

# High-sensitivity hydrocarbon sensors based on tungsten oxide nanowires†

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Hydrocarbon (LPG) sensors based on the nanostructures of  $V_2O_5$  do not exhibit satisfactory characteristics, while sensors based on  $WO_{2.72}$  nanowires show high sensitivity ( $\sim 1800$ ) for 2000 ppm of LPG at 200 °C as well as relatively short recovery and response times. Impregnation of  $WO_{2.72}$  nanowires with Pt in the 0.1–1.0 at% range, significantly improves the sensor characteristics, the sensitivity increasing with Pt concentration and reaching a value of  $\sim 10^6$  for 2000 ppm of LPG in the 100–200 °C range with 1 at% Pt. The sensitivity remains high even for 50 ppm of LPG, and is not affected significantly by repeated cycles or humidity. The mechanism of sensing of hydrocarbons by  $WO_{2.72}$  nanowires is explained on the basis of adsorbed oxygen species.

## Introduction

Many of the semiconducting metal oxides have been found to be good candidates for gas sensing since they exhibit significant variations of the electrical resistance on contact with ambient gases and vapours. Thus, ZnO, SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> have been employed in different forms to sense gases and vapours such as hydrogen, carbon monoxide, ethanol and NO<sub>2</sub>. In spite of considerable effort, good sensors for hydrocarbons have not been found hitherto, the problem being of vital significance to industry as well as to the general public. It is, therefore, not surprising that there is considerable interest in developing reliable and efficient hydrocarbon sensors having good sensitivity. Wide band gap semiconducting oxides such as SnO<sub>2</sub> and ZnO have been studied for making efficient hydrocarbon sensors with noble metal additives such as palladium and platinum.<sup>1–4</sup> The sensitivity of the sensors employing these oxides is well within 100 at the 2000 ppm level. Other materials examined for hydrocarbon sensing include WO<sub>3</sub>,<sup>5</sup>  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> loaded with PtO<sub>6</sub> and nanocrystalline Ni<sub>1-x</sub>Co<sub>x</sub>Mn<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub>.<sup>7</sup> The sensitivity (generally defined as the ratio of the resistance in air to that in the hydrocarbon) and response times of these sensors are not entirely satisfactory. V<sub>2</sub>O<sub>5</sub> supported on ZrO<sub>2</sub> is reported to be a good sensor for n-propane–butane mixtures at 625 K,<sup>8</sup> but the maximum sensitivity found is around 3 at the 2000 ppm level. Thick films of nano-sized SnO<sub>2</sub> exhibit a sensitivity of 90 for 1000 ppm of liquefied petroleum gas (LPG).<sup>9</sup> SnO<sub>2</sub> samples sintered at 600 °C show a sensitivity of 100 at 350 °C for 1000 ppm of LPG.<sup>10</sup> In another report, thick-film gas sensors based on pure and Ru-doped nanostructured SnO<sub>2</sub> are found to have a maximum sensitivity of 375 for 1000 ppm of LPG.<sup>11</sup> Liu *et al.*<sup>12</sup> have reported a LPG sensor based on

multi-walled carbon nanotubes coated with SnO<sub>2</sub> with a sensitivity of  $\sim 20$  at 335 °C for 1000 ppm of LPG.

In the present work we have studied the hydrocarbon sensing characteristics of different nanostructures of V<sub>2</sub>O<sub>5</sub> as well as nanowires of tungsten oxide ( $WO_{2.72}$ ) over the concentration range of 50–2000 ppm, after characterizing the nanostructures by X-ray diffraction, electron microscopy and Raman spectroscopy. In addition to studying the sensing characteristics of the as-prepared nanowires of tungsten oxide, we have investigated the effect of impregnating the tungsten oxide nanowires with 0.1, 0.5 and 1 at% Pt. We have found excellent sensing characteristics of  $WO_{2.72}$  nanowires towards LPG (propane–butane mixture) at relatively low temperatures in the range of 50–200 °C with satisfactory response and recovery times. The sensitivity is enhanced markedly on impregnating the  $WO_{2.72}$  nanowires with Pt. The sensing characteristics are not affected significantly even at a relative humidity of 90% and on repeated cycling.

