

Accepted Manuscript

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Authors: Mohamad Hijazi, Mathilde Rieu, Valérie Stambouli, Guy Tournier, Jean-Paul Viricelle, Christophe Pijolat



PII: S0925-4005(17)31934-2
DOI: <https://doi.org/10.1016/j.snb.2017.10.036>
Reference: SNB 23340

To appear in: *Sensors and Actuators B*

Received date: 17-3-2017
Revised date: 4-10-2017
Accepted date: 5-10-2017

Please cite this article as: Mohamad Hijazi, Mathilde Rieu, Valérie Stambouli, Guy Tournier, Jean-Paul Viricelle, Christophe Pijolat, Ambient temperature selective ammonia gas sensor based on SnO₂-APTES modifications, Sensors and Actuators B: Chemical <https://doi.org/10.1016/j.snb.2017.10.036>

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Ambient temperature selective ammonia gas sensor based on SnO₂-APTES modifications

Mohamad HIJAZI ^a, Mathilde RIEU ^{a,*}, Valérie STAMBOULI ^b, Guy TOURNIER ^a, Jean-Paul VIRICELLE ^a, Christophe PIJOLAT ^a

^a *École Nationale Supérieure des Mines, SPIN-EMSE, CNRS:UMR5307, LGF, F-42023 Saint-Étienne, France*

^b *LMGP, Université Grenoble-Alpes, Grenoble INP-MINATEC, 3 parvis Louis Néel, CS 50257, 38016 Grenoble Cedex 1, France*

* Corresponding author: Mathilde Rieu, *E-mail address*: rieu@emse.fr, Tel.: +33 4 77 42 02 82

Highlights Molecular functionalized sensors were elaborated by two steps modification.

- Characterization of modified sensors was carried out by ATR-FTIR.
- Testing the sensors under gases was performed at room temperature.
- Ester modified SnO₂ sensor was sensitive and selective to ammonia gas.

ABSTRACT

In order to deal with the well-known lack of selectivity of SnO₂ based gas sensors, the functionalization of SnO₂ was performed. Liquid silanization by 3-aminopropyltriethoxysilane (APTES) was used as an intermediate step, followed by functionalization with molecules bearing acyl chloride with alkyl or ester end functional groups. Modified sensors with APTES, alkyl and ester end functional groups were successfully characterized by Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR). No response was observed for APTES and alkyl modified SnO₂ sensors to ammonia gas at room temperature while the SnO₂ sensor modified with ester end group was found to be sensitive and selective to ammonia gas at room temperature. This implies that the response is generated by ester functional groups. Working at low temperature is also one of the advantages of these sensors as well as the selectivity with respect to other gases like acetone and ethanol.

Keywords: SnO₂; Functionalization; APTES; Ammonia gas; Room temperature detection

1. Introduction

Breath analysis is considered as noninvasive and safe method for the detection of diseases [1]. Gas sensors have shown to be promising devices for selective gas detection related to disease diagnosis [2,3]. These sensors can be used to detect the gases emanated from the human body. For example, ammonia is a disease marker for liver problems. Indeed, ammonia in humans is

converted to urea in the liver and then passes in the urines through the kidney, while unconverted ammonia is excreted in breath of 10 ppb for healthy subjects [4]. The ammonia concentration increases in case of malfunctioning of liver and kidney reaching more than 1 ppm in presence of renal failure [5,6].

SnO₂ sensors have been well investigated from a very long time [7–9], since they can detect many gases with high sensitivity and low synthesis cost [10,11]. The interactions of SnO₂ material with gases have been extensively studied [12,13]. The chemical reactions of target gases with SnO₂ particle surface can generate variations in their electrical resistances. SnO₂ is n-type semiconductor, in this case, the adsorbed oxygen on particle surface takes electrons from the conduction band at elevated temperature, generating depletion layer between the conduction band and the surface (space-charge region). Reducing gases such as CO are oxidized on the surface, then they consume the adsorbed surface oxygen giving back the electrons to the conduction band. This decrease in the depletion layer decreases the resistance of whole film [14]. However, like other metal oxides, SnO₂ sensors have lack of selectivity and operate at high temperature (350–500 °C), except if some particular activation with light for example, is carried out [15,16]. Many techniques were applied to enhance the selectivity such as (i) the addition of gas filter [17], or small amount of noble metals [18–20], (ii) the use of oxides mixture [21,22], or hybrid film of SnO₂ and organic polymers [23,24].

Since several years, there is a high request to develop analytical tools which are able to work at temperature lower than 200 °C in order to incorporate them in plastic devices and to reduce the power consumption [25,26]. For such devices, researchers are now focused on the development of room temperature gas sensors. The first reported metal oxide gas sensor was based on palladium nanowires for the detection H₂ [27]. Concerning SnO₂ gas sensors, the more recent studies at room temperature are related to NO₂ detection [15,16] or to formaldehyde sensors [18].

As exposed previously, for breath analysis, there is also a high demand for ammonia sensors working at room temperature. Among the current studies, it can be mentioned the sensors using tungsten disulfide (WS₂) [28] or carbon nanotubes (CNTs) [29] as sensing material, and especially the ones based on reduced graphene oxide (RGO) [30–32], or on polyaniline (PANI) [33–36].

Molecular modification of metal oxide by organic film is another way to enhance the selectivity and to decrease the sensing temperature (room temperature gas sensors) [37–39]. The need of selective sensors with high sensitivity in presence of humidity at low gases concentration pushes the research to modify SnO_2 sensing element in order to change its interaction with gases. The modifications with organic functional groups having different polarities could change the sensor response to specific gases (e.g. ammonia) depending on their polarity [38]. In the literature, a functionalization based on APTES (3-aminopropyltriethoxysilane) combined with hexanoyl chloride or methyl adipoyl chloride was investigated on silicon oxide field effect transistors [39]. These devices were tested under some aliphatic alcohol and alkanes molecules. The functionalized field effect transistors have shown responses to a wide variety of volatile organic compounds like alcohols, alkanes etc. The response of such sensors to gases is derived from the change in electrostatic field of the molecular layer which can generate charge carriers in the silicon field effect transistor interface. Interactions with volatile organic compounds on the molecular layer can take place in two types: the first type is the adsorption on the surface of the molecular layer and the second type is the diffusion between the molecular layers [38,39]. However, these field effect transistor sensors is still lacking of selectivity.

