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GO: Ag Composites Materials for Dynamic Humidity Sensing Applications

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Abstract

Silver crystallite-graphene oxide (Ag-Nps/GO) composites are widely used for various applications and are an attractive material for next-generation nano-electronic devices, and we demonstrate their use in humidity sensors. Silver crystallite (Ag-Nps) is prepared through a single step by reduction method at room temperature. The resulting crystallite is a pure phase as confirmed through X-ray diffraction (XRD) without any traces of oxides or secondary impurities. The crystallite size is around 1 μm. These crystallites are blended with synthesized graphene oxide in a different weight ratio to make the composite. Various characterization techniques like scanning electron microscopy (SEM), UV spectroscopy, and XRD are used to understand structures and surface morphology. The composite is dropped on Al printed sensor (IDE). The humidity is varied from 5% to 55%, the conductivity decreases with an increase in humidity. The sensor has a fast response/recovery time reproducible. In conclusion, the present work describes a low-cost, novel strategy for synthesizing humidity sensor applications. The sensors can be used in applications like biomedical, food processing, agriculture, pharmaceutical, and microelectronics.

Keywords: *Graphene oxide, silver crystallite, composites, Scherrer formula, Rietveld refinement, Inter-Digitated Electrodes(IDE), humidity sensor.*

1.0 Introduction

In recent years as the technology shifted toward automated systems, the need for various kinds of physical and chemical sensors gained importance. It is well known that humidity plays a key role in all biological activities, making humidity sensors a basic component for industrial automation devices, agriculture, and human comfort. Among the various types of humidity sensors, the ones which are based on electrical properties such as capacitance and resistance are best suited for automatically controlled systems [1].

The emergence of nanotechnology has led to the synthesis of nanomaterials, inorganic nano-particles with high conductivity and surface area. Silver crystallites with graphene and its derivatives like graphene oxide (GO). These developments further widen the opportunity for microelectronics, sensors, and conductive inks for printing technology and have been increasingly used to replace conventional semiconductor devices [2]. Graphene oxide enhances the electrochemical properties of the composite as compared to using each nanoparticle individually. Silver crystallites show excellent catalytic activity in the field of sensors. Purity, shape, size, electrochemical properties, and the matrix of the composite extensively affect the performance of the sensors [3].

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In the present study, this paper briefly discusses the fabrication of high-performance, low-cost humidity sensors and simple one-step synthesis of highly conductive silver crystallite through the chemical reduction process and its composites with graphene oxide. Synthesis of highly pure and small particles was achieved and different compositions of Ag/GO were coated on the IDE and their I/V characteristics at different relative humidity were evaluated at room temperature.

Materials

All chemicals and reagents are used without any further purification. Sodium nitrate $NaNO_3$ (SD fine chemicals ltd 99% pure), Sulphuric acid H_2SO_4 (97% pure Thermo fisher scientific India Pvt Ltd), Potassium permanganate $KMnO_4$ (99% pure Loba chemicals Pvt Ltd), anhydrous Ethanol C_2H_5OH, Graphite Powder (98% pure Loba chemicals Pvt Ltd), hydrogen peroxide H_2O_2 (30% w/w solution Thermo fisher scientific India Pvt Ltd), Hydrochloric acid HCL (Thermo fisher scientific India Pvt Ltd), cellulosic dialysis membrane (Sigma Aldrich, 12kDa). All experiments were performed in de-ionized (DI) water (specific resistance 18.5 Mohm).

Preparation of Silver Crystallite

Silver crystallite was synthesized by reduction of silver nitrate ($AgNO_3$). 0.4944 mmol of $AgNO_3$ was weighed and taken in a hydrothermal reactor with 42ml of ethylene glycol and 2.3847 mmol of ascorbic acid. The solution was stirred for homogenous dispersion of the chemicals. The hydrothermal reactor was put in an oven for 8 hours with 1ºC increase per minute till the oven temperature reaches a maximum of 180ºC. After 8 hours the reactor was cooled to room temperature. The dark brown solution was decanted into a centrifuge tube, the solution was kept till the silver crystallite settles down. The top solution was discarded and the crystallites were washed with anhydrous ethanol to remove traces of elements left. Silver crystallite was dried overnight at room temperature.