## Experimental

For the synthesis of V<sub>2</sub>O<sub>5</sub> nanoparticles, 1 g of NH<sub>4</sub>VO<sub>3</sub> (Merck, 99.5% pure) was taken in a 100 ml Teflon-lined autoclave containing 80% volume of ethylenediamine (Merck, 99% pure) and heated at 220 °C for 24 h. The final product obtained after cooling the autoclave to room temperature was washed with deionized water and then anhydrous alcohol several times and dried at 80 °C for 24 h. The powder was then heated slowly at 450 °C for 2 h in air.

V<sub>2</sub>O<sub>5</sub> nanobelts were prepared by adding 0.01 mol (1.17 g) of analytically pure NH<sub>4</sub>VO<sub>3</sub> into 50 ml (2 g l<sup>-1</sup>) poly(ethylene glycol)-4000 (Loba Chemie, 99% pure) solution under stirring and the pH of the mixture was adjusted to 2–3 by adding HNO<sub>3</sub> (Rankem, 72% pure) dropwise. The solution was transferred into a 100 ml Teflon-lined autoclave. The autoclave was kept at 200 °C for 24 h and then allowed to cool. The final product was washed several times with deionized water and ethanol.

In order to prepare V<sub>2</sub>O<sub>5</sub> nanowires, an aqueous solution of sodium metavanadate was passed through a cation exchange column (DOWEX) to get vanadic acid. A polycarbonate

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membrane (Nucleopore Track-Etch membrane, 0.02  $\mu\text{m}$ ; Whatman, Kent, UK) was immersed in the vanadic acid solution and kept for 24 hours at 50  $^{\circ}\text{C}$ . The polycarbonate membrane containing nanowires was slowly heated at 500  $^{\circ}\text{C}$  for 6 h.

Tungsten oxide nanowires were prepared by solvothermal synthesis. Tungsten hexachloride (1 g; Aldrich, 98% pure) was taken in a 25 ml autoclave filled with ethanol (Merck, 99.8% pure) up to 90% of its volume. Solvothermal synthesis was carried out at 200  $^{\circ}\text{C}$  for 24 h. The product obtained by centrifugation was washed with ethanol.

The various nanostructures of  $\text{V}_2\text{O}_5$  and nanowires of tungsten oxide were characterized by X-ray diffraction (Cu K $\alpha$  radiation), scanning electron microscopy (LEICA S440i), transmission electron microscopy (JEOL JEM 3010) and micro-Raman spectroscopy (LABRAMAN-HR) using a He-Ne laser (632.81 nm) in the back scattering geometry. The XRD patterns (Fig. 1a) showed the  $\text{V}_2\text{O}_5$  nanostructures had the orthorhombic structure (lattice parameters:  $a = 11.52 \text{ \AA}$ ,  $b = 3.5 \text{ \AA}$ ,  $c = 4.3 \text{ \AA}$ , JCPDS no: 41-1426). The Raman bands observed for  $\text{V}_2\text{O}_5$  nanoparticles, nanobelts and nanowires (Fig. 1b) showed all the samples are crystalline  $\text{V}_2\text{O}_5$  and are in line with literature data.<sup>13,14</sup> The XRD pattern of the tungsten oxide nanowires (Fig. 1a) had the monoclinic structure (lattice parameters:  $a = 18.33 \text{ \AA}$ ,  $b = 3.78 \text{ \AA}$ ,  $c = 14.03 \text{ \AA}$ , JCPDS no: 36-101) characteristic of  $\text{WO}_{2.72}$ .<sup>15,16</sup> The XRD peak intensity of the (010) reflection was relatively higher than that of other reflections. This implies that the nanowires grow along the (010) direction. The four Raman bands at 270, 328, 713 and 805  $\text{cm}^{-1}$  (Fig. 1b) observed were in agreement with those of monoclinic  $\text{WO}_{2.72}$ .<sup>17,18</sup>

