A Comparative Study of Structural and Ethanol Gas Sensing Properties of Pure, Nickel and Palladium Doped SnO₂ Nanorods Synthesised by the Hydrothermal Method

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ABSTRACT: SnO₂ nanostructures are usually modified with some metal dopants in order to improve its gas sensing properties. In this work, pure tin oxide (SnO₂), nickel (Ni) doped SnO₂ (Ni:SnO₂) and palladium (Pd) doped SnO₂ (Pd:SnO₂) nanorods were successfully synthesised via hydrothermal method at low temperature (180°C) without templates or further calcination. All the samples were systematically analysed using X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). The sensor response (R = R₀/Rg) towards 1000 ppm ethanol gas was investigated using nitrogen gas as a carrier gas. XRD results confirmed that all samples consisted of rutile tetragonal-shaped SnO₂. It was found that the average diameter of nanorods formed in Ni:SnO₂ and Pd:SnO₂ were decreased to ~6 nm and ~10 nm, compared with nanorods formed in pure SnO₂ (~25 nm). The gas sensing results indicated that the sensor properties of SnO₂ were enhanced after the doping process. At 450°C, the Pd:SnO₂ nanorod sensor recorded the highest response value towards 1000 ppm ethanol gas which is 15 times higher than pure SnO₂ nanorods. Interestingly, all samples showed similar response time, ~ 40 s. However, pure SnO₂ and Ni:SnO₂ nanorods sensors exhibited longer recovery
time compared to Pd:SnO$_2$ nanorods. Pd:SnO$_2$ nanorods recorded only 12 min of almost 100% recovery. It is proposed that Pd:SnO$_2$ sensor could be a promising candidate for the detection of ethanol gas.

Keywords: Hydrothermal, Pd doped, Ni doped, tin oxide, nanorods, gas sensor

1. INTRODUCTION

The application of metal oxide as a gas sensor has attracted many researchers’ attention ever since Seiyama et al. discovered that the adsorption and desorption of gases on the surface of zinc oxide (ZnO) films caused rapid changes in electrical conductivity. Since then, various types of metal oxides have been extensively studied for the detection of a wide variety of air pollutants, toxic, combustible and process gases. Among them, one-dimensional (1-D) tin oxide (SnO$_2$) nanostructures as a gas sensor has great advantages such as high sensitivity towards various reducing and oxidising gases, large surface-to-volume ratio, low cost and compatibility with microfabrication. Nevertheless, the sensing properties of pure SnO$_2$ still needs to be further improved due to their poor sensitivity, selectivity and lengthy recovery time. To overcome these disadvantages, an efficient method is the doping of SnO$_2$ with transition or noble metals. The fundamental theory of doping is to enhance its catalytic activity and modify its electric resistance for the gas sensor.

Several studies have been reported on noble metals-doped (e.g., Pt, Pd, Ag, Au, etc.) SnO$_2$ sensors. These sensors are sensitive to a wide number of toxic and explosive gases including ethanol gas. Among them, Pt and Pd are the most commonly used dopants in enhancing the sensing properties of SnO$_2$, owing to their high oxidation catalytic properties. For instance, Lee et al. reported that Pd-doped SnO$_2$ nanorod thin films prepared by plasma-enhanced chemical vapour deposition (PECVD) method showed 2.5 times higher sensor response with full recovery towards 1000 ppm ethanol gas at 300°C compared to un-doped SnO$_2$. It was suggested that changes in the oxidation state of Pd was the key factor that promoted the gas sensing properties of Pd-doped SnO$_2$. Meanwhile, Ivanov et al. fabricated an ethanol gas sensor using Pt-doped SnO$_2$ where the detection limit was at sub-ppb level and with high sensitivity and fast response.

In contrast, transition metal dopants such as Ni, Co and Fe are well known for crystal growth inhibitors. Wu et al., in a study, explained that the interaction on the boundaries between the host and dopant crystallites resisted the motion of crystallites and stunted crystal growth. As a result, the size of crystallites was decreased by the doping process. Besides that, the incorporation of transitional
metal doping also increased oxygen vacancies and subsequently enhanced the sensor performance of SnO$_2$ nanostructures. In our previous study, we found that the ethanol sensor response was greatly enhanced (by approximately 13 times) after SnO$_2$ was doped with 5 mol% Ni.\textsuperscript{16} It was proposed that the thickness of charge depletion layer and the presence of oxygen vacancies mainly contributed to the high sensor response.

