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Detection of Harmful Gasses Using Composites with MXene Nanomaterials

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Abstract

MXene composites have emerged as promising materials for gas-sensing applications due to their unique properties. This overview delves into the utilization of MXene composites for the detection of ammonia, a critical pollutant in various industries and a biomarker indicating problems with liver and kidney function. The abstract will focus on the advantages of MXene composites in enhancing the sensitivity, selectivity, and stability of ammonia sensors. By examining recent advancements and potential applications, this paper highlights the growing significance of MXene composites in facilitating the development of efficient and reliable sensing technologies for monitoring ammonia levels.

Keywords: MXene composites, Gas sensing; Ammonia detection; Nanomaterial; Chemical sensors; Breath analysis; diagnosis; semiconducting; nanorods.d Accreditation of Laboratory Animal Care; HDPE: High-Density Polyethylene; ZDEC: Zinc Diethyldithiocarbamate; SLS: Sodium Lauryl Sulfate

Introduction

Harmful gasses monitoring is of importance, especially in industry applications where the risk is high. Of the different harmful and toxic gases, ammonia (NH_3) is one of the most intensive and even in lower concentrations can cause damage to the respiratory system [1]. Monitoring ammonia (NH_3) concentrations is of importance in different areas, as it is toxic in water [2] and also important for monitoring the concentration in breath [3], for early health problems diagnosis or even as a first indicator for liver and kidney health check. Sources of pollution of air are the agriculture industry, livestock [4], transportation and food processing plants [5], and microelectronics (for example, in the production of silicon nitride by chemical vapor deposition, NH_3 is one of the precursors) [6].

NH_3 can be detected by using sensors based on nanomaterials [7]. One of these nanomaterials are MXenes. MXenes are a class of 2D nanomaterials and are being explored for increasing the sensitivity of other nanomaterial-based sensors for harmful gases. MXenes are produced by selective etching of crystal MAX phase, where M is a transition metal, A is aluminum or silicon, and X is carbon or nitrogen. After etching the aluminum or silicon from the MAX phase, left is the MX layered structure from nanosheets, for example, titanium carbide (Ti_3C_2) (Figure1). As such, the strengths of MXenes, important for use in sensing applications, are high electric conductivity and high surface area [8].

MXenes are terminated with -OH, -O, -F groups, depending on the etching method of the A elements in the MAX phase, and because of these groups, the target molecules of interest can bind more easily on the surface, which increases the sensitivity of the materials [10] [11]. By incorporating them with semiconducting nanomaterials, such as nanosheets [8], nanorods [12] or quantum dots [13], it is possible to increase sensitivity toward harmful gasses compared to pristine MXenes or semiconducting nanomaterials.

These nanomaterials can be used as sensing layers in resistive sensors, which means that the electrical resistance of the nanomaterials changes when in contact with specific molecules. The change in resistance is measured and the concentration of the molecules in question can be determined.

Resistive sensors' electrical resistance increases or decreases under the influence of the target molecules, depending on the interactions between the target molecules and the sensing layer, and on the sensing layer's type of conductivity.

The response of the sensors is given in percentage change of the resistance, calculated by the formula:

$$R = \left(\frac{R_a - R_g}{R_a}\right) \times 100\% \qquad (1)$$

where is the resistance in air and is the resistance of the sensor when exposed to the influence of NH_3.

Increasing the response of sensors is of interest for broadening their possible applications, so they can be used both in the industry environment and for healthcare through the monitoring of biomarkers. Improving the sensitivity of a sensor towards a target gas can be done by UV illumination, where the UV photons generate conduction electrons which play a role in the sensing mechanism [14], surface functionalization with metal nanoparticles (NPs), where the affinity toward the target gas can be increased, depending on the metal, and also possible creation of a barrier between the metal NPs and the sensing layer which can impact the sensing mechanism [15], or by combining different materials, utilizing their properties, such as large surface area and conductivity, to make composites with improved sensitivity and stability compared to its self-standing components [16].

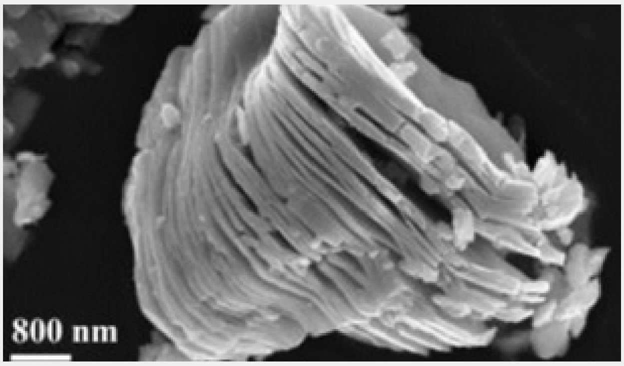

Figure 1: FESEM image of $Ti_3C_2T_x$ MXene [9]

In this paper, different approaches, incorporating MXenes with sensing materials and comparison of the responses of the sensors are briefly reviewed to conclude best candidates for precise monitoring of NH_3 in the environment but also in human breath.

