Study on Graphene-Metal Oxide Semiconductor Nanocomposite Based Sensors for Detection of Volatile Organic Compounds at Low Temperature

(Index no.: 38/20/Chem./27)

ABSTRACT

Non-invasive diagnosis of different diseases via human exhaled breath analysis has been recognized as a promising technology. It's worth mentioning that in exhaled human breath several VOCs are present at ppm/ppb level concentration and some of them are identified as breath biomarkers; viz., ammonia for renal diseases, acetone for diabetes, toluene for lung cancer, etc. Though recently certain spectroscopic techniques are being used for non-invasive diagnosis of diseases; however, real-time application requires development of selective VOC sensors for precise detection of low concentration VOC.

In this purpose, among various types of sensors, chemiresistive metal oxide semiconductor (MOS) based sensors already proved their efficacy. Although MOS-based sensors are suitable for versatile gas sensing applications, but, in pristine form their potential applications are hindered due to their high operating temperature, low sensitivity, poor selectivity, etc. Different strategies are being adopted to get rid of the short-comings of MOS-based sensor, either engineering of heterojunction-based nanocomposites or metal ion doping in pristine lattice. Such functionalizations of pristine lattice facilitate the sorption of gas molecules via defect site generation and thereby boost the sensing response. Carbonaceous nanomaterials are regarded as highly promising composite materials due to their high charge carriers' mobility that facilitates the electronic interaction during gas sensing. Now, reduced graphene oxide (rGO) is one of the best carbonaceous materials which provide a large specific surface area with enhanced number of active sites for adsorption of gas molecules. Therefore, less activation energy is required for the interaction between gas molecules and the sensing materials which reduces the operating temperature of the sensor. The elimination of the heating element makes the fabrication of the sensor very simple and its durability also improves. Therefore, in the proposed Ph. D. dissertation work, the prime goal was to develop graphene-metal oxide semiconductor nanocomposite based sensors for selective detection of VOCs at a low operating temperature.

At first, $ZnO-SnO_2$ binary nanocomposites were synthesized and further decorated with rGO. The optimum rGO decorated $ZnO-SnO_2$ nanocomposite showed a significant decrease in optimum operating temperature from 300°C to 150°C. The sensors exhibited their high

performance to detect very low concentration (~ 1 ppm) of acetone and ethanol in presence of many other interfering gases with quite good stability. The primary objective of this work was to obtain the optimum operating temperature at ambient conditions, i.e., at room temperature. Therefore, in the next chapter, rGO decorated $NiO-SnO_2$ nanocomposite based sensors were fabricated and VOCs (acetone and ethanol) detection was achieved at room temperature. Nevertheless, the selectivity to a specific VOC was still remained as a challenge.

Among higher transition metal oxides, WO_3 is a prolific gas sensing material and so in the following work pristine WO_3 was doped with Fe^{3+} and further nanocomposite was synthesized with rGO to obtain a promising VOC sensor. The as-prepared nanocomposite-based sensor exhibited an excellent selectivity towards acetone with rapid response/recovery time and long term stability; however, the operating temperature of the sensor was a little bit higher (~ 130°C). Low temperature operated selective acetone sensor was obtained, by changing the dopant ion from Fe^{3+} to Cr^{3+} in rGO decorated WO_3. This induced crystalline phase change from monoclinic to hexagonal WO_3, accounted for room temperature acetone sensing performance with better sensing response.

Among lower transition metal oxides, iron oxide is considered as conventional gas sensing material; so in the dissertation work, iron oxide was doped with Cr^{3+} followed by decorated with rGO. This work revealed a temperature dependent transition of sensing response from n-type (at higher temperature) to p-type (at lower temperature). Even these sensors also demonstrated a selective acetone sensing performance at room temperature.

Some of the developed room temperature operated sensors also implemented for discrimination of exhaled breath of diabetic person from healthy person in terms of sensing response towards the acetone concentration present in those breath samples.

In a nutshell, in this thesis work, VOC sensing performance of different MOSs based sensors were delineated. Their sensing performance was improved in terms of working temperature reduction, enhancement of sensing response, and selective acetone sensing, either by formation of binary nanocomposite or by doping of metal ions and further introduction of rGO. The sensing mechanism of the sensors was elucidated by schematic band diagram modeling. This dissertation work unveiled the selective ppm-level acetone sensing performance at ambient condition and paved the way for non-invasive diabetes detection via exhaled human breath analysis.

Susmita Kundu 27/02/24
डॉ सुष्मिता कुंडु
Dr. Susmita Kundu
प्रमुख वैज्ञानिक / Principal Scientist
कार्यात्मक पदार्थ एवं उपकरण विभाग
Functional Materials & Devices Division
सीएसआईआर-केंद्रीय काँच एवं सिरामिक अनुसंधान संस्थान
CSIR-Central Glass & Ceramic Research Institute
१९६, राजा एस. सि. मल्लिक रोड,196, Raja S. C. Mullick Road
कोलकाता-७०० ०३२, भारत, Kolkata-700 032, India

Sovandeb Sen 27/2/24