Our literature search shows that there are not many comparative studies on ethanol gas sensing properties of pure, transition metal and noble metal-doped SnO$_2$ being reported. Furthermore, it can be difficult comparing the gas sensing properties between numerous research works since the synthesis routes and reaction conditions are different. Hence, in this study, we prepared pure SnO$_2$, Ni and Pd-doped SnO$_2$ nanorods by using a facile hydrothermal method. A comparative study was carried out exploring the role of transition metal dopants and noble metal dopants in promoting the ethanol gas sensor performance.

2. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were of analytical grade without any further purification. Tin(IV) chloride pentahydrate, SnCl$_4$$\cdot$5H$_2$O (98%), was obtained from Sigma Aldrich, United States. Nickel chloride hexahydrate, NiCl$_2$$\cdot$6H$_2$O was purchased from Hamburg Chemical GmbH, Germany and palladium chloride, PdCl$_2$ was obtained from QRec. Chemical Co. Ltd, Thailand. Sodium hydroxide, NaOH and absolute ethanol, C$_2$H$_5$OH were procured from QRec Asia Sdn. Bhd., Malaysia.

2.2 Synthesis of SnO$_2$ Nanorods

The hydrothermal method for synthesis, pure and Ni-doped SnO$_2$ (Ni:SnO$_2$) nanorods had been reported in previous works.\textsuperscript{16,17} In brief, the precursor, including SnCl$_4$$\cdot$5H$_2$O (4.8 mmol), and a calculated amount of NiCl$_2$$\cdot$6H$_2$O (5 mol% Ni) and PdCl$_2$ (5 mol% Pd) were dissolved in 30 ml of an absolute ethanol-distilled water solvent (1:1 v/v) separately, with vigorous stirring to obtain a homogeneous solution. The pH of the solution was then adjusted to pH 13 by adding an equal volume of 6 M NaOH solution and absolute ethanol, simultaneously. The final volume of the reaction mixture was filled to 40 ml by adding ethanol-distilled water (1:1 v/v) mixture and was then transferred to a 50 ml Teflon-lined stainless-steel autoclave, sealed and heated at 180°C for 15 h. The product was centrifuged and
repeatedly washed with distilled water and ethanol, and later oven-dried at 55°C overnight. The pure SnO$_2$ sample was prepared as per the previously-mentioned process, except that heat treatment was carried out for 24 h without dopant.

2.3 Sample Characterisations

The crystal structure of the samples was determined by XRD (PW 3040/60 X’PERT PRO, PANalytical, Malvern, United Kingdom) using Cu Kα radiation with a scanning step size of 0.0340°. The structural parameters were calculated by applying Rietveld analysis (semi-automatic mode) using the PANalytical X’Pert Highscore Plus (version 2.2) software. The surface composition was investigated using X-ray photoelectron spectroscopy (XPS, Axia Ultra DLDXPS, Kratos, Manchester, United Kingdom) with a monochromatic Al Kα X-ray source (1486.6 eV of photons) and background pressure of 10–7 Pa. All the reported binding energy (BE) data were calibrated using the C 1s line at 284.6 eV. CASAXPS (version 2.3.17) software was used for analysing the XPS spectra. A GL (30) Gaussian (70%)-Lorentzian (30%) profile and a standard Shirley background were applied for fitting the components. The morphologies of the samples were examined by FESEM (LEO 1525, 30 kV, New York, United States) and high-resolution transmission electron microscopy (HRTEM, TECNAI G2 20 S-TWIN, FEI, China) at 200 kV. For FESEM characterisation, the as-synthesised SnO$_2$ samples were sputtered on aluminium stub which was covered with carbon tape. The samples were then coated with a thin layer of gold to increase the electron conduction which subsequently improved the quality of images. Meanwhile, for HRTEM analysis, the as-synthesised SnO$_2$ powder samples were dispersed in absolute ethanol and ultrasonicated for 30 min. The dispersion was then dropped on carbon-copper grids.