Preparation of Graphene Oxide

Graphite oxide (GO) is initially synthesized by oxidizing graphite using the Hummers Method [4]. The contents of a round bottom flask equipped with a Teflon coated magnetic stir bar are added to a round bottom flask provided with a Teflon coated magnetic stir bar, and the contents are aggressively agitated; to prevent temperature increase, the flask is kept in an ice bath. Over 15 minutes, potassium permanganate (15g) is progressively added to the flask. When potassium permanganate is added to the solution in the flask, it changes into a green-colored suspension. The ice bath is then replaced with a 35°C water bath, and the suspension is vigorously churned for three hours, confirming graphite oxide development when the suspension turns a viscous dark brown color.

After that, the reaction flask is placed in an ice bath while 230 mL of ultrapure deionized (DI) water is gently added. By mixing 12 mL hydrogen peroxide with 700 mL ultrapure DI water, the remaining potassium permanganate is converted to manganese dioxide. Allowing the suspension to sit overnight changes the color to a brownish yellow color. Three cycles of centrifugation (8230g for 5 min), decantation, and re-suspension in 4 wt. per cent aqueous HCl solution wash the resultant graphite oxide; the 3-cycle procedure is repeated with ultrapure DI water. The sample was washed, rinsed, and centrifuged many times with ultra-pure DI water. To obtain GO powder, the sample was vacuum filtered and dried in a vacuum dryer at 50°C.

Preparation of Humidity Sensor

A fully flexible Inter-Digitated Electrode (IDE) was developed by Shridhar PM. The nano-composite of Ag/GO was sonicated for uniform dispersion and dropped on top of the IDE for uniform deposition. The IDE coated with Ag/GO was placed in a humidity-controlled environmental chamber for evaluating the humidity response of the fabricated sensor. The sensor was connected to the device via crocodile clips to experiment with variable relative humidity. The response of the printed device was recorded using Keithley 2450EC workstation equipped with Lab View program and analyzed using a custom LabVIEW application on a PC.

Results and Discussions

Scanning Electron Microscopy Analysis

Figure 1 shows scanning electron microscopy of graphene oxide. The sample was prepared by dropping prepared graphene oxide on a carbon tape, on magnification it shows that graphite layers were exfoliated during the oxidation process. From the images, it can be observed that the micrograph of graphene oxide film has a sponge-like porous structure. The sheets are not continuous; this distortion in the graphene sheets may be seen because of oxygen and different functional groups attached to graphene sheets