The aim of the functionalization performed in this work was to passivate the surface states on the SnO_2 sensors by molecular layer aiming to optimize their interactions with ammonia gas. One SnO_2 sensor was coated with molecules having mostly nonpolar (functional) side groups (SnO_2 -APTES-alkyl) and two others were coated with molecules having mostly polar side groups (SnO_2 -APTES and SnO_2 -APTES-ester) in order to discover their interactions with ammonia which is a polar molecule. It was explored by testing the different functionalized sensors under ammonia which is the target gas. The changes in the response of the modified sensors were compared with pure SnO_2 . Another objective is to reduce the power consumption by decreasing the operating temperature, since the sensor will be used later for smart devices and portable applications.

In the present work, we focus on the change in sensitivity and selectivity of SnO_2 sensors after functionalization with amine (APTES), alkyl (CH_3), and ester (COOCH_3) end functional groups. The sensors are firstly functionalized by APTES followed by covalent attachment of alkyl or ester end functional groups molecule. Functionalization is characterized with FTIR analysis, and

then detection performances of resulting sensors are investigated in regards of ammonia detection.

2. Experimental

2.1. Fabrication of SnO_2 sensors

Thick SnO_2 films were deposited on alumina substrate by screen-printing technology. A semi-automatic Aurel C890 machine was used. The procedure for preparing the SnO_2 ink and sensor fabrication parameters has been described elsewhere [17]. SnO_2 powder (Prolabo Company) was first mixed with a solvent and an organic binder. SnO_2 ink was then screen-printed on an alpha-alumina substrate ($38 \times 5 \times 0.4 \text{ mm}^3$) provided with two gold electrodes deposited by reactive sputtering. The SnO_2 material was finally annealed for 10 h at 700°C in air. Film thickness was about 40 microns. SnO_2 particles and agglomerates sizes were found to be between 10 nm and 500 nm. A photographic image of the two sensor faces is presented in Fig. 1.

2.2. Molecular modifications of SnO_2 sensor

The functionalization was carried out by two-step process. In the first step, 3-aminopropyltriethoxysilane (APTES, ACROS Organics) molecules were grafted on SnO_2 (silanization). Silanization in liquid phase has been described elsewhere [40]. SnO_2 sensors were immersed in 50 mM APTES dissolved in 95% absolute ethanol and 5% of distilled water for 5 h under stirring at room temperature. Hydroxyl groups present on the surface of SnO_2 allow the condensation of APTES. To remove the unbounded APTES molecules, the sensors were rinsed with absolute ethanol and dried under N_2 flow (sensor SnO_2 -APTES). In a second step, SnO_2 -APTES sensors were immersed in a solution of 10 mM of hexanoyl chloride (98%, Fluka, alkyl: $\text{C}_6\text{H}_{11}\text{ClO}$) or methyl adipoyl chloride (96%, Alfa Aesar, ester: $\text{C}_7\text{H}_{11}\text{ClO}_3$) and 5 μL of triethylamine (Fluka) in 5 mL of chloroform as solvent for 12 h under stirring. The terminal amine groups of APTES allow the coupling reaction with molecules bearing acyl chloride group. The sensors were then rinsed with chloroform and dried under N_2 flow (sensors: SnO_2 -APTES-alkyl and SnO_2 -APTES-ester). The functionalization of SnO_2 sensors leads to covalent attachment of amine, ester, and alkyl end functional groups. A schematic illustration of the two steps functionalization is reported in Fig. 2.

2.3. Characterization of molecularly modified SnO_2

Modified molecular layers were characterized by Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR), the sample being placed face-down on the diamond crystal, and a force being applied by pressure tip. FTIR spectra were recorded in a wavelength range from 400 to 4000 cm^{-1} . The scanning resolution was 2 cm^{-1} . The entire ATR-FTIR spectrums were collected using a Golden Gate Diamond ATR accessory (Bruker Vertex 70).

2.4. Sensing measurements of modified sensors

In the test bench, the sensor was installed in 80 cm^3 glass chamber under constant gas flow of 15 l/h. The test bench was provided with gas mass flow controllers which allow controlling the concentrations of different gases at same time by PC computer. A cylinder of NH_3 gas (300 ppm, diluted in nitrogen) was purchased from Air Product and Chemicals Company. In addition, the test bench was equipped with water bubbler to test the sensors under different relative humidity (RH) balanced with air at 20 °C. Conductance measurements were performed by electronic unit equipped with voltage divider circuit with 1 volt generator that permits measuring the conductance of the SnO_2 film. Before injecting the target gas in the test chamber, the sensors were kept 5 h at 100 °C, and then stabilized under air flow for 5 h at 25 °C. Gas sensing properties were then measured to different concentrations of ammonia gas balanced with air with different RH. The normalized conductance was plotted to monitor the sensor response as well as to calculate response and recovery times. The normalized conductance is defined as G/G_0 , where G is the conductance at any time and G_0 is the conductance at the beginning of the test (i.e. $t=0$). Response/recovery times are defined hereafter as the time to reach 90% of steady-state sensor response. In addition, the curve of relative response ($(G_N - G_A)/G_A$, with G_N : conductance after 20 min of ammonia injection, and G_A : conductance under air with 5%RH) versus ammonia concentration was plotted for different sensors to compare their sensitivity. Sensitivity is defined as the slope of the calibration curve. Limit of detection (LOD) was also evaluated and it corresponds to a signal equal 3 times the standard deviation of the conductance baseline noise. Values above the LOD indicate the presence of target gas. The selectivity of SnO_2 -APTES-ester was tested versus acetone and ethanol gases.

3. Results and Discussions

3.1. Characterization of modified molecular layers

Molecular characterization of the grafted films on SnO₂ sensors was carried out by ATR-FTIR. Spectra of SnO₂ (red curve), SnO₂-APTES (green curve), SnO₂-APTES-alkyl (blue curve), and SnO₂-APTES-ester (black curve) are presented in Fig. 3 between 800 and 4000 cm⁻¹. All the sensors showed similar features in the range between 1950 and 2380 cm⁻¹ which is not exploitable as it corresponds to CO₂ gas contributions in ambient air.

With respect to first step of functionalization which is the attachment of APTES on SnO₂, most significant absorption bands were found between 800 and 1800 cm⁻¹ (Fig. 3, green curve). The peak at 938 cm⁻¹ is attributed to Sn-O-Si bond in stretching mode. The ethoxy groups of APTES hydrolyze and react with the hydroxyl groups presented on the surface of SnO₂ grains. In addition, the hydrolyzed ethoxy groups to hydroxyl react with another hydroxyl of the neighbor grafted APTES molecule, which leads to SnO₂ surface covered with siloxane network [41]. This feature is shown by the wide band between 978 cm⁻¹ and 1178 cm⁻¹ which is attributed to siloxane groups (Si-O-Si) from polymerized APTES. The -NH₃⁺ and -NH₂ vibrational signals of SnO₂-APTES are found at 1496 cm⁻¹ and 1570 cm⁻¹ respectively. Regardless the pure SnO₂, the CH₂ stretch peaks for all modified sensor founded at 2935 cm⁻¹ are related to the backbone of the attached molecules. Thus, from these peaks, the presence of characteristic features of APTES on the surface of SnO₂ is confirmed.