2.4 Sensor Preparation and Ethanol Gas Sensing Measurement

Details of the sensor preparation and the configuration of custom-built gas sensing measurement instrumentation can be found in our previous work. In brief, a proper amount of as-synthesised SnO$_2$ samples were mixed in sensor ink separately to form a slurry. Subsequently, the slurry was coated onto an Au-interdigitated alumina substrate covering a dimension of 5 mm × 5 mm (Case: Western Reserve University, Cleveland, United States). In order to stabilise the sensor material, the substrates were heat-treated at 450°C in argon gas flow prior to use. For the purpose of determining the optimum operating temperature, gas sensing measurement was performed at 200°C–450°C using the pure SnO$_2$ nanorods sensor, with 1000 ppm ethanol C$_2$H$_5$OH in nitrogen (N$_2$) gas environment. The total flow rate was maintained at 200 sccm throughout the experiment. It was found that at 450°C,
the pure SnO₂ nanorods sensor demonstrated good sensing properties. Further gas sensing measurements were recorded at 450°C. The sensor response at different concentrations (50–1000 ppm) was investigated by diluting 1000 ppm ethanol gas with nitrogen gas. The response to ethanol gas is defined as $R_0/R_g$ where $R_0$ and $R_g$ are the resistances of SnO₂ sensor materials in nitrogen gas and in C₂H₅OH gas, respectively. The response time is expressed as the duration taken by the sensor to achieve 90% of the total resistance changes upon the adsorption of C₂H₅OH gas. The recovery time is defined as the duration taken by the sensor to achieve 90% of total resistance changes upon the removal of C₂H₅OH gas.

3. RESULTS AND DISCUSSION

3.1 Compositional and Morphological Analysis

The XRD patterns of pure SnO₂, Ni:SnO₂ and Pd:SnO₂ nanorods samples are presented in Figure 1. The unit cell parameters were calculated by means of the Rietveld refinement which are listed in Table 1. All the diffraction peaks can be indexed as rutile tetragonal phase SnO₂ (SG, $P4_2/mnm$) (ICSD no. 98-005-7394, $a = b = 4.7380$ Å and $c = 3.1870$ Å). No trace of other phases (e.g., SnO, PdO, Pd, Ni, NiO, etc.) were detected. It was found that the addition of dopants (5 mol% Pd and 5 mol% Ni) in SnO₂ crystal structures induced a broadening and an intensity alteration of peaks, indicating a reduction in particle size and crystallinity. The Rietveld refinement showed that the lattice parameters of pure SnO₂ nanorods were $a = 4.7503$ Å and $c = 3.1838$ Å, whereas, slight changes in lattice parameters and crystallite size were recorded after doping with Ni and Pd. This phenomenon could be due to the substitution of Sn⁴⁺ ions with Ni²⁺ and Pd²⁺ ions. It is worth noting that the lattice parameters and crystallite size of Pd:SnO₂ is slightly larger than Ni:SnO₂, which is most likely due to the ionic radii of Pd²⁺ ion (86 pm) which is larger than Ni²⁺ (69 pm). Hence, the substitution of Ni²⁺ in SnO₂ lattice structure leads to more significant variations in lattice parameters and crystallite size compared to Pd doping. Moreover, as a dopant, Ni is known to inhibit the growth of crystals. The high intensity peaks of (110), (101) and (211) indicate the preferential crystal planes of nanorods.
Figure 1: XRD patterns of as-synthesised SnO\textsubscript{2} samples. The experimental data and Rietveld refinement fitting are represented with symbols and solid lines, respectively (ref. ICSD no. 98-005-7394).

Table 1: The lattice parameters and the mean crystallite size calculated using Rietveld refinement.

| Samples    | Lattice parameters (Å) | Mean crystallite size, nm |
|------------|------------------------|---------------------------|
|            | a          | c          |                            |
| Pure SnO\textsubscript{2} | 4.7503     | 3.1838     | 28.3                      |
| Ni:SnO\textsubscript{2}   | 4.7473     | 3.1800     | 6.2                       |
| Pd:SnO\textsubscript{2}  | 4.7481     | 3.1820     | 7.3                       |
The morphology and size of as-synthesised SnO$_2$ nanorod samples were characterised by both FESEM and HRTEM. The FESEM images (Figure 2) confirmed the formation of nanorods in all three SnO$_2$ samples. From the results, it can be seen clearly that the nanorods grew into closely packed flower-like bunches. It is worth noting that even in the absence of dopants (pure SnO$_2$), similar morphology was obtained. This observation led to the conclusion that in this study, the shape of the particles was not influenced by the dopants. However, evidence shows that higher amount of dopants could act as a structure-directing agent in metal oxide nanostructures.$^5,^{24}$

