Synthesis and Characterization of Zinc Cobalt Ferrite Embedded into PAN Nanofibers for Humidity Sensing Applications

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In this work, composite materials were prepared by mixing different concentrations of ferrites with polyacrylonitrile (PAN) polymer. Using the electrospinning technique, these composites were deposited on a p-type silicon wafer. The prepared samples demonstrated nanofibers in both pure PAN polymers and their composites with ferrite. Prior to examining the humidity sensing effectiveness with a percentage of relative humidity at a frequency of 10 kHz, based on ambient temperature and a relative humidity range of 50–100%, the composite nanofibers demonstrated stronger humidity sensing compared to the pure PAN nanofibers, which demonstrated a powerful resistance response. More precisely, the PAN@ferrite nanocomposite showed a broad adsorption/desorption hysteresis loop.

Keywords: Nanocomposites; Zinc ferrite; Cobalt ferrite; Electrospinning
Received: 19 January 2024; Revised: 14 July 2024; Accepted: 06 July 2024

1. Introduction

In nanofibers and nanocomposites, polymers are one of the materials mostly used in nanotechnology. These nanofibers and nanocomposites offer unique and controlled features such as cheap cost, ease of fabrication, low density, insulation, and chemical inertness [1]. The nanocomposites have the potential to produce materials with adjustable properties those are highly interested by materials scientists. These composites are composed of inorganic nanoparticles scattered in a polymer matrix. These nanoparticles exhibit many optical, thermal, electrical, and electrochemical properties that depend on their quantity, size, and form [2]. Its wide variety of applications includes biological implants, wear-resistant coatings, microelectronics, and optical coatings. Nanostructured materials, such as nanosheets and nanofibers, are gaining popularity due to the increased sensitivity of thin film semiconductors [3]. The PAN@ferrite nanocomposite demonstrated a broad adsorption/desorption hysteresis loop [4,5]. The two main types of humidity sensors are relative humidity (RH%) sensors and absolute humidity sensors (sometimes called hygrometers). People widely use relative humidity (RH%) sensors due to their ease of use, superior quality, and lower cost, all of which contribute to human comfort [6]. The two types of sensors used to measure relative humidity are impedance sensors and capacitive sensors. Commercial, industrial, and meteorological monitoring applications often use capacitive relative humidity sensors. The advantage of a capacitive humidity sensor is that its dielectric constant varies in a manner that is almost precisely proportional to the surrounding air's relative humidity (RH). Humidity resistance sensors are transducers that convert variations in humidity into variations in resistance. Humidity resistance tests have primarily tested electrolytes, polymers, and ceramics. These materials have properties that make them resistant to humidity; hence, one way to evaluate humidity is to measure the resistance [7]. It is possible to find polymer-based humidity sensors that are resistant to moisture. Many studies have looked at the durability of polymer films that depend on many chemical properties, such as hydrophilic, molecular, and ionic forms, as well as the characteristics of these devices, like humidity sensitivity. Researchers also demonstrated the non-linear moisture-resistance properties of these polymers [8,9].

This study reports on the successful development of PAN@$ZnFe_2O_4$ and PAN@$ZnCoFe_2O_4$ composite nanofibers using electrospinning technique for humidity sensing applications. Polyacrylonitrile (PAN), $ZnFe_2O_4$, and $ZnCoFe_2O_4$ nanoparticles were prepared hydrothermally as filler material to increase the sensitivity of flexible humidity sensors.