To fabricate thick film sensors, an appropriate quantity of diethylene glycol was added to the desired nanostructure of

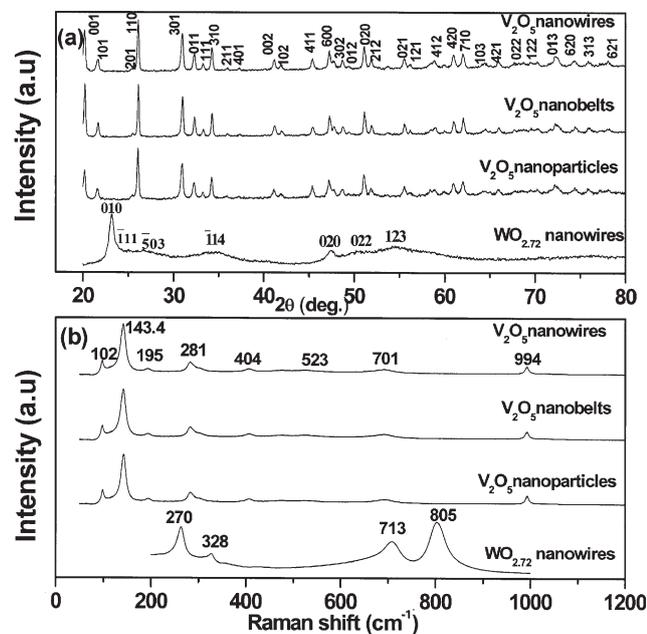


Fig. 1 (a) XRD patterns of  $\text{V}_2\text{O}_5$  nanowires, nanobelts, nanoparticles and  $\text{WO}_{2.72}$  nanowires, (b) Raman spectra of  $\text{V}_2\text{O}_5$  nanowires, nanobelts, nanoparticles and  $\text{WO}_{2.72}$  nanowires.

$\text{V}_2\text{O}_5$  or nanowires of  $\text{WO}_{2.72}$  to obtain a paste. The paste was coated on to an alumina substrate (5 mm  $\times$  20 mm, 0.5 mm thick) attached with a comb-type Pt electrode on one side, the other side having a heater. The films were dried and annealed at 350  $^{\circ}\text{C}$  for 1 h. The  $\text{WO}_{2.72}$  films were impregnated with Pt by dipping the metal oxide film in an aqueous solution of  $\text{H}_2\text{PtCl}_6$  of concentration 0.01 M, 0.05 M or 0.1 M. The thick films were dried and fired at 350  $^{\circ}\text{C}$  for 30 min to promote the decomposition of the platinum precursor into metallic platinum. The extent of impregnation was confirmed by EDAX analysis (see Fig. 2 for a typical EDAX pattern).

Gas sensing properties were measured using a home-built computer-controlled characterization system consisting of a test chamber, a sensor holder, a Keithley multimeter-2700, a Keithley electrometer-6517A, mass flow controllers and a data acquisition system. The test gas was mixed with dry air to achieve the desired concentration and the flow rate was maintained at 200 sccm using mass flow controllers. The current flowing through the samples was measured using a Keithley multimeter-2700. The working temperature of the sensors was adjusted by changing the voltage across the heater side. By monitoring the output voltage across the sensor, the resistance of the sensor in dry air or in test gas can be measured. The gas sensitivity (response magnitude) of the sensor,  $S$ , was determined as the  $R_{\text{air}}/R_{\text{LPG}}$  ratio, where  $R_{\text{air}}$  is the resistance of the thick film sensor in dry air and  $R_{\text{LPG}}$  is the resistance in the different concentration of LPG (commercial propane-butane mixture). The resistance of the sensors based on  $\text{V}_2\text{O}_5$  was in the 120–0.05  $\text{M}\Omega$  range, whereas the resistance of the sensors based on tungsten oxide was in the 200–0.1  $\text{M}\Omega$  range in dry air in the 50–200  $^{\circ}\text{C}$  range. The response time is defined as the time required for the conductance to reach 90% of the equilibrium value after the test gas is injected. The recovery time is the time necessary for the sensor to attain a conductance 10% above the original value in air. Details for the fabrication of the sensors and experimental set-up is given in our earlier report.<sup>19</sup> The sensitivity of thick film

