

PAPER

Cite this: *Nanoscale*, 2015, 7, 12460Hierarchical nanostructured WO₃–SnO₂ for selective sensing of volatile organic compounds†Arpan Kumar Nayak,^a Ruma Ghosh,^b Sumita Santra,^c Prasanta Kumar Guha^b and Debabrata Pradhan^{*a}

It remains a challenge to find a suitable gas sensing material that shows a high response and shows selectivity towards various gases simultaneously. Here, we report a mixed metal oxide WO₃–SnO₂ nanostructured material synthesized *in situ* by a simple, single-step, one-pot hydrothermal method at 200 °C in 12 h, and demonstrate its superior sensing behavior towards volatile organic compounds (VOCs) such as ammonia, ethanol and acetone. SnO₂ nanoparticles with controlled size and density were uniformly grown on WO₃ nanoplates by varying the tin precursor. The density of the SnO₂ nanoparticles on the WO₃ nanoplates plays a crucial role in the VOC selectivity. The responses of the present mixed metal oxides are found to be much higher than the previously reported results based on single/mixed oxides and noble metal-doped oxides. In addition, the VOC selectivity is found to be highly temperature-dependent, with optimum performance obtained at 200 °C, 300 °C and 350 °C for ammonia, ethanol and acetone, respectively. The present results on the cost-effective noble metal-free WO₃–SnO₂ sensor could find potential application in human breath analysis by non-invasive detection.

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Introduction

Low-cost, ultrasensitive and highly selective chemical sensors which can sense trace amounts of volatile organic compounds (VOCs) have become indispensable for environmental monitoring, biomedical and industrial applications.¹ One of the vital biomedical applications of such ultrasensitive sensors can be in breath analyzers, in which an array of sensors are needed to detect very low concentrations of VOCs such as acetone (in the case of diabetics), nitric oxide (in the case of asthma) and ammonia (in the case of renal diseases) from exhaled human breath.² The current breath analysers are based on gas chromatography and mass spectrometry, which are large, expensive, and require pre-concentration procedures for reliable measurement.^{3–5} One of the suitable alternatives is portable metal oxide-based chemo-resistors with high sensitivity and selectivity towards a particular biomarker.⁶

Metal oxide-based chemo-resistive sensors have shown significant potential because of their high sensitivity towards

different analytes with fast response and recovery.⁷ However, selectivity has always been an issue for metal oxide-based sensors. In recent years, several metal oxides (such as SnO₂, In₂O₃, TiO₂, ZnO and CuO) have been widely explored for different gas detections.^{8–12} Among these, SnO₂ is one of the very promising and widely-studied sensing materials. WO₃ is another important gas sensing material, and various forms of WO₃, such as thin films, nanocrystals, hollow spheres, nanofibers and nanorods, have been extensively used for the detection of several gases and VOCs.^{13–19} In the majority of these studies, precious noble metals (Ag, Au, Pd and Pt) are either doped or decorated into/on the metal oxides to improve the sensing performance (sensitivity and selectivity).^{20–27} However, the use of noble metals increases the cost of the device, prompting researchers to explore non-noble metal-based sensors with competent performance for large-scale applications. There have been a few studies on metal-doped and mixed metal oxides with much improved gas sensing properties.^{28–30} In particular, Kim *et al.* reported an exceptionally fast CO response and recovery using NiO-doped hierarchical SnO₂ sensors.³¹ Xu *et al.* have fabricated In₂O₃–CeO₂ nanotubes which acted as bifunctional gas sensors to detect H₂S at low temperature (25–110 °C), and acetone at relatively high temperature (300 °C).³² Recently, Kida *et al.* used SnO₂ nanoparticles to control the porosity of WO₃ nanolamellae to enhance the NO₂ sensitivity.³³

Considering the effectiveness of SnO₂ and WO₃ nanostructures for sensing different gases, we report here the *in situ*

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hydrothermal synthesis of WO_3 - SnO_2 mixed metal oxides, for the first time, which can sense different VOCs selectively. The as-synthesized mixed metal oxides are composed of WO_3 nanoplates decorated with SnO_2 nanoparticles. The SnO_2 nanoparticles, of three different concentrations, were grown on the WO_3 nanoplates using a single-step hydrothermal technique by varying the tin precursor. Three important VOCs, ammonia, ethanol and acetone, were tested on WO_3 - SnO_2 -based sensors, and their performances have been compared with those of pure WO_3 nanoplates and SnO_2 nanoparticles. Not only was an improved sensing performance obtained with the WO_3 - SnO_2 , but also with highly temperature-dependent selectivity towards different analytes. The high sensing response is ascribed to the multiple depletion regions formed between WO_3 and WO_3 , SnO_2 and SnO_2 , and WO_3 and SnO_2 . Furthermore, the limit of detection (LOD) calculation shows that the present WO_3 - SnO_2 -based sensors can sense VOCs at the ppb level (with a LOD for ammonia of 520 ppb, a LOD for ethanol of 131 ppb and a LOD for acetone of 2.68 ppm), and thus they are appropriate for applications where trace amounts of analytes need to be detected (*e.g.* in breath analyzers). The importance of this work lies in the following aspects: (i) the simple and cost-effective *in situ* synthesis of WO_3 - SnO_2 mixed metal oxide nanomaterials, (ii) the sensors having a large response towards three VOCs which are commonly used as biomarkers, and (iii) the as-fabricated sensors being highly selective. This suggests that the development of such sensors will be highly beneficial for new generation highly sensitive and selective chemo-resistive sensors.

Experimental section

Chemicals

Sodium tungstate hydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and stannous chloride hydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were from SRL, India; hydrochloric acid (HCl) of about 35% v/v and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were from Merck, India, and ethanol ($\text{C}_2\text{H}_5\text{OH}$) was from Changshu Yangyuan Chemical, China. All the above reagents were analytical grade and used without further purification.

Synthesis of WO_3 nanoplates

WO_3 flower-like structures, self-assembled from nanoplates, were prepared by using a facile hydrothermal method. In a typical synthesis, 1.6 g sodium tungstate hydrate (0.12 M) was dissolved in 40 mL distilled water. Then, 4 mL of concentrated HCl was added dropwise to the above transparent solution while stirring. The resulting solution turned yellow. Upon adding 1 g oxalic acid (0.2 M) to the above solution, it became transparent again. The final transparent solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was heated at 200 °C in a muffle furnace for 12 h and then cooled to room temperature naturally. The precipitated product was collected by centrifugation and washed with ethanol and distilled water. The washed product

was dried at 60 °C for 4 h and then calcined at 400 °C for 2 h under air.

Synthesis of SnO_2 nanoparticles

0.54 g stannous chloride hydrate (0.06 M) was dissolved in 40 mL distilled water and the solution was stirred for 5 min. Then, 1 mL of concentrated HCl was added and stirred vigorously for 30 min, prior to transferring it into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 200 °C for 12 h and cooled naturally to room temperature. The as-synthesized product was washed and calcined as described for WO_3 .

In situ synthesis of WO_3 - SnO_2 mixed oxides

In the WO_3 synthesis as described above, upon adding oxalic acid to the mixture of sodium tungstate hydrate (0.12 M) and concentrated HCl, the solution becomes transparent. A pre-determined quantity of stannous chloride hydrate (0.27 g, 0.54 g or 1.08 g) was then added, and the mixture stirred vigorously for 10 min before transferring it to the autoclave. The autoclave was heated at the same temperature for the same duration (*i.e.* at 200 °C for 12 h) and then cooled naturally to room temperature. The precipitated product was collected by centrifugation, washed, dried, and calcined as described for WO_3 .

Characterization

The surface morphology of the as-synthesized products was investigated using a Carl Zeiss SUPRA 40 field-emission scanning electron microscope (FESEM). The structural properties of the products were measured with a PANalytical High Resolution XRD (PW 3040/60) operated at 40 kV and 30 mA with Cu K α X-rays (1.54 Å) in the 2 θ angular range 20–80°. A FEI TECNAI G2 transmission electron microscope (TEM) was employed to investigate the microstructures of the samples in detail. Energy-dispersive X-ray (EDX) analysis of the samples was carried out using an EVO 60 Carl Zeiss SEM with an Oxford EDS detector. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI 5000 VersaProbe II Scanning XPS Microprobe with a monochromatic Al K α source (1486.6 eV), with a typical energy resolution of 0.4–0.5 eV full width at half-maximum. The effective Brunauer–Emmett–Teller (BET) surface areas of the as-synthesized samples were measured using a Quantachrome ChemBET analyzer.

