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# Enhanced gas sensitivity in $TiO_2$ nanoneedles grown on upright $SnO_2$ nanoplates

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In situ growth of upright-standing $SnO_2$ nanoplates connected to horizontally pointed $TiO_2$ nanoneedles to form a new, high surface area hierarchical nanostructure is proposed for the first time and envisaged in ammonia and liquid petroleum gas sensors. The increased surface area due to a hierarchical nanostructure accounts for enhanced gas sensitivity.


*Keywords:* $Tio_2$ nanoneedles; $SnO_2$ nanoplates; Gas sensor; Structural elucidation; Raman analysis

Liquid petroleum gas (LPG) and ammonia ($NH_3$) are combustible gases. They are potentially hazardous because of their explosive nature; accidents might be caused when they leak out accidentally or are not handled with care. So the detection of these gases with a high level of accuracy in the domestic environment is highly desirable. In recent years, there has been extensive interest in developing binary and ternary metal oxide-based gas sensors. Nanostructures of several metal oxides (e.g. ZnO, $WO_3$ and $Bi_2O_3$) have proven to have excellent sensing properties [1–4]. Tin oxide ($SnO_2$), an *n*-type direct band gap (3.6 eV) semiconductor, has excellent optical and electrical properties [5] and has been used in a variety of devices, such as gas sensors [6], transparent conductors, lithium ion batteries [7], solar cells [5] and catalyzers. The performance of the material in these applications is basically size and morphology dependent [8]. The metal oxides used in gas sensors can be in a variety of forms, including pellets of pressed powder, and thick and thin films. To increase the selectivity and sensitivity, they usually are doped with different cations or modified with elements that exert a catalytic effect to enhance the conductivity response towards certain gases [9]. A variety of chemical techniques to synthesize $SnO_2$ nanostructures have been proposed in the literature [10–13], and in many reports the effects of the modifying elements under doping have been investigated.

It should be noted that gas adsorption occurs on metal additive particles and that gas molecules do not interact directly with the semiconductor substrate. The chemical or catalytic mechanism is mediated by a spillover process of gas molecules from the surface of the metal particles to the surface of the semiconductor oxide. First, the gas molecules are chemisorbed onto the surface of the metal, where they are activated (dissociated). Later, these activated species migrate to the semiconductor surface (spillover). Thus, the conductivity of the semiconductor could change as a result of: (i) the adsorbed species acting as a donor (acceptor) to induce an accumulation (depletion) layer; or (ii) the adsorbed species reacting with the lattice atoms to alter the stoichiometry of the substrate [14–17]. Thus, the electronic conductivity of these kind of sensors is greatly affected by: (i) the type and nature of the electrical contacts between the semiconductor and the electrodes [18]; (ii) the electronic state of the surfaces [19]; (iii) the presence of additives; (iv) the impurities present therein [20]; and (v) differences in the mean pore and grain sizes [21,22].

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Ionic contributions to the conductivity from the adsorbed gas species have also been investigated [19]. Most of the commercial gas detectors available at present make the use of $SnO_2$ as a gas-sensing element and are considered as surface sensors, whereas titanium dioxide ($TiO_2$) represents a thermodynamically controlled bulk defect sensor, as schematically represented in Figure 1. The gas-sensing mechanism of mixed oxide systems such as $TiO_2$–$SnO_2$ has not yet been fully resolved. In many studies the sensing response is carried out on polycrystalline materials of one form only – perhaps because it is not straightforward to synthesize dual forms directly on the substrate surface [22].

In this communication, we propose, for the first time, a gas sensor application of $SnO_2$–$TiO_2$ with a hierarchical nanostructure. A 3.2 μm film, composed of upright-standing nanoplates, was initially obtained using a simple and cost-effective wet chemical method. Next, these nanoplates were modified to a $SnO_2$–$TiO_2$ hierarchical form using $TiCl_4$ surface treatment. The samples were synthesized using a simple and cost-effective wet chemical method. A possible growth mechanism for the hierarchical growth is proposed. We further employed these nanostructures for the detection of LPG and $NH_3$ gases.

The $SnO_2$ nanoplates were synthesized directly on glass substrates by dipping the substrates into a deposition solution containing 0.3 M tin (IV) chloride pentahydrate and 0.6 M thioacetamide in ethanol in 50 ml capacity Falcon tubes. The solution was heated to 80 °C in a water bath for 90 min, then the substrates were removed and washed with ethanol, dried with a stream of argon and annealed in air at 500 °C for 30 min. The crystal structure and phase of the $SnO_2$ nanoplates and $SnO_2$–$TiO_2$ hierarchical nanostructures were elucidated using X-ray diffratometry (XRD; Rigaku D/MAX 2500 V, Cu $K_\alpha$, $\lambda = 0.15418$ nm). To confirm the thickness and nanoforms, cross and surface field-emission scanning electron microscopy (FE-SEM; Hitachi S-4200) digital photo-images were recorded. Raman analysis was also carried out. The chemical surface composition was identified using energy-dispersive X-ray analysis (EDX).