The second step of sensors modification was the attachment of a film on SnO₂-APTES, ended with alkyl or ester groups. These modifications were carried out by reaction of amines with acyl chlorides leading to the production of one equivalent acid, which forms a salt with unreacted amine of APTES and diminish the yield. The addition of triethylamine base is to neutralize this acid and leads to push the reaction forward. From the FTIR spectra in Fig. 3 (blue and black curves), the alkyl and ester sensors exhibit two peaks at 1547 cm⁻¹ and 1645 cm⁻¹ which correspond to carbonyl stretch mode and N-H bending mode of amide respectively. An additional broad peak between ~ 3000 and ~ 3600 cm⁻¹ corresponds to N-H stretch of amide. These peaks confirm the success of the reaction between amine group of APTES and acyl chloride groups. Asymmetrical C-H stretching mode of CH₃ for SnO₂-APTES-alkyl and for SnO₂-APTES-ester appears at 2965 cm⁻¹. The stretching peak of carbon double bounded to oxygen of ester group of SnO₂-APTES-ester is found at 1734 cm⁻¹ (Fig. 3, black curve). These results show that SnO₂ sensors are modified as expected with alkyl and ester end groups.

As a conclusion, FTIR analysis confirms that functionalization is effectively achieved on SnO_2 by showing the presence of attached APTES molecules on SnO_2 after silanization, as well as the existence of ester and alkyl molecules on SnO_2 -APTES after reaction with acyl chloride products.

3.2. Sensing measurements of different functionalized SnO_2 sensors

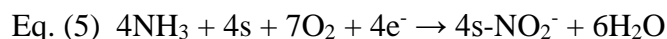
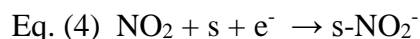
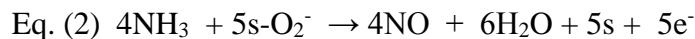
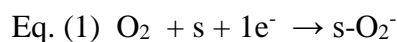
The first part of the test under gases was to show the characteristic of the response of different sensors to ammonia gas. SnO_2 , SnO_2 -APTES, SnO_2 -APTES-alkyl and SnO_2 -APTES-ester sensors were tested under 100 ppm of ammonia balanced with 5% RH air at 25 °C. The four sensors responses (normalized conductance) are reported in Fig. 4.

3.2.1. SnO_2 sensor

First we have to mention that the conductance of SnO_2 at room temperature is measurable as reported by Ji Haeng Yu et al. [44]. Indeed, stoichiometric SnO_2 is known to be insulator at room temperature. But the used SnO_2 sensitive film contains defects and the experiments were performed with 5%RH which lead to the formation of hydroxyl groups adsorbed on SnO_2 surface. These two effects explain the measurable conductance base line under air balanced with 5%RH of pure SnO_2 . Furthermore, the conductance was still measurable even when the test was switched to dry air as the hydroxyl groups stayed adsorbed at room temperature.

The conductance of pure SnO_2 decreases upon exposure to ammonia gas (Fig. 4). This type of response has been found before by Kamalpreet Khun Khun et al. [42] at temperature between 25 to 200 °C. They supposed that ammonia reacts with molecular adsorbed oxygen ion (O_2^- , created as shown in Eq 1) producing nitrogen monoxide gas (NO) according to Eq 2. In presence of oxygen and at low temperature, NO can be easily transformed into NO_2 which is very good oxidizing agent (Eq 3). The reaction of NO_2 with SnO_2 at ambient temperature causes the decrease of sensor conductance. NO_2 adsorbs on SnO_2 surface adsorption sites (s) and bring out electrons from the conduction band (Eq 4) [43]. Thus, the overall reaction of ammonia with SnO_2 at room temperature can be written as in Eq 5. Therefore, this reaction confirms the obtained results because the conductance was actually decreased when SnO_2 sensor is exposed to ammonia. Thus, according to published results, the overall reaction of ammonia with SnO_2 at room temperature could be written as in Eq 5. Such a mechanism is consistent with a

conductance decrease upon ammonia exposure. However, actually, we have no experimental proof of such a mechanism.



where s is an adsorption site.

3.2.2. *SnO₂-APTES sensor*

When SnO₂-APTES sensor was exposed to ammonia gas, no response was observed. Formation of APTES film on SnO₂ prevents the water molecules to adsorb on the surface because the active sites of SnO₂ are occupied by O-Si bond of APTES, and because of the hydrophobic nature of APTES film. Therefore, in the following discussion, the conventional mechanism of interaction of SnO₂ with gases cannot be taken in consideration as no reactive sites are available. SnO₂-APTES shows no change in conductance upon exposure to ammonia (Fig. 4). This implies that no significant interactions occur between the grafted APTES and ammonia gas. In term of polarity and other chemical properties like acidity, the amine and ammonia groups are almost the same, since amine is one of the derivatives of ammonia. Hence, such result was expected for SnO₂-APTES. In addition, this behavior indicates that the SnO₂ surface is well covered by APTES molecules because the negative response observed on pure SnO₂ is totally inhibited.

3.2.3. *SnO₂-APTES-alkyl and SnO₂-APTES-ester sensors*

SnO₂-APTES-alkyl and SnO₂-APTES-ester exhibit increase in conductance upon exposure to 100 ppm of ammonia gas as shown in Fig. 4. However, the response of SnO₂-APTES-ester is more important than for SnO₂-APTES-alkyl. These responses could be related to the different polarities of the attached end groups. Indeed, Wang et al. [38,39] reported that the response of some functionalized sensitive films is derived from the change in electrostatic field of the attached molecular layer. Ester is a good electron withdrawing group, while alkyl is mostly considered as