Gas sensing tests

The sensors were fabricated by dispersing WO_3 , SnO_2 and WO_3 - SnO_2 mixed metal oxide powders in ethanol and then drop-casting them on Pt-based interdigitated electrodes (IDEs) (Synkera Technologies) with 100 μm inter-finger gaps. The gas test measurements were carried out in a custom-made gas test set-up. The set-up contains an airtight stainless steel chamber assembled with a heater, thermocouple and probes. Mass flow controllers were used to vary the flow rates of gas analytes. An Agilent 34972A LXI data acquisition card was used as an inter-

facing unit between the gas test set-up and the computer, to record the resistance values of sensor samples at every 5 s interval. The sensors were initially purged with dry air for 20 min to stabilize the baseline resistance at a particular temperature. They were then exposed to target gases for 5 min, followed by 10 min of dry air purging.

Results and discussion

Morphology

The morphology of the as-synthesized samples was studied by FESEM, as shown in Fig. 1. Fig. 1(a) shows a representative FESEM image of WO_3 nanoplates, which are found to be self-assembled to near-spherical structures. The inset of Fig. 1(a) shows a magnified FESEM image of the nanoplates, which are 40–400 nm in length/width and 20–60 nm in thickness. Fig. 1(b) shows a FESEM image of uniform SnO_2 nanoparticles, of diameter <20 nm. Fig. 1(c)–(f) show FESEM images of WO_3 –(x) SnO_2 mixed oxides, synthesized by varying the mass of the tin

precursor (x), *i.e.* 0.27 g, 0.54 g and 1.08 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, respectively, while keeping that of the tungsten precursor [$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.6 g, 0.12 M)] constant. The plate-like morphology of the WO_3 building blocks and their self-assembly to a spherical flower-like morphology remains the same upon addition of the tin precursor. Moreover, the density and size of the SnO_2 nanoparticles on the WO_3 nanoplates were found to increase with increasing initial $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration. At a lower tin precursor concentration, *i.e.* WO_3 –(0.27 g) SnO_2 , very fine particles of size 5–10 nm were observed on the nanoplates, as shown in Fig. 1(c). These nanoparticles appear slightly brighter on the nanoplates, as shown in the inset FESEM image of Fig. 1(c). With increasing the mass of tin precursor to 0.54 g and 1.08 g, the sizes of the SnO_2 nanoparticles were found to increase to ~20 nm and 20–40 nm, respectively, as shown in Fig. 1(d)–(f). The insets of Fig. 1(d)–(f) show magnified FESEM images clearly depicting bright SnO_2 nanoparticles deposited on the WO_3 nanoplates. At a higher tin concentration, *i.e.* 1.08 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, agglomeration of SnO_2 nanoparticles was found at a few locations, as shown in Fig. 1(f).

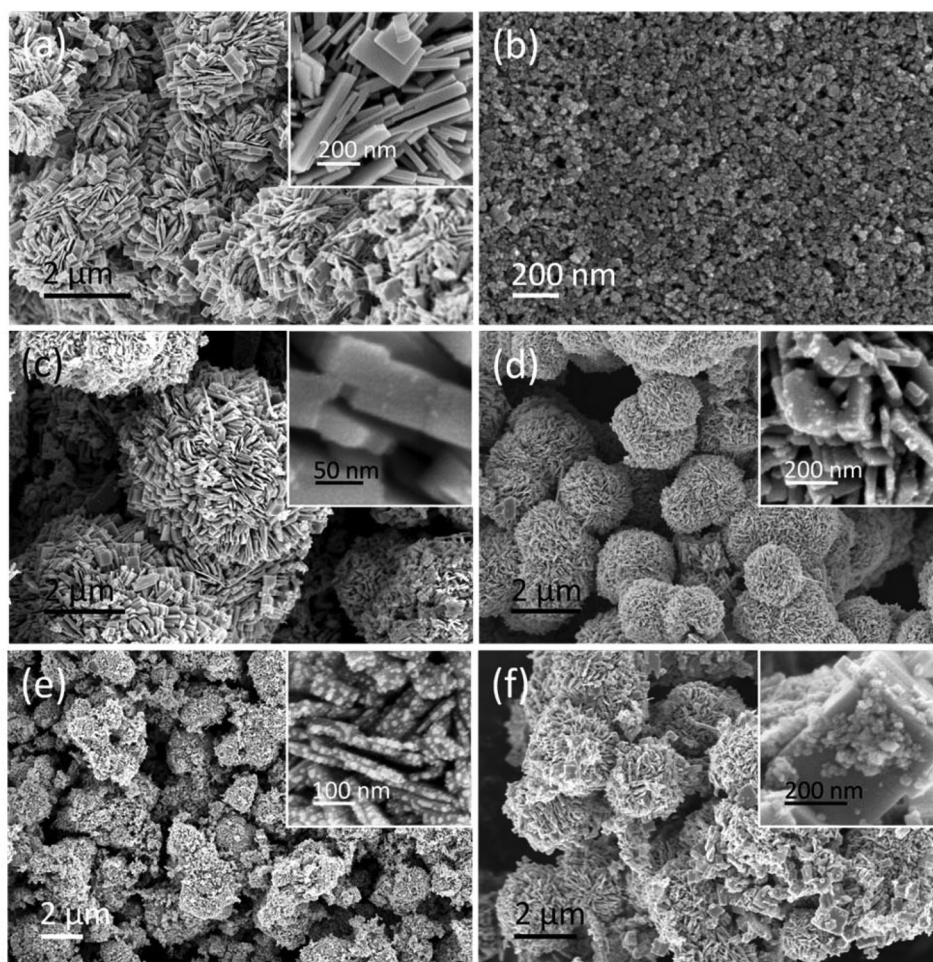


Fig. 1 FESEM images of (a) WO_3 nanoplates, (b) SnO_2 nanoparticles, and (c) WO_3 –(0.27) SnO_2 , (d) WO_3 –(0.54) SnO_2 and (e, f) WO_3 –(1.08) SnO_2 mixed oxides, prepared by varying the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration. The insets show magnified FESEM images of the corresponding samples. All the samples were prepared hydrothermally at 200 °C in 12 h.

Structural and microstructural analysis

Fig. 2 shows the XRD patterns of WO_3 nanoplates, SnO_2 nanoparticles and WO_3 - SnO_2 mixed oxides. The sharp diffraction features suggest the crystalline nature of all the samples. The XRD peaks of the WO_3 nanoplates [Fig. 2(a)] are readily indexed to the monoclinic crystal structure with lattice parameters (in Å) of $a = 7.3$, $b = 7.53$ and $c = 3.83$ ($a = 7.384$, $b = 7.512$ and $c = 3.846$, JCPDS no. 00-005-0363). The XRD pattern [Fig. 2(b)] of the SnO_2 nanoparticles matches the tetragonal cassiterite structure of SnO_2 with lattice constants $a = 4.74$ and $c = 3.18$ ($a = 4.738$ and $c = 3.188$, JCPDS no. 00-021-1250). The