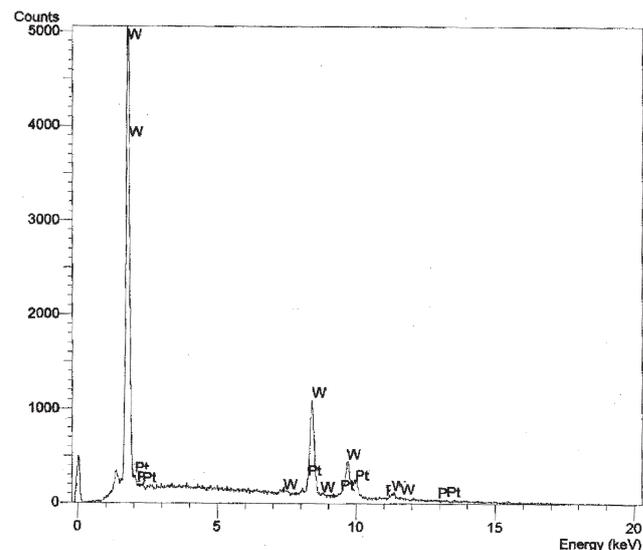
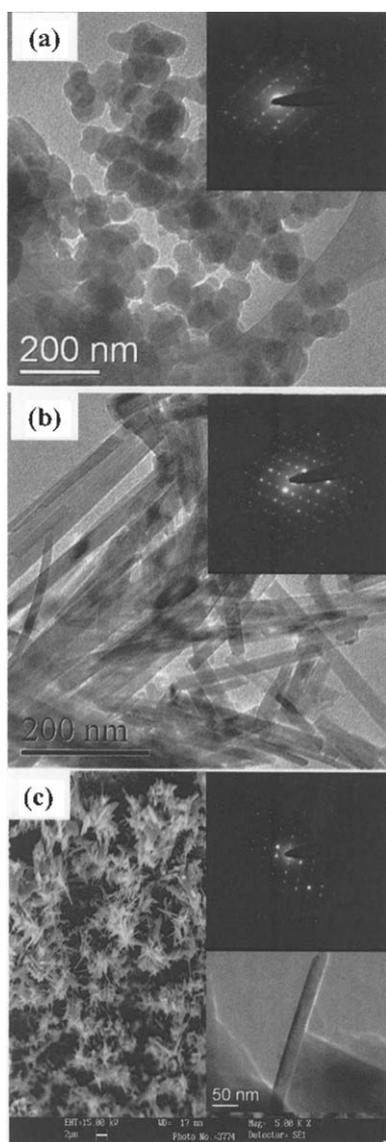


Fig. 2 EDAX pattern of 1 at% Pt impregnated tungsten oxide nanowires.

sensors was also measured in atmospheres with different relative humidities.

## Results and discussion

In Fig. 3a, we show a typical TEM image of  $V_2O_5$  nanoparticles with the inset showing the selected area electron diffraction (SAED) pattern. The average size of these nanoparticles was in the 30–50 nm range. The SAED pattern indicates the particles to be single crystalline. Fig. 3b shows the TEM image of  $V_2O_5$  nanobelts, with the SAED pattern as the inset. The TEM image reveals that the belts are 500–1000 nm long and 20–50 nm wide. Fig. 3c shows the SEM image of the  $V_2O_5$  nanowires with the inset showing the SAED pattern and a TEM image. The diameter of the nanowires was in



