



Cite this: *RSC Adv.*, 2017, 7, 49605

# CuO/V<sub>2</sub>O<sub>5</sub> hybrid nanowires for highly sensitive and selective H<sub>2</sub>S gas sensor†

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Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) nanowires decorated with CuO nanoparticles on their surface have been prepared by a facile chemical route. The gas-sensing performance of the CuO/V<sub>2</sub>O<sub>5</sub> nanohybrids has been examined against H<sub>2</sub>S, CO, and NO<sub>2</sub> gases over a range of gas concentrations from 7 to 60 ppm and working temperatures from 100 to 400 °C, and compared with that of pristine V<sub>2</sub>O<sub>5</sub> nanowires without the decoration. The CuO/V<sub>2</sub>O<sub>5</sub> nanohybrids exhibit a greatly enhanced sensitivity toward H<sub>2</sub>S gas selectively and are relatively indifferent to CO and NO<sub>2</sub> gases. The gas-sensing response of the nanohybrids increases by nearly 18 times (from 1.84 to 31.86) when tested against 23 ppm of H<sub>2</sub>S gas at 220 °C. The nanohybrids remain stable when detecting H<sub>2</sub>S gas for a period of two weeks. This selective enhancement is attributable to the local p–n junction formed at the interface together with the reversible chemical reaction that occurs when CuO is exposed to H<sub>2</sub>S gas at the temperature employed.

Received 14th June 2017  
 Accepted 10th October 2017

DOI: 10.1039/c7ra06657k

rsc.li/rsc-advances

## Introduction

Hydrogen sulphide (H<sub>2</sub>S) is a “broad-spectrum” poison, namely it is toxic to several systems in the human body, however the nerve system is most affected. Enzymes that exist in the human body are capable of detoxifying H<sub>2</sub>S by oxidation to harmless sulfates. However, the oxidative enzymes become overwhelmed when the H<sub>2</sub>S concentration exceeds a certain threshold level of about 300–350 ppm on average.<sup>1</sup> To avoid harmful incidents occurring, the design of commercial H<sub>2</sub>S gas sensors capable of detecting minute gas concentrations at ppm levels often requires a detection level as low as 5–15 ppm under moderate working temperatures. In this regard, chemiresistor-type sensors based on one-dimensional metal oxide semiconductors (MOSS) are attractive since they are capable of providing gas-sensing ability for the stable detection of trace amounts of hazardous gases with a wide range of chemical attributes. To detect H<sub>2</sub>S gas specifically, various MOS sensing materials such as WO<sub>3</sub>, SnO<sub>2</sub>, ZnO, In<sub>2</sub>O<sub>3</sub> and CuO have been explored.<sup>2</sup> The MOS sensors still suffer from major drawbacks such as cross-sensitivity, sensitivity to humidity, long-term signal drifting and slow sensor response.<sup>3</sup> In particular, the poor selectivity remains a challenge to overcome and often limits their practical applicability.<sup>2–4</sup>

In the literature, the gas-sensing properties of one-dimensional n-type vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) has seldom

been addressed, despite its promising potential in gas detection.<sup>5–10</sup> Liu *et al.* first prepared V<sub>2</sub>O<sub>5</sub> nanobelts decorated with either Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or SnO<sub>2</sub> nanoparticles by a hydrothermal method.<sup>5,6</sup> The hybrid nanobelts showed a moderately enhanced sensing response ( $S = 2.0$ – $3.1$  at 100 ppm ethanol) when compared to the pristine V<sub>2</sub>O<sub>5</sub> nanobelts ( $S = 1.7$ ) at 200 °C. Since then, V<sub>2</sub>O<sub>5</sub> nanostructures have been investigated as gas sensors for detecting mostly organic vapours.<sup>7–10</sup> Among them, Raible *et al.* reported a high sensitivity against organic amines such as 1-butylamine, with a detection limit as low as 30 ppb using V<sub>2</sub>O<sub>5</sub> nanofibres.<sup>7</sup> Raj *et al.* chemically prepared V<sub>2</sub>O<sub>5</sub> nanostructures and found that V<sub>2</sub>O<sub>5</sub> showed a slightly improved sensitivity toward ethanol at ppm levels compared to ammonia with identical concentrations at room temperature.<sup>8,9</sup> Mondafferri *et al.* also demonstrated the sensing response against ammonia gas over a concentration range of 0.85–8.5 ppm at 200–250 °C using electrospun V<sub>2</sub>O<sub>5</sub> nanofibres.<sup>10</sup> Recently, the use of V<sub>2</sub>O<sub>5</sub> nanostructures for the detection of inorganic, hazardous gases has begun to emerge.<sup>11–13</sup> Yan *et al.* reported the room-temperature sensing capability of a porous silicon/V<sub>2</sub>O<sub>5</sub> nanorod composite with a selective, substantially enhanced sensitivity toward NO<sub>2</sub> gas at low concentrations (3 ppm). This compares favourably to that of organic gases such as ethanol, methanol and acetone with an even higher concentration (100 ppm).<sup>11</sup> Mane *et al.* prepared V<sub>2</sub>O<sub>5</sub> and Pd-decorated V<sub>2</sub>O<sub>5</sub> nanorods on glass substrates by chemical spraying and subsequent thermal treatment.<sup>12,13</sup> They also found an enhanced selectivity against NO<sub>2</sub> gas compared to other gases including NH<sub>3</sub>, H<sub>2</sub>S, CO, and SO<sub>2</sub>.<sup>13</sup>

The use of V<sub>2</sub>O<sub>5</sub> nanostructures as sensors for detecting inorganic toxic gases requires more work to assess their applicability. We herein report the decoration of CuO nanoparticles

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra06657k



onto  $V_2O_5$  nanowires to form hybrid nanostructures and investigate the gas sensitivity/selectivity of these nanostructures toward the toxic gases  $H_2S$ ,  $CO$  and  $NO_2$ . The reason for selecting  $CuO$  for the hybrid structure lies in the fact that there are reports about enhanced selective sensing achieved with p-type  $CuO$  semiconductors exposed to  $H_2S$  gas.<sup>14–17</sup> For the first time, the  $CuO/V_2O_5$  nanohybrids have been found to exhibit highly sensitive and selective detection toward  $H_2S$  gas at ppm levels continuously over a prolonged period of time (up to two weeks) and are relatively indifferent to  $CO$  and  $NO_2$  gases over the moderate temperature range examined.