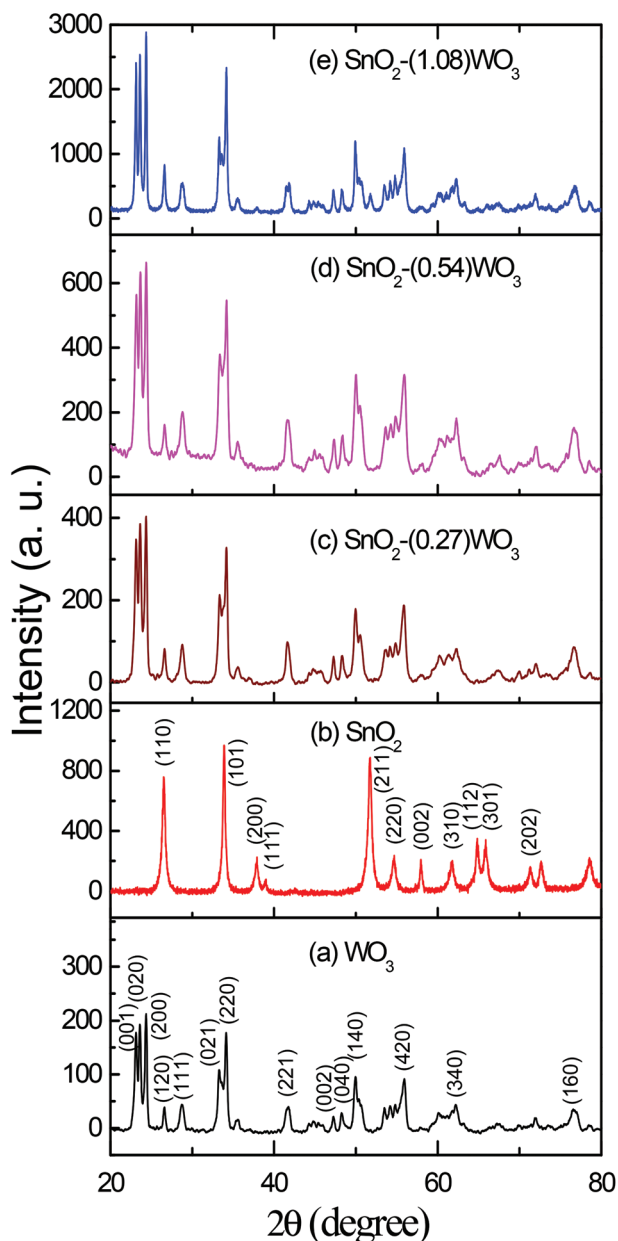


Fig. 2 Powder XRD patterns of (a) WO_3 nanoplates, (b) SnO_2 nanoparticles, and (c) WO_3 -(0.27) SnO_2 , (d) WO_3 -(0.54) SnO_2 and (e) WO_3 -(1.08) SnO_2 mixed oxides, prepared by varying the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration in the hydrothermal process at 200 °C for 12 h.

XRD patterns of all the WO_3 - SnO_2 mixed oxide samples match the monoclinic crystal structure of WO_3 without any other phases such as Sn or SnO_2 , suggesting no change in the WO_3 crystal structure.³³ The absence of SnO_2 diffraction features in the mixed oxide samples is believed to be due to the small quantity of SnO_2 present. Nonetheless, the XRD intensity of the WO_3 peaks was found to increase with increasing SnO_2 in the sample, *i.e.* for WO_3 -(0.27) SnO_2 , WO_3 -(0.54) SnO_2 and WO_3 -(1.08) SnO_2 mixed oxides, as shown in Fig. 2(c)-(e), respectively. This increase in diffraction intensity indicates an increase in the crystallinity, which can be attributed to the incorporation of a small amount of Sn into the WO_3 lattice, as reported earlier.³⁰

The microstructures of the as-synthesized WO_3 nanoplates, SnO_2 nanoparticles and WO_3 - SnO_2 mixed oxides were examined by TEM. Fig. 3(a) shows a TEM image of the WO_3 nanoplates, of either square or rectangular shape, with sizes in the range of 40–400 nm. A high-resolution TEM (HRTEM) image [Fig. 3(b)] taken at an edge of a nanoplate shows a continuous lattice with a spacing of 3.77 Å, which corresponds to the (020) plane.³³ The regular spot selected area diffraction pattern (SAED) shown in the inset of Fig. 3(b) confirms the single crystalline nature of the WO_3 nanoplates. Fig. 3(c) shows a TEM image of the SnO_2 nanoparticles, of size around 20 nm. An HRTEM image [Fig. 3(d)] of the SnO_2 nanoparticles shows the lattice fringe with a spacing of 2.65 Å, indicating the crystalline nature of the particles. The distinct diffraction spots on the ring SAED pattern [inset, Fig. 3(d)] further suggests the single crystalline nature of individual SnO_2 nanoparticles in accordance with the XRD analysis.

Fig. 4 shows TEM images of the WO_3 -(x) SnO_2 mixed oxides. The dark spots of size <10 nm on the WO_3 nanoplates in Fig. 4(a) are believed to be SnO_2 nanoparticles of WO_3 -(0.27) SnO_2 . Upon increasing the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ precursor to 0.54 g and 1.08 g in the synthesis, the size of the SnO_2 nanoparticles was found to increase to ~20 nm [Fig. 4(b)] and 20–40 nm [Fig. 4(c)], respectively, as clearly revealed in the TEM images. The number density of the SnO_2 nanoparticles was also found to increase with the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration. The HRTEM and spot SAED indicate no change in the crystal structure of the WO_3 upon addition of the tin precursor in the synthesis. Fig. 4(d) shows a HRTEM image of WO_3 nanoplates of the WO_3 -(1.08) SnO_2 mixed oxide, with a lattice spacing of 3.78 Å, corresponding to the (020) planes of pure WO_3 . It is important to note that no separate SnO_2 nanoparticles are found on the TEM grids for the WO_3 - SnO_2 samples. This suggests that the SnO_2 nanoparticles are grown and chemically bonded to the WO_3 nanoplates. Furthermore, sensing experiments proved the presence of heterojunctions in the mixed oxide samples, resulting in an enhanced response (discussed later), which could only be possible for chemically bonded materials.

Composition and chemical states

The elemental compositions of the as-synthesized samples were measured using energy-dispersive X-ray (EDX) spec-

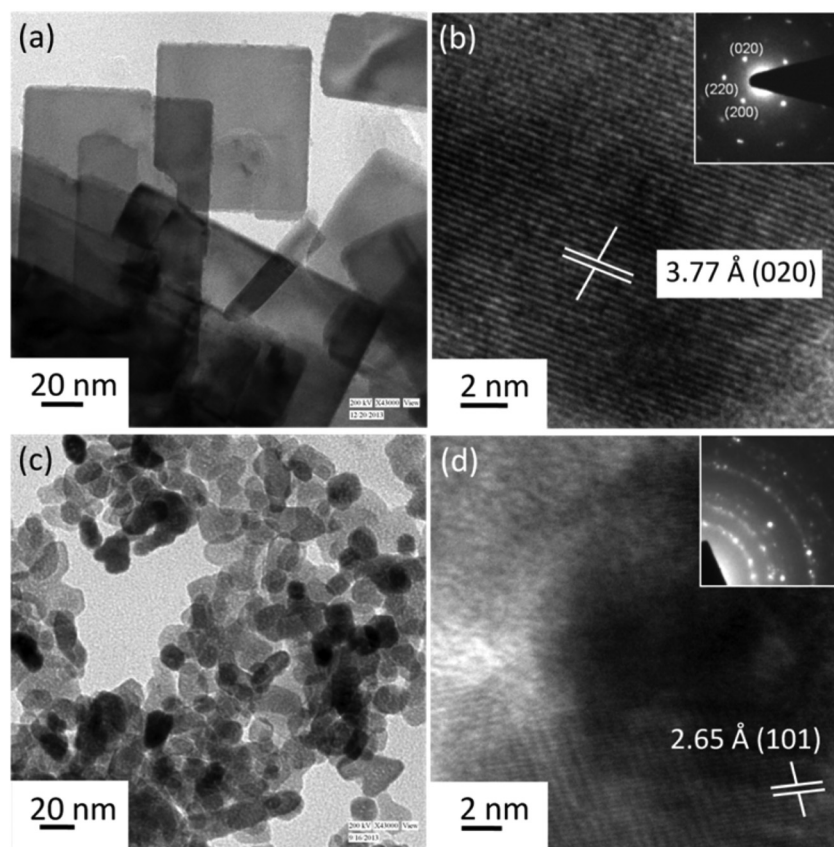


Fig. 3 (a, c) TEM and (b, d) HRTEM images of (a, b) WO_3 nanoplates and (c, d) SnO_2 nanoparticles. The insets of (b) and (d) display the corresponding SAED patterns.

troscopy. Fig. 5 shows the EDX spectra of pure WO_3 nanoplates, SnO_2 nanoparticles and WO_3 –(0.54) SnO_2 mixed oxides. For the pure WO_3 nanoplates, the stoichiometric ratio of W to O matches closely to WO_3 with a slight oxygen deficiency. However, the rest of the samples show a higher oxygen composition than that anticipated from their stoichiometric ratio, indicating surface oxygen and amorphous hydroxides. The EDX spectrum [Fig. 5(b)] from the SnO_2 nanoparticles shows almost 6 at.% higher oxygen, which can be ascribed to surface hydroxide $[\text{Sn}(\text{OH})_4]$, since tin is often found in the +4 state. Moreover, the Sn% was found to increase with increasing initial $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration used for the synthesis of the WO_3 – SnO_2 mixed oxides. This supports the morphology and microscopic results [Fig. 1 and 4] on the increasing size and density of SnO_2 nanoparticles on the WO_3 nanoplates with increasing tin precursor concentration for the synthesis of the mixed oxides.