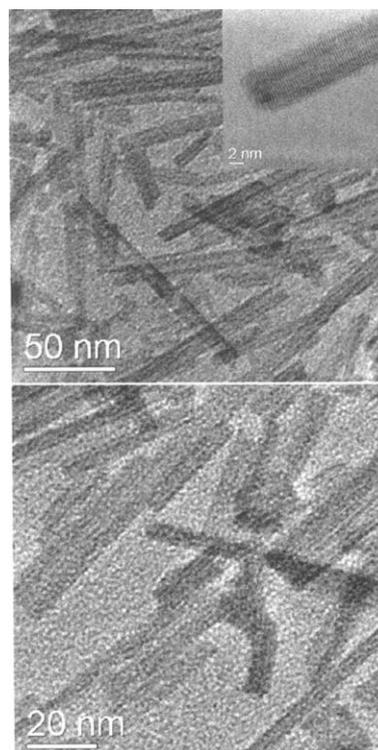
**Fig. 3** (a) TEM image of  $V_2O_5$  nanoparticles with the inset showing the electron diffraction pattern, (b) TEM image of  $V_2O_5$  nanobelts with the inset showing the electron diffraction pattern, (c) SEM image of  $V_2O_5$  nanowires with the inset showing a TEM image and the electron diffraction pattern.

the 20–50 nm range with lengths of several micrometers. The SAED pattern confirms the nanowires to be single crystalline.

In Fig. 4, we show TEM images of the  $WO_{2.72}$  nanowires. The average diameter of the nanowires is in the range 5–15 nm and the length is in the 100–200 nm range. A high-resolution TEM image is also shown as an inset in Fig. 4 and confirms the single crystalline nature of the nanowires.

In Fig. 5a, we show the sensing characteristics of  $V_2O_5$  nanoparticles towards 2000 ppm of LPG. The highest sensitivity found is 10 at 200 °C and  $\sim 7$  at 100 °C. The LPG sensing characteristics of the as-prepared  $V_2O_5$  nanobelts and nanowires are shown in Fig. 5b and c respectively. A maximum sensitivity of 24 was obtained with  $V_2O_5$  nanobelts at 200 °C and the sensitivity at lower temperature decreases drastically. With the nanowires of  $V_2O_5$ , the maximum sensitivity at 200 °C is  $\sim 10$ . Thus, the sensitivities found with the  $V_2O_5$  nanostructures are unsatisfactory, with the response and recovery times also being on the high side.

In Fig. 6a, we show the LPG sensing characteristics of the  $WO_{2.72}$  nanowires. A maximum sensitivity of 1800 is found with 2000 ppm of LPG at 200 °C with the as-prepared  $WO_{2.72}$  nanowires. Even at 50 °C, the sensitivity is 225 for these nanowires. The response as well as recovery times are in the range of 25–80 s for 500 ppm of LPG. Variation of the sensitivity of the  $WO_{2.72}$  nanowires with the concentration of LPG (50–2000 ppm) at 200 °C is shown in Fig. 6b. The nanowires show a sensitivity of 13 for 50 ppm of LPG at 200 °C. In Fig. 7a, we show the variation of the response and recovery times over the temperature range of 50–200 °C. With increasing working temperature, the response and recovery



**Fig. 4** TEM images of  $WO_{2.72}$  nanowires with the inset showing HREM image.

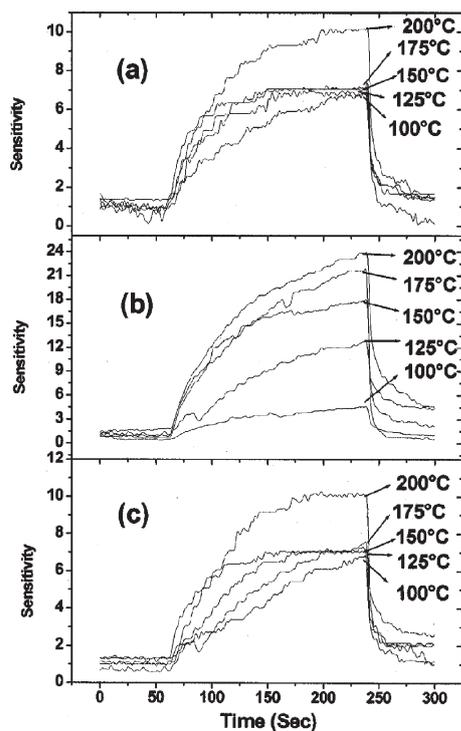


Fig. 5 Gas sensing characteristics of (a)  $V_2O_5$  nanoparticles, (b)  $V_2O_5$  nanobelts, (c)  $V_2O_5$  nanowires for 2000 ppm of LPG.

times decrease as expected. The response times vary in the range of 28–65 s, and the recovery time in the range of 55–80 s.

