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Synthesis And Characterization Of Nano-fibres Graphene Oxide For Sensing Humidity

M. Arif[1], N. Saba[2], A. Naveed[1], M. Sadiq[3], S. Afridi[1], F.H. Khan[5], M. Asif[2]*

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Abstract

Relative humidity is the prime parameter in industrial processes, which are measured through the ceramic, metal oxide and polymeric sensors. Ceramic and metal oxide sensors show nonlinear resistive behaviours with increasing relative humidity and high sintering temperature for hydro-desorption. The transformation of ceramic and metallic sensors with polymeric sensors is due to its eco-friendly synthesis fabrication, less heat-intensive and high sensitivity. In this research work, a polymeric sensor of enhanced electric properties with sustainable captive and resistive response was synthesised from nano-fibres graphene oxide for sensing humidity. The synthesized graphene oxide through the modified Hammer method was mixed with poly-vinyl alcohol (GO/PVA) in the ratio of 5 wt % for four hours at 90 ºC. Nano fibres of graphene oxide and poly-vinyl alcohol (GO/PVA) solutions were obtained at the 24V DC electric field; 0.5 ml/h feed rate and 10 cm tip-to-collector distance through electrospinning. GO/PVA fibres were deposited on the silver inter-digited electrodes of 8mm and five combs of 20ìm consecutive distance. SEM analysis shows that the fibres were in the nano-range with no major cracks while XRD and FTIR spectrum investigated the fingerprints and functional groups of GO and GO/PVA respectively. The parametric study of resistive and capacitive was analysed at different response and recovery times at various frequencies in the range of 0 % to 82% relative humidity.

Keywords: Electric Characterization; Electrospinning; Graphene Oxide; Inter-digited Electrodes;

1. Introduction:

Humidity is an important factor of consideration in the synthesis, manufacturing and fabrication of many industrial processes [1]. It is mostly expressed in terms of relative humidity (RH). Relative humidity is the term for the ratio of the actual moisture density to the saturation vapour density at a given temperature [2]. These vapours in the atmosphere are a key ingredient to some process but to others, it proves catastrophe which can be measured through various electronic equipment such as Psychomotor, lithium chloride dew point, resistive humidity, capacitive humidity, thermal conductivity and Gravimetric humidity sensors [3]. RH sensors are further separated into three classes: ceramic, metal oxide semiconductor and organic polymers on basis of the dielectric material used in it. Both inorganic and polymeric sensors are used in the processes for various applications. [4].

Inorganic ceramic-type sensors can be designed by exploiting either semiconducting or dielectric metal oxide composites [5]. They are not compatible with

[1] *Center for Advanced Studies in Energy, University of Engineering and Technology, Peshawar, Pakistan*

[2] *Department of Electronics, University of Peshawar, Peshawar, Pakistan*

[3] *Department of Mechanical Engineering University of Engineering and Technology, Peshawar, Pakistan*

[5] *Department of Industrial Engineering, University of Engineering and Technology, Peshawar, Pakistan*

Corresponding Author: arif.khattak@uetpeshawar.edu.pk

the standard of IC fabrication technologies because of nonlinear resistive behaviour concerning increasing humidity. Furthermore, Ceramic physical and chemical stability are good, but desorption of water molecules for ceramic sensors is difficult, which usually needs an external heat cleaning process [6]. On the other hand, polymeric-based humidity sensors are environment friendly and their capacitance increase sharply with RH level, change of conductivity in organic humidity sensor is due to ionic and electronic conduction, and response/recovery time is high in resistive mode [7]. The transformation of ceramic and metallic sensors with polymeric sensors is due to its eco-friendly synthesis fabrication, less heat-intensive and high sensitivity [7-8]. These polymeric-based sensors show excellent electronic, and optical properties and high sensitivity due to functional groups [9].

Polymeric-based sensors are made of organic macromolecules that measure the quantity of moisture as a stimulus in the atmosphere [10]. The moisture filling of micro-pores of the sensing polymeric film is responsible for the physical change. Furthermore, polymeric sensors are flexible, small areas, low cost and lightweight technology used in light-emitting diodes, organic lasers, solar cells and field-effect transistors [11]. In addition to it, the performance of the sensor can be manipulated accordingly simply by adjusting the shape of the pores, and the size of the active sensing layer, and in effect prompting a better response behaviour towards relative change in surrounding humidity [12]. However, the synthesis of polymeric sensors is expensive and complex due to multiple steps.