Elemental and surface chemical states information was further obtained using X-ray photoelectron spectroscopy (XPS). Fig. 6 shows representative XPS spectra of the WO_3 –(1.08) SnO_2 mixed oxide. The survey spectrum [Fig. 6(a)] confirms the presence of W, Sn and O, along with surface impurity carbon. The absence of peaks related to either Na or Cl (present in the pre-

cursors) in the survey spectrum suggests the high purity of the sample. The atomic percentages of W, Sn and O were estimated to be 16.7%, 11.1% and 72.2%, respectively. The stoichiometry of WO_3 and SnO_2 is well matched to the atomic percentages. Fig. 6(b)–(d) display the W 4f, Sn 3d and O 1s region XPS spectra, respectively. The XPS peaks at 35.62 and 37.75 eV can be assigned to W 4f_{7/2} and W 4f_{5/2} of WO_3 , respectively, with a spin-orbit splitting of 2.13 eV.^{34–36} Similarly, the photoelectron peaks at 487.0 and 495.4 eV are assigned to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively.^{37,38} The Sn XPS peaks confirm the +4 oxidation state contributed from SnO_2 . The O 1s shows an intense peak at 530.5 eV from oxides, and the broad O 1s peak at 531.8 eV can be assigned to surface hydroxides.³⁶

Gas sensing

The as-synthesized nanostructured mixed oxide materials were drop-casted on platinum interdigitated electrodes to prepare the sensor devices. In chemoresistive sensors, the resistance of the sensing layer changes in the presence of the detectable gas. For testing the sensor devices, ammonia, ethanol and acetone were selected because they are vital biomarkers.

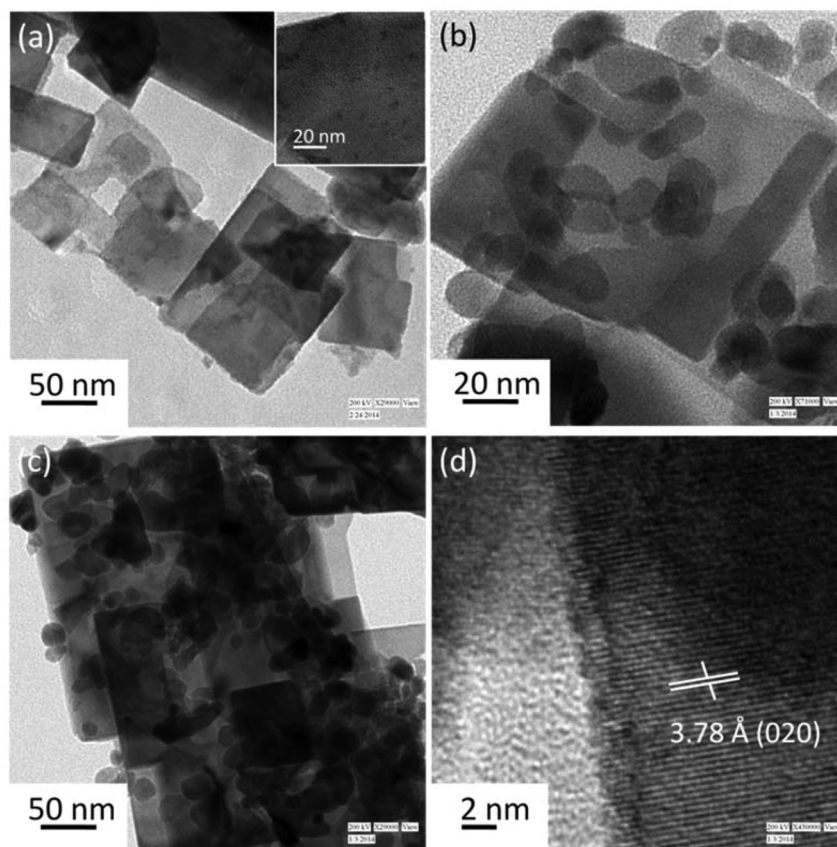


Fig. 4 TEM images of (a) WO_3 -(0.27) SnO_2 , (b) WO_3 -(0.54) SnO_2 and (c, d) WO_3 -(1.08) SnO_2 mixed oxides, prepared by varying the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration. The inset of (a) shows a corresponding magnified image. Panel (d) shows a HRTEM image of an edge of the WO_3 nanoplate shown in (c).

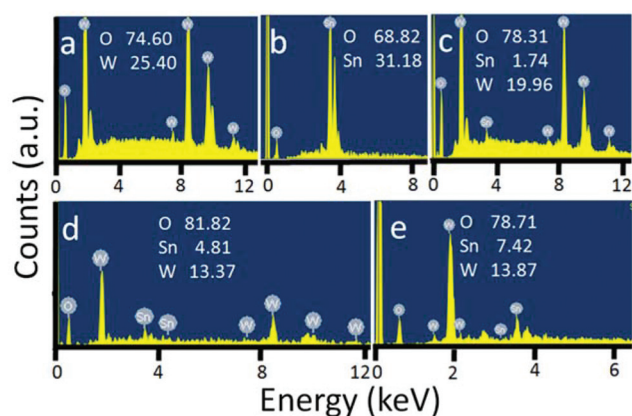


Fig. 5 EDX spectra of (a) WO_3 nanoplates, (b) SnO_2 nanoparticles and (c) WO_3 -(0.27) SnO_2 , (d) WO_3 -(0.54) SnO_2 and (e) WO_3 -(1.08) SnO_2 mixed oxides, prepared by varying the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration.

The responses of the chemoresistive sensors were calculated using eqn (1):

$$\text{Response} = \frac{R_{\text{air}}}{R_{\text{VOCs}}}, \quad (1)$$

where R_{VOCs} is the resistance of the sensor material in the presence of VOCs (ammonia/ethanol/acetone) and R_{air} is the resistance of the sensor material in the presence of air. To explore the optimum performance of the different sensor materials, temperature profiles of each of them were carried out for all the VOCs. Fig. 7(a)–(c) show the sensitivity response as a function of operating temperature for ammonia (1200 ppm), ethanol (350 ppm) and acetone (1000 ppm). The optimum response was obtained at 200 °C for ammonia, 300 °C for ethanol and 350 °C for acetone. These optimum temperatures are valid for all the sensing materials studied in the present work, except for the sensing of acetone. In the case of acetone, the WO_3 -(0.54) SnO_2 and WO_3 -(1.08) SnO_2 samples demonstrated an optimum response at 300 °C. The WO_3 - SnO_2 mixed oxides were found to show higher responses towards ammonia and ethanol compared to the pure oxides (WO_3 and SnO_2). With increasing SnO_2 content in the mixed oxides, the response towards ammonia increased at the optimum temperature of 200 °C as shown in Fig. 7(a), whereas the WO_3 -(0.54) SnO_2 mixed oxide showed the best sensing response for ethanol [Fig. 7(b)]. However, the pure SnO_2 nanoparticles sample was found to show the maximum response in the presence of acetone [Fig. 7(c)].