In order to achieve improved sensing characteristics with the  $WO_{2.72}$  nanowires, we carried out studies after impregnating them with 0.1, 0.5 and 1 at% Pt. In Fig. 8a and b we present the

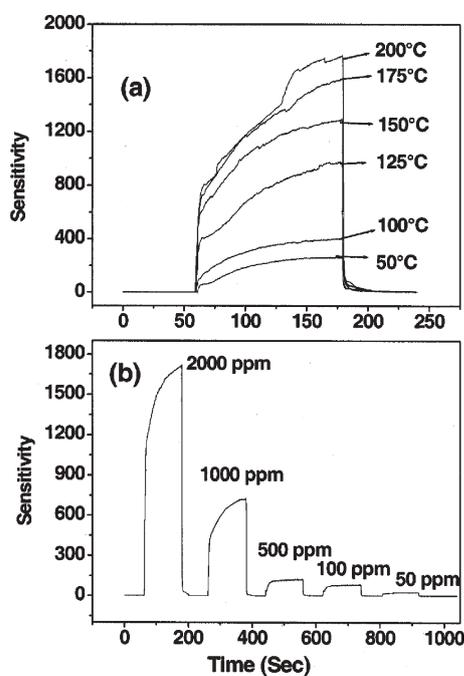


Fig. 6 (a) Gas sensing characteristics of  $WO_{2.72}$  nanowires for 2000 ppm of LPG, (b) variation of sensitivity with concentration of LPG at 200 °C.

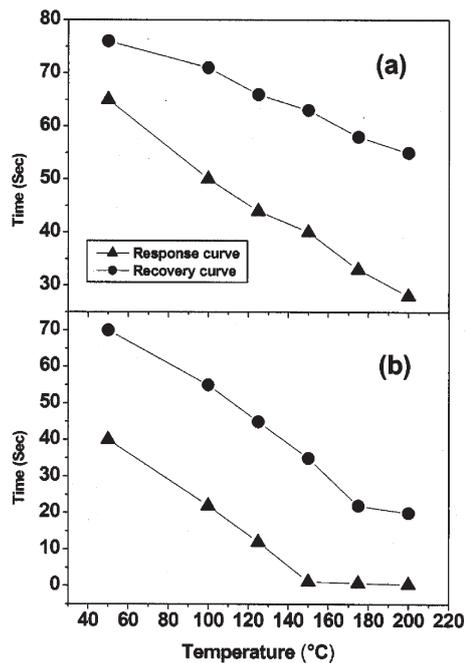


Fig. 7 Response and recovery curves for the (a) pure  $WO_{2.72}$  nanowires, (b) 1 at% Pt impregnated  $WO_{2.72}$  nanowires for 2000 ppm LPG.

sensing characteristics of 0.1 at% Pt impregnated  $WO_{2.72}$  nanowires. We readily notice the very high sensitivity ( $\sim 2200$ ) for 2000 ppm of LPG at 200 °C. The sensitivity is 110 at 50 °C and goes well above 500 at 125 °C. In Fig. 8b, we show the sensing characteristics of 0.1 at% Pt impregnated  $WO_{2.72}$