nonpolar. Ammonia molecule is a good nucleophilic molecule (donating), thus the interaction is between electron withdrawing (ester) and electron donating groups. In this case, dipole-dipole interaction is taking place. However, in the case of SnO_2 -APTES-alkyl, the interaction is of induced dipole type because ammonia is a polar molecule and alkyl end group is mostly nonpolar. It is likely that the adsorption process occurs through interaction between the nitrogen of ammonia and the end functional group of the molecular layer (alkyl and ester). It was reported before by B. Wang et al. [38], that the dipole-dipole interaction is always stronger than induced dipole interaction. This can explain the difference in the response between the SnO_2 -APTES-alkyl and SnO_2 -APTES-ester sensors to ammonia gas. As mentioned previously, the interaction can also result from diffusion of the gas in the molecular layer. This type of interaction is favorable only for SnO_2 -APTES-alkyl. It is difficult for ammonia molecules to diffuse in the molecular layer of SnO_2 -APTES-ester, because of the steric hindrance induced by ester end groups. This phenomenon can explain the response of SnO_2 -APTES-alkyl to ammonia in addition to the induced dipole interaction. These two interactions (i.e. dipole-dipole and induced-dipole) result in a modification in the dipole moment of the whole film. The variation in the molecular layer's dipole moment affects the electron mobility in SnO_2 film which modifies the conductance [45,46]. The exposure to ammonia leads to increase in electron mobility (proportional to conductance). The same behavior was founded to a selection of polar and non-polar gases but on ester, and alkyl silicon oxide functionalized substrate [38].

According to the above discussion, the response of the molecular modified sensors does not obey the conventional mechanism of direct interaction with SnO_2 . The response comes powerfully from the interaction of ammonia molecules with end function group of the attached layer. The response of SnO_2 -APTES-ester is generated from dipole-dipole interaction, while the response of SnO_2 -APTES-alkyl is produced from induced dipole interaction which has less significant effect.

3.2.4. Sensors sensitivity

Regarding the different sensors sensitivity against ammonia concentrations, Fig. 5 shows the relative responses versus ammonia concentrations of SnO_2 -APTES-ester in comparison with pure SnO_2 , SnO_2 -APTES and SnO_2 -APTES-alkyl sensors. Sensitivity is defined as the slope of the relative response curve versus ammonia concentrations, i.e., how large is the change in the sensor signal upon a certain change in ammonia concentration. Pure SnO_2 and SnO_2 -APTES sensors

have almost no sensitivity to different ammonia concentrations. In addition, SnO₂-APTES-alkyl gives no significant response between 0.5 ppm and 30 ppm, but its sensitivity starts to increase from 30 ppm of ammonia. It can be noticed that SnO₂-APTES-ester exhibit constant sensitivity between 0.5 ppm and 10 ppm, around 0.023 ppm⁻¹. After this concentration the sensor starts to become saturated and the sensitivity continuously decreases down to nearly zero at 100 ppm NH₃. However, the sensitivity of SnO₂-APTES-ester at concentrations higher than 30 ppm is still more significant than the sensitivity of SnO₂-APTES-alkyl. The calculated LOD for ester modified SnO₂ was 80 ppb.

To summarize this section, SnO₂-APTES-ester sensors showed good sensitivity to ammonia gas in a range of concentration compatible with breath analysis applications (sub-ppm). This sensor is studied in more details in the following part.

3.3. Focus on SnO₂-APTES-ester sensor

3.3.1. Effect of humidity on the response

As known, human breath contains high amount of humidity (100 % RH at 37 °C). Water molecule presents high polarity, hence it can affect the response to ammonia gas. In order to check this effect, SnO₂-APTES-ester was tested to ammonia gas under different amount of relative humidity ranging from 5 to 50% RH. Figure 6 shows the sensor response of SnO₂-APTES-ester to 100 ppm in dry and humid air at 25 °C. Upon exposure to ammonia gas the sensor conductance increases in the four cases (dry air, 5%RH, 26%RH, and 50%RH) with fast response and recovery times. In dry air and 5%RH, the sensor shows almost the same response magnitude, 1.46 and 1.45 respectively, which decreases to 1.25 and 1.06 in 26%RH and 50%RH respectively. This means that a small quantity of relative humidity does not affect the sensor response, while at elevated amount the response starts to be less significant. A potential explanation is that the attached ester film is saturated by water molecules or adsorbed hydroxyl groups at high RH. Hence, during exposure to ammonia, there is a limitation of response due to adsorption competition between water and ammonia. For the future tests, the humidity will be kept at 5%RH.

In these conditions, 5%RH at 25 °C, the response and recovery times (as defined in section 2.4) are 98 s and 130 s respectively, which is quite noticeable for a tin oxide based sensors working at room temperature.

3.3.2. *Effect of operating temperature*

In the most cases, the increase of the operating temperature of SnO₂ sensors increases the sensitivity to gases. In contrast, in the case of SnO₂-APTES-ester, the increase of temperature generates decrease of ammonia sensor response. As shown in Fig. 7, the response of SnO₂-APTES-ester to ammonia decreases from 1.45 (25 °C) to 1.18 and 1.06 when the operating temperature is increased to 50 °C and 100 °C respectively. Therefore, the interaction of ammonia with ester attached to SnO₂ is more significant at low temperature (25 °C) than at higher one (50 and 100 °C).

So, interesting conclusion is that SnO₂-APTES-ester has to be operated close to room temperature (25 °C), without any power consumption for the sensitive detection of ammonia.

3.3.3. *Effect of ammonia concentration on sensor response*

The influence of ammonia concentrations on sensor response was studied at the optimum conditions defined previously, 5%RH at 25 °C. Figure 8 shows the change in conductance of SnO₂-APTES-ester upon exposure to different concentrations of ammonia gas (0.2-100 ppm). The curve at low concentrations (Fig. 8a) was used to calculate the limit of detection (LOD) of the sensor to ammonia gas which is around 80 ppb. Such a value confirms the potentiality of ammonia detection for breath analysis application.

Figure 8b also shows the stability of the sensor with time. The stability of metal oxide is a challenge mostly for room temperature gas sensors. Present results show quite good stability of the baseline. The drift is around 0.98% over 16 hours.

3.3.4. *Selectivity*

Human breath contains a wide variety of volatile organic compounds which are polar or non-polar, oxidant or reductant. It's well known that SnO₂ sensor which usually operates at temperature between 350-500 °C can give a response to most of these types of gases, unfortunately without distinction (selectivity) or even with compensating effect for oxidant/reducing gases [47]. Field effect transistors functionalized with ester end group have

shown responses to a wide variety of volatile organic compounds like alcohols and alkanes [39]. This implies that these sensors also have a lack of selectivity. To check the selectivity to ammonia of the developed SnO₂-APTES-ester, such sensors were tested with respect to ethanol and acetone gases.