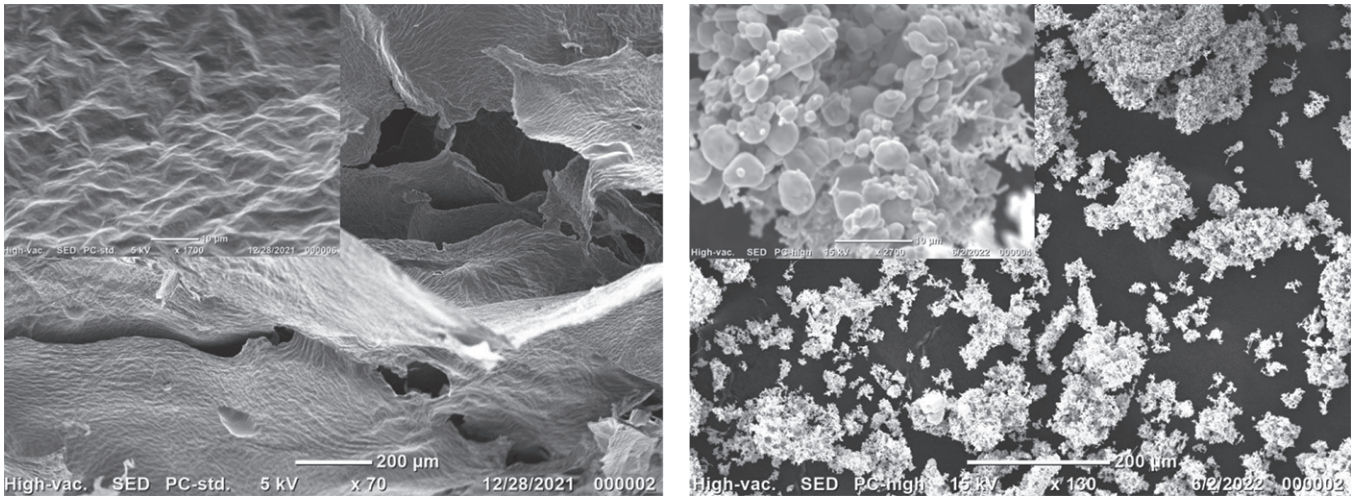

Figure 1: An SEM images of graphene oxide (b) graphene oxide at higher magnification (c) silver crystallites (d) silver crystallites at higher magnification.

during the exfoliation of graphite. On further magnification, it can be observed that graphene oxide has a discontinuous wrinkled sheet scaffold.

The SEM micrograph of silver crystallite was synthesized by hydrothermal reduction of silver nitrate; the SEM samples are prepared by dropping the crystallite on the carbon tape on magnification which is observed that spherical-shaped silver crystallite was formed. The average diameter of silver crystallite was found to be 0.5µm. The silver nanoparticles are seen aggregated which indicates that the particles are in direct contact. The shapes of silver particles are spherical and particles are aggregated into an irregular structure with an ambiguous morphology.

X-Ray Diffraction

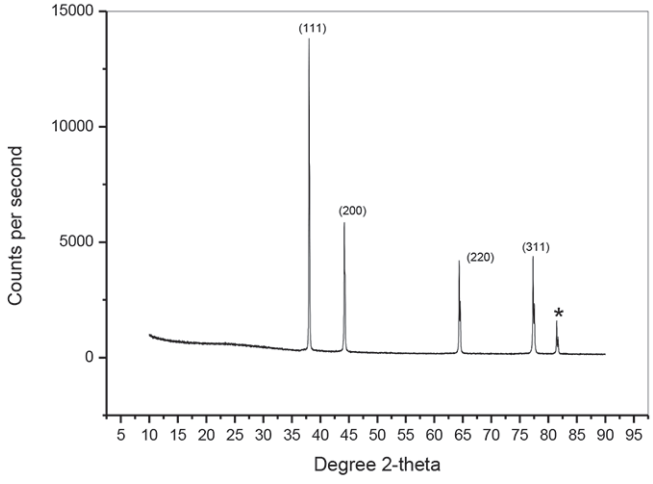

Figure 2: X-ray diffraction pattern of silver crystallites

Crystalline size and structure of silver crystallites were analyzed by XRD. Silver crystallites synthesized by chemical reduction of silver nitrate were confirmed by observing the peaks of the XRD image. Five distinct XRD peaks of 2θ of 35.1°, 44.3°, 64.7°, 77.5°, 82° can be assigned the planes (1 1 1), (2 0 0), (2 2 0), (3.1 1) this planes formation indicates face centre cubic (FCC) structure of silver crystallites. The average particle size can be calculated by the

Debye–Scherer formula $\left(D=\frac{K\lambda}{\beta\cos\theta}\right)$

Where D is particle size, K is Scherrer constant with the value ranging from 0.9 to 1, λ is the wavelength of the x-Ray source deployed in XRD, and β is the full width at half maximum of a peak located at any 2θ in the figure and θ is the angle measured [5].

EDX

The elemental analysis of the two nanocomposites was done by EDX (JOEL JCM-6000PL) at a probe current of 7.475 nA, acc voltage of 15kV, and energy range between 0-20kev to detect the purity of the composition. From Figure 3a optical absorption characteristic peak of carbon and oxygen is observed which indicates the presence of graphene oxide and further silver peak can be seen at 2.983 keV, indicating the presence of L-Ag. The elemental composition like Carbon (C) at 23.61%, Oxygen (O) at 5.27%, and Silver (Ag) at 71.11%. Similarly, from figure 3b it is observed the optical absorption peak of carbon and oxygen was seen at 0.277kev indicating the presence of graphene oxide, and another peak at 2.983kev indicating the presence of silver. The composition of elements like