Discussion on MXene/nanomaterials composites

Mxenes/Au/Pt

A sensing layer made from $Ti_3C_2T_x$ MXenes and Au or Pt nanoparticles, where the resistance of the material increases under the influence of NH_3 molecules has been reported [17]. The sensing mechanism has been explained by the fact that oxygen, in the adsorption process on the sensor surface, takes electrons from the material and becomes a negatively charged species, as a result a hole accumulation layer forms and the material's resistance is changed. After the reaction between the present NH_3 molecules and the oxygen, the electrons go back to the material and thus the resistance of the sensor changes again. Another important fact is that Au and Pt particles help with their catalytic roles toward the NH_3 gas. Also of importance is the reported Schottky barrier formation between the Au or Pt particles and the MXenes by which the depletion region has an effect on the sensing mechanism. Good selectivity has been reported toward NH_3 and after a high number of bending cycles, the response of both structures decreases slowly, indicating stability for possible applications in flexible sensors.

Mxenes/GaN

Another approach has been reported by fabricating a GaN nanorods-$Ti_3C_2T_x$ composite for the sensing material [11]. N-type behavior of the composite has been reported, which means that the GaN nanorods dominate the sensing mechanism?. A heterojunction is formed between the p-type MXenes and n-type GaN, and by the reaction of NH_3 with the adsorbed oxygen, electrons are given back to the material with which the depletion layer becomes narrower and thus the resistance of the material decreases. The reported lower detection limit of the composite is 20 times lower than that of GaN nanorods and with a 3.4 times higher response than that of self-standing MXenes. These structures have good stability after aging, where the response variation is under 4.8 % after 90 days.

Mxenes/WS_2

Fabrication of composite between $Ti_3C_2T_x$ MXene and WS_2 nanosheets has been reported, where both components are p-type in the composite, and by the reactions of NH_3 with oxygen, when the electrons are given back to the material they recombine with holes increasing the resistance of the sensor [8]. The reported structures have higher selectivity toward NO_2 than NH_3, which is confirmed by DFT simulations, where the calculated adsorption energies are -1.64 eV for NO_2 and -1.2eV for NH_3.

Mxenes/SnO_2

In another work, sensors prepared with $Ti_3C_2T_x$ MXenes and SnO_2 quantum dots have been reported, where the resistance increases under the influence of NH3 molecules [13]. An increase in response by 13.35% at 50 ppm of $Ti_3C_2T_x$ Mxenes by sputtering of a SnO_2 layer over them has been reported. The resistance of this composite also increases [18]. A decrease in response time has been reported by these approaches, compared to pristine MXenes. However, in another study, fabrication of composite has been reported by using the same materials, namely $Ti_3C_2T_x$ MXenes and SnO_2 quantum dots, where the resistance of the material decreases when NH_3 molecules are adsorbed [19]. This is in agreement with the n-type SnO_2 nanoparticles, and the difference can be due to the different concentrations of SnO_2 in the composite, and possible differences in the sizes of the quantum dots in both studies. This ratio determines which material is dominating the sensing process. Here, the sensing mechanism is also explained by returning electrons to the conduction band when NH_3 reacts with the adsorbed oxygen. Also, it has been reported that by adjusting the concentrations of the components of the composite, a higher response or wider detection range can be achieved.

Mxenes/In_2O_3

A strong response has been reported from a sensor produced with In_2O_3 microtubes and $Ti_3C_2T_x$ MXene. The structure also has very fast response and recovery times, good stability and selectivity towards NH_3 [20]. The proposed mechanism is the same, meaning that the NH_3 molecules react with O_2^- species and by doing so, trapped electrons from the conduction band of the material are given back, which increases the conductance of the material. Another approach has been reported by creating a composite with $Ti_3C_2T_x$ MXenes and In_2O_3 NPs [21], with very good selectivity towards NH_3, and with increase in resistance under the influence of NH_3, and explained reason is that in this case the sensing mechanism depends on the MXenes. Another composite of $Ti_3C_2T_x$ MXenes and In_2O_3 NPs with high response and very good selectivity has been reported [22].