The XRD patterns of $SnO_2$ nanoplates and $SnO_2$–$TiO_2$ hierarchical nanostructures are presented in Figure 2(a). All the diffraction peaks for the products match well to the primitive tetragonal $SnO_2$ profile (JCPDS-41-1445). Polycrystalline nature of $SnO_2$ is confirmed from the respective XRD pattern. The particle size calculated from Scherer's formula is around 17.2 ± 1 nm.

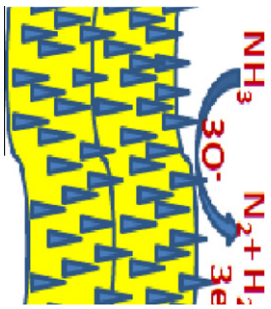


**Figure 1.** Schematic illustration of the gas-sensing mechanism of an $SnO_2$–$TiO_2$ hierarchical nanostructure.

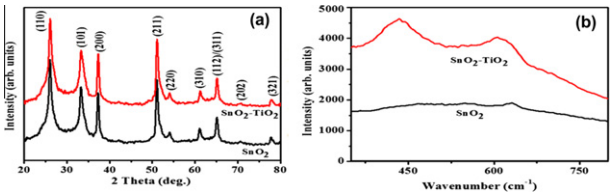


**Figure 2.** (a) XRD and (b) Raman measurements of $SnO_2$ nanoplates and $SnO_2$–$TiO_2$ hierarchical nanostructures.

There is no significant change in the XRD pattern following $TiO_2$ surface treatment, indicating that $TiO_2$ might be in either a porous or nanocrystalline form. The XRD peak positions of $SnO_2$ are shifted slightly towards the lower angle side after $SnO_2$–$TiO_2$ hierarchical nanostructure formation, indicating effective coupling between $SnO_2$ and $TiO_2$ due to favourable lattice matching.

Figure 2(b) shows the Raman scattering spectra of the $SnO_2$ and $SnO_2$–$TiO_2$ hierarchical nanostructures, from which the formation of $TiO_2$ on $SnO_2$ can be proved due to the difference in their respective peaks. The pristine $SnO_2$ nanoplate shows a Raman peak close to 625 $cm^{-1}$. Two major peaks, at 447 and 612 $cm^{-1}$, corresponding to $E_g$ and $A_{1g}$ as active modes, are seen in the $SnO_2$–$TiO_2$ film, confirming the formation of $TiO_2$ over $SnO_2$ [23–25]. The form of the $TiO_2$ is rutile, as the peak positions for anatase are at 515 and 640 $cm^{-1}$ [26].

FE-SEM digital photo-images of $SnO_2$ and $SnO_2$–$TiO_2$ are presented in Figure 3(a–d) at different magnifications. The low-magnification (Fig. 3(a)) FE-SEM image confirms the uniform coverage of the $SnO_2$ nanoplates, whereas, under closer inspection, stereospecific growth, perpendicular to the FTO substrate surface, can be noticed. These nanoplates are 50–60 nm in width and 200–300 nm in length (Fig. 3(c)), and are well connected in the form of a spider's web.

After $TiCl_4$ treatment, nanoplates of $SnO_2$ were changed to a hierarchical nanostructure (Fig. 3(b and d)). We presumed that these $SnO_2$ nanoplates could have changed in form; however, Raman, XRD and EDX (discussed later) measurements suggested that there was additional growth of rutile $TiO_2$ nanoneedles over the $SnO_2$ nanoplates to form the hierarchical nanostructure, indicating that the nanoplates act as nucleation centers for horizontally growing nanoneedles. As nanoplates are composed of several small-sized interconnected

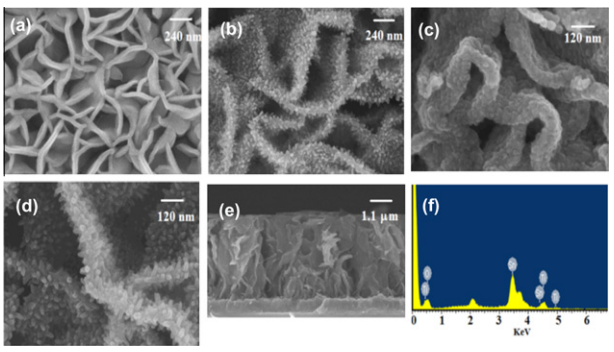


**Figure 3.** (a–e) FE-SEM surface and cross-section images of $SnO_2$ and $SnO_2$–$TiO_2$, confirming the formation of a hierarchical nanostructure; (f) EDX analysis showing the presence of $TiO_2$ over $SnO_2$.