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Preparation and sensing characterization of hybrid iron oxide/polyaniline/reduced graphene oxide at room temperature

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Abstract

Building materials, plants, paints, chemicals, and fossil fuels combustions all emanate volatile organic compound (VOC), which influence our health and everyday lives. Therefore, the ability to detect VOCs at room temperature is very essential. This study focused on interdigitated electrode (IDE) sensor based on the hybrid nanoparticles of iron oxide (Fe_3O_4), polyaniline (PANI) and reduced graphene oxide (rGO) and its sensing mechanism towards 300ppm acetone was investigated. The hybrid material was synthesized through in-situ method and deposited on the IDE using drop-cast method. X-ray diffraction shows that all unary materials were present in the hybrid nanoparticles and the crystallite size calculated was 4.49nm. The response and recovery time for the hybrid material towards 300ppm acetone was 2.73min and 2.67min, respectively which shows a great improvement compared to response and recovery time of single material of Fe_3O_4. The IDE based on hybrid materials sensor in sensitive and reversible, making it suitable for human health and environmental safety application.

Keywords: Interdigitated electrode (IDE), hybrid material, volatile organic compound (VOC), sensing application

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1. Introduction

One of the major sources of environmental problems in recent years has been the emission of hazardous compounds from various factories. To ensure a safe living environment, trace sensing devices are required to detect these gases [1, 2]. Sensors for detecting these gases at trace levels are critical for maintaining a safe living environment. In this way, many forms of gas sensors were used for detecting these gases such as calorimetric [3], conductometric [4], potentiometric [5], catalytic [6] and chemical [7]. The chemiresistive sensors were widely used because of their high selectivity, sensitivity, ease of processing, compact in size, lower process temperature and low electrical consumption. Due to some drawbacks of the sensors mentioned above, nowadays, the advances in low temperature processing nanomaterials have enabled alternate ways for embedding sensor layers on diverse substrates in a straightforward manner like IDE [8].

IDE is one of the most promising approaches to dealing with the problems of sensitivity, simple, user-friendly, reliable, fast, less expensive, portable and multi-analyte detection. Sensors of various types have been developed for food, water, security, agriculture, military, and medical quality control which has been a promising platform as it provides miniaturization of electrodes in sensor devices [9-12]. Despite of the design of the sensor platform, the selection of materials as the active layer of the sensor also plays a crucial part to improve the performance of the sensor.

Metal oxide-based gas sensors are the most promising for monitoring hazardous volatile organic compounds (VOC). They are in high demand in a variety of fields, owing to their numerous advantages, which include strong response, small dimensions, ease of use, fast response, stable repeatability for reuse in the same process, simplicity in fabrication, low detection limits, inexpensive and low energy consumption [13-15]. Among the huge variety of materials studied, inorganic semiconductor oxides (usually SnO_2, ZnO, TiO_2 and Fe_2O_3) have garnered the

greatest attention and constitute a significant portion of commercially available gas sensors [16-18]. In recent years, there have been further advancement in the comprehension of metal oxide that can be exploited for gas sensing application and new material hybridization have been recognized that may improve the sensor performance such as lowering the operating temperature of metal oxide semiconductor (MOX) sensor [19, 20].

Carbon nanotubes and graphene stand out among the carbon-based materials due to their high carrier mobility (conductive qualities), high quality crystal lattices, and low electrical noise. Furthermore, their excellent mechanical and thermal qualities make them ideal for flexible electrical devices. While having great conducting properties, carbon nanostructures have a number of drawbacks for sensor applications, including a long recovery time, insufficient selectivity, and poor interaction with gas molecules. Carbon nanomaterials can therefore be synthesized by functionalizing or combining them with other materials to create hybrid platforms with improved sensing capability, for the detection of VOC [21].

As a result, in this study, we will functionalize graphene with metal oxide nanomaterial to open a large energy gap in graphene via the quantum confinement effect in order to increase sensor performance.

2. Materials and methods

2.1. Materials

Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), iron (III) nitrate ($FeNO_3)_3.9H_2O$, nitric acid (65%), hydrochloric acid (37%), ascorbic acid and graphene oxide (GO) paste (95 wt% purity) was all purchased from Merck. De-ionized (DI) water is used in all preparations. IDE with size of 5mm × 5mm was purchased from NovaScientific.