2. Experimental Part

To prepare nanofiber films, dimethylformamide (DMF) is dissolved with polyacrylonitrile (PAN) that has a molecular average of $1.5x10^6$ g/mol and a purity of ≥99%. PAN nanofibers with and without ferrite nanostructure which is made by a hydrothermal process. We produce PAN@ferrite by embedding these nanoparticles into the PAN solution. After dissolving 0.65 g of PAN polymer in 6 ml of DMF and agitating it for two hours with a magnetic stirrer, the precursor solutions become homogenous and clear. We grafted 0.065 g of $ZnFe_2O_4$ and $ZnCoFe_2O_4$ with a polymer solution using the hydrothermal technique. We individually dissolved 1.94 g of zinc nitrate and ferric chloride in 30 ml of distilled water in each of two beakers to prepare $ZnFe_2O_4$. We separately stir the cobalt nitrate, iron chloride, and zinc nitrate aqueous solutions on a magnetic stirrer for 10 minutes. Next, we add iron chloride to the zinc nitrate solution and stir it for fifteen minutes to achieve complete dissolution, resulting in 60 ml of the mixing solution. Next, they transfer the autoclave, bake it at 120 °C for 10 hours, and then cool the oven to room temperature for the next day. The solutions are fully dried to a powder. We moved the powder to an oven and burned it for 2 hours at 400 °C to stabilize its phase. We ground it until it was ready to mix with a polymer to create the composites PAN@$ZnFe_2O_4$ and PAN@$ZnCoFe_2O_4$. We conducted the electrospinning as shown in Fig. (1), using the following parameters: a voltage of 18 kV and a distance of 8 cm between the tip and collector.

The percentage relative humidity (RH) and humidity sensing efficiency were measured using a digital LCR meter (E4980) operating at a frequency of 10 kHz after placing the composite nanofibers onto an interdigitated electrode. According to room temperature data in the range of 50% to 100% relative humidity, the composite nanofibers had the strongest humidity sensing performance compared to the PAN nanofibers without addition, which demonstrated a strong resistive response.

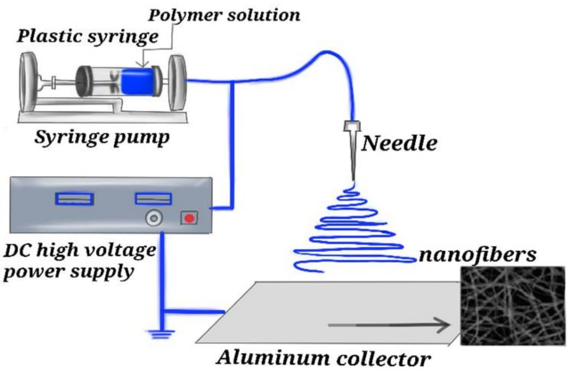

Fig. (1) Design for the electrospinning apparatus assembly

3. Results and Discussion

The FE-SEM images in Fig. (2) display the collected fibers. The morphological analysis demonstrated the success of the electrospinning parameters used to produce soft polymeric nanofibers. The inset figure illustrates the PAN nanofiber diameter.

Figure (3) illustrates how FTIR spectra look into vibration modes. Along with a high absorption for the compound $ZnFe_2O_4$ at 642 cm^{-1} that belongs to the C-H, there is another absorption at 1029 and 1034 cm^{-1} that belongs to the C-O. These absorptions indicate that elements or compounds have metal-oxygen stretching vibrations. Additionally, there is absorption at 1373 and 1450 cm^{-1}, associated with the C-H stretches, which typically span 1663 and 1739 cm^{-1} to belong to C=O, as well as absorption at 2243 and 2390 cm^{-1}, spanning from 2100 to 2500 cm^{-1}. Compounds or element-induced absorption includes C-H stretching vibration at 2935 cm^{-1}, spanning from 2922 to 3426 cm^{-1}, and O-H stretching vibration at 3459 cm^{-1}, often spanning from 3426 to 3779 cm^{-1}.

