Influence of TiO_2 precursor variation in GO/TiO_2 composite for gas sensing applications using quartz crystal microbalance

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1. Introduction

Graphene based materials are highly used as conductors or insulators. However, Literature has shown that graphene-metal oxide hybrid composite provide a higher output in sensor applications upon chemical modification. The choice of the second material combined with graphene or graphene oxide (GO) depened on the type of the application. Among such applications, gas sensing is expected to progress by graphene oxide hybridization with metal oxide and by advancing the sensing techniques [1].

TiO_2 has been prepared by various research groups using different precursor materials. By changing the precursor materials, precursor amount, calcination temperature, additives and acidity, TiO_2 with different morphologies, phases, and sizes could be obtained [2]. The key point of this variation of the TiO_2 and incorporating it with other materials is directly related to its applications. The outcome of the applications is highly dependent on the properties of the material.

The main aim of this research is to develop a graphene oxide based novel composite incorporating TiO_2, which could be utilized as a gas sensor at room temperature. Quartz crystal microbalance (QCM), which provides precise readings, would be used as the measuring technique. Gases causing the change of oscillation frequency after adsorption can be achieved via coating a layer of sensitive substrate on the surface of the quartz crystal electrode regardless of its conductivity. The choice of sensing material is particularly crucial to the working mechanism of the QCM gas sensor, but not the type of gas, as long as a nanogram mass change is taking place in the system.

2. Methodology

In this research, GO has been prepared using typical the modified hummers method. The initial preparation of GO/TiO_2 composite, was conducted using ammonium hexaflorotitanate (AHFT) as the TiO_2 precursor under liquid phase deposition method. However, this composite preparation does not undergo any annealing process, which is usually followed by TiO_2 preparation to remove any unrelated elements. The main reason behind using the non-annealing procedure is that the composite needs to preserve the GO structure the same way, without turning into reduced GO (RGO). In addition to the use of AHFT, three other Ti precursors ($TiCl_4$, titanium (IV) isopropoxide, titanium (IV) butoxide) have been used for the preparation of the GO/TiO_2 composite via sol-gel method. Further, all the TiO_2 types and composites are characterized in detail to find the elements available in the material.

A domestic gas sensing device which functions by dynamic flow method, has been used to conduct all the gas sensing experiments. QCM oscillator circuit is designed to drive the quartz at its resonance frequency and to use it as a gas sensor. N_2 gas has been used as a carrier gas and ethanol vapor has been used for initial sensing trials of the materials.

3. Results and discussions

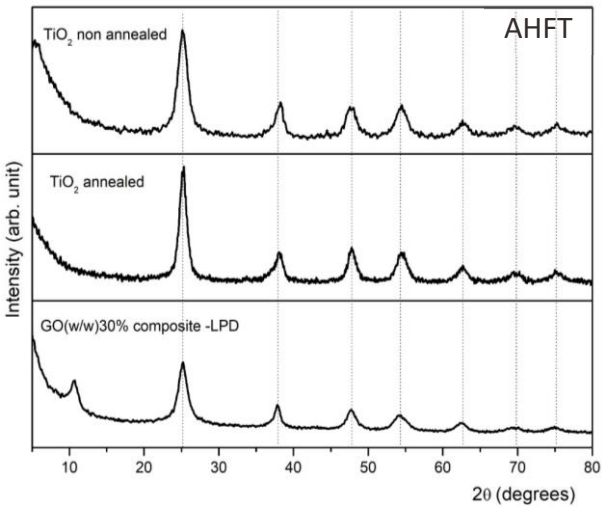

Fig. 1 XRD patterns of annealed TiO_2, non-annealed TiO_2 and GO/TiO_2 composite [GO(w/w) = 30% in the precursor solution] prepared with AHFT

The anatase phase of which the peaks at 2θ values of 25.2º, 38.3º, 48.5º, 54.1º and 63.1º are correctly identified for all the X-ray diffractograms of TiO_2 with AHFT. (**Fig. 1**) The vital factor is that AHFT utilized non-annealed TiO_2 and composite has comparable crystallite size showing proper crystalline particle formation. Upon the formation of the GO/TiO_2 composite, only AHFT utilized composite displays both GO as well as the TiO_2 peaks properly.

According to **Fig. 2**, composites prepared with

TTIP, and TTBO showed some peaks related to C=C and C-O with Ti-O-C peak region around 1000-1400 cm^{-1} in FTIR. However, such peaks are not clearly observed for $TiCl_4$ utilized composite. Further, a peak at 1400 cm^{-1} is observed for AHFT used composite, indicating that N-H could be attached to the surface of the sample. Since a peak at 1208 cm^{-1} is not observed, we can interpret that no F is bonded to C as C-F but available on the TiO_2 surface.