2.2. Synthesis of iron oxide (Fe_3O_4)

Fe_3O_4 was synthesized using Massart's procedure as mentioned in [22, 23] by mixing $FeCl_3$ and $FeCl_3$ together. The mixture was added to ammonium hydroxide solution. The instantaneous black magnetite precipitate (Fe_3O_4) was formed. The solution was washed with DI water a few times and nitric acid was added to it. Finally, ferric nitrate solution was mixed in the solution to obtain the final product. The procedure is illustrated in Figure 1.

2.3. Synthesis of polyaniline (PANI)

The conducting polymer, PANI was prepared by chemical oxidative polymerization of aniline. In the presence of hydrochloric acid HCl and ammonium peroxydisulphate (APS) were used as oxidants. First, 1 M of HCl protonic acid and 0.2M of aniline monomer solution were placed in a beaker and mixed at a temperature of about -4°C. Then 0.25M of APS was added into the above solution in an aqueous medium using the dropped wise method. Both solutions were mixed in a beaker and stir to polymerize the mixture. The precipitate PANI was collected, filtrate and washed as mentioned in the previous work [22].

2.4. Synthesis of RGO

The rGO was prepared according to previous work [24, 25, 26] where 10g of ascorbic acid with 100ml of distilled water and stirred in 0.1mg/ml of GO solution. The, the sample was heated up at 95˚C for 1 hour and sonicated for about 15mins, filtered, and washed with distilled water.

2.5. Synthesis of the hybrid material

The hybrid material was prepared using in-situ method where 10wt% of iron oxide and PANI were dissolved in GO paste with ascorbic acid solution and heated up for 1 hour at 95˚C before being centrifuged and washed for few times.

3. Results and discussion

3.1. Microstructural study analysis (XRD)

Figure 2 shows the typical XRD pattern of Fe_3O_4 nanoparticles (NPs) synthesized using Massart's procedure. It is clear that the cubic spinel structure of Fe_3O_4 NPs occurred at the angles of 2θ = 30.4°, 35.6°, 43.1°, 57.2° and 62.7° with planes of (200), (311), (400), (511) and (440), respectively. All diffraction peaks are indexed to cubic spinel structure of Fe_3O_4 NPs with lattice constant, a = 8.39 Å. The results are consistent with pure Fe_3O_4 NPs phase (ICDD No. 96-151-3305). The diffraction pattern of PANI can be observed at a range of 2θ: 9.21°, 14.96°, 20.79°, 25.43°, 27.01° and 29.89° which corresponding to d9.6, d5.9, d4.2, d3.5, d3.3 and d2.9. Based on the XRD pattern of RGO, a small peak can be seen approximately at 16.3°. According to Jayachandiran et al. (2018), when reducing rGO from Graphene Oxide (GO), the diffraction peak at around 11° will disappeared and will be replaced by a new peak at around 24° which correlate to the removal of oxygen functional groups during the reduction process of GO [27].

However, in Figure 3, a broad peak was present approximately at 4-14° and 25-40°. This might be due to incomplete process of reduction from GO to rGO. The incomplete process is because of the concentration of GO in the solution [28]. The peak of the hybrid material occurred at the angles of 2θ=25.36°, 30.45°, 35.72°, 43.47°, 57.43° and 63.02°. These peaks are in accordance with all the single materials where the peaks along 2θ: 14-30° is related to the interaction of PANI and graphene and the rest of the peaks are in accordance with Fe_3O_4. The crystallite size of

these materials was calculated using Debye-Scherrer Equation,

$$\mathbf{D = \frac{K\lambda}{\beta cos\theta}}$$

Where D is the average crystallite size in nm, k is the shape factor, often assigned a value of 0.9, λ is the x-ray wavelength of x-ray radiation (1.54Å), β is the full width at half maximum (FWHM) measured in radians, θ is the half angle measured in degrees. The crystallite size of Fe_3O_4, PANI and hybrid sample was calculated to be 6.34, 5.5 and 4.49nm respectively.

3.2. Sensing characterization

The sensor responses of the single material Fe_3O_4 and the hybrid that contains 10wt% of Fe_3O_4 and PANI were shown in Figure 4 and 5 upon exposure to 300ppm of acetone. The single material Fe_3O_4 was conducted at 300°C while the hybrid sample was conducted at room temperature. All samples were first purged with nitrogen for about 5min and purged with acetone. The sensor's response as a change in resistance and the response as well as the recovery time were studied. The change in the response of the sensor is due to the change in the texture and size of the active material [8]. The base resistance of the single material is higher compared to the hybrid sample. The response of the hybrid sample was decreased to 2.6%.