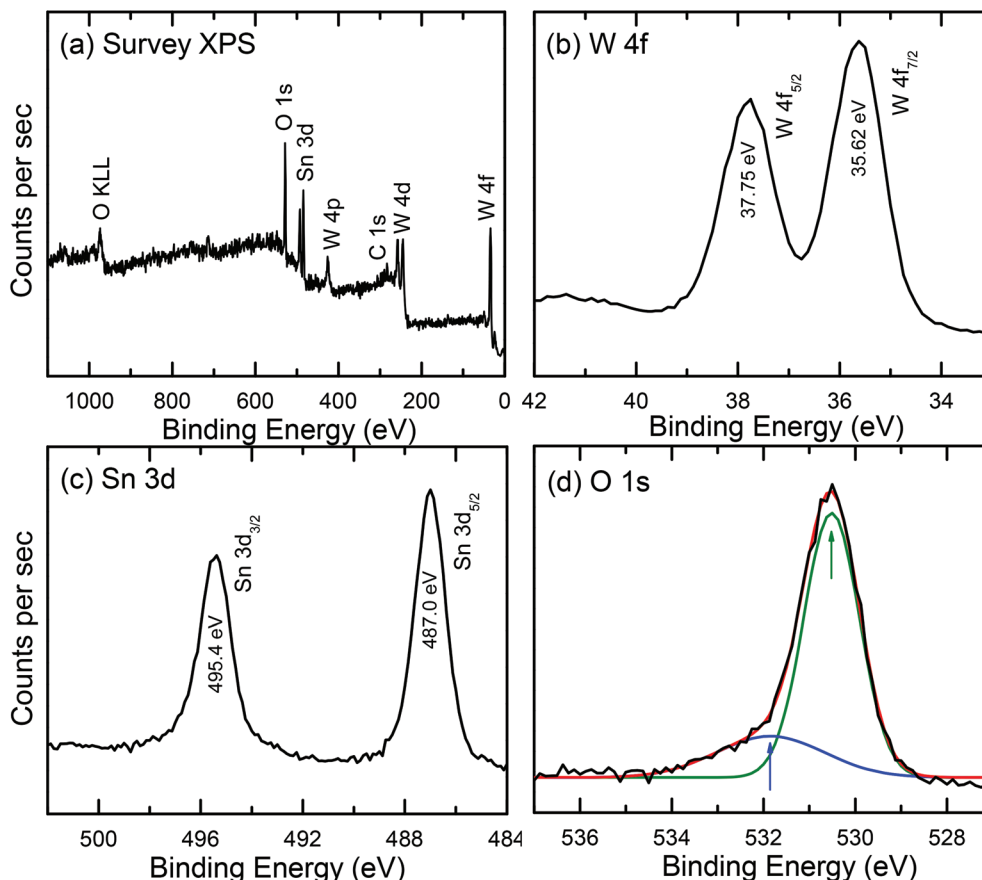


Fig. 6 (a) Survey spectrum, and (b) W 4f, (c) Sn 3d and (d) O 1s region XPS spectra of the $\text{WO}_3\text{--}(1.08)\text{SnO}_2$ mixed oxide.

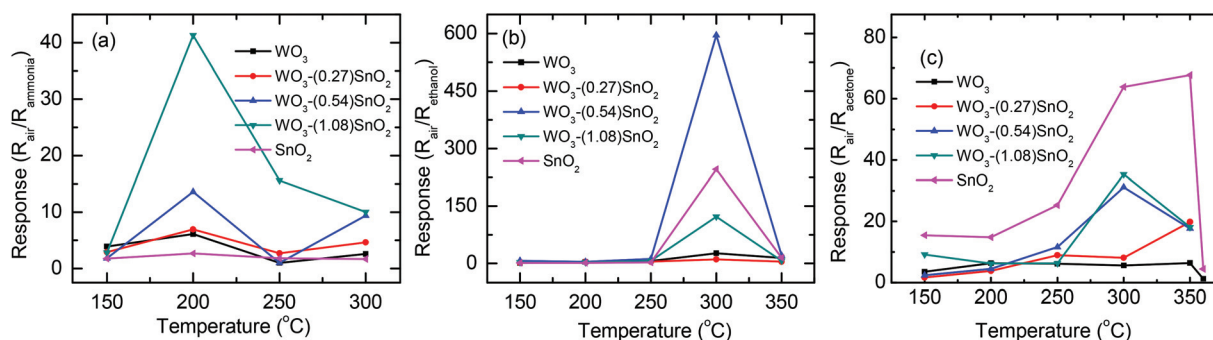


Fig. 7 Response of different samples as a function of operating temperature towards (a) ammonia (1200 ppm), (b) ethanol (350 ppm) and (c) acetone (1000 ppm).

The sensing tests were further carried out for different concentrations of VOCs (ammonia – 400 to 2800 ppm, ethanol – 180 to 2800 ppm and acetone – 1000 to 4000 ppm) using all five samples [(i) WO_3 , (ii) $\text{WO}_3\text{--}(0.27)\text{SnO}_2$, (iii) $\text{WO}_3\text{--}(0.54)\text{SnO}_2$, (iv) $\text{WO}_3\text{--}(1.08)\text{SnO}_2$ and (v) SnO_2]. The dynamic response–recovery curves with different VOC concentrations are shown in Fig. 8(a)–(c) for ammonia, ethanol and acetone, respectively. In particular, $\text{WO}_3\text{--}(1.08)\text{SnO}_2$ [iv of Fig. 8(a)] showed a 35 times (400 ppm) to 54 times (2800 ppm) response

against ammonia, and $\text{WO}_3\text{--}(0.54)\text{SnO}_2$ [iii of Fig. 8(b)] exhibited a ~ 392 times (180 ppm) to 1476 times (at 2800 ppm) response towards ethanol. We have further performed methanol sensing using $\text{WO}_3\text{--}(0.54)\text{SnO}_2$ (sample iii) at an optimum temperature of 300 °C (results not shown), which exhibited a ~ 15 times response towards 1000 ppm of methanol. Although the response was found to be much less than that of ethanol, the mixed oxide can still be used for methanol sensing. This substantiates the important role of mixed oxides in the

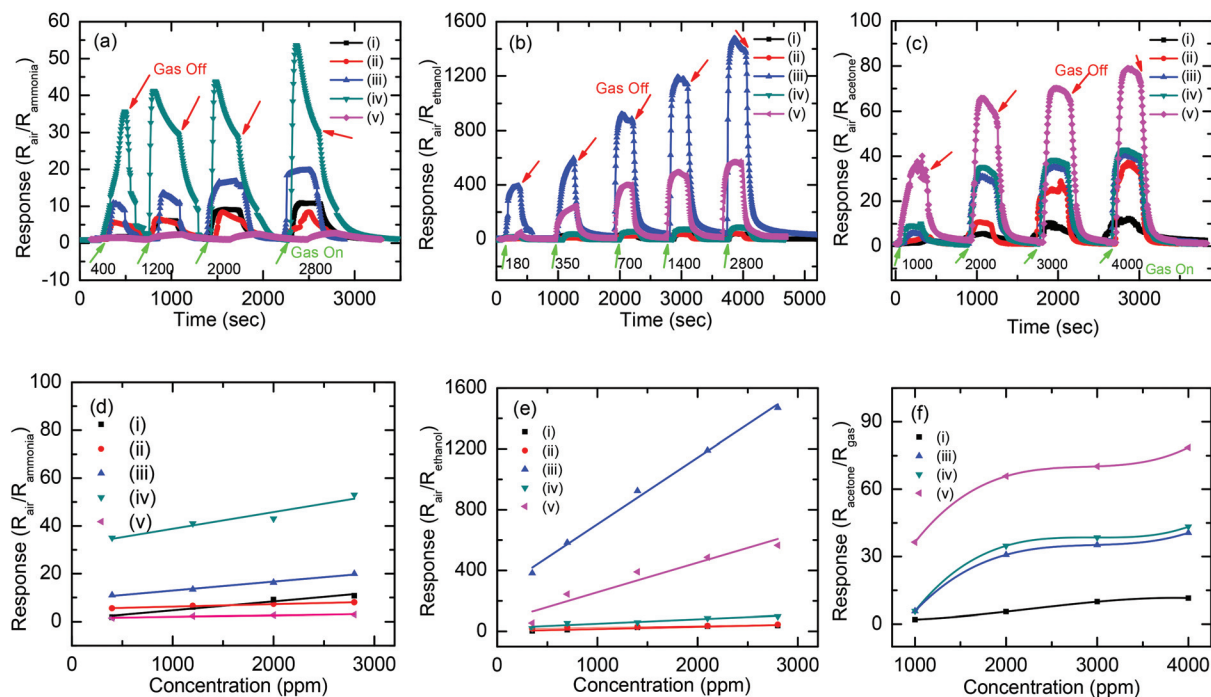


Fig. 8 The dynamic response curves of five sensors with different gas concentrations for (a) ammonia at 200 °C, (b) ethanol at 300 °C and (c) acetone at 300 °C as a function of time. The sensor materials are (i) WO_3 , (ii) $\text{WO}_3-(0.27)\text{SnO}_2$, (iii) $\text{WO}_3-(0.54)\text{SnO}_2$, (iv) $\text{WO}_3-(1.08)\text{SnO}_2$ and (v) SnO_2 . (d, e) Linear fitted response as a function of (d) ammonia and (e) ethanol concentration. (f) The third order polynomial fitted response as a function of acetone concentration.