Figure 2: FESEM images of as-synthesised samples for (a) pure SnO$_2$, (b) Ni:SnO$_2$ nanorods, and (c) Pd:SnO$_2$ nanorods.
Figure 3: HRTEM images of: (a and b) pure SnO$_2$, (c and d) Ni:SnO$_2$, and (e and f) Pd:SnO$_2$ nanorods, respectively.
Further morphology characterisation was studied using HRTEM analysis. Figure 3(a, c and e) exhibits the morphologies of as-synthesised SnO\textsubscript{2} nanorods. Meanwhile, Figure 3(b, d to f) shows the enlarged images of all the samples, where the lattice fringes can be observed clearly. The nanorods formed in pure SnO\textsubscript{2} typically had an average diameter of \(\sim 25 \text{ nm}\). Meanwhile, the average diameter of nanorods in Ni:SnO\textsubscript{2} and Pd:SnO\textsubscript{2} were \(\sim 6 \text{ nm}\) and \(\sim 10 \text{ nm}\), respectively. This finding is supported by XRD data (broadening of peaks), where the particle size was reduced in Ni:SnO\textsubscript{2} and Pd:SnO\textsubscript{2} nanorods samples. On the other hand, the lattice fringes of all the samples confirmed the single crystal nature of the SnO\textsubscript{2} nanorods.\textsuperscript{25} The lattice spaces in pure SnO\textsubscript{2} (Figure 3(b)) were \(\sim 0.336 \text{ nm}\) and \(\sim 0.265 \text{ nm}\), which attributed to (110) and (101) planes of the tetragonal rutile crystal structure. Meanwhile, for Ni:SnO\textsubscript{2} nanorods, as shown in Figure 3(d), the lattice fringe were found to be \(\sim 0.336 \text{ nm}\) and \(\sim 0.331 \text{ nm}\), which were assigned to plane (110) tetragonal rutile indicating that the preferential growth direction was [001].\textsuperscript{26} Likewise, lattice spaces for Pd:SnO\textsubscript{2}, shown in Figure 3(f) were identified as \(\sim 0.331 \text{ nm}\) and \(\sim 0.268 \text{ nm}\) which corresponded to plane (110) as well as (101) respectively. This result is in good agreement with XRD patterns where the planes (110) and (101) were among the strongest peaks recorded for all the three SnO\textsubscript{2} samples.

The chemical composition and chemical state of the as-synthesised SnO\textsubscript{2} samples were investigated using XPS. In our previous paper, we discussed in detail the XPS result of pure SnO\textsubscript{2} and Ni:SnO\textsubscript{2} nanorods samples.\textsuperscript{16} In brief, XPS results of pure SnO\textsubscript{2} and Ni:SnO\textsubscript{2} nanorods samples confirmed the formation of SnO\textsubscript{2}. The presence of O 1s lattice oxygen (O-Sn-O) peak was detected, and another peak corresponding to oxygen ions in deficient regions were identified in both pure and Ni doped SnO\textsubscript{2} samples, respectively. An additional O 1s peak, which ascribed to surface absorbed oxygen ions was identified in Ni:SnO\textsubscript{2}. Also, no other peaks such as Ni, Ni\textsubscript{2}O\textsubscript{3} or NiO were found in the Ni:SnO\textsubscript{2} sample.

In this current work, we only focused on the XPS result of Pd:SnO\textsubscript{2}. Figure 4 exhibits the XPS high resolution spectra of the Pd:SnO\textsubscript{2} sample. Unlike the pure SnO\textsubscript{2} and Ni:SnO\textsubscript{2} nanorods samples, two types of Sn species were identified in Pd:SnO\textsubscript{2}. The main peaks were assigned as Sn\textsuperscript{4+} 3d\textsubscript{5/2} (486.2 eV) and Sn\textsuperscript{4+} 3d\textsubscript{3/2} (494.6 eV), which confirmed the presence of SnO\textsubscript{2}.\textsuperscript{27} Also, the peaks of Sn\textsuperscript{2+} 3d\textsubscript{5/2} and Sn\textsuperscript{2+} 3d\textsubscript{3/2} were detected in Pd:SnO\textsubscript{2} samples, suggesting that Sn\textsuperscript{4+} ions were partially reduced to Sn\textsuperscript{2+} during the doping process. This observation is similar to a previous study by Aragón et al.\textsuperscript{20} On the other hand, the region of O 1s in Pd:SnO\textsubscript{2} could be de-convoluted into three different oxygen peaks. The higher binding energy O 1s peak was ascribed to , O\textsuperscript{2-} and OH\textsuperscript{2-} at oxygen deficient regions.
which played an important role in influencing gas sensing properties. The peak at the binding energy of 529.9 eV was assigned to lattice oxygen $O^{2-}$ in the O-Sn-O bond. Another peak was recorded at the higher binding energy of 531.1 eV, which corresponded to the coordination of oxygen in Sn-O-Pd. This result is supported by the Pd$^{2+}$ 3d peaks as shown in Figure 4(c). The doublet peaks at 342.3 eV and 336.5 eV were binding energies of Pd$^{2+}$ 3d$^{3/2}$ and Pd$^{2+}$ 3d$^{5/2}$, respectively, which suggests that Pd-O is bonded in Sn-O-Pd. Unlike Ni:SnO$_2$, metallic Pd$^0$ peaks were identified in Pd:SnO$_2$ sample. Based on the above mentioned data, the Pd:SnO$_2$ nanorods sample could contain Pd clusters such as Pd and PdO as surface species.

