



# Electrochemical impedance characterisation of tungsten trioxide–polyaniline nanocomposites for room temperature acetone sensing



Stephen M. Hicks, Anthony J. Killard\*

Centre for Research in Biosciences, Department of Biological, Biomedical and Analytical Sciences, University of the West of England, Coldharbour Lane, Bristol BS16 1QY, UK

## ARTICLE INFO

### Article history:

Received 26 October 2013  
Received in revised form 9 December 2013  
Accepted 11 December 2013  
Available online 18 December 2013

### Keywords:

Acetone  
Tungsten trioxide  
Polyaniline  
Nanocomposite  
Impedance spectroscopy  
Gas sensing

## ABSTRACT

Composites of  $\text{WO}_3$  nanoparticles and water-soluble polyaniline (PANI) particles doped with dodecyl benzenesulphonic acid at different mass ratios were deposited onto interdigitated electrodes and characterised using electrochemical impedance spectroscopy in air and in acetone vapour. The nanocomposites displayed an approximate equivalent circuit model of a parallel resistance and small inductance due to the PANI and a constant phase element (CPE) due to the  $\text{WO}_3$ . The contribution of the CPE increased with increased  $\text{WO}_3$  loading. The nanocomposites mostly displayed increases in their real impedance on exposure to acetone at frequencies below 1 kHz, as well as a small increase in imaginary impedance. However, low  $\text{WO}_3$  loadings and low acetone concentrations resulted in decreases in film resistance. This effect is due to the balance of charge carriers in the film. The resulting sensors were able to detect 10 ppmv acetone at room temperature.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Acetone is a volatile organic compound (VOC) produced in the body when fats are metabolised for energy [1]. It is detectable in the breath and human studies have found mean breath acetone concentrations of 300–900 ppbv in healthy subjects, rising to more than 1800 ppbv in diabetic patients [2]. Consequently, acetone in breath has been reported to be a potential non-invasive marker for diabetes [3]. The potential of acetone in breath as a biomarker for diabetes is currently limited by the availability of sensors for detecting acetone at these low ppbv concentrations. At present, only cumbersome and expensive instruments have the required sensitivity, and these are not suitable for miniaturisation as compact devices for patient use [4]. For breath acetone to be of value in the self-monitoring of diabetes, a small and portable sensor device that can be mass produced for low cost is required.

The use of metal oxides as sensing elements in gas sensors is well-recognised. In these sensors, the metal oxide functions as a chemoresistor whereby interaction with a target gas causes a change in resistance [5]. With regards to acetone sensing, one of the more promising sensitive and selective metal oxide gas sensing candidates to emerge is tungsten (VI) oxide ( $\text{WO}_3$ ). Absorbed

oxygen species on the  $\text{WO}_3$  nanoparticles causes the transfer of electrons from the  $\text{WO}_3$  conduction band to form  $\text{O}_2^-$  and  $\text{O}^-$  species. The presence of a reducing gas such as acetone reacts with the chemisorbed oxygen species, releasing an electron back to the conduction band of  $\text{WO}_3$ , decreasing its resistance. Sensors fabricated from screen-printed  $\text{WO}_3$  films have shown the ability to measure acetone over a concentration range of 25–75 ppm, at an operating temperature of 300 °C [6]. Flame spray pyrolysis (FSP) has also been used to produce Cr-doped  $\text{WO}_3$  nanoparticle sensors that responded to acetone down to a concentration of 0.2 ppm, at an operating temperature of 400 °C [7]. In this study, the Cr doping was used to stabilise  $\text{WO}_3$  in the  $\epsilon$  phase, and the findings showed the sensor to have good selectivity to acetone over ethanol, methanol, NO,  $\text{NO}_2$ ,  $\text{NH}_3$ , and CO. FSP has also been used to fabricate Si-doped  $\text{WO}_3$  nanoparticle sensors (Si doping was again used to stabilise  $\text{WO}_3$  in the  $\epsilon$  phase) that, at an operating temperature of 400 °C, detected acetone down to 20 ppb in air with a relative humidity of 90%, a level that would typically be encountered in breath samples [8]. This sensor also showed a much higher sensitivity to acetone than either ethanol or water vapour, thus demonstrating selectivity towards acetone.