In this research, a humidity sensor was fabricated with a miniature size and simple structure to shrink the fabrication cost and efficient working mechanism and sensing properties. Graphene Oxide and polyvinyl alcohol nano-fibres are cast-off as the sensing material and emplaced on top of the silver inter-digited electrodes. The performance of the sensors made through nano-fibres is compared and measured with various commercial humidity sensors.

2. Materials and Characterization:

2.1 Synthesis of Graphene Oxide (GO)

In the present study, GO is extracted by the modified Hummer method. In modified Hummer's method, GO is prepared by oxidizing graphite without using $NaNO_3$, which proved that H_2SO_4 and $KMnO_4$ are capable enough to oxidize graphite [12]. GO is prepared by oxidizing graphite without using NaNO3, which proved that H2SO4 and KMnO4 are capable enough to oxidize graphite. A dark black solution was obtained by mixing graphite powder of 1 gram with 25 ml of sulphuric acid (H2SO4) for 2 hours. A dark green solution was obtained when potassium permanganate (KMnO4) of 3 grams was added slowly at 20 ºC. The prepared solutions were oxidized through 100 ml of deionized water while hydrogen peroxide was added to stop the reaction. Prepared graphene oxides were washed with hydrochloric acid (HCl) and deionized water solutions several times to remove the Mn^{2+} ions and other impurities. GO was dried at 90 ºC for 24 hours [14].

2.2 Synthesis of Graphene Oxide Nano-fibres and Sensor:

Prepared GO was mixed with poly-vinyl alcohol were mixed in 10 ml of deionized water for two hours at 90 °C. To control the parametric morphology electrospinning was done at the 24V DC electric field; 0.5 ml/h feed rate and 10 cm tip-to-collector distance. Prepared GO/PVA fibres were deposited on the silver inter-digited electrodes of 8mm and five combs of 20ìm consecutive distance. GO/PVA fibres were deposited on inter-digited electrodes through deionized water. The electrode was heated at 60°C to make it completely dry on electrodes for good electric contact.

3. Results and Discussions:

3.1 X-Ray Diffraction (XRD) Analysis

The XRD characterization of the synthesized sample is shown in Figure 1. It has similar characteristics to commercially available pure graphene. The peaks are detected at the same angle. The major peak shows the crystalline structure of both GO. However, smaller peaks are also observed in synthesized GO, which is attributed to the presence of impurities in the sample.

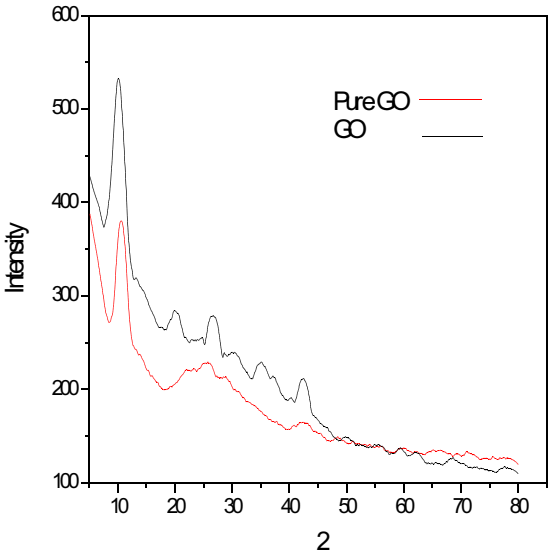

Figure 1: XRD of Pure GO and Synthesized GO

3.2 Fourier Transform Infrared Spectroscopy (FTIR):

The FTIR results for GO, PVA powder and GO/PVA nano-fibres are shown in Figure 2. The results show that the GO and PVA when in powdered form, exhibit a smaller peak of the OH group but once the nano-fibres are formed, the peak gets sharper in the 3000 to 3500 range on the x-axis. Similarly, the -COOH bound is visible in the 1500 to 2750 range on the x-axis; other epoxy groups are also visible in Figure 2. It is evident that after GO/PVA nanofibres the OH group becomes more dominant, increasing the hydrophilicity of the nano-fibres.