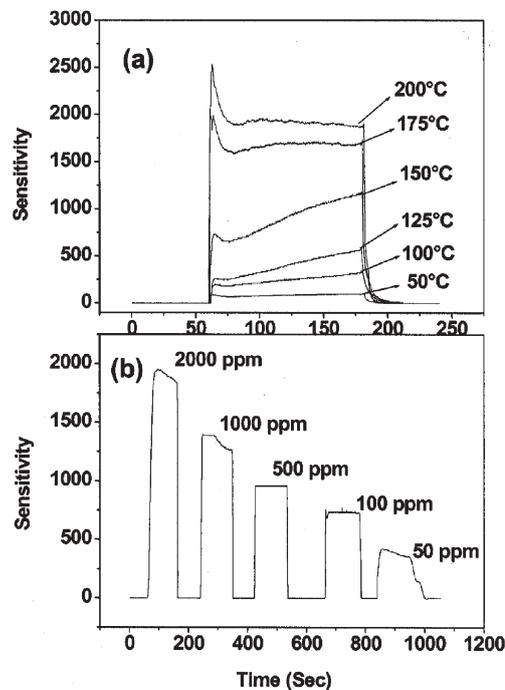
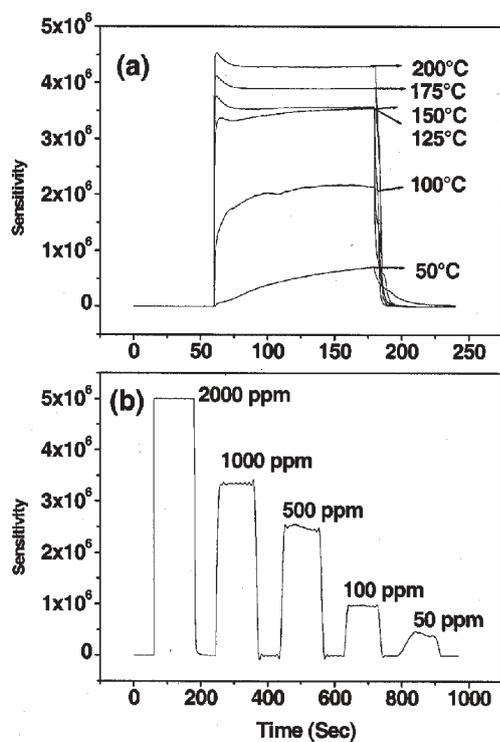


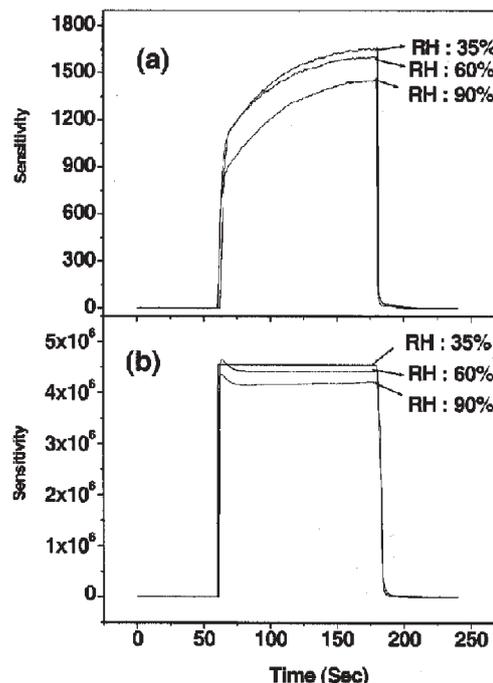
Fig. 8 (a) Gas sensing characteristics of  $WO_{2.72}$  nanowires impregnated with 0.1 at% Pt for 2000 ppm of LPG, (b) variation of sensitivity with concentration of LPG at 200 °C.