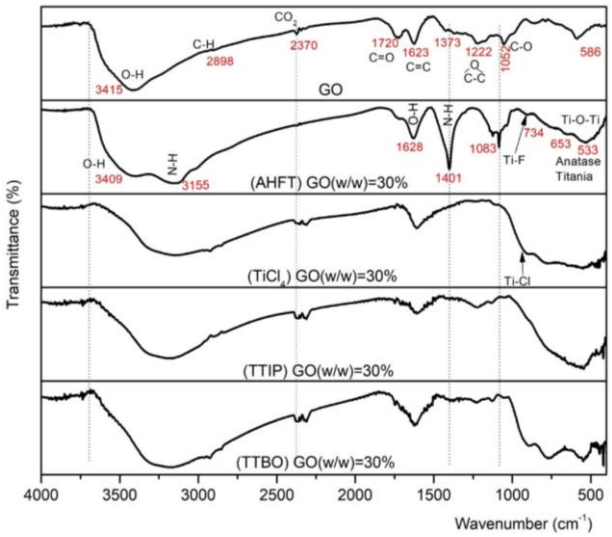

Fig. 2 Figure 4.6 GO and GO/TiO_2 composite of 30% GO(w/w) prepared with different TiO_2 precursors

From the dynamic gas flow device with QCM, the EtOH vapor detection range has been obtained from 20,000 ppm to 12 ppm. The annealed TiO_2 samples showed the typical gas sensing patterns where the frequency shift value is higher for TTBO utilized TiO_2 sample.

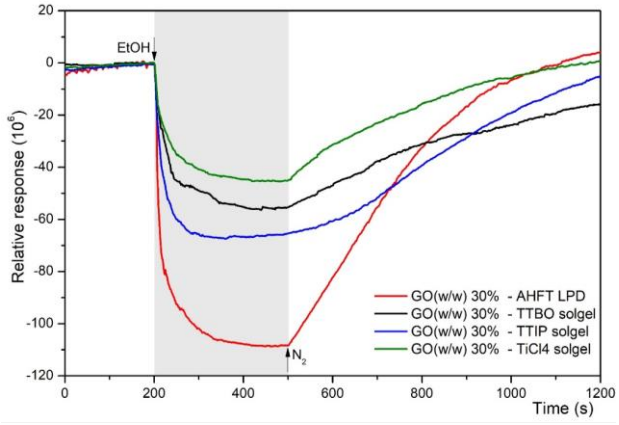

Fig. 3 Response graphs for GO/TiO_2 composite (30% GO) with different TiO_2 precursors upon exposure to 5000 ppm EtOH

Fig. 3 shows the vapor adsorption ability of GO/TiO_2 composite (30% GO w/w) prepared with for different TiO_2 precursors. The composite prepared with $TiCl_4$, TTIP, and TTBO displayed lower ethanol vapor adsorption as well as a slow desorption process. Here, the most acceptable gas sensing behavior was observed by the composite prepared with AHFT precursor. The AHFT TiO_2 utilized composite and the bare TiO_2 under annealed and non-annealed conditions followed a similar gas sensing pattern. Since the frequency shift value reaches to the initial level during the desorption process, it is safe to indicate that all the reaction taking place during adsorption are physisorption.

4. Conclusions

The most acceptable gas sensing behavior was observed by the composite prepared with the AHFT TiO_2 precursor. The GO/TiO_2 composite prepared with AHFT follows a similar gas adsorption and desorption patterns to the bare TiO_2 prepared under annealed and non-annealed conditions. The ethanol adsorption sensor response value is higher for the GO/TiO_2 composite for all the Ti precursors compared with TiO_2 only samples. Since fluorine is a highly electronegative element, the attachment of fluorine on the surface creates more surface-active sites. Therefore, we can conclude that among different TiO_2 precursor materials used for the preparation of GO/ TiO_2 composite, the most suitable one for sensing is composite prepared with AHFT utilized TiO_2. Additionally, the composite sensing ability was tested with different GO ratios in the AHFT precursor solutions. The results revealed that depending on the type of testing vapor, the most suitable composite can vary between 30% GO and 50% GO. Further we can conclude that QCM based room temperature gas sensor is quite capable in real time sensor measurements. Depending on the variation in surface substrate, the gas adsorption of different vapor kinds are easyly detected using this kind of QCM gas sensor.

References

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