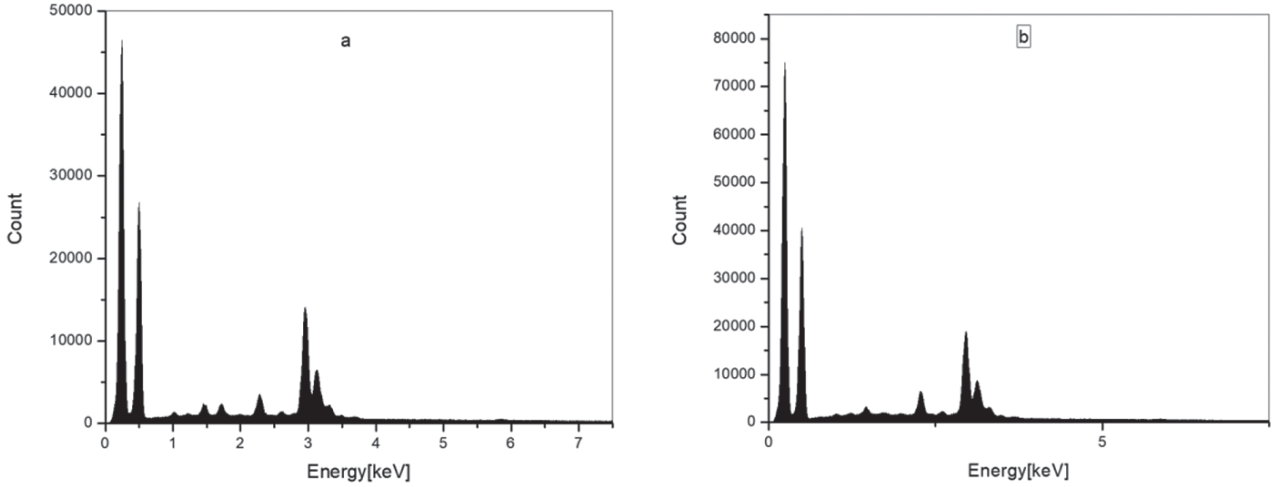

Figure 3: Energy Dispersive X-Ray Analysis (a) Ag/GO composite in the ratio of 1:1 (b) Ag/GO composite in the ratio of 3:7.