## Results and discussion

Fig. 1(a) shows the morphology of the hydrothermally prepared  $V_2O_5$  nanowires.  $V_2O_5$  nanowires with a uniform diameter of 100 to 250 nm, a length of 10 to 20  $\mu m$  and a smooth topography have been obtained. The XRD pattern in Fig. 1(b) shows characteristic diffraction peaks in good agreement with those of the orthorhombic  $V_2O_5$  structure (JCPDS no. 41-1426). Fig. 2 shows that the  $V_2O_5$  nanowires are of single crystal morphology. The lattice-fringe spacings in Fig. 2(b) are 0.434 and 0.343 nm, corresponding to the (001) and (110) planes of orthorhombic  $V_2O_5$ , respectively. The nanowires grow along the [110] direction preferentially.

The  $V_2O_5$  nanowires served as a backbone for the preparation of  $CuO/V_2O_5$  hybrids with decorative  $CuO$  nanoparticles. Fig. 3(a) shows that the  $CuO$  nanoparticles with a diameter of

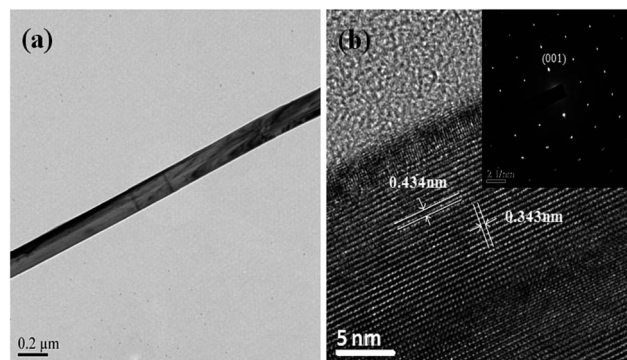


Fig. 2 (a) Bright-field TEM image, (b) HRTEM image and SAED pattern (inset) of a single  $V_2O_5$  nanowire.

about 50 nm are well dispersed on the  $V_2O_5$  surface. Fig. 3(b) shows a typical TEM bright-field image of the  $CuO/V_2O_5$  hybrids, in which discrete  $CuO$  nanoparticles seem to adhere onto the  $V_2O_5$  surface. The black dots are monoclinic  $CuO$  which was verified by TEM (Fig. S1 in the ESI†). Fig. 3(c) displays an XRD pattern of the  $CuO/V_2O_5$  hybrids prepared *via* a deposition process, with a heat-treatment temperature of 400 °C. Well-defined crystalline phases have been found for the orthorhombic  $V_2O_5$  and monoclinic  $CuO$  (JCPDS no. 48-1548), without the formation of any intermediate alloying compounds. It is worthwhile to note that the heat-treatment temperature turned out to be critically important for the successful preparation of  $CuO/V_2O_5$  hybrids. If the temperature was raised to 500 °C, the hybrids became irregular fragments as shown in Fig. 3(d), suggesting that the  $V_2O_5$  nanowires had partially melted or softened (note that the melting temperature of pure bulk  $V_2O_5$  is about 690 °C) so the structure of the hybrid was destroyed.

Fig. 4 shows the sensing response of the pristine  $V_2O_5$  and the  $CuO/V_2O_5$  hybrid nanowires against 23 ppm  $H_2S$  gas over a temperature range from 100 to 380 °C. Two important findings have been observed. Firstly, the bell-shaped distribution reveals an optimum working temperature at which the sensing response is highest. This bell-shaped temperature dependence is ascribed to two main reasons.<sup>17</sup> On the one hand, the adsorption, desorption and diffusion reactions involved, between the target gas and the semiconducting oxide surface, are all thermally activated processes. Hence the response increases with the working temperature.<sup>3</sup> On the other hand, electrons in oxide semiconductors are more likely to attain sufficient energy to jump to the conduction band from the valence band at elevated temperatures. This leads to an increased concentration of free electrons so that electrical resistance is reduced accordingly. A combination of the thermally activated process, together with the increased probability of free-electron formation as the temperature was increased, results in an optimal temperature at which the electrical resistance (and hence the sensing response) is highest. In this regard, we have demonstrated for the first time that the optimal sensing temperature can be tailored to a lower temperature, against the model  $H_2S$  gas at ppm levels, through the decoration

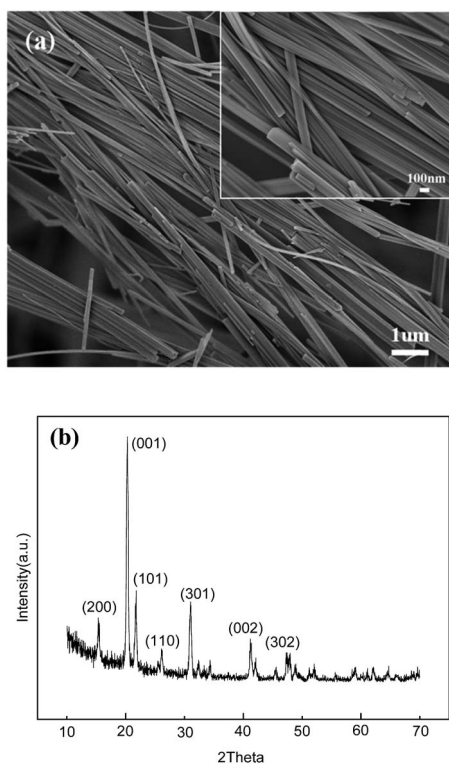


Fig. 1 (a) FE-SEM image and (b) XRD pattern of the hydrothermally prepared  $V_2O_5$  nanowires.