sensing performance of ammonia and ethanol. However, the pure SnO_2 nanoparticles [v of Fig. 8(c)] showed a ~ 40 times (1000 ppm) to ~ 80 times (4000 ppm) response against acetone. The responses of all the samples increased linearly with increase in the concentrations of ammonia and ethanol, as shown in Fig. 8(d) and (e), respectively. However, in the case of acetone, the response increased initially and then saturated at higher concentrations, as shown in Fig. 8(f). This could be due to the fact that, at higher concentrations, the gas molecules do not find sufficient reaction sites. In addition, an anomaly of a rapid decrease in response with time after reaching a maximum is observed for ammonia with $\text{WO}_3-(1.08)\text{SnO}_2$ [iv of Fig. 8(a)]. This instability is believed to be due to structural transformation, materials poisoning, bulk diffusion, and/or generation of electron acceptor species, such as NO_x in the present case, that abridge the sensing response.³⁹ A similar instability in response as a function of time has been reported in recent literature.⁴⁰ Further study is needed to find the exact cause of such instability.

The lowest limit of detection (LOD) for all three VOCs was theoretically calculated from the experimental data obtained here. The details of the LOD calculation are provided as ESI.† The LOD was calculated to be 520 ppb for ammonia, 131 ppb for ethanol and 2.68 ppm for acetone. This suggests that these sensors can be used to detect trace levels of VOCs (except for acetone, which requires a detection ability of ~ 1 ppm for a sensor to be usable) for biomedical applications, and thus are

suitable for breath analysis.⁴¹ The performances of the best sensor materials for different VOCs are summarized in Table 1. The present results are further compared with recent literature on these VOCs, presented in Table 2. It is found that the sensing performance of the present $\text{WO}_3\text{-SnO}_2$ mixed oxide is not only superior to several other oxide materials, but is also better than those of the noble metal-doped/decorated oxides.^{27,42–50}

The sensing results revealed an apparent temperature-dependent selectivity towards the VOCs, as shown in Fig. 7, *i.e.* 200 °C for ammonia, 300 °C for ethanol and 350 °C for acetone. To further explore their selectivity, the best sensing samples were exposed to toluene, hexane and chloroform, because all these vapors have biological or environmental consequences. Fig. 9(a)–(c) show the comparative response bar plots of different VOCs with 1200 ppm at 200 °C [using $\text{WO}_3-(1.08)\text{SnO}_2$], with 350 ppm at 300 °C [using $\text{WO}_3-(0.54)\text{SnO}_2$] and with 2000 ppm at 350 °C [using SnO_2], respectively. A stand-out temperature-dependent selective response can be clearly noticed for the respective analytes.

Sensing mechanism

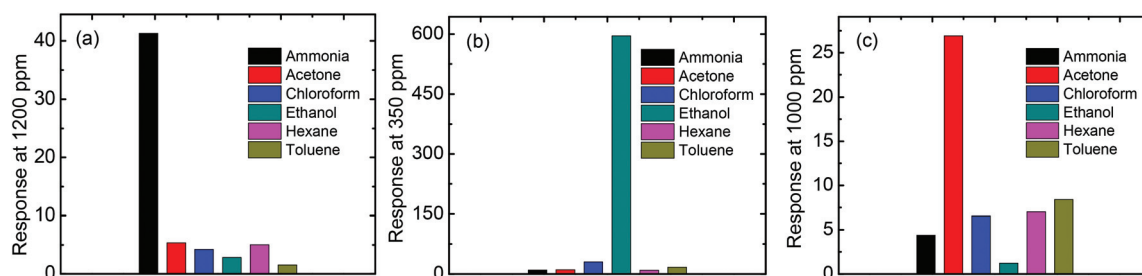
The optimum responses towards the three analytes were observed in three different samples, *i.e.* the best responses towards ammonia, ethanol and acetone were shown by $\text{WO}_3-(1.08)\text{SnO}_2$, $\text{WO}_3-(0.54)\text{SnO}_2$ and SnO_2 , respectively. For almost all the samples, the optimum response occurred at three

Table 1 Summary of the performances of the sensor materials for different VOCs

VOCs	Sensor material with highest response	Response			Calculated LOD
		With lowest VOC concentration	With highest VOC concentration	Optimum response temperature	
Ammonia	WO ₃ -(1.08)SnO ₂	35 times (400 ppm)	54 times (2800 ppm)	200 °C	520 ppb
Ethanol	WO ₃ -(0.54)SnO ₂	392 times (180 ppm)	1476 times (2800 ppm)	300 °C	131 ppb
Acetone	SnO ₂	40 times (1000 ppm)	80 times (4000 ppm)	350 °C	2.68 ppm

Table 2 Comparison of the best sensing performances of different materials towards ammonia, ethanol and acetone

VOCs	Sensing material	Concentration (best response)	Present best results	Ref.
Ammonia	Cr-doped WO ₃	50–500 ppm (9–50 times)	400 ppm (35 times)	40
Ammonia	Metal-doped SnO ₂ (Pt, Au, Cr, Pd, In, Cu)	450 ppm (26 times) best with Pt	400 ppm (35 times)	41
Ammonia	Metal-doped WO ₃ (Pd, Pt, Au)	400–4000 ppm (4–44 times)	400–2800 ppm (35–54 times)	27
Ethanol	SnO ₂	1–1000 ppm (10–280 times)	180–1500 ppm (400–1470 times)	42
Ethanol	MoO ₃	10–500 ppm (10–50 times)	180–1500 ppm (400–1470 times)	43
Ethanol	Gallia-SnO ₂	300 ppm (120 times)	350 ppm (600 times)	44
Ethanol	WO ₃	10–500 ppm (1.5–2.4 times)	350 ppm (600 times)	45
Ethanol and ammonia	SnO ₂ /ZnO	Ethanol 25–500 ppm (3–17 times) Ammonia 100 ppm (2 times)	Ethanol 350 ppm (600 times) Ammonia 100 ppm (35 times)	46
Acetone	SnO ₂ -Pt	800 ppm (3.3 times)	1000 ppm (37 times)	47
Acetone	WO ₃	1000 ppm (20 times)	1000 ppm (37 times)	48

**Fig. 9** Comparative response bar plots of different VOCs: (a) with 1200 ppm at 200 °C using the WO₃-(1.08)SnO₂ sample, (b) with 350 ppm at 300 °C using the WO₃-(0.54)SnO₂ sample, and (c) with 2000 ppm at 350 °C using the SnO₂ sample.

different temperatures, *i.e.* at 200 °C for ammonia, at 300 °C for ethanol and at 350 °C for acetone.

Effect of the sensing material. The sensing mechanism of the heterogeneous metal oxide structure is explained through schematics shown in Fig. 10.

The basic mechanism of sensing by metal oxides has been discussed in detail in the literature.¹⁷ Briefly, when air comes into contact with the metal oxide surface, the oxygen molecules in the air get adsorbed and form different oxygen species (O⁻, O₂⁻, O₂⁻ and O₂²⁻) by trapping the free surface electrons from the conduction band of the n-type sensing layer (WO₃ and SnO₂), as shown in Fig. 10(b). This leads to electron depletion on the metal oxide surface, which contributes towards the large base line resistance of the sensing material. These adsorbed oxygen sites act as active sites for the targeted gas molecules to get attached. Upon introducing target reducing gases such as ammonia, ethanol and acetone, they are

oxidized by reactive oxygen species, resulting in release of electrons to the sensing material (metal oxide), and thereby its resistance decreases. To explain the effect of the material on the sensor performance, the following points need to be considered.