nanowires for different concentrations of LPG at 200 °C. A sensitivity of 405 is obtained for 50 ppm of LPG. The sensing characteristics of WO<sub>2.72</sub> nanowires show further improvement on impregnating with 1 at% Pt. We found a maximum sensitivity of  $\sim 4.3 \times 10^6$  for 2000 ppm at 200 °C (Fig. 9a). Even at a temperature of 50 °C, the sensitivity is in the 10<sup>5</sup> range. In Fig. 9b, we show the variation of sensitivity at 200 °C with the LPG concentration in the 50–2000 ppm range. We have examined the effect of impregnating WO<sub>2.72</sub> nanowires with 0.5 at% Pt on LPG sensing and found the sensing characteristics of these nanowires to fall in between those for the 0.1 at% and 1 at% Pt impregnated samples. A maximum sensitivity of  $\sim 5 \times 10^6$  was obtained for 2000 ppm of LPG at 200 °C. In Fig. 7b, we show the variation of the response and recovery times with temperature in the 50–200 °C range for 1 at% Pt impregnated WO<sub>2.72</sub> nanowires. The response times vary in the 1–40 s range and recovery times in the 20–70 s range. Above 150 °C the response and recovery times are around 1 s and 20 s respectively.

We carried out LPG sensing with as-prepared and 1 at% Pt impregnated WO<sub>2.72</sub> nanowires over several cycles over two weeks and found practically no change in the sensitivity as well as the response and recovery times after 200 cycles. We have studied the effect of humidity on the LPG sensing characteristics of the as-prepared and 1 at% Pt impregnated WO<sub>2.72</sub> nanowires sensors in the range of 35–90% relative humidity. We illustrate the effect of humidity on the sensitivity at 200 °C for 2000 ppm of LPG in Fig. 10a and b. There is a slight decrease in the sensitivity on pure WO<sub>2.72</sub> nanowires with an increase in the humidity. However, there is not much change in



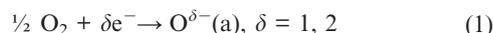
**Fig. 9** (a) Gas sensing characteristics of WO<sub>2.72</sub> nanowires impregnated with 1 at% Pt for 2000 ppm of LPG, (b) variation of sensitivity with concentration of LPG at 200 °C.



**Fig. 10** Effect of humidity on the sensitivity of (a) pure WO<sub>2.72</sub> nanowires, (b) WO<sub>2.72</sub> nanowires impregnated with 1 at% Pt.

the sensor characteristics of 1 at% Pt impregnated WO<sub>2.72</sub> nanowire sensors even at a relative humidity of 90%.

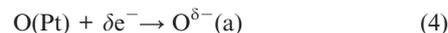
Hydrocarbon sensing by an oxide such as WO<sub>2.72</sub> involves oxygen species<sup>2,3</sup> such as O<sup>-</sup> and O<sup>2-</sup> adsorbed on the oxide surface as given by the reaction



Here, O<sup>δ-</sup>(a) is a charged oxygen species adsorbed on the oxide surface. LPG hydrocarbons (HC) first get adsorbed on the oxide to give the HC(a) species which react with O<sup>δ-</sup>(a),



Reactions (2) and (3) release electrons to decrease the resistivity of the oxides. In the presence of Pt, oxygen is dissociatively adsorbed as O(Pt), which spills over to the oxide and forms the charged oxygen species as shown in reaction (4).



Reactions (2) and (3) would follow reaction (4), thereby explaining the increased sensitivity of Pt impregnated WO<sub>2.72</sub> nanowires.

## Conclusions

We have successfully demonstrated that WO<sub>2.72</sub> nanowires are good for hydrocarbon (LPG) sensing with a sensitivity of the order of 10<sup>3</sup> or more at 200 °C for 2000 ppm of LPG. The response and recovery times are in the 25–80 s range.

Impregnation of the WO<sub>2.72</sub> nanowires with Pt has a profound effect on the sensor characteristics, the sensitivity increasing from 2200 for 0.1 at% Pt to  $4.3 \times 10^6$  for 1 at% Pt at 200 °C for 2000 ppm of LPG. The sensitivity is 405 and  $4.5 \times 10^5$  for 50 ppm of LPG with 0.1 and 1 at% Pt impregnation. It is remarkable that even 90% relative humidity has negligible effect on the sensor characteristics of the Pt impregnated WO<sub>2.72</sub> nanowires. The results can be understood on the basis of the interaction of charged surface oxygen species and the hydrocarbons.

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