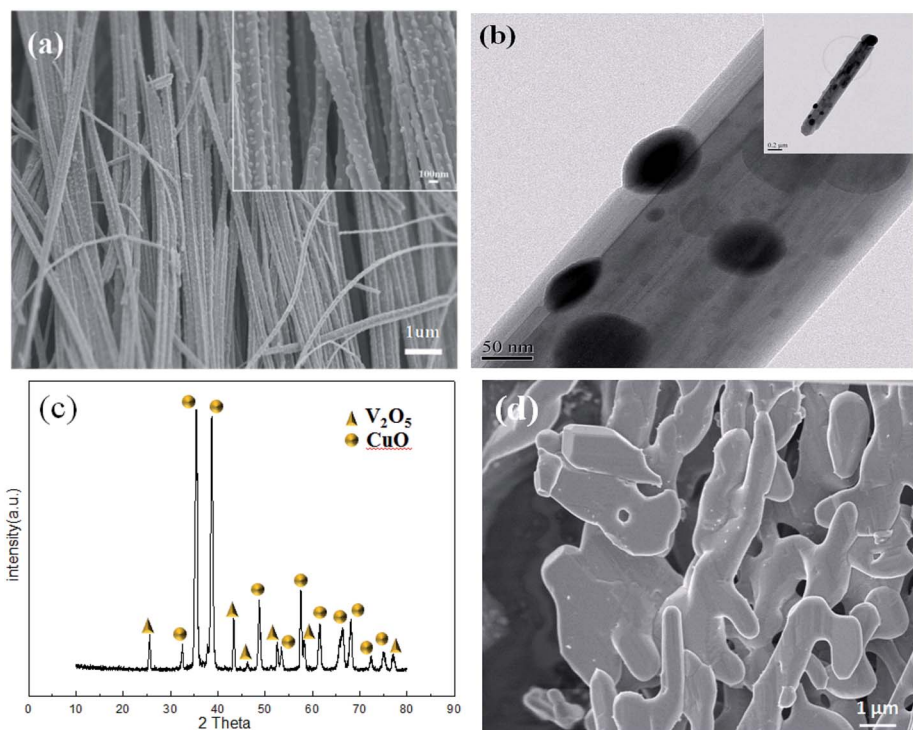


Fig. 3 (a) FE-SEM, (b) bright-field TEM and (c) XRD pattern of the CuO/V<sub>2</sub>O<sub>5</sub> hybrids prepared at 400 °C. (d) FE-SEM image of the CuO/V<sub>2</sub>O<sub>5</sub> hybrids prepared at 500 °C.

of CuO nanoparticles onto V<sub>2</sub>O<sub>5</sub> nanowires in Fig. 4. Secondly, we have found that the CuO/V<sub>2</sub>O<sub>5</sub> hybrids show a response as high as 31.86 against H<sub>2</sub>S gas at ppm levels at 220 °C. For the first time, this compares favourably with that of the pristine V<sub>2</sub>O<sub>5</sub>, for which the highest response is merely 1.84 at 300 °C. The increased sensitivity is ascribed to the hybridization of V<sub>2</sub>O<sub>5</sub> with the CuO nanoparticles together with the decorative hybrid structure, and will be discussed in later sections.

The CuO/V<sub>2</sub>O<sub>5</sub> hybrid nanowires also display a significantly enhanced gas selectivity which is highly desirable in practical sensing applications. To illustrate this, the dynamic resistance behaviour of the pristine V<sub>2</sub>O<sub>5</sub> nanowires is displayed in Fig. 5 against H<sub>2</sub>S, CO, and NO<sub>2</sub> gases at 300 °C. Responses of the

V<sub>2</sub>O<sub>5</sub> nanowires are 1.84 for 23 ppm H<sub>2</sub>S gas, 1.48 for 60 ppm CO gas and 1.46 for 30 ppm NO<sub>2</sub> gas.

In addition, the response times toward detection of H<sub>2</sub>S, CO, and NO<sub>2</sub> gases are 196, 174, and 212 s, respectively, as shown in Fig. 6(a–c), for the above gas concentrations. The sensing properties are primarily ascribed to the exchange of charge carriers between the adsorbed gas molecules and the V<sub>2</sub>O<sub>5</sub> surface. In an air atmosphere, chemisorbed oxygen species, such as O<sup>2-</sup>, O<sup>-</sup> and O<sub>2</sub><sup>-</sup>, trap electrons from the conduction band of the n-type V<sub>2</sub>O<sub>5</sub> semiconductor, resulting in a space-charge depletion near the surface.<sup>18</sup> After the introduction of the reducing H<sub>2</sub>S or CO gas into the testing chamber, the gas molecules would react with the previously chemisorbed oxygen

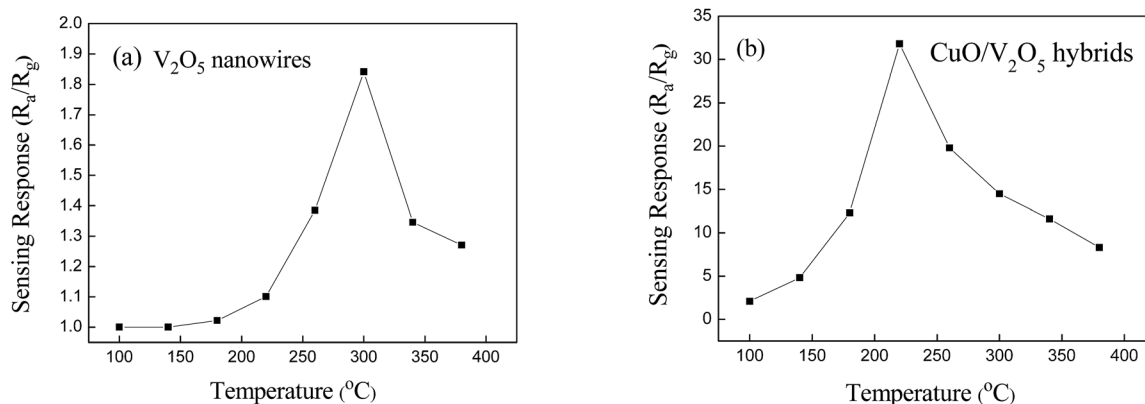


Fig. 4 Gas-sensing response of the (a) pristine V<sub>2</sub>O<sub>5</sub> nanowires and (b) CuO/V<sub>2</sub>O<sub>5</sub> hybrids against 23 ppm H<sub>2</sub>S over a broad temperature range.