Figure 4: The XPS spectra of Pd:SnO$_2$ nanorod sample.
3.2 Gas Sensing Measurement

In order to evaluate the gas sensing properties, all the as-synthesised SnO₂ nanorods sensors were first tested with 1000 ppm ethanol (C₂H₅OH) gas at an optimum operating temperature of 450°C in nitrogen gas flow. Figure 5 presents responses to 1000 ppm of C₂H₅OH gas for the pure SnO₂, Ni:SnO₂ and Pd:SnO₂ nanorods sensors. From the results obtained, it can be seen that pure SnO₂ nanorods revealed a very low sensor response, \(R_0/R_g \approx 1.1 \times 10^3\). However, the response recorded a drastic increase after the doping process. The response values of Ni:SnO₂ and Pd:SnO₂ sensors were \(R_0/R_g \approx 1.4 \times 10^4\) and \(R_0/R_g \approx 1.7 \times 10^4\), respectively.

![Figure 5: As-synthesised SnO₂ nanorods sensors response to 1000 ppm C₂H₅OH/N₂ gas at operating temperature of 450°C.](image)

Figure 6 shows the resistance curves for as-synthesised SnO₂ nanorod sensors. It was observed that the initial resistances of Pd:SnO₂ was much higher than pure SnO₂ and Ni:SnO₂ nanorods sensors. A similar result was also observed by Chen et al. and Fedorenko et al.²⁸,²⁹ It was explained that the presence of two forms of Pd clusters (Pd and PdO) in the SnO₂ sensor system influenced the initial resistance. This is because more chemisorption of oxygen takes place at the common edge between Pd/PdO and SnO₂, which eventually increased the initial resistance of the sensor. All the samples revealed the same response time, 40 s, but had different recovery times. It is worth noting that the recovery time of Ni:SnO₂ was improved compared to pure SnO₂, where the recovery time was found to be considerably longer. On the contrary, Pd:SnO₂ showed almost 100% recovery in 12 min. Thus, Pd:SnO₂ shows a high sensor response with fast recovery as well as response time.
Ethanol Gas Sensing Properties

Figure 6: The resistance curves of as-synthesised SnO₂ nanorod sensor.

Figure 7: Continuous response-recovery curves of Pd:SnO₂ nanorod sensor for various C₂H₅OH gas concentrations at 450°C.
Upon further investigation, the Pd:SnO$_2$ nanorod sensor was tested with different C$_2$H$_5$OH gas concentrations (50 ppm, 100 ppm, 200 ppm, 500 ppm and 1000 ppm). Figure 7 shows the real-time response curve of Pd:SnO$_2$ nanorods sensor to C$_2$H$_5$OH. It was observed that the responses gradually increased from $6.4 \times 10^2$, $7.6 \times 10^2$, $6.9 \times 10^3$, $1.0 \times 10^4$ and $1.7 \times 10^4$ with the increase of C$_2$H$_5$OH gas concentration of 50 ppm, 100 ppm, 200 ppm, 500 ppm and 1000 ppm, respectively. The response time reduced from 40 s to 30 s as the concentration decreased from 1000 ppm to 50 ppm. Similarly, the recovery time also reduced from 12 min to 8 min. Meanwhile, Figure 8 shows that the linearity of the Pd:SnO$_2$ nanorods sensor performed better at higher concentration range (200–1000 ppm) of C$_2$H$_5$OH gas than the lower concentration range.

