive materials can be poisoned easily in some gas atmospheres, which can lead to reduction in sensitivity and stability. Iron has been considered an appropriate candidate for doping TiO_2, as the radius of Fe^{3+} being similar to that of Ti^{4+}. Therefore, Fe^{3+} ions might easily be incorporated into TiO_2 lattice [8]. As the band gap of iron is 2.6 eV, it will

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reduce the band gap of TiO_2, thereby increasing the performance of the sensor at lower temperature with large response and lower recovery time.

TiO_2 and Fe doped TiO_2 thin films were deposited by different methods, such as sol–gel process [9], chemical spray pyrolysis [10,11], sputtering [12], hydrothermal technique [13], reactive pulsed laser deposition [14] and electron beam physical vapour deposition [15]. Among which spray pyrolysis offers a number of advantages over other deposition processes, such as scalability of the process, cost-effectiveness, easiness of doping, operation at moderate temperatures and large uniform surface area. Fe-functionalized Brookite TiO_2 nanowires were assessed to detect a range of gases, but their sensing properties toward ethanol gas were not reported as far as we know. Hence, in the present work a novel ethanol sensor based on TiO_2 films were fabricated by spray pyrolysis technique. The effect of Fe doping on the structural, optical, and morphological properties of TiO_2 were investigated for enhancing sensing performance of TiO_2 towards ethanol at room temperature.

2. Experimental procedure

Aqueous solution of Titanium isopropoxide (TTIP) and Ferric chloride ($FeCl_3$) were used as precursors for the production of TiO_2 and Fe doped TiO_2 thin films. The solution was atomized by pneumatic spray system using compressed air as the carrier. TiO_2 and Fe doped TiO_2 thin films were coated using spray pyrolysis unit as discussed by the author elsewhere [16]. Parameters like solution flow rate, nozzle to substrate distance and deposition time were optimized during deposition to obtain good quality films. TiO_2 and Fe doped TiO_2 films were deposited using a pulsed solution feed at a flow rate of 5 ml per min. The distance between nozzle and the substrate was 30 cm. The substrate temperature was kept at a constant value of 350 °C. The mixed aqueous solution was sprayed over hot substrate, which undergoes thermal decomposition, TiO_2 film and Fe doped TiO_2 film was obtained. These films were further used to investigate the structural, vibrational and optical properties. The structural characterization was done using X pert Pro X-ray diffractometer with Cu $K\alpha$ radiation. Fourier transform infrared spectral analysis was made using FTIR spectrometer. The optical band gap energy of the films was investigated using Lambda 35 UV visible spectrometer. Surface morphology of films was studied using Scanning electron microscope.

3. Results and discussion

3.1. Effect of Fe doping on the structure of TiO_2 thin films

XRD pattern of the films only show the characteristic peaks of brookite phase at $2\theta = 31.78$ (JCPDS card no. 15-0875) without any characteristic peaks of Fe_2O_3 as shown in Fig. 1(a). Fe could not be observed in XRD as Fe^{3+} and Ti^{4+} have similar ionic radii, so Fe can easily substitute Ti^{4+} ions in the crystal framework of TiO_2 film. Ranjit et al., has also reported that Fe ions can be superseded by TiO_2 [17]. The characteristic peaks for Fe-doped TiO_2 thin films however, were shifted slightly to lower 2θ values when iron dopant was incorporated as shown in Fig. 1(b). The incorporation of Fe into TiO_2 gives rise to the structural expansion of the crystalline lattice, subsequently its structural distortion. The increase in the interplanar distance of the brookite framework causes the XRD peak patterns to shift to lower 2θ direction. Thus, the peak shift can be regarded as indirect evidence of successful iron doping into the TiO_2 crystal framework. The crystalline sizes (D) were calculated from peak broadening of principal peaks by Debye Scherer's formula [18],

$$\mathbf{D} = \frac{0.9\,\lambda}{\beta\ \mathbf{cos}\ \theta} \qquad (1)$$

where β is the full-width half maximum (FWHM) of the diffraction peak, λ is the X-ray wavelength (nm) and θ is the diffraction angle. Intensity of brookite TiO_2 phase decreased significantly after Fe doping which can be ascribed to substitution of Fe into TiO_2 lattice, also the iron oxide content influences the particle size. From the diffraction patterns it is also obvious that materials prepared are in the form of small particles, as the peaks are broad. It can be concluded from Scherer equation that doping iron-ion with proper content decreases the crystal size. For, pure TiO_2 film the crystallite size was found to be 215.7 nm, which decreased drastically to 71.87 nm for Fe doped TiO_2 film implying that the inclusion of strain due to Fe^{3+} has marginal impact on the average crystallite size. Thus, doping modifications may prevent particle agglomeration forming well defined film with high surface area.

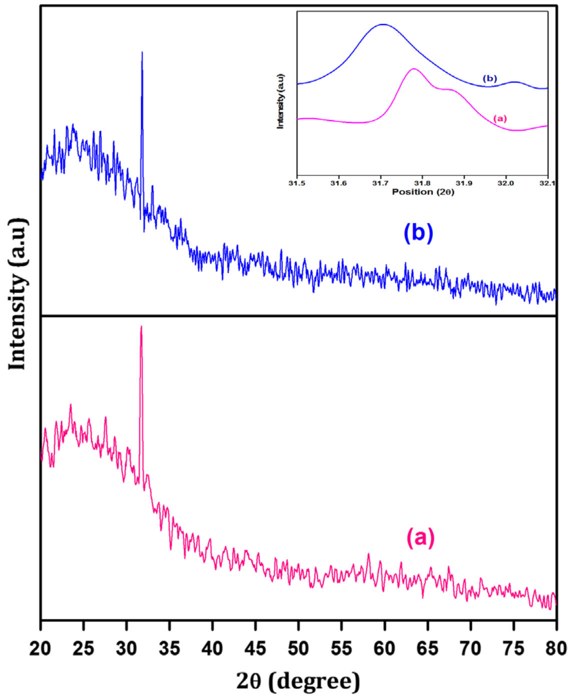

Fig. 1. XRD patterns of (a) pure TiO_2 and (b) Fe doped TiO_2 thin films.

3.2. Influence of Fe doping on the vibrational spectra of TiO_2 thin film

Fig. 2 shows the characteristic peaks of undoped and Fe doped TiO_2 samples. The IR bands at 3518 cm^{-1} revealed the presence