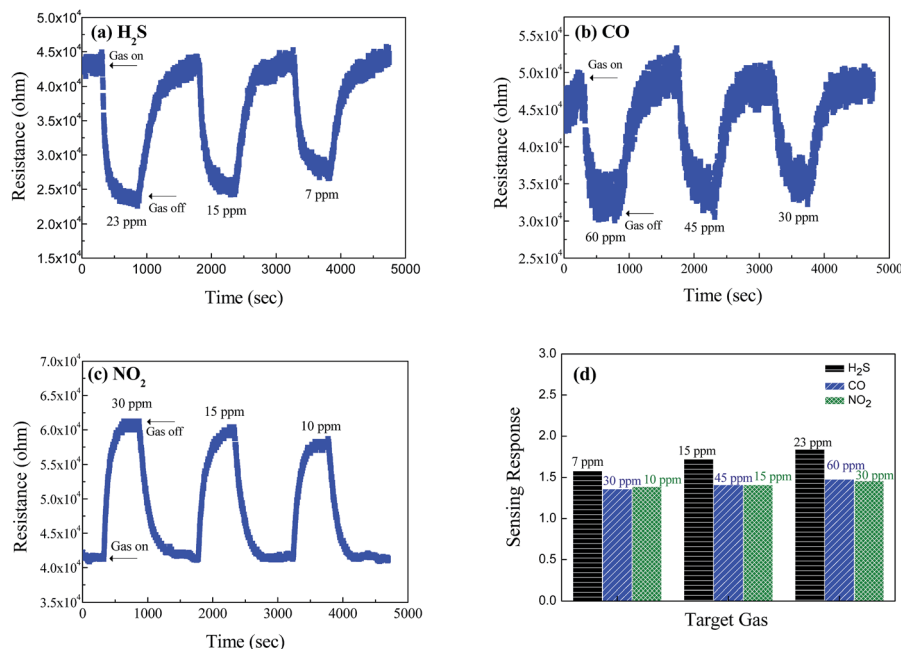
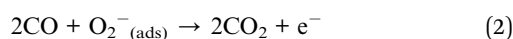
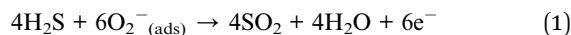


Fig. 5 Dynamic resistance change of the pristine  $V_2O_5$  nanowire sensors against (a)  $H_2S$ , (b)  $CO$  and (c)  $NO_2$  gases, at ppm-level concentrations at  $300\text{ }^\circ\text{C}$ . (d) A summary of the responses of the  $V_2O_5$  nanowires against  $H_2S$ ,  $CO$ , and  $NO_2$  gas at  $300\text{ }^\circ\text{C}$ .

ions, so that the electrons trapped by the absorbed oxygen would subsequently be released into the bulk  $V_2O_5$  nanowires, according to the following reactions (1) and (2):



This produces free electrons and hence decreases the electrical resistance. When the reducing gases were removed from the atmosphere, oxygen molecules spontaneously adsorb onto the  $V_2O_5$  surface reversibly to trap free electrons, which causes the electrical resistance to increase, returning back to its initial value. In contrast, the adsorption of oxidizing  $NO_2$  gas would

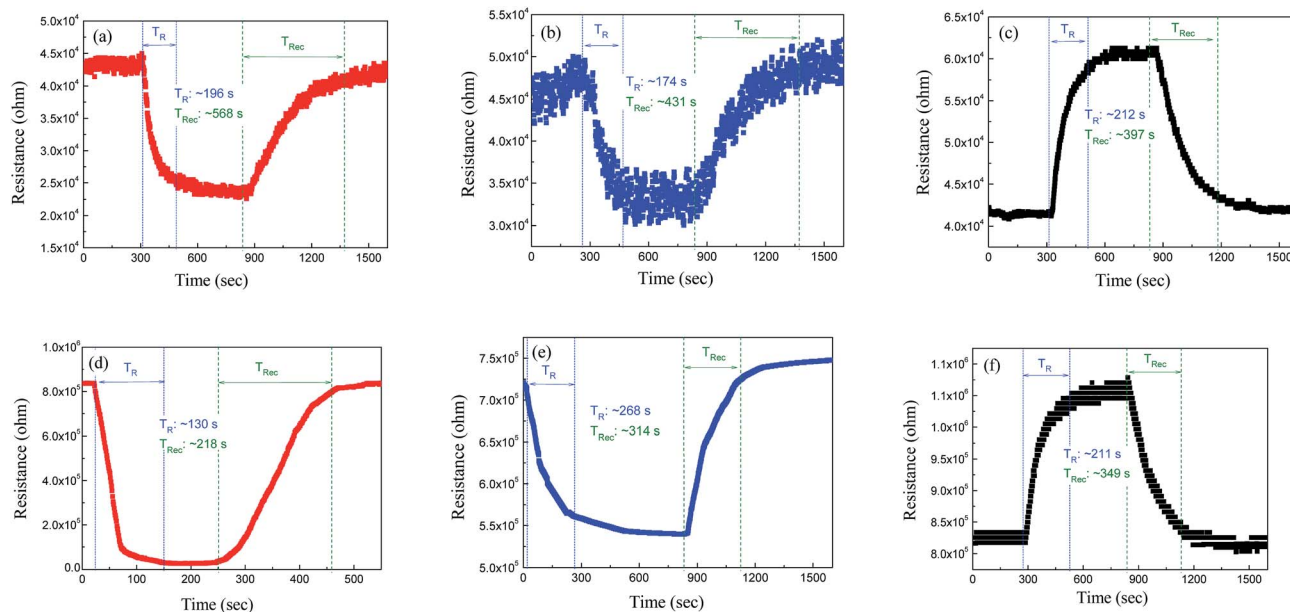


Fig. 6 Response time ( $T_R$ ) and recovery time ( $T_{Rec}$ ) of the pristine  $V_2O_5$  nanowires against (a)  $H_2S$  (23 ppm), (b)  $CO$  (60 ppm) and (c)  $NO_2$  (30 ppm) at  $300\text{ }^\circ\text{C}$ , respectively.  $T_R$  and  $T_{Rec}$  of the  $CuO/V_2O_5$  hybrid nanowires against (d)  $H_2S$  (23 ppm), (e)  $CO$  (60 ppm) and (f)  $NO_2$  (30 ppm) at  $220\text{ }^\circ\text{C}$ , respectively.