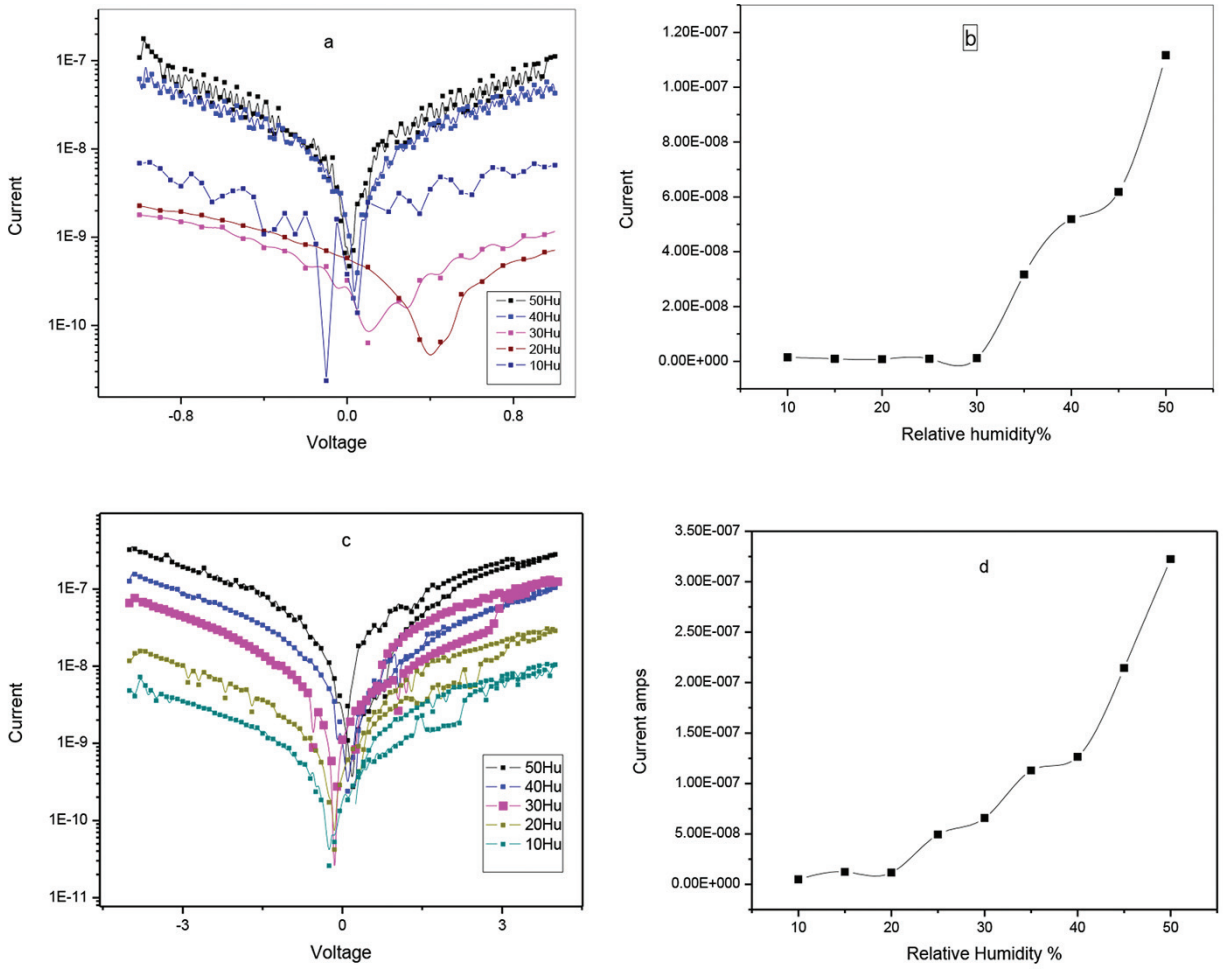

Figure 4: Current-voltage characteristics of silver crystallites with graphene oxide (a) I-V characteristics of Ag/GO of composition 1:1 at relative humidity ranging from 50 to 10, (b) variation of current with relative humidity% of Ag/GO of composition 1:1, (c) I-V characteristics of Ag/GO of composition 30:70 at relative humidity ranging from 50 to 10, (d) variation of current with relative humidity% of Ag/GO of composition 3:7.

Carbon(C) 28.79%, Oxygen(O) 4.92%, Silver(Ag) 66.29%, indicating a higher quantity of graphene oxide compared to the previous composition.

Humidity Sensing Properties

The commercially available humidity sensors are complex and expensive to fabricate. The proposed method will be useful for the fabrication of a simple humidity sensor. Synthesized silver composites with graphene oxide are used and the I-V curves are recorded. The logarithmic current-voltage is plotted from a potential of ±1V at room temperature 300 K. As it is evident from the I-V curve of the Figure (4a), Ag/GO of equal composition shows low conductivity of (11.16 μA) for an applied voltage of 1 V at 50% relative humidity. It is observed that the curve is symmetric in both the reverse and forward bias regions. The symmetry of forward and reverse bias indicates Ohmic charge transport. From Figures 4a and 4b it is observed that the current value decreases with a decrease in relative humidity %. A similar logarithmic plot of current-voltage has been plotted from a potential ranging ±4V at 300 K. From Figure 4c it is observed that the composition shows a relatively lower value of current (32.3 μA) for an applied voltage of 4V at 50% relative humidity. From the I-V curve in Figure 4c, it is evaluated that as relative humidity is decreased by 10 the value of current is reduced by half due to which formation of a parabolic pattern is observed in the characteristic graph of current-relative humidity in Figure 4d.

3.0 Conclusion

The present work includes the fabrication of a humidity sensor. Synthesis of Ag crystallites by simple thermal reduction and graphene oxide by chemical oxidation and exfoliation was carried out. A composition of Ag/GO on an IDE was fabricated and used for analyzing the change in relative humidity. At room temperature, the humidity is varied from a range of 50-10 to a decrement of 10. A decrease in current is seen as the relative humidity decreases. Finally, the developed sensor is showing excellent moisture detecting properties and can be used for moisture sensing applications.

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