This is because smaller sample have higher surface area which can absorb more analyte and eventually increase the sensitivity of the sensor. The response and recovery time for both Fe_3O_4 and hybrid samples were 2.19/3.6min and 2.73/2.67min, respectively. This shows an increasing of response time and decreasing of recovery time after the sample is being hybridized, however the operational temperature of the sensor has been reduced to room temperature. It is clear that IDE sensor based on the hybrid materials has better sensitivity when compared to single material Fe_3O_4.

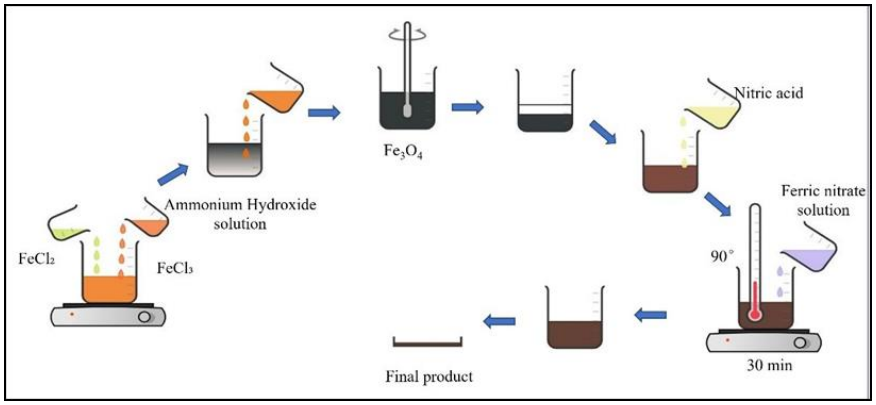

Fig. 1: Synthesis procedure of Fe_3O_4

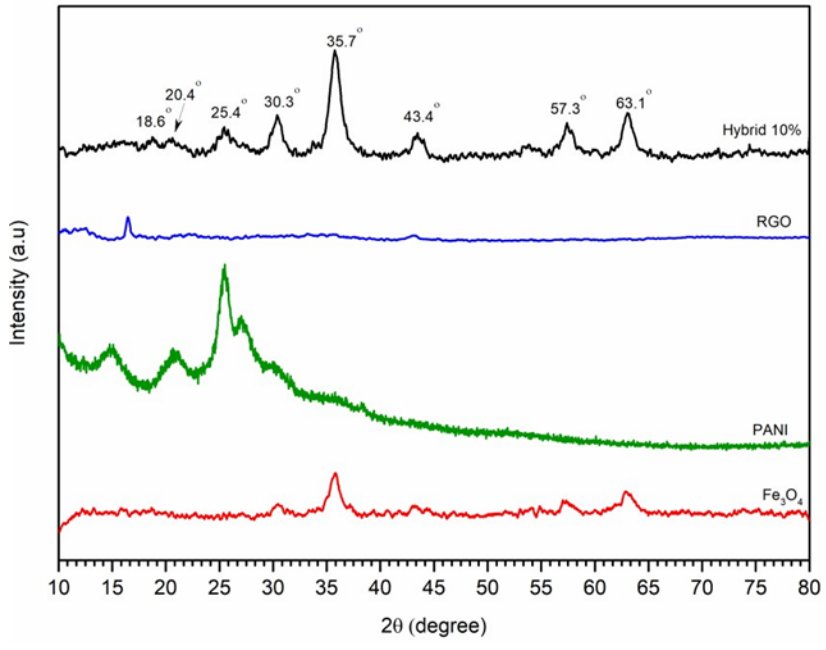

Fig. 2: XRD pattern for all samples

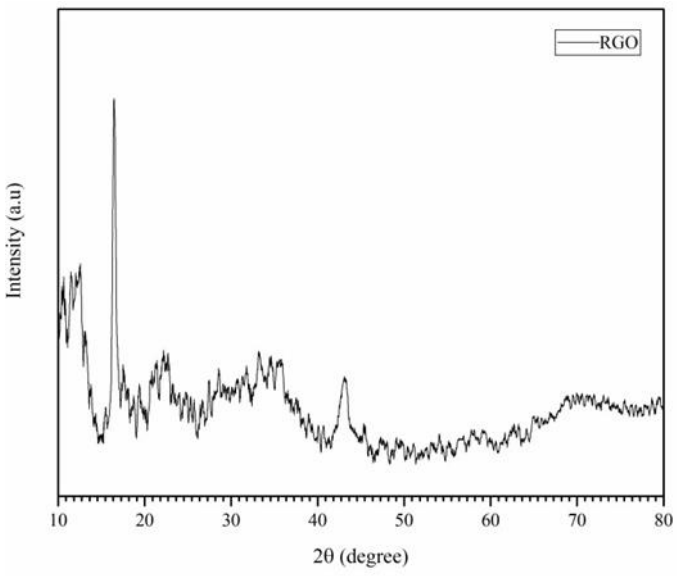

Fig. 3: XRD pattern for rGO

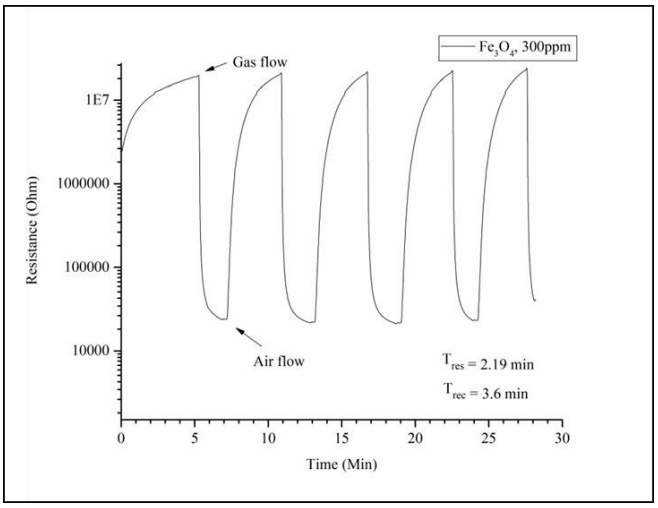

Fig. 4: Sensor response for single material Fe_3O_4 at 300°C

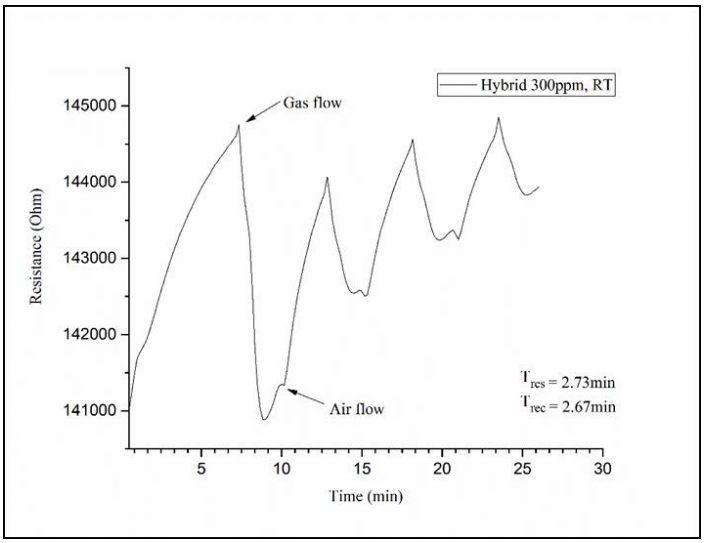

Fig. 5: Sensor response for hybrid nanomaterial at room temperature

4. Conclusions

In general, the fabrication of ternary hybrid nanocomposite materials has been synthesized and the characterization analysis shows that the ternary hybrid material exhibits a great composition where they can blend homogenously together. XRD analysis showed that all peaks from the hybrid nanocomposite matched well with the individual materials and the crystallite size calculated are less than 10nm. From the sensing characteristic, the response and recovery time of unary material Fe_3O_4 was 2.19min and 3.6 min, respectively at operational temperature of 300°C. However, when it was hybridized with PANI and rGO, the operational temperature can be lowered down to room temperature and response and recovery time was 2.73min and 2.67min, respectively. This shows that the hybrid material can create a great synergistic effect as active sensing material to improve the sensing performance of the IDE. However, further studies need to be done to investigate the chemical and physical characteristic of the active materials so that alteration can be made to further lower down the response and recovery time as well as improve the sensitivity of the sensor.

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