deplete the number of charge carriers in the surface layer of the  $V_2O_5$  nanowires. This widens the depletion region, resulting in an increase in the electrical resistance accordingly. The desorption of gas molecules from the pristine  $V_2O_5$  appears to be more difficult than the adsorption, so that a “tail” was found in Fig. 6(a–c).

In addition, Fig. 5(d) summarizes the sensing response of the pristine  $V_2O_5$  nanowires. The lack of gas selectivity is apparent, however the sensor does provide a decent response to a change in concentration of the target gases over ppm concentrations, examined at the given working temperature.

Fig. 7 shows the dynamic resistance change of the  $CuO/V_2O_5$  hybrids against  $H_2S$ , CO, and  $NO_2$  gases. The responses of the hybrids are 1.33 against 60 ppm CO gas, and 1.29 against 30 ppm  $NO_2$  gas at 220 °C. The result resembles that of the pristine  $V_2O_5$  nanowires at 300 °C, despite the fact that the sensing temperature employed was reduced. A significantly enhanced sensing performance was found for the  $CuO/V_2O_5$  hybrids toward  $H_2S$  gas selectively. Fig. 7(a) shows the resistance change of the  $CuO/V_2O_5$  hybrids against  $H_2S$  gas of various concentrations at 220 °C; the responses are 31.86 at 23 ppm, 20.89 at 15 ppm and 7.86 at 7 ppm. This result indicates a dramatic enhancement of the sensing response from 1.84 for the pristine  $V_2O_5$  nanowires to 31.86 for the  $CuO/V_2O_5$  hybrids upon exposure to 23 ppm  $H_2S$ . Compared to the rather indifferent sensitivity of the hybrid nanowires against CO and  $NO_2$  gases, a significantly increased sensing performance, nearly 18 times that of the pristine  $V_2O_5$  nanowires, has been discovered toward  $H_2S$  gas selectively over the various gases and gas concentrations examined, as summarized in Fig. 8. Not to mention the fact that this occurs at a slightly lower working

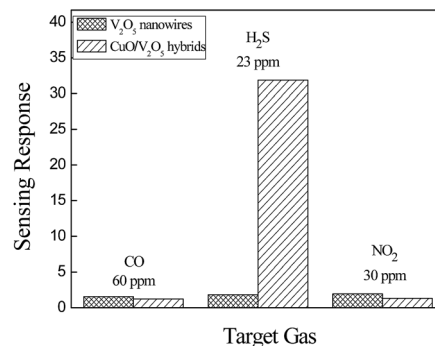


Fig. 8 Selectivity of  $V_2O_5$  nanowires and  $CuO/V_2O_5$  hybrids toward  $H_2S$ , CO and  $NO_2$  gases at the optimal working temperature (300 °C for  $V_2O_5$ , 220 °C for  $CuO/V_2O_5$ ).

temperature (220 °C). In addition, Fig. 6(d) shows that the response time of the hybrid is 130 s for  $H_2S$  gas at a 23 ppm concentration. Therefore, the enhanced selective sensitivity is obtained with a simultaneously shortened response time. In comparison, the response times to detect CO and  $NO_2$  gases are 268 and 211 s for the hybrids, respectively, which are similar to that of the pristine counterpart. Similar results have been found for the recovery times. The detection limit of the hybrid  $CuO/V_2O_5$  nanowires has been determined experimentally, in which no response was detectable when the  $H_2S$  concentration was below 3 ppm.

The selective enhancement and increased sensitivity toward  $H_2S$  gas sensing of the  $CuO/V_2O_5$  hybrids may be explained by the p–n junction formed at the dissimilar interface and

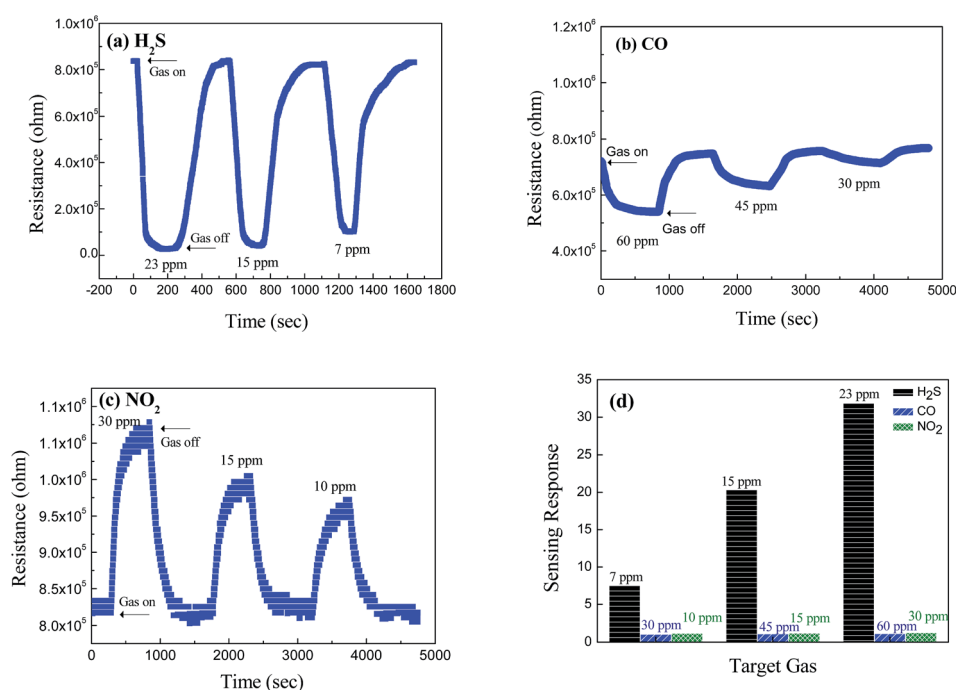


Fig. 7 Dynamic resistance change of the  $CuO/V_2O_5$  hybrids against (a)  $H_2S$ , (b) CO and (c)  $NO_2$  at ppm-level concentrations at 220 °C. (d) A summary of the gas response of the  $CuO/V_2O_5$  hybrids against  $H_2S$ , CO and  $NO_2$  at 220 °C.