Besides screen printing and FSP fabrication methodologies, other techniques have also been used to produce  $\text{WO}_3$  sensors for the detection of acetone. A sol–gel method was used to produce a  $\text{WO}_3$  nanocrystal sensor, which, at an operating temperature of 300 °C, could detect acetone down to 0.05 ppm. The sensor showed

\* Corresponding author. Tel.: +44 117 3282147.

E-mail address: [tony.killard@uwe.ac.uk](mailto:tony.killard@uwe.ac.uk) (A.J. Killard).

approximately a 3–9 times higher response to acetone than other interfering gases such as methanol, chlorine, hydrogen, ammonia, hydrogen sulfide, benzene, ethanol and formaldehyde [9]. A sol–gel method was also used to prepare Cr<sub>2</sub>O<sub>3</sub>-doped WO<sub>3</sub> thin-film sensors, which showed that a 5 mol% Cr<sub>2</sub>O<sub>3</sub>-doped WO<sub>3</sub> sensor could detect acetone down to 0.5 ppm, at an operating temperature of 320 °C [10]. Furthermore, at this operating temperature, the sensor demonstrated selectivity to acetone compared to ethanol, ammonia, methanol, n-butanol and carbon dioxide. Therefore there is good evidence that WO<sub>3</sub> is a sensitive and selective metal oxide for the detection of acetone.

However, metal oxide gas sensors have several limitations. They require operating temperatures of several hundred degrees centigrade, which has power consumption implications for any battery-operated device for measuring breath acetone, as well as potential safety and lifetime issues. Ideally, a sensor for measuring breath acetone should operate at ambient temperatures. Many metal oxide sensors also employ relatively costly semiconductor manufacturing technologies. The fabrication of exotic forms of WO<sub>3</sub> such as the  $\epsilon$  phase using FSP requires complex and expensive equipment and only yields low quantities of material. The high cost associated with these fabrication methodologies limits their potential for use in commercially viable devices for point of care measurement of breath acetone. Ideally, a sensor for measuring breath acetone should be able to be produced cheaply, using facile techniques that can be scaled for mass production.

Conducting polymers such as polyaniline (PANI) also have chemoresistive properties that can change upon exposure to acetone [11]. However, they can be difficult materials to optimise with respect to sensitivity and selectivity. Such materials alone have not proven suitable for the measurement of acetone in breath [12]. However, they have been employed as conductive support matrices for active materials such as metallic nanoparticles [13]. In this way, the nanoparticles can be maintained in a highly dispersed manner with good diffusion of analytes to the particle surface, maximisation of the available surface area, while also allowing them to remain in electronic contact with one another. It is hypothesised that a nanocomposite of conducting polymer and WO<sub>3</sub> may exhibit synergies that may make it suitable for acetone sensing.

In this work, water-soluble composites of dodecyl benzenesulphonic acid-doped PANI particles with WO<sub>3</sub> nanoparticles were prepared and deposited onto interdigitated electrodes. Their electrochemical impedance spectroscopic characteristics were studied in air and acetone and the sensors were shown to be capable of measurement of acetone in air at room temperature.

## 2. Materials and methods

### 2.1. Polyaniline nanoparticle synthesis

Water-soluble particles of polyaniline (PANI) were synthesised using a method developed by Ngamna et al. [14]. In summary, these were synthesised by adding 3.4 g of 0.25 M DBSA to 40 mL of deionized water. This was stirred at 20 °C until the DBSA had fully dissolved. To the DBSA solution, 0.36 g of APS was added and stirred until fully dissolved. This was followed by 0.6 mL of distilled aniline and was allowed to mix for 2.5 h. After this time, 20 mL of 0.05 M SDS was added to the DBSA/APS/aniline solution which appeared thick and dark green in colour. The DBSA/APS/aniline/SDS solution was then centrifuged at 5000 rpm for 30 min. The supernatant was transferred to dialysis tubing and dialyzed against 0.05 M SDS for 48 h and analysed by thermogravimetry. The particles were characterised by dynamic light scattering (Malvern Mastersizer 2000) and UV-vis spectroscopy (Perkin Elmer Lambda XLS). Average particle size was found to be 100 ± 10  $\mu\text{m}$ . Spectroscopy showed localised polaron bands at 785 nm and approximately 420 nm, and a  $\pi$ - $\pi^*$

band at approximately 350 nm. The localised form of the band at 785 nm is indicative of doped PANI forming a “compact coil” conformation, and the overlapping of the bands at 350 nm and 420 nm suggests a high level of doping [15].