Figure 9 shows that the SnO₂-APTES-ester sensors have almost no change in conductance upon exposure to 50 ppm of acetone and ethanol at 25 °C. This means that ester modified sensor is relatively selective to ammonia, at least in regards of the two tested gases. This particular selectivity derives from the way of interactions of the grafted layer on SnO₂ with ammonia gas. As mentioned previously, interactions occur between the ester end group which is strongly electron withdrawing, and the ammonia molecule which is electron donating. Hence, electrons are withdrawn by the attached ester end group from the ammonia molecules adsorbed on it during exposure. These interactions lead to the significant response of SnO₂-APTES-ester sensor. Other molecules like ethanol and acetone do not have this high affinity to donate the electrons to SnO₂-APTES-ester, explaining minor changes in conductance upon exposure to these gases.

4. Conclusion

Mohamad Hijazi received his master's degree in Synthesis Catalysis and Sustainable Chemistry from Claude Bernard University Lyon 1 (France) in 2014, and is currently pursuing PhD degree in Solids and Instrumentation Processes **and Sensors** at Ecole des Mines of Saint-Etienne. His research is focused on the development of gas sensing materials in breath analysis field.

Mathilde Rieu received her PhD degree in Material Science and Engineering in 2009 from Toulouse University (France). She worked on the SOFC technology and after a post-doctoral position at CEA Grenoble she was recruited in 2010 as assistant professor at the Ecole des Mines de Saint-Etienne (France). She works in the field of chemical gas sensors at the Center for Chemical Engineering "SPIN" in the department of Processes and Reactivity of solid-gas systems, Instrumentation and Sensors.

Valérie Stambouli received her PhD in 1991 in Paris-Sud University (France). Then she moved to E.P.F.L. (Switzerland) where she was involved in physical and chemical characterizations to study the oxidization and tribological behavior of Fe based alloys. Since 1994, she is a full-time researcher of the Center National de la Recherche Scientifique (CNRS). She worked on the elaboration of metallic and dielectric films using P.V.D. techniques for microelectronics and microsystems. In 2002, she joined the LMGP in Grenoble where she initiated an interdisciplinary research program. She focuses on the elaboration and functionalization of thin metal oxide films for label-free biosensing.

Guy Tournier received his PhD in 1979 from the University Claude Bernard at Lyon. He enters at Ecole des Mines de Saint-Etienne in 1982 as research engineer. Since 1984, he works in the

department of Processes and Reactivity of solid-gas systems, Instrumentation and Sensors attached to SPIN Research Center (Natural and Industrial Process Sciences) in Ecole des Mines of Saint-Etienne. His field of activity is the development of tin oxide gas sensors and their used in industrial applications.

Jean-Paul Viricelle received his Ph.D. in Chemical Engineering in 1994 at Ecole des Mines of St-Etienne (France). He has worked as a post-doctoral student on the oxidation of ceramic composite materials in University of Limoges (France) from 1995 to 1997. Since 1998, he has been working as associate professor in MICC department (Microsystems, Instrumentation and Chemical Sensors) attached to SPIN research centre (Natural and Industrial Process Sciences) in Ecole des Mines of St-Etienne. He now manages PRESSIC department (Process and Reactivity of solid-gas systems, Instrumentation and Sensors). His research activity is focused on electrical properties of solids for development of chemical gas sensors, solid oxide fuel cells and micro-preconcentrators.

Christophe Pijolat is Professor of Chemical Engineering and Microsystems at Ecole des Mines of Saint-Etienne (France), he is deputy director of SPIN research center (Natural and Industrial Process Sciences). Since 1980, he has been working in the field of electrical properties of solids and on the development potentiometric and semi-conductor sensors. He has contributed to several technological transfers of sensors into industrial applications.

Molecularly modified SnO₂ thick films were produced by screen printing and wet chemical processes. The functionalizations were carried out first by grafting of 3-aminopropyltriethoxysilane followed by reaction with hexanoyl chloride or methyl adipoyl chloride. Then, tests under gases were performed. Pure SnO₂ sensor and APTES modified SnO₂ didn't show any significant sensitivity to NH₃ (0.5-100 ppm) at 5%RH, 25 °C, while the sensitivity to NH₃ gas starts to increase from 30 ppm for alkyl modified sensor. On the contrary, ester modified sensor exhibit fast response and recovery time to NH₃ gas with a limit of detection estimated to 80 ppb at 5%RH, 25 °C. In addition, this sensor shows constant sensitivity between 0.5 and 10 ppm of NH₃ (0.023 ppm⁻¹). Moreover, ester modified sensor is selective to NH₃ gas with respect to reducing gases like ethanol and acetone. However, the relative humidity higher than 5% decreases the response. Working at room temperature, ester modified sensor may be a good candidate for breath analysis applications for the diagnosis of diseases related to ammonia gas biomarker. Such sensor could be coupled with a condenser to reduce the amount of humidity in the analyzed breath sample to 5 %RH. The sensing mechanism of ester modified SnO₂ and the selectivity in regards of various volatile organic compounds have to be investigated in further work.

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Figure captions

Fig. 1. Photograph of the two SnO₂ sensor sides deposited by screen printing.

Fig. 2. Schematic illustration of SnO₂-APTES, SnO₂-APTES-alkyl, and SnO₂-APTES-ester synthesis steps. Hexanoyl chloride represent the molecule C₅H₈ClOR with R: CH₃ and methyl adipoyl chloride is the molecule C₅H₈ClOR with R: COOCH₃.

Fig. 3. ATR-FTIR spectra of SnO₂ (red curve), SnO₂-APTES (green curve), SnO₂-APTES-alkyl (blue curve), and SnO₂-APTES-ester (black curve) films.

Fig. 4. The sensor response of SnO₂ ($G_0=1.4\times10^{-5} \Omega^{-1}$), SnO₂-APTES ($G_0=7.9\times10^{-6} \Omega^{-1}$), SnO₂-APTES-alkyl ($G_0=1.5\times10^{-5} \Omega^{-1}$), and SnO₂-APTES-ester ($G_0=9.5\times10^{-6} \Omega^{-1}$) to 100 ppm ammonia gas balanced with humid air (5%RH) at 25 °C.

Fig. 5. Relative response of pure SnO₂, SnO₂-APTES, SnO₂-APTES-alkyl, and SnO₂-APTES-ester sensors versus ammonia concentrations balanced with 5% RH air at 25 °C.

Fig. 6. The sensor response curves of SnO₂-APTES-ester to 100 ppm of ammonia gas balanced with dry air, 5%RH, 26%RH, and 50%RH at 25 °C.

Fig. 7. The sensor response of SnO₂-APTES-ester to 100 ppm ammonia gas balanced with humid air (5%RH) at 25 °C, 50 °C, and 100 °C.