sulfuration of the decorative CuO. The intrinsic  $V_2O_5$  and CuO are n- and p-type semiconductors, respectively. The decoration of CuO onto  $V_2O_5$  in the hybrids forms local p-n junctions at the interface.<sup>14-17,19,20</sup> The width of the space-charge region ( $W$ ) at the interface can be estimated from eqn (3) and (4) for n- $V_2O_5$  and p-CuO, respectively:<sup>20,21</sup>

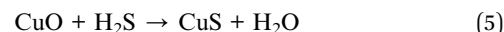
$$W_{V_2O_5} = \left[ \frac{2\varepsilon_{V_2O_5} V_o}{q} \times \frac{N_{CuO}}{N_{V_2O_5}(N_{V_2O_5} + N_{CuO})} \right]^{1/2} \quad (3)$$

$$W_{CuO} = \left[ \frac{2\varepsilon_{CuO} V_o}{q} \times \frac{N_{V_2O_5}}{N_{CuO}(N_{V_2O_5} + N_{CuO})} \right]^{1/2} \quad (4)$$

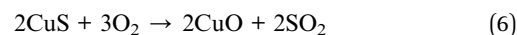
where  $\varepsilon$  is the permittivity ( $2.25 \times 10^{-11}$  F m<sup>-1</sup> for  $V_2O_5$  and  $2.123 \times 10^{-10}$  F m<sup>-1</sup> for CuO),<sup>20,22</sup>  $V_o$  ( $= 0.6$  eV) is the contact potential which is equal to the amount of the energy band bending between  $V_2O_5$  and CuO ( $\phi_{CuO} - \phi_{V_2O_5}$ ),  $q$  is the electrical charge of the carrier ( $1.6 \times 10^{-19}$  C), and  $N$  is the carrier concentration ( $N_{V_2O_5} = 1.48 \times 10^{18}$  cm<sup>-3</sup> and  $N_{CuO} = 1 \times 10^{19}$  cm<sup>-3</sup>, at room temperature).<sup>20,23</sup> The calculated space-charge widths are 9.97 nm for  $V_2O_5$  and 4.53 nm for CuO. These estimates are used for the plot of the energy-band diagram of CuO/ $V_2O_5$  p-n junction in air and  $H_2S$ , in Fig. 9(a). Energy-band bending at the interface is apparent. The band gap ( $E_g$ ), electron affinity ( $\chi$ ) and work function ( $\phi$ ) of  $V_2O_5$  are 2.3, 3.99, and 4.7 eV, respectively.<sup>24,25</sup> Those of CuO are 1.35, 4.07, and 5.3 eV, respectively.<sup>20</sup> Note that the calculated space-charge widths are an estimate since the carrier concentrations used in the calculation are the values at room temperature. A more precise determination of the  $W_{V_2O_5}$  and  $W_{CuO}$  needs information about the carrier concentrations at the working temperature (220 °C) employed. Nonetheless, the electrical transport channel is suppressed by the presence of local p-n junctions, according to the estimates of the space-charge region. This would hence lead to a higher base resistance (as observed in Fig. 6 where the base resistance values of the CuO/ $V_2O_5$  hybrids were 10 to 20 times greater than that of the pristine  $V_2O_5$ ) and a larger change in electrical resistance (and hence sensing

response) for the CuO/ $V_2O_5$  hybrid nanowires compared to that of the pristine  $V_2O_5$  counterpart.

An energy-band diagram shown in Fig. 9(b) further demonstrates how the sulfuration of the decorative CuO affects the response and recovery processes at the p-n junctions in the hybrids. In an air atmosphere, the potential barrier at the p-n junction impedes the electron flow through the interface. When  $H_2S$  gas is introduced into the testing chamber with a concentration exceeding a certain critical level (about 7 ppm determined experimentally in the present study), the CuO is spontaneously converted to CuS by the following chemical reaction:<sup>14-16</sup>



CuS is a metallic conductor, thus, the p-n junction as well as the charge-depletion region transform into a metal-n-type heterostructure. The potential barrier at the p-n junction is then expected to be lowered; therefore, the conversion from CuO to CuS facilitates the electron flow, leading to the drastic decrease in the electrical resistance. After the inflow of  $H_2S$  gas is terminated and air is re-introduced into the chamber, CuS changes back to CuO by oxidation:



The electrical resistance accordingly returns to its initial level. It may be interesting to note that the  $V_2O_5$  surface, without being decorated by the CuO nanoparticles as in the CuO/ $V_2O_5$  hybrid, may also be involved in the gas sensing when  $H_2S$  is introduced. As yet, this appears not to contribute substantially to the  $H_2S$  selectivity.