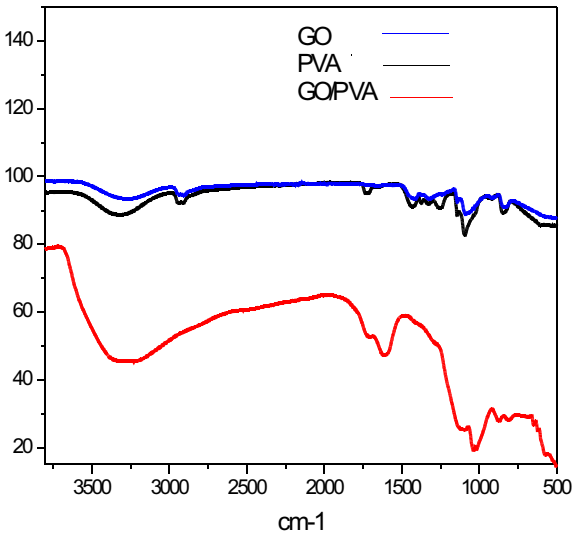

Figure 2: FTIR of the GO, PVA and GO/PVA fibres

3.3 Scanning Electron Microscopy Analysis:

The surface morphology of the fibres is investigated using an atomic force microscope (SEM) as shown in Figure 3. Results show that GO and PVA are blended well and exhibit smooth surface morphology of the fibres. They are very thin, having a diameter in the nano range. Few beads appeared at a distance attributed to the slight increase in speed during electro-spinning.

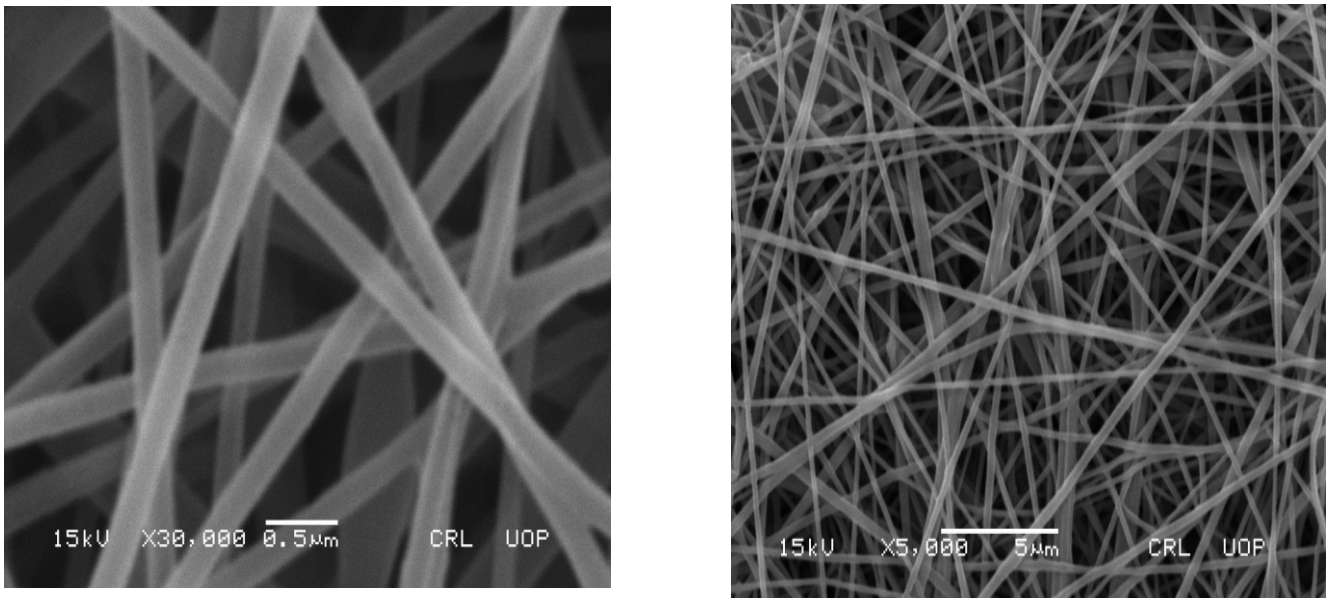

Figure 3: Surface Morphology of GO/PVA fibres

3.4 Resistive Response of the Sensor:

The resistive response of the sensor was measured by varying humidity concerning resistance at a certain frequency as shown in Figure 4. The relative humidity was increased from 30% to 85% while measuring the relative decrease in resistance concerning RH. The results show that with an increase in RH, the resistance decreases and saturates beyond 70% of the RH.