Fig. 8. The change in conductance of SnO₂-APTES-ester upon exposure to different concentrations of ammonia gas in humid air (5%RH) at 25 °C, a) [NH₃] ranging from 0.2 to 5 ppm and b) [NH₃] ranging from 5 to 100 ppm.

Fig. 9. The sensor response of SnO₂-APTES-ester upon exposure to 50 ppm of ammonia, ethanol, and acetone gases in humid air (5%RH) at 25 °C.

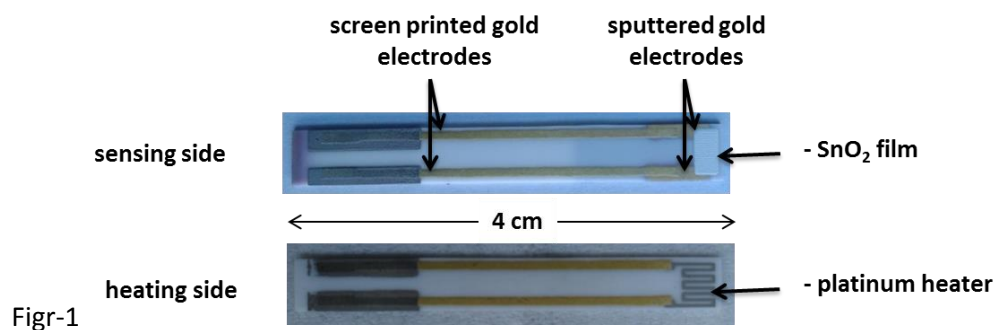


Fig. 1. Photograph of the two SnO_2 sensor sides deposited by screen printing.

Figr-2

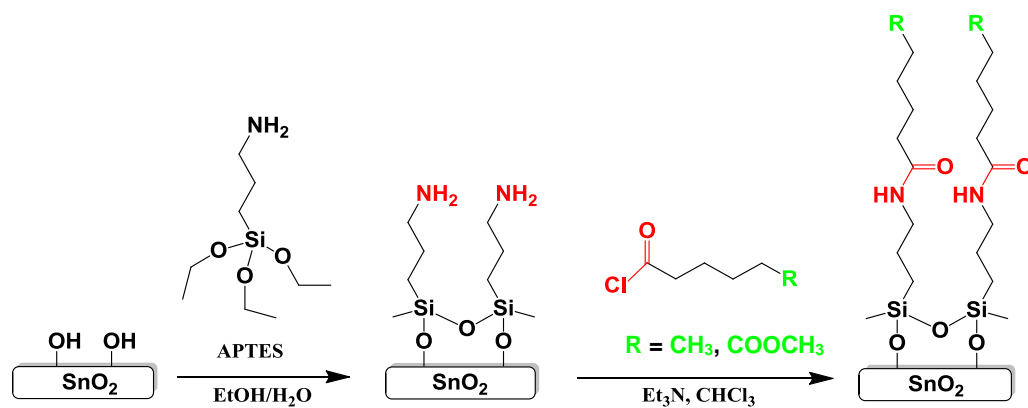
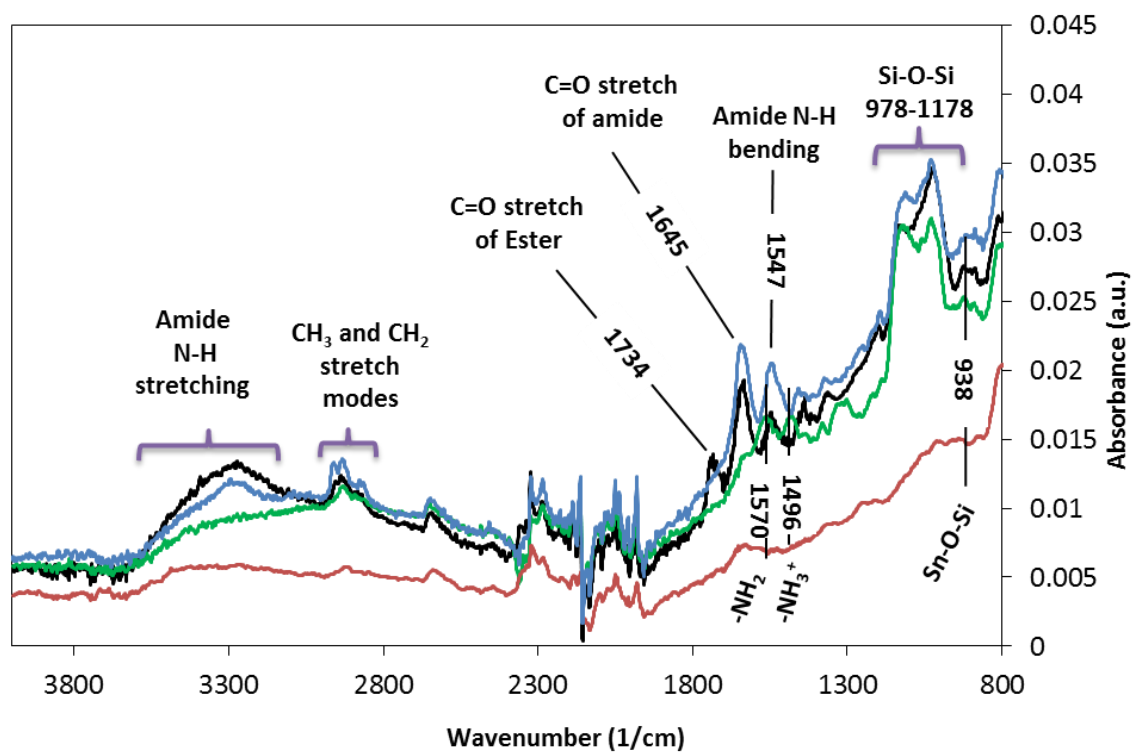