The gas-sensing stability of the CuO/ $V_2O_5$  nanohybrids has been examined against 15 ppm  $H_2S$  for a long period of time. In Fig. 10, the sensing response remains relatively stable with an average sensitivity of 21.1 during the continuous two-week measurement. Note that every response value is in fact an average of seven measurements (as shown in the inset for the first data point). This finding indicates that the CuO/ $V_2O_5$

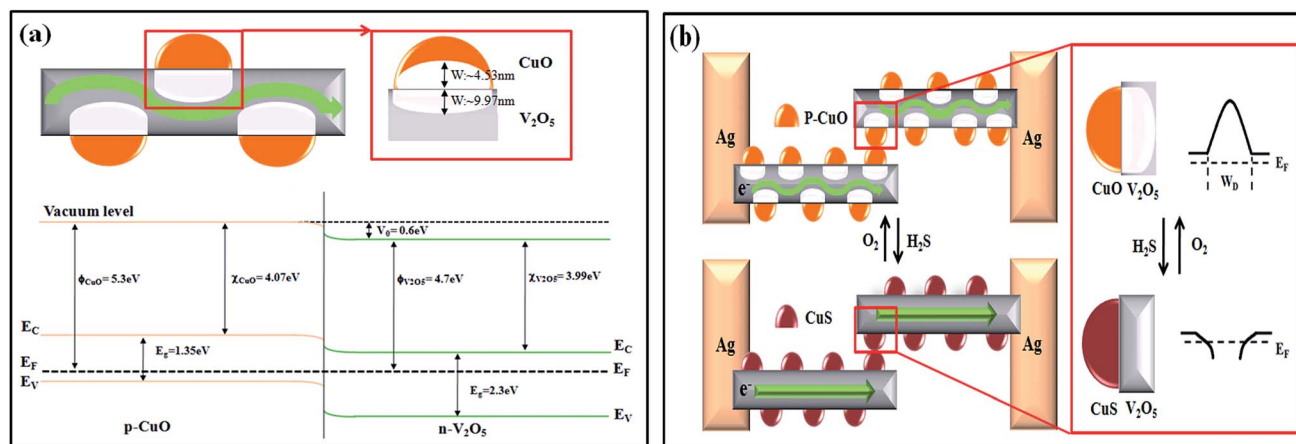


Fig. 9 (a) The band bending diagram and depletion-layer width at the p-n junction. (b) The energy-band diagram of the CuO/ $V_2O_5$  p-n junction in an air and  $H_2S$  gas atmosphere.



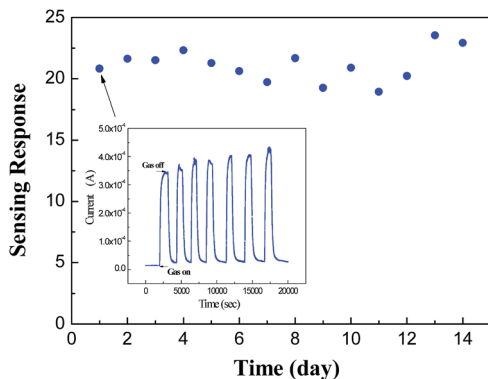


Fig. 10 Gas-sensing stability of the CuO/V<sub>2</sub>O<sub>5</sub> nanohybrids against 15 ppm H<sub>2</sub>S at 220 °C.

nanohybrids may be used in practical sensing applications for the selective detection of hazardous H<sub>2</sub>S gas, despite more work being required to elucidate the applicability.

## Experimental section

### A. Materials

CuO-functionalized V<sub>2</sub>O<sub>5</sub> nanowires were prepared by a facile two-step route, involving hydrothermal and wet-deposition processes. In the hydrothermal process, crystalline V<sub>2</sub>O<sub>5</sub> nanowires were synthesized from a solution mixture consisting of 0.285 g V<sub>2</sub>O<sub>5</sub> powder in 9 ml de-ionized water, with dropwise addition of 1 ml hydrogen peroxide (35%) under vigorous agitation for 1 h. The solution was then placed in a Teflon-lined stainless-steel autoclave and kept at 180 °C for 24 h before being cooled down to room temperature naturally. The resultant V<sub>2</sub>O<sub>5</sub> nanowires were washed repeatedly with de-ionized water, centrifuged and then dried at 80 °C. In the wet-deposition process, the as-prepared V<sub>2</sub>O<sub>5</sub> nanowires were dispersed in a mixed solution consisting of 10 ml of ethanol and 0.06 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O. The suspension was then heated to 80 °C for the removal of ethanol. The powder was then placed in an alumina boat and fed into the centre of a three-zone horizontal quartz-tube furnace. The tube was first evacuated until the pressure inside reached  $6 \times 10^{-2}$  torr, before the introduction of a gaseous mixture containing 85 sccm argon (standard cubic centimetres per min at STP) and 15 sccm oxygen. The temperature was then increased to 400 °C with a heating rate of 20 °C per min and held isothermally for 1 h with a continuous flow of the mixed gas during the entire heating process to prepare CuO nanoparticles decorated on V<sub>2</sub>O<sub>5</sub> nanowires.

### B. Characterization

The morphology and crystalline structure of the V<sub>2</sub>O<sub>5</sub> and CuO/V<sub>2</sub>O<sub>5</sub> hybrid nanowires were examined by field-emission scanning electron microscopy (FE-SEM), X-ray diffractometry (XRD) with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm) and transmission electron microscopy (TEM).

### C. Fabrication of the gas sensing devices

The gas sensors were fabricated by mixing the CuO/V<sub>2</sub>O<sub>5</sub> hybrids or pristine V<sub>2</sub>O<sub>5</sub> nanowires with methanol. The suspensions were then dispensed on alumina substrates with pre-configured, inter-digitated Ag electrodes. Analysis of the sensing properties was carried out in a self-assembled tubular furnace system along with a mass-flow controller, so that the concentration of various gases including air, H<sub>2</sub>S, CO and NO<sub>2</sub> gases, could be precisely tuned. The electrical resistance was recorded by a volt-amperometric Keithley 2410 every 1 s over a wide range of gas concentrations (7 to 60 ppm) and working temperatures (100 to 400 °C) against target gases such as H<sub>2</sub>S, CO and NO<sub>2</sub>. For each test, the nanowire sensor was stabilized in air for 10 min before the target gas was introduced into the reaction chamber. The gas response ( $S$ ) is defined as the ratio of the electrical resistance measured in fresh air ( $R_a$ ) to the resistance measured in the presence of target gas ( $R_g$ ). Either  $R_a/R_g$  or  $R_g/R_a$  was used for the determination of  $S$ , depending on the oxidising or reducing target gas used. The response time and recovery time are defined herein as the time it takes for the sensor to achieve 90% of its equilibrium level for the entire resistance change for adsorption and desorption of the target gas, respectively.