Mxenes/$Na_2Ti_3O_7$-PANI

Another strong response has been reported by preparing a sensitive material with MXenes, sodium titanate nanofibers and encapsulating the composite with polyaniline (PANI), with good stability, where PANI is the reason for the increased moisture resistance and has an effect on the stability of the structure [23]. The surface structure of the $Ti_3C_2T_x$-$Na_2Ti_3O_7$-PANI is fibrous, and the surface has a very large area, which partly can contribute toward the increased response because of the increased available active sites where the reaction of the sensing mechanism can take place.

In Table 1 the reviewed reported responses and their response and recovery times of the different materials under the given conditions are compared.

Table 1: Response in percent and response and recovery times of different MXene composites.

Material	Concentration	Response/ recovery time	Response	Ref.
Au- $Ti_3C_2T_x$ Pt- $Ti_3C_2T_x$	100 ppm	87/217s	16% (RH=0%); 14.5% (RH=30%) 8.2% (RH=0%); 7% (RH=30%)	[17]
GaN- $Ti_3C_2T_x$	100 ppm	21/23s	51% (RH=20% to 80%)	[12]
WS_2- $Ti_3C_2T_x$	5 ppm	-/-	29% (RH = 33%)	[8]
SnO_2- $Ti_3C_2T_x$	100 ppm	34/-s	10.4% (RH=40%)	[13]
SnO_2- $Ti_3C_2T_x$	100 ppm	109/342s	41% (RH = 40 to 55%)	[19]
SnO_2- $Ti_3C_2T_x$	50 ppm	24.9/86.5 s	13.35 % (RH=45%)	[18]
In_2O_3- $Ti_3C_2T_x$	100 ppm	1/3.25s	180% (RH = 24.8%)	[20]
In_2O_3- $Ti_3C_2T_x$	30 ppm	42/209s	63.8 % (RH = 40%)	[21]
In_2O_3- $Ti_3C_2T_x$	20 ppm	60/300s	100.7% (RH=35%)	[22]
$Ti_3C_2T_x$-$Na_2Ti_3O_7$-PANI	100 ppm	231.2/165.4s	185.44% (RH=45%)	[23]

Table abbreviations: Ref. (Reference); RH (Relative Humidity).

The structures' behavior under humidity makes them potentially applicable in monitoring NH3 from human breath. Increased NH3 concentrations in blood can be a marker for health problems, such as problems with liver function. It is a byproduct of protein metabolism and if the levels are high, it is an indicator of problems with the NH3 metabolism in the body, as it is converted to urea slower [24]. Another example of why NH3 measuring is important is in monitoring hemodialysis [25].

If the humidity and temperature of the environment have an effect on the sensors' response, breath detection of NH3 with such sensors becomes a little more complicated. For that reason, the sensors' response depending on the humidity and temperature should be measured precisely. In addition, calibration of the sensor is needed, or for better precision, a sensor for RH and temperature in close proximity with the NH_3 sensor should be used, and by knowing the NH_3 sensors' response dependence on RH and temperature, correct concentrations of NH_3 can be calculated independent of these factors, and false positives or negatives avoided. Another important criterion for breath detection is the response time of the sensor, as it should be short so that the measurement does not inconvenience the patient by needing multiple exhales.

By these criteria, the most applicable materials for breath NH_3 detection are In_2O_3/MXene and PANI/MXene. PANI/MXene composite has been reported to have an increased response to NH_3 with RH increase, that means if it is closer to the mouth of the patient it should be in contact with more H_2O molecules which will increase its sensitivity, which means it makes it the suitable for measuring NH_3 levels in human breath, however, the response time is longer compared to In_2O_3/MXene (Table 1). The fastest response times and the high response of In_2O_3(microtubes)/MXene makes this composite most suitable for sensors for human breath analysis, from the reviewed works. However, more tests are needed for different combinations of RH, temperatures above room temperature, closer to body temperature and aging, so that the potential materials can be characterized for the intended environment.

Conclusion

MXenes are proven to be of importance in the fabrication of sensors for harmful gasses operating at room temperatures, as they are conductive and with a high surface-to-volume ratio, thus having the potential for increased sensitivity when used as a composite material as compared to the pure self-standing MXenes and semiconducting nanoparticles. A comparative review has been done of some of the nanocomposites with MXenes reported recently considering their sensitivity toward ammonia. They show high potential for further research and development of sensing composite materials. One of the main mechanisms for sensing is oxygen adsorption and electron trapping from the materials when they are exposed to air. When ammonia molecules react with the adsorbed oxygen species, the trapped electrons are transferred back to the material. As a consequence the resistance of the material changes, depending on the type of junctions between the components and the dominating component in the sensing mechanism of the composite material. For breath analysis, it was concluded that In_2O_3/MXene was the most suitable material due to the fastest response and recovery times compared to the other reviewed materials.

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