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Figr-3

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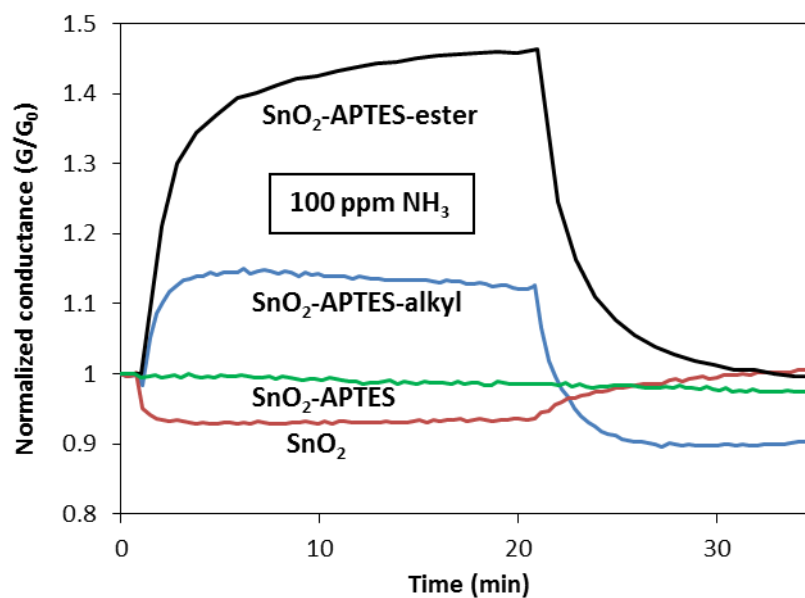


Fig-4

Fig. 4. The sensor response of SnO_2 ($G_0=1.4\times10^{-5} \Omega^{-1}$), SnO_2 -APTES ($G_0=7.9\times10^{-6} \Omega^{-1}$), SnO_2 -APTES-alkyl ($G_0=1.5\times10^{-5} \Omega^{-1}$), and SnO_2 -APTES-ester ($G_0=9.5\times10^{-6} \Omega^{-1}$) to 100 ppm ammonia gas balanced with humid air (5% RH) at 25 °C.

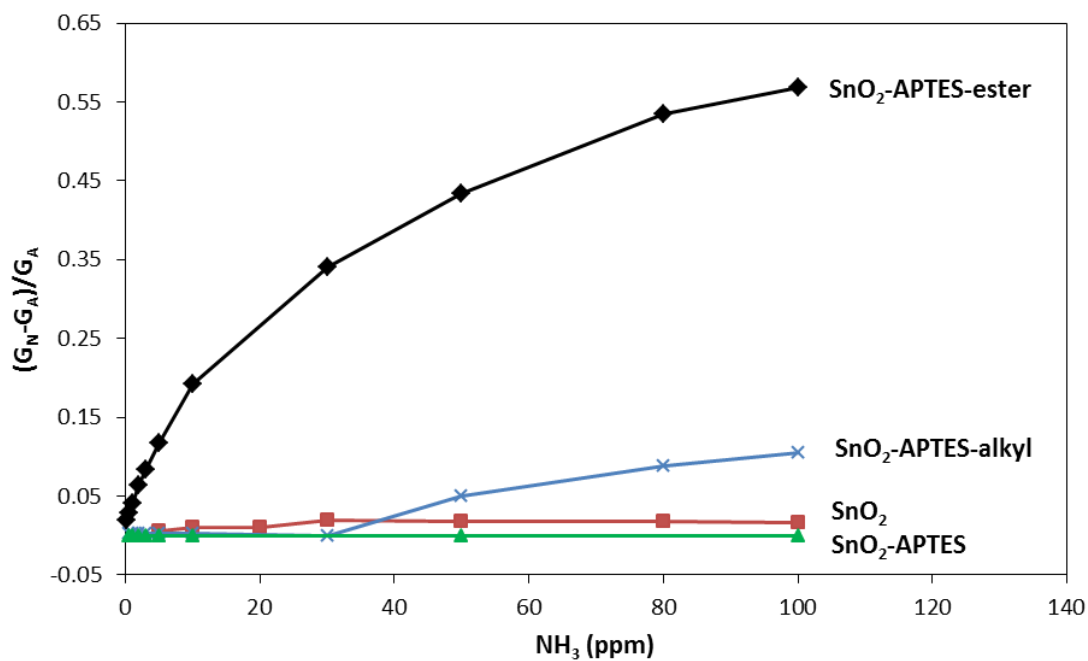


Fig-5

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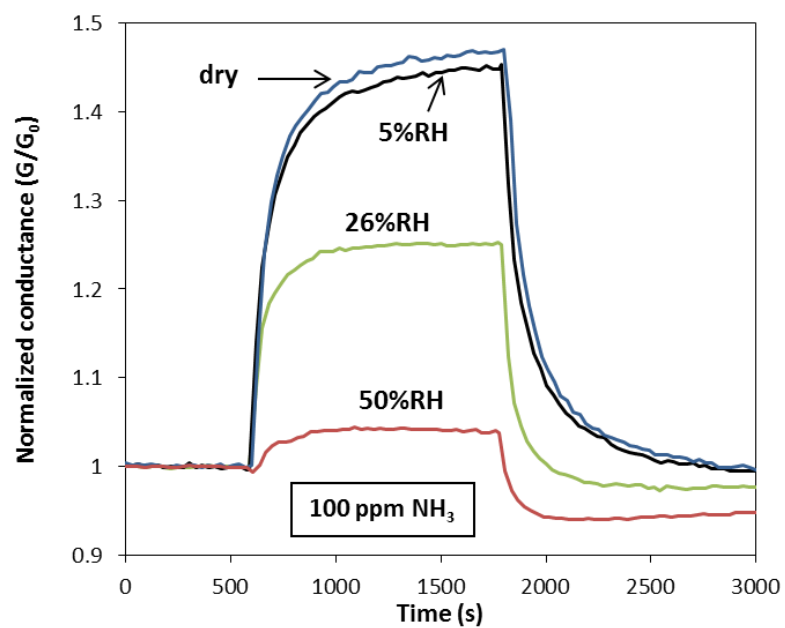


Fig-6

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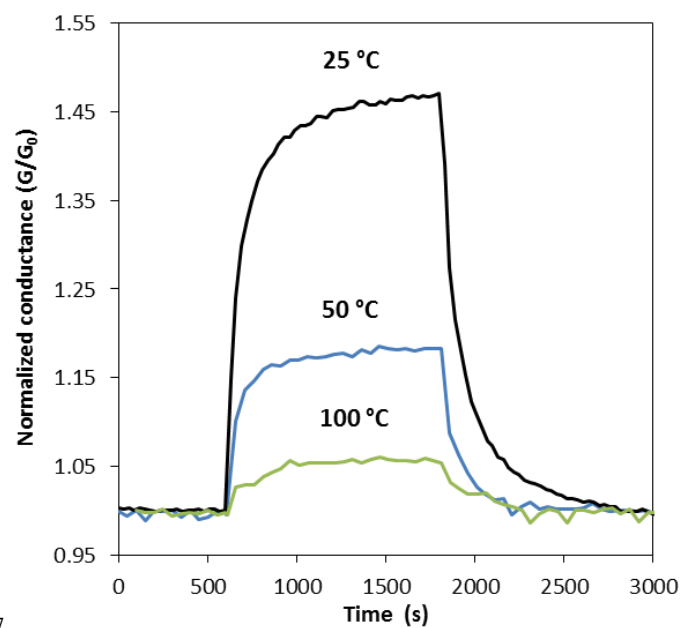


Fig-7

Fig. 7. The sensor response of SnO_2 -APTES-ester to 100 ppm ammonia gas balanced with humid air (5%RH) at 25 °C, 50 °C, and 100 °C.