## Conclusion

Hybrid p-CuO/n-V<sub>2</sub>O<sub>5</sub> nanowires were prepared *via* a facile chemical route and their gas-sensing properties were investigated. The formation of local p–n junctions at the nanometre scale CuO/V<sub>2</sub>O<sub>5</sub> interface, together with the reversible sulfuric/oxidative reactivity when exposed to cyclic H<sub>2</sub>S gas/air at moderate temperatures, significantly enhanced the response and selectivity toward H<sub>2</sub>S gas sensing. The hybrid nanowires showed a rather indifferent response when CO and NO<sub>2</sub> were used as the target gas. This unique selectivity toward H<sub>2</sub>S gas at precise ppm levels means that hybrid p-CuO/n-V<sub>2</sub>O<sub>5</sub> nanowires are anticipated to be used in a stable and reliable sensing device suitable for practical alarm applications.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We would like to dedicate this article to the late Professor Yung-Chiun Her who has inspired many friends and students alike with his boundless spirit and enthusiasm. His greatness is not merely reflected by the amount of wisdom he gave in and out of classroom, but even more by the way he always practiced what he preached. This study was supported financially by the Ministry of Science and Technology (Taiwan) under contract no. NSC101-2221-E005-033-MY3. Experimental assistance from students at the National Taichung First Senior High School is also gratefully acknowledged.



## References

- 1 S. Ramasamy, S. Singh, P. Taniere, M. J. S. Langman and M. C. Eggo, *Am. J. Physiol.: Gastrointest. Liver Physiol.*, 2006, **291**, 288–296.
- 2 V. E. Bochenkov and G. B. Sergeev, Sensitivity, selectivity, and stability of gas-sensitive metal-oxide nanostructures, in *Metal Oxide Nanostructures and Their Applications*, ed. A. Umar and Y.-B. Hahn, American Scientific Publishers, 2010, ch. 2, pp. 31–52.
- 3 H.-J. Kim and J.-H. Lee, *Sens. Actuators, B*, 2014, **192**, 607–627.
- 4 S. M. Kanan, O. M. El-Kadri, I. A. Abu-Yousef and M. C. Kanan, *Sensors*, 2009, **9**, 8158–8196.
- 5 J. Liu, X. Wang, Q. Peng and Y. Li, *Adv. Mater.*, 2005, **17**, 764–767.
- 6 J. Liu, X. Wang, Q. Peng and Y. Li, *Sens. Actuators, B*, 2006, **115**, 481–487.
- 7 I. Raible, M. Burghard, U. Schlecht, A. Yasuda and T. Vossmeier, *Sens. Actuators, B*, 2005, **106**, 730–735.
- 8 A. D. Raj, P. S. Kumar, Q. Yang and D. Mangalaraj, *Phys. E*, 2012, **44**, 1490–1494.
- 9 A. D. Raj, T. Pazhanivel, P. S. Kumar, D. Mangalaraj, D. Nataraj and N. Ponpandian, *Curr. Appl. Phys.*, 2010, **10**, 531–537.
- 10 V. Modafferi, G. Panzera, A. Donato, P. L. Antonucci, C. Cannilla, N. Donato, D. Spadaro and G. Neri, *Sens. Actuators, B*, 2012, **163**, 61–68.
- 11 W. Yan, M. Hu, D. Wang and C. Li, *Appl. Surf. Sci.*, 2015, **346**, 216–222.
- 12 A. A. Mane, M. P. Suryawanshi, J. H. Kim and A. V. Moholkar, *Appl. Surf. Sci.*, 2017, **403**, 540–550.
- 13 A. A. Mane, M. P. Suryawanshi, J. H. Kim and A. V. Moholkar, *J. Colloid Interface Sci.*, 2017, **495**, 53–60.
- 14 X. Xue, L. Xing, Y. Chen, S. Shi, Y. Wang and T. Wang, *J. Phys. Chem. C*, 2008, **112**, 12157–12160.
- 15 F. Shao, M. W. G. Hoffmann, J. D. Prades, R. Zamani, J. Arbiol, J. R. Morante, E. Varechkina, M. Rummyantseva, A. Gaskov, I. Giebelhaus, T. Fischer, S. Mathur and F. Hernández-Ramírez, *Sens. Actuators, B*, 2013, **181**, 130–135.
- 16 T.-S. Wang, Q.-S. Wang, C.-L. Zhu, Q.-Y. Ouyang, L.-H. Qi, C.-Y. Li, G. Xiao, P. Gao and Y.-J. Chen, *Sens. Actuators, B*, 2012, **171–172**, 256–262.
- 17 S. Ahlers, G. Müller and T. Doll, *Sens. Actuators, B*, 2005, **107**, 587–599.
- 18 R. Wang, S. Yang, R. Deng, W. Chen, Y. Liu, H. Zhang and G. S. Zakharova, *RSC Adv.*, 2015, **5**, 41050–41058.
- 19 Y.-C. Her, B.-Y. Yeh and S.-L. Huang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9150–9159.
- 20 S.-W. Choi, A. Katoch, J.-H. Kim and S. S. Kim, *J. Mater. Chem. C*, 2014, **2**, 8911–8917.
- 21 B. G. Streetman and S. K. Banerjee, in *Solid State Electronic Devices*, Pearson Education Inc., New Jersey, 2005, pp. 144–238.
- 22 R. M. Abdel-Latif, *Phys. B*, 1998, **254**, 273–276.
- 23 F. K. Butt, C. Cao, F. Idrees, M. Tahir, R. Hussain and A. Z. Alshemary, *New J. Chem.*, 2015, **39**, 5197–5202.
- 24 H.-J. Zhai and L.-S. Wang, *J. Chem. Phys.*, 2002, **117**, 7882–7888.
- 25 V. Shrotriya, G. Li, Y. Yao, C. Chu and Y. Yang, *Appl. Phys. Lett.*, 2006, **88**, 073508.