![Figure 8: Sensor response of Pd:SnO$_2$ nanorods for different C$_2$H$_5$OH gas concentrations (50–1000 ppm) at 450°C.](image)

### 3.3 Ethanol Gas Sensor Mechanism

In general, gas sensor response is defined as the transfer of electrons on the sensor material when gas sensing reaction takes place.$^{31}$ In this study, the Pd:SnO$_2$ nanorod sensor showed high C$_2$H$_5$OH sensing response and fast recovery time. It is postulated that the introduction of Pd into SnO$_2$ nanorods can bring several changes in physical and chemical properties which lead to the enhancement of gas sensor properties. Firstly, the interface between two forms of Pd/PdO and SnO$_2$ remarkably increased the chemisorption of oxygen.$^{10,30}$ It is worth noting
that the initial resistance, $R_a$, greatly depends on the chemisorbed oxygen content. Secondly, the 1-D SnO$_2$ nanorods with considerably smaller sizes (~10 nm) could provide a large surface-to-volume ratio which contributed to more active sites to react. Thirdly, Pd dopants can act as a catalytic site in facilitating oxidation reaction. Lastly, oxygen vacancies at oxygen deficient regions also play a vital effect on the sensor properties of Pd:SnO$_2$.

Based on the results obtained, we propose a mechanism for C$_2$H$_5$OH gas sensing in the Pd:SnO$_2$ system. At ambient temperature, oxygen molecules in the air adsorbed at the interface of active additives and SnO$_2$ (Equation 1). At temperatures of 150°C–300°C, oxygen molecules ionised into oxygen species, for instance O$_2^-$, O$^-$ and O$_2^{2-}$ ions, by trapping the electrons from conductive bands and subsequently forming negatively-charged surface potential (Equation 2). As the operating temperature increased to 450°C, atomic ion species (O$^-$ and O$_2^{2-}$) dominated. Thus, the near surface layer of the sensor material became depleted by electrons. This eventually impeded the transfer of electron in the sensor material. As a result, the initial resistance increased drastically. Moreover, the presence of oxygen vacancies in oxygen deficient regions also partly contributed to the amount of surface oxygen ions. When the sensor was exposed to C$_2$H$_5$OH gas, the ethanol gas reacted with the chemisorbed oxygen ion species on the active sites and eventually transferred back the electrons which in turn reduced the depletion layer (Equations 3 and 4). Hence, a decrease in resistance was recorded. It should be noted that the high sensor response not only depends on the amount of chemisorb oxygen, but also on the temperature where the high catalytic activity was obtained at 450°C. During the recovery process, the sensor returned to its initial condition by trapping the electrons again.

$$\text{O}_2^\text{gas} \rightarrow \text{O}_2^\text{chemisorbed}$$  \hspace{1cm} (1)

$$\frac{\alpha}{2}\text{O}_2^\text{chemisorbed} + \beta e^- \rightarrow \text{O}_\alpha^\beta^-$$  \hspace{1cm} (2)

where $\alpha = 1$ for atomic oxygen, $\alpha = 2$ for oxygen molecule, $\beta = 1$ for singly ionised, and $\beta = 2$ for doubly ionised.

$$\text{C}_2\text{H}_5\text{OH} \text{ (gas)} + 6\text{O}^- \text{ (chemisorbed)} \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O} (\text{g}) + 6e^-$$  \hspace{1cm} (3)

$$\text{C}_2\text{H}_5\text{OH} \text{ (gas)} + 6\text{O}_2^- \text{ (chemisorbed)} \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O} (\text{g}) + 12e^-$$  \hspace{1cm} (4)
4. CONCLUSION

The pure SnO$_2$, Ni:SnO$_2$ and Pd:SnO$_2$ nanorods were successfully synthesised through a template-free hydrothermal method. The diameter of nanorods were found to be reduced after the doping process. The XPS result of Pd:SnO$_2$ revealed that there were more than one Pd clusters (Pd and PdO) formed during the hydrothermal synthesis. The gas sensing measurement showed that the Pd:SnO$_2$ nanorod sensor drastically improved the C$_2$H$_5$OH sensor response and recovery time compared to pure SnO$_2$ and Ni:SnO$_2$ nanorods sensors. Overall, we conclude that the chemical state of Pd, the oxygen vacancies and the 1-D nanostructure of Pd:SnO$_2$ are mainly responsible for the high C$_2$H$_5$OH gas sensing response.

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