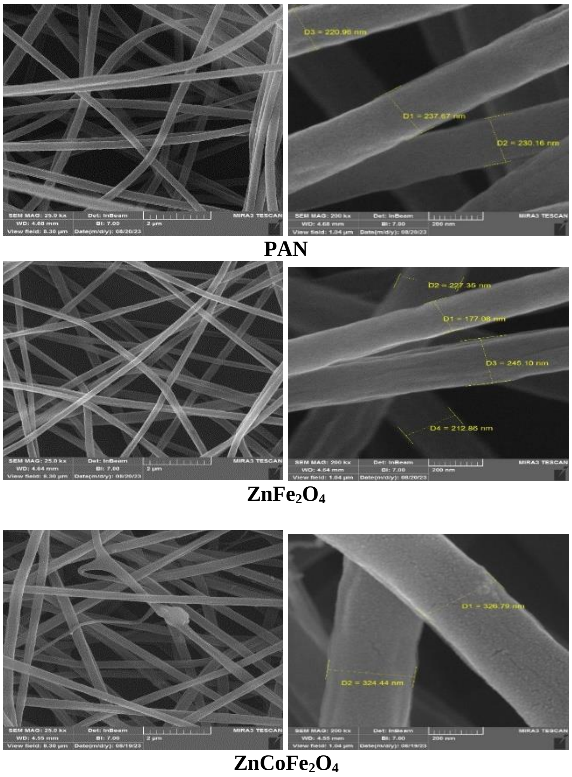

Fig. (2) FE-SEM images of the prepared PAN@ferrites composites

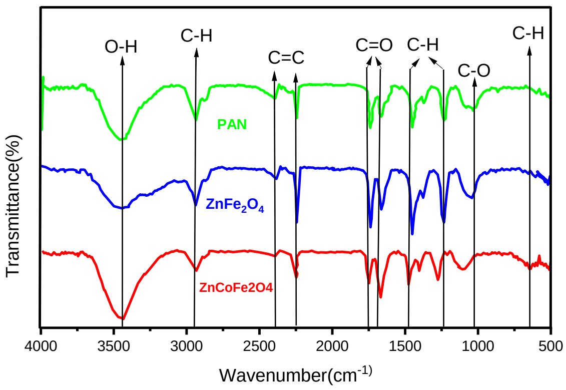

Fig. (3) FTIR spectra of (a) PAN NFs, (b) PAN@$ZnFe_2O_4$, (c) PAN@$ZnCoFe_2O_4$

Figure (4) displays the current-voltage characteristics of both pure PAN NFs and their composites with ferrites. Because the I-V characteristic curve is symmetric, it shows photoconductive behavior for pure PAN and PAN@$ZnFe_2O_4$. However, it shows Schottky behavior for PAN@$ZnCoFe_2O_4$ NFs. The current flow between electrodes is generally low at low voltages, but it increases at high bias voltages. However, in reverse bias, the current is less than at forward bias voltages, resulting in rectifier behavior, as seen in Fig. (4). When adding cobalt to ferrite lattices, the high radius of the cobalt cation causes distortion, leading to this phenomenon.