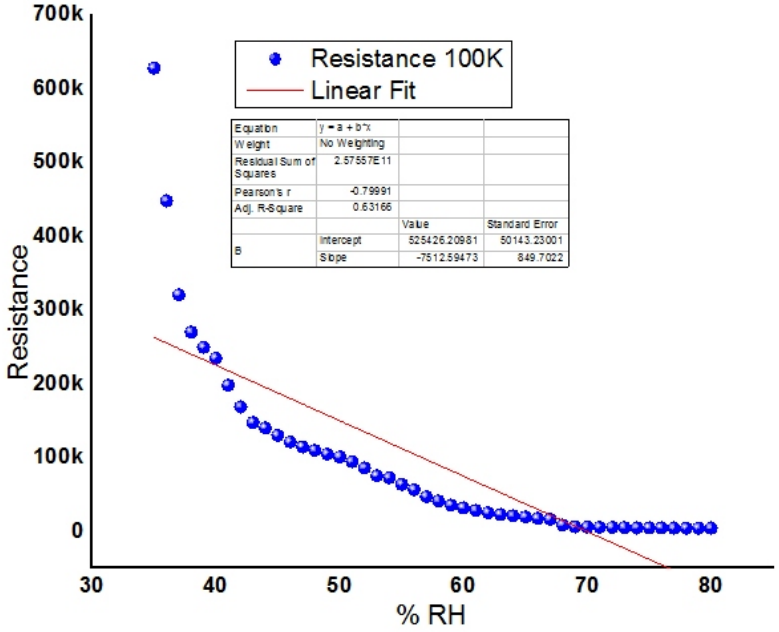

Figure 4: Resistive response of the sensor

3.5 Capacitive Response of the Sensor:

The capacitive response of the sensor is shown in Figure 5. The Dielectric of the capacitor increases when Sensor performance is measured at 100 KHz, 250 KHz, 500 KHz, 750 KHz and 1 MHz frequencies. The response of the sensor at 1 MHz is much more linear as compared to other frequencies. With the increase of the RH, the capacitive response of the sensor also increases, almost following a linear fit at higher RH.

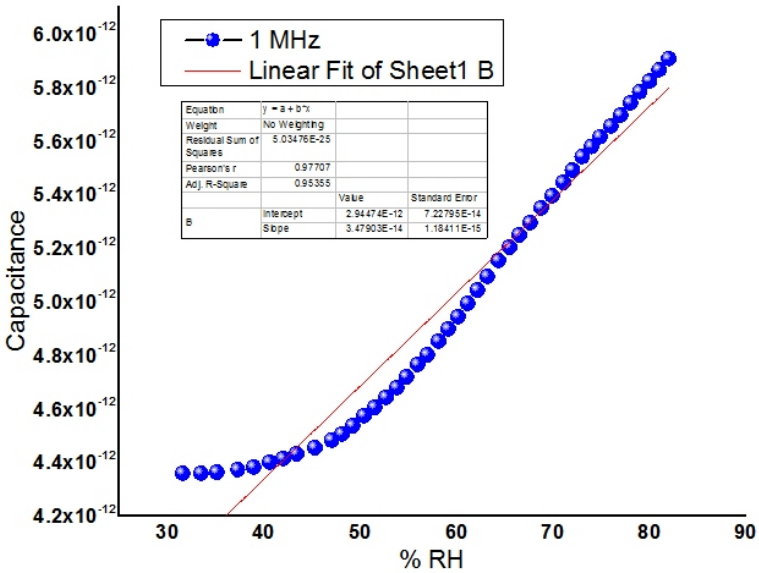

Figure 5: Resistive response of the sensor.

3.6 Response and Recovery time:

The response and recovery time are two important factors, which evaluate the behaviour of the sensor. GO/PVA sensor response and recovery time were studied at different frequencies, that is 100 KHz, 250 KHz, 500 KHz, 700 KHz and 100 KHz as shown in Figure 6. The Capacitance of the sensor is recorded at various frequencies with different levels of RH percentages. The rise and fall time of the sensor was recorded. The rise time of the sensor was recorded to be 140 seconds and the fall time of the sensor was 180 seconds for RH percentages of 31% and 82% respectively.