Firstly, in a WO₃-SnO₂ mixed oxide heterostructure, the electron transport mechanism is different from that of individual metal oxides (WO₃ and SnO₂) because of the presence of multiple junctions. In a WO₃-SnO₂ mixed oxide, three different potential barriers exist, and those are between WO₃ and WO₃, WO₃ and SnO₂, and SnO₂ and SnO₂. The schematic band diagram of a WO₃-SnO₂ heterojunction is shown in Fig. 10 (e and f). As the position of the Fermi level in WO₃ is higher than that of SnO₂, electron transfer takes place from WO₃ to SnO₂ by band bending, and a potential barrier is established at the heterojunction, as shown in Fig. 10(f). These two kinds of potential barriers (two potential barriers at homojunctions and one potential barrier at heterojunction) are

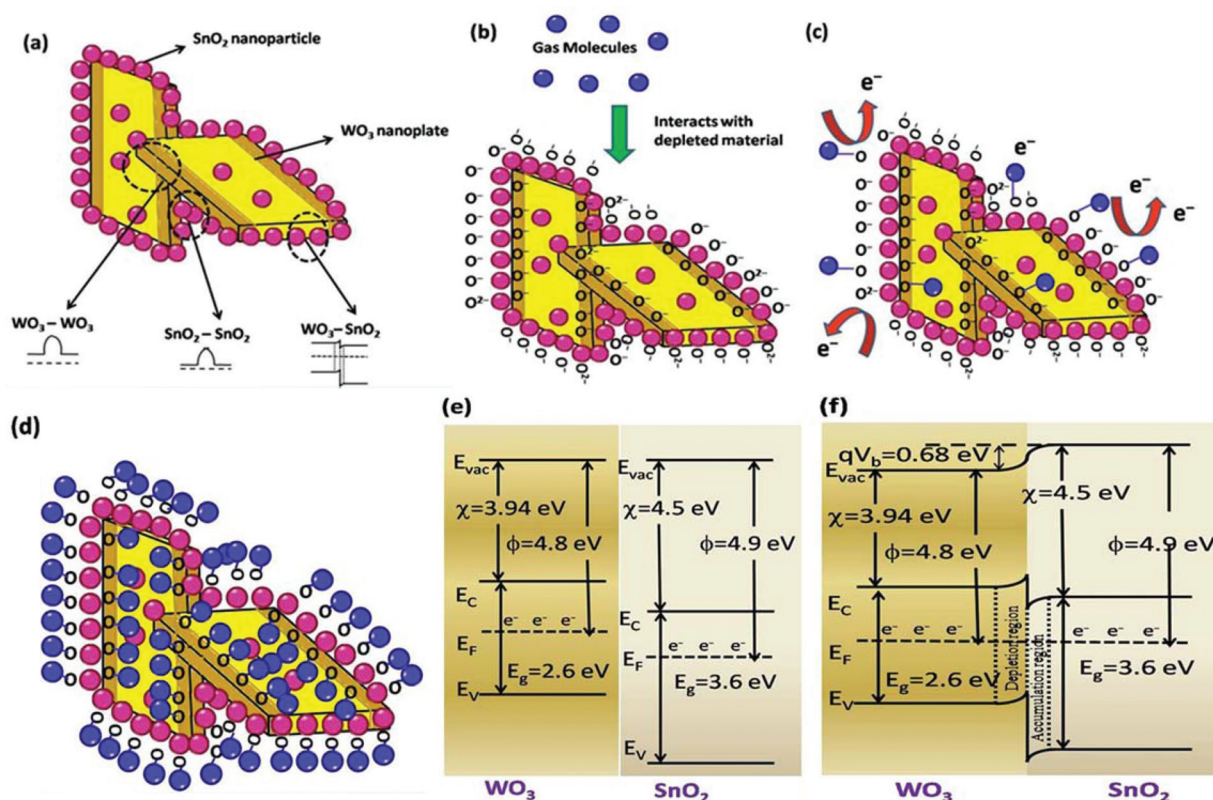
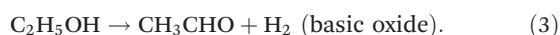
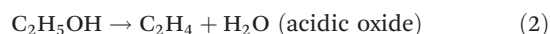


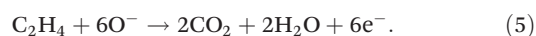
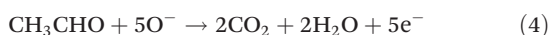
Fig. 10 Schematic representation of (a) WO₃-SnO₂ mixed oxides with available barrier potentials, (b) different species of oxygen adsorbed on the surface of the heterostructured metal oxide upon exposure to dry air, (c) reaction and attachment of gas molecules with the adsorbed oxygen, (d) complete covering of active sites with the gas molecules, (e) the energy band structures of WO₃ and SnO₂, and (f), the energy band structure of a WO₃-SnO₂ mixed metal oxide.

tions and one potential barrier at a heterojunction) hinder the electron transport through the nanostructures; thus, they provide extra electrons for more oxygen species to adsorb on the surface of the sensing layer, which significantly increases the sensor response.

Secondly, ethanol decomposition [eqn (2) and (3)] is related to the acid-base properties of the mixed metal oxides:⁵¹



WO₃ is acidic in nature, whereas SnO₂ has both acidic and basic properties.^{49,52} In the case of WO₃, only dehydration to the intermediate C₂H₄ is expected, whereas both dehydration and dehydrogenation would occur in the case of a mixed oxide. The intermediate states (CH₃CHO and C₂H₄) can react with oxygen ions to produce CO₂ and H₂O [eqn (4) and (5)]:



These reactions also release electrons which decrease the sensing layer resistance. Thus, the WO₃-SnO₂ mixed

oxide gives a larger ethanol response than the single metal oxides.

Thirdly, there has been a recent report that the heterostructure's sensing performance also depends on the ability of the test molecules to reach the heterojunction.⁵³ As the size of the ammonia molecule is smallest (kinetic diameter 0.26 nm)⁵⁴ among the three chemical analytes tested in this work, ammonia has the maximum probability to reach not only depleted homojunctions (SnO₂/SnO₂ and WO₃/WO₃), but also SnO₂/WO₃ depleted heterojunctions. The kinetic diameters of ethanol and acetone molecules are 0.45 nm and 0.469 nm, respectively.⁵¹ In the present case, the highest density of SnO₂ particles on WO₃ nanoplates is found in sample iv [WO₃-(1.08) SnO₂], which shows the highest sensitivity towards ammonia. The high selectivity of ammonia towards sample iv [WO₃-(1.08)SnO₂] is thus attributed to it having the highest SnO₂ density (and, thereby, the maximum heterojunction area), and to the smaller kinetic diameter of ammonia allowing it to reach the junction at the interface of WO₃ and SnO₂. However, as the molecular size of the ethanol molecule is larger than that of ammonia, ethanol molecules have a lower probability of reaching the heterojunctions where SnO₂ nanoparticles are agglomerated on WO₃ nanoplates at all, as is evident from the FESEM image [Fig. 1(f)]. Hence, the sensitivity towards

ethanol is lower for sample iv [$\text{WO}_3\text{--}(1.08)\text{SnO}_2$], with its dense SnO_2 nanoparticles. However, in the case of sample iii [$\text{WO}_3\text{--}(0.54)\text{SnO}_2$], the ethanol molecules can access both the homo- and heterojunctions due to the SnO_2 nanoparticles being evenly dispersed on the WO_3 nanoplates. Hence, the ethanol sensitivity is found to be highest for sample iii. This argument can similarly be applicable for the acetone, because of its largest kinetic diameter among the VOCs we have chosen. Thus a sensing layer with a heterojunction is less effective for acetone.