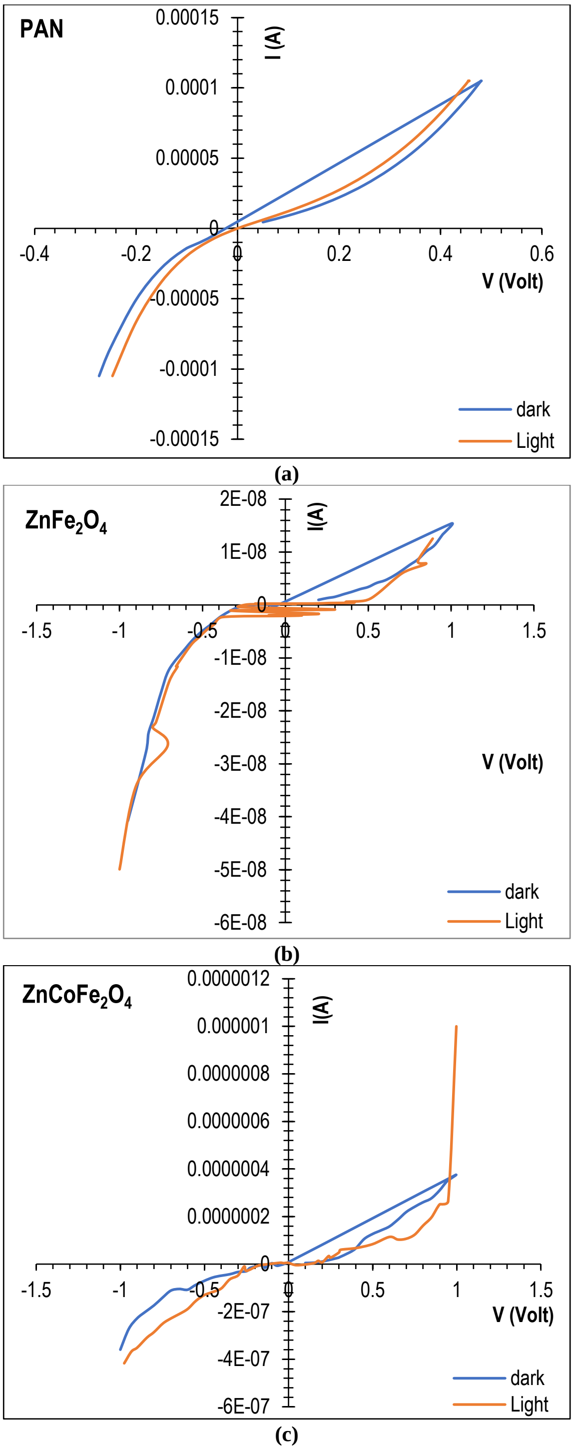

Fig. (4) I-V characteristic of (a) PAN NFs, (b) PAN@$ZnFe_2O_4$, (c) PAN@$ZnCoFe_2O_4$

The hydrophilicity of PAN NFs encourages us to create a humidity sensor and investigate whether adding ferrite increases the sensor's sensitivity to H_2O vapor. Figure (5) shows the setup we used to assess sensor performance [10]. The study examined the process of humidity sensing in sensors that use electro spun nanofibers (PAN). Figure (6) illustrates the dynamic adsorption and desorption behavior of the PAN nanofibers under various humidity conditions. Humidity sensors use a variety of processes to function, but capacitive sensing is a popular one. By absorbing or desorbing water vapor from the air, a humidity-sensitive substance (often a polymer) modifies its dielectric constant. This shift alters the capacitance of the sensor, leading to the electrical determination of the relative humidity. Resistive sensing is an additional technique that modifies the resistance of a material that is sensitive to changes in humidity. We applied a specific voltage across the ohmic contact and measured the electrical resistance within the humidity range of 20-100% RH. We study the PAN@$ZnFe_2O_4$ and PAN@$ZnCoFe_2O_4$ NFs surface-type humidity sensor at a frequency of 10 kHz, and figure (6) shows the normalized resistance as a function of relative humidity (RH%).

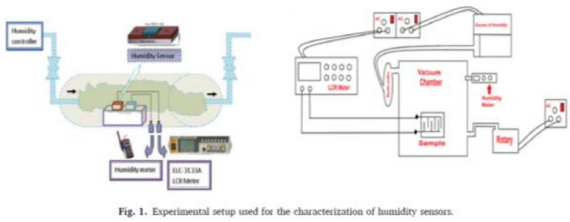

Fig. (5) The experimental setup of humidity sensor characterization [10]

Figure (6a) displays a minuscule hysteresis loop and minimal sensitivity to H_2O vapor. Figure (6b) depicts the enlargement of the hysteresis loop upon the addition of zinc ferrite nanoparticles, while figure (6c) demonstrates the enlargement of the hysteresis loop across wide regions upon the addition of zinc cobalt ferrite, suggesting a higher detection of humidity with the PAN@$ZnCoFe_2O_4$ loop. Water molecule adsorption on PAN@$ZnFe_2O_4$ and PAN@$ZnCoFe_2O_4$ surfaces drives the mechanism of humidity sensing. It is possible to indirectly find the rough and smooth surfaces of nanocomposites by adding ferrite nanoparticles to the hydrophilic polymer matrix. This makes the nanocomposite's surface area much larger and increases the number of water molecules that can stick to the sensing material [11]. In contrast, the establishment of hydrogen bonds between hydrophilic PAN and water molecules improves the humidity sensing response [12]. We considered two categories of adsorption interactions chemisorption and physisorption to understand the humidity sensing process [13]. The present investigation began with the nanofiber composite exposed to water molecules at low relative humidity. The extra water molecules were adsorbed on the hydrophilic PAN's surface via intermolecular hydrogen bonding and recognized as a chemisorbed layer [14]. As the relative humidity increased, a physisorption layer formed because hydrogen interaction between two neighboring hydroxyl groups created a water multilayer [15].