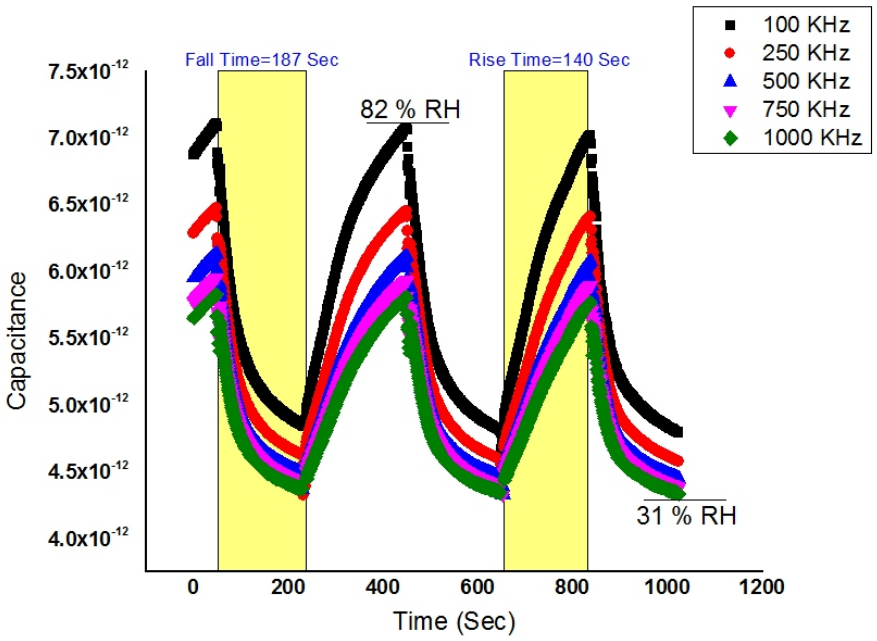

Figure 6: Response and recovery time

3.7 Hysteresis:

The hysteresis of the humidity sensor is shown in Figure 7. During the measurements, the humidity was infused in the chamber and the capacitive response of the sensor was noted. Followed by the removal of humidity, to check the capacitive response of the sensor. The capacitance was recorded for the decrease in humidity for 128 seconds. The humidity was first increased from 0-80%, followed by a decrease back to 0%. Consequently, the capacitance reaches back to 4.4×10^{-12}.

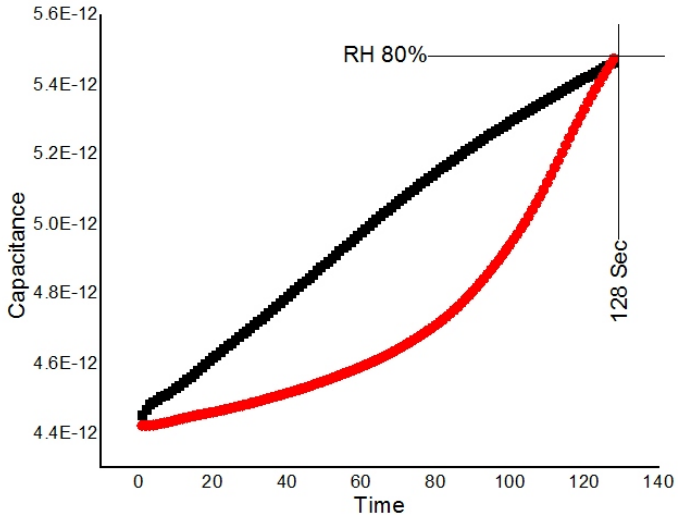

Figure 7: Hysteresis (Capacitance Vs Time)

The linear increase in hysteresis shows that, as hysteresis increases, the sensitivity of the sensor also increases.

4. Conclusions:

In this work, a humidity sensor was fabricated in which graphene was oxidized through Hummer's method. Later on, a specific quantity of GO was mixed with PVA through continuous stirring and sonification. Structural characterization of GO performed using XRD showed consistent results with commercially available graphene. Fibres morphology, diameter and other characteristics were monitored using SEM. The presence of various bonds formation was observed using FTIR. Electrical characterization of the sensor shows that GO/PVA fibres have a good capacitive response as compared to a resistive response. Go/PVA fibres are potential candidates for utilization as sensors, due to easy fabrication, low cost and stability for a longer duration.

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