### 2.2. Preparation of WO<sub>3</sub>-PANI nanocomposites

The PANI particles were mixed with WO<sub>3</sub> nanoparticles (Sigma-Aldrich) at different mass ratios to produce composite dispersions with increasing loadings of WO<sub>3</sub>. Mixing was achieved using a micropipette. Composite dispersions with the following mix ratios of WO<sub>3</sub>:PANI were produced: 0:1 (PANI), 5:1, 10:1, 20:1, 40:1, 60:1, 80:1, 100:1, 200:1, 300:1 and 400:1.

### 2.3. Fabrication of sensors

Silver interdigitated electrodes were screen printed onto polyethylene terephthalate (PET; thickness, 175  $\mu\text{m}$ ) (HiFi films Ltd., Dublin) using a silver ink (Acheson Electrodeag PF-410) on a DEK 248 screen-printer (DEK, Weymouth, Dorset, UK) and cured at 150 °C for 30 min, similar to those used elsewhere [16]. Films of the WO<sub>3</sub>-PANI nanocomposites were cast onto the screen-printed IDEs by pipetting 50  $\mu\text{L}$  aliquots. Deposited films were left to dry at room temperature.

### 2.4. Composite characterisation

WO<sub>3</sub>-PANI nanocomposites were characterised using UV-vis spectroscopy (Perkin Elmer Lambda XLS), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis (Philips XL30) and cyclic voltammetry in 1 M HCl at 100 mV s<sup>-1</sup> vs. Ag/AgCl (Autolab PGSTAT 128N). Sensors were characterised using electrochemical impedance spectroscopy (Autolab FRA2 module) using a 10 mV rms sinusoidal waveform in a two-electrode configuration from 0.1 to 10<sup>6</sup> Hz. Sensors were studied either in air or in gas jars containing acetone vapour in air from 0 to 100 ppmv. All studies were performed at room temperature.

## 3. Results and discussion

### 3.1. Physical characterisation of the WO<sub>3</sub>-PANI nanocomposites

Scanning electron micrographs and EDX spectra of the 0:1 (PANI), 20:1, 60:1, 200:1 and 400:1 WO<sub>3</sub>-PANI nanocomposite blends are shown in Fig. 1. PANI alone shows the low contrast typical of films composed of purely organic polymers. The introduction of WO<sub>3</sub> introduces high contrast features. At low WO<sub>3</sub> loadings, these are distinct and dispersed within the polymer. However, at higher loadings, the WO<sub>3</sub> begins to form aggregates. In addition, the shift in contrast on the electron microscope makes it appear that the PANI polymer is no longer present. This effect has been seen in previous SEM studies of PANI composites [17]. However, the WO<sub>3</sub> material remains embedded in the conducting polymer matrix. The EDX spectral data also indicates the presence of increasing levels of W in the films, consistent with the increased loadings. PANI alone presented distinctive peaks for the presence of C, O, Na and S. C and O are major components of the PANI, as well as the underlying PET film and S and Na are also from the dodecyl benzenesulphonic acid and sodium dodecyl sulphate present in the PANI formulation. Increasing WO<sub>3</sub> loadings yielded increased contributions from W and also from O, demonstrating the presence of WO<sub>3</sub>-PANI nanocomposite films.

Cyclic voltammograms of the PANI and 80:1 and 400:1 WO<sub>3</sub>-PANI composites drop-cast onto glassy carbon electrodes in 1 M HCl at 100 mV s<sup>-1</sup> vs. Ag/AgCl are shown in Fig. 2. PANI alone shows the distinctive voltammogram previously demonstrated for

Download English Version:

<https://daneshyari.com/en/article/742882>

Download Persian Version:

<https://daneshyari.com/article/742882>

[Daneshyari.com](https://daneshyari.com)