Fourthly, the particle size is also known to play a critical role in gas sensing behavior.⁵⁵ A good approximation of the optimal particle size for gas sensing applications can be obtained from the Debye length. It is well known that a particle with a diameter nearly twice the Debye length depletes completely when interacting with oxygen molecules, and thus the whole particle can take part in gas sensing. In the case of SnO_2 , the Debye length is around 3 nm at 250 °C and it increases ($\propto \sqrt{T}$) with temperature.⁵⁶ This explains why the SnO_2 sample (particle size 5–10 nm) exhibits the highest sensitivity towards acetone, compared to the other samples. Thus the heterojunction depletion layer did not play a critical role in the case of acetone; rather, the large surface to volume ratio of the SnO_2 nanoparticles (the concentration of increased adsorbed oxygen species) was the major factor.

Another factor that plays an important role in sensing behaviour is the porosity of hierarchical materials.^{57–59} The Knudsen diffusion and molecular gas diffusion processes are described for the smaller (2–100 nm) and larger (above 100 nm) pore diameters of sensing materials, respectively.⁶⁰ Thus we have further measured the effective BET surface area and porosity of the as-synthesized materials. Fig. 11 displays the nitrogen adsorption–desorption isotherms of (a) WO_3 nanoplates, (b) SnO_2 nanoparticles, (c) $\text{WO}_3\text{--}(0.54)\text{SnO}_2$ and (d) $\text{WO}_3\text{--}(1.08)\text{SnO}_2$. The effective surface area is measured to be the largest ($19.5 \text{ m}^2 \text{ g}^{-1}$) for the SnO_2 nanoparticles and the smallest ($11.38 \text{ m}^2 \text{ g}^{-1}$) for the WO_3 nanoplates, as expected. The effective surface areas of $\text{WO}_3\text{--}(0.54)\text{SnO}_2$ and $\text{WO}_3\text{--}(1.08)\text{SnO}_2$ were measured to be 13.87 and $17.9 \text{ m}^2 \text{ g}^{-1}$, respectively. The average pore size was estimated to be in the range of 25 to 35 nm, suggesting mesoporous samples. Although the effective BET surface area of the as-synthesized samples is highly correlated to the surface morphology, the sensing behaviour of samples is found to be not directly dependent on the surface area. This confirms the important role of the heterojunction in the sensing material, along with sensing gases and temperature.

Effect of temperature. The present VOC sensing behavior clearly ascertains the temperature-dependent gas selectivity, as outlined before. It is known that at lower temperature (<200 °C), $\text{O}_{2(\text{ads})}^-$ and $\text{O}_{2(\text{ads})}^{2-}$ are predominant whereas at higher temperature, atomic reactants $\text{O}_{(\text{ads})}^-$ and $\text{O}_{(\text{ads})}^{2-}$ are found in abundance.⁶¹

First, in the case of ammonia, the following reactions [eqn (6) and (7)] are feasible:⁵⁵

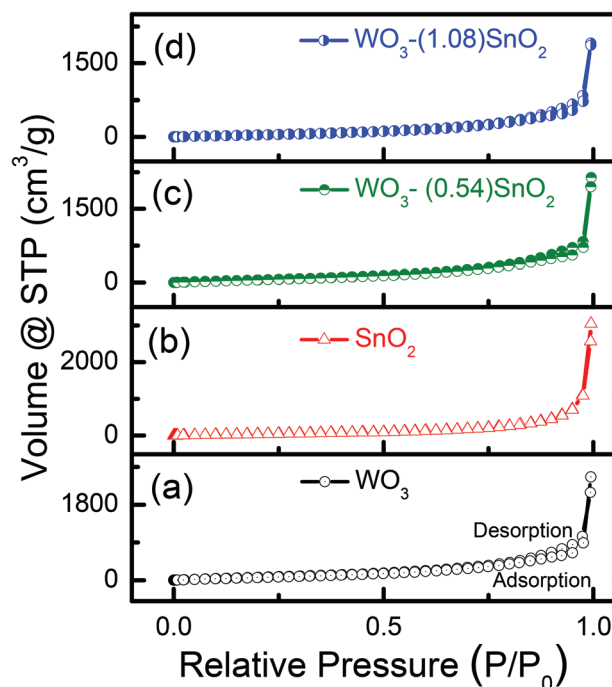
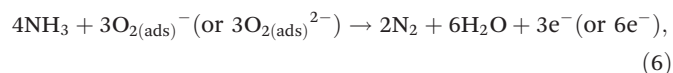
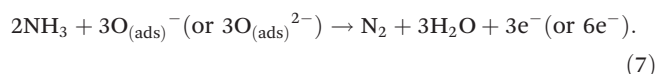


Fig. 11 Nitrogen adsorption–desorption isotherms of the (a) WO_3 nanoplates, (b) SnO_2 nanoparticles, (c) $\text{WO}_3\text{--}(0.54)\text{SnO}_2$ and (d) $\text{WO}_3\text{--}(1.08)\text{SnO}_2$.

at 200 °C,



and at 300 °C,



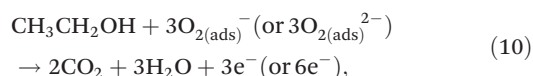
The above chemical reactions show the release of the same number of electrons at lower and at higher temperature. But along with the aforementioned reactions, the oxidation reactions that occur primarily depend on the operating temperature and the nature of the metal oxides. This will lead to the formation of NO_x , as shown in reactions (8) and (9) below:^{40,62}



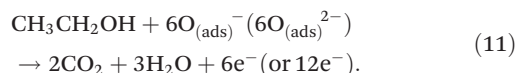
Thus, at higher temperature, NH_3 being the donor molecule results in a decrease in the resistance of the metal oxides, alongside NO_x being acceptor molecules which withdraw electrons, thereby resulting in an increase in the resistance of the $\text{WO}_3\text{--}\text{SnO}_2$ sensors. Hence, the effective response of the nanoparticles towards ammonia decreases at higher temperatures.

The following chemical reactions [eqn (10) and (11)] could occur on the surface of the sensing material in the case of ethanol:⁶³

at 200 °C,



and at 300 °C,



Our experimental results showed a maximum ethanol response at 300 °C for all the samples, suggesting a higher interaction on the surface. However, at a higher temperature (350 °C), the ethanol–metal oxide interaction is expected to be weakened, resulting in a poor response, as shown in the following reaction [eqn (12)]:⁶⁴

at 350 °C,

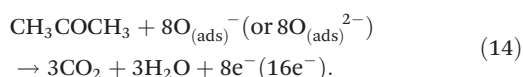


On the other hand, acetone releases only a single electron when it reacts with oxygen ions below 300 °C [eqn (13)], so the change in the sensing layer resistance is less. However, above 300 °C, the number of electrons released is much higher, as shown in the reaction below [eqn (14)]. This is believed to be due to there being insufficient active sites at lower temperature (<300 °C) for all the molecules to be oxidized, whereas at higher temperature (350 °C), the reaction products get desorbed at a faster rate, and hence the new gas species find enough active sites for attachment.⁵⁸

At <300 °C,



but at >300 °C,



This is attributed to the maximum response obtained at 350 °C in the case of acetone.

Conclusions

Here, we demonstrate the synergy of two active oxide materials, *i.e.* WO₃ nanoplates and SnO₂ nanoparticles, for the temperature-dependent sensing behavior of three important biomarkers (ammonia, ethanol and acetone). The SnO₂ nanoparticle size and density on the WO₃ nanoplates was controlled by varying the mass of the SnCl₂·2H₂O precursor, using a facile *in situ* hydrothermal synthesis technique. This leads to an optimum ratio of SnO₂ nanoparticles on WO₃ nanoplates, which played a crucial role in the sensing selectivity of VOCs. In particular, their smaller kinetic diameter meant that the ammonia molecules could easily approach the interface of the WO₃–SnO₂ junction in the case of the high-density SnO₂ nanoparticle-covered WO₃ nanoplates sample, showing maximum sensitivity. On the other hand, the best performance was obtained for ethanol with sparsely coated SnO₂ nanoparticles

on WO₃ nanoplates, due to the bigger kinetic diameter of ethanol molecules. The sensing performances being higher in the present work than those in previous reports is attributed to the formation of a heterojunction at the interface of the two oxides. The as-fabricated chemoresistive sensor, using noble metal-free oxide materials, has strong potential for biomedical and environmental applications, both in terms of cost effectiveness and performance.

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