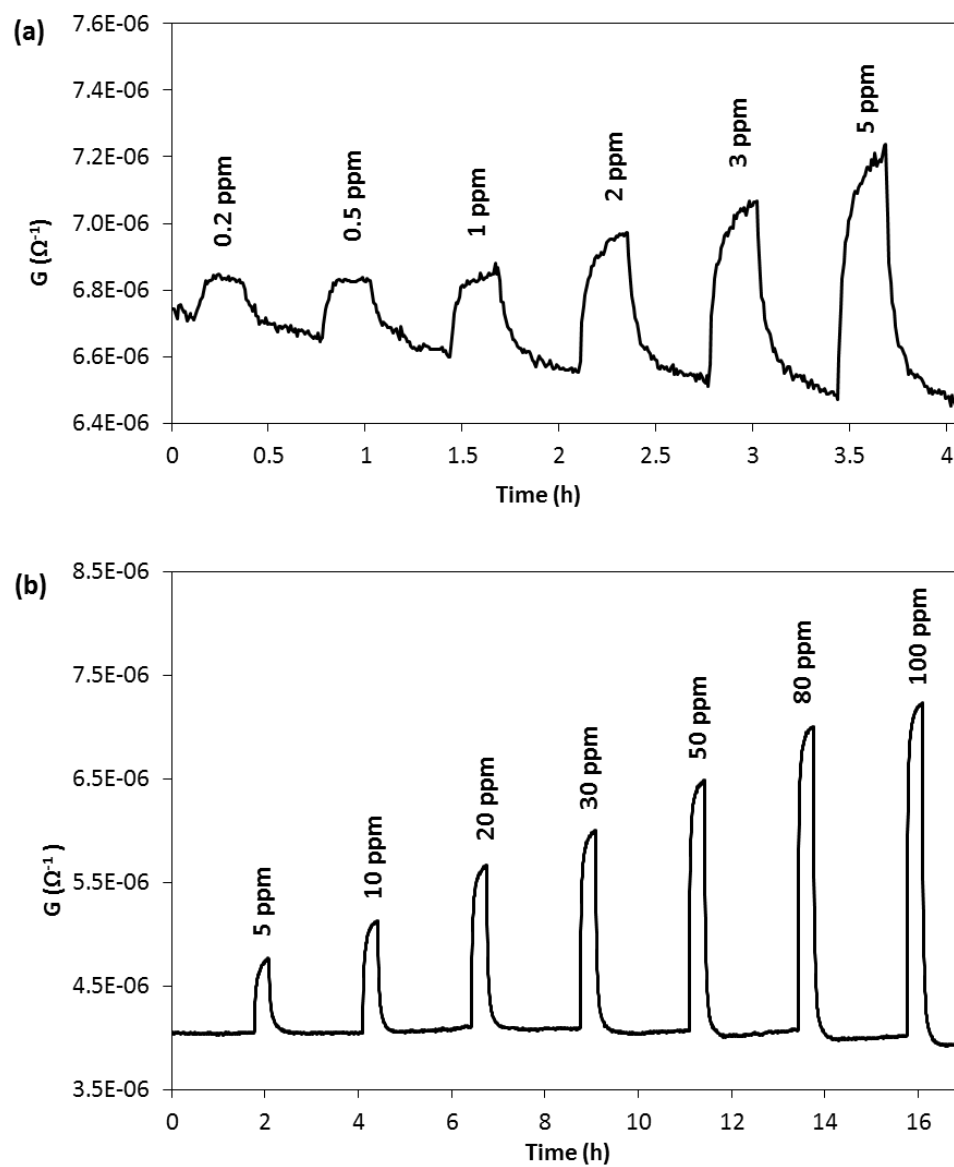


Fig-8

Fig. 8. The change in conductance of SnO_2 -APTES-ester upon exposure to different concentrations of ammonia gas in humid air (5%RH) at 25 °C, a) $[\text{NH}_3]$ ranging from 0.2 to 5 ppm and b) $[\text{NH}_3]$ ranging from 5 to 100 ppm.

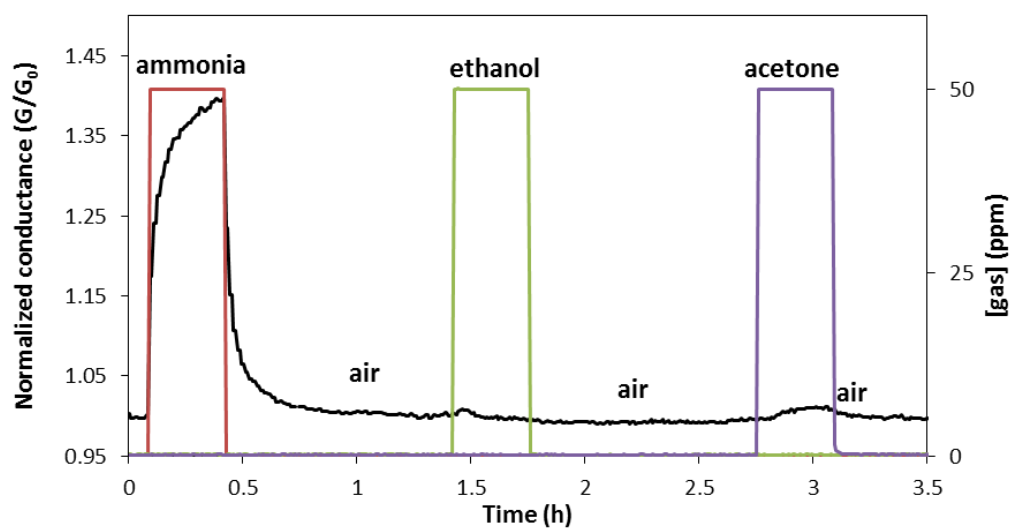


Fig-9

Fig. 9. The sensor response of SnO₂-APTES-ester upon exposure to 50 ppm of ammonia, ethanol, and acetone gases in humid air (5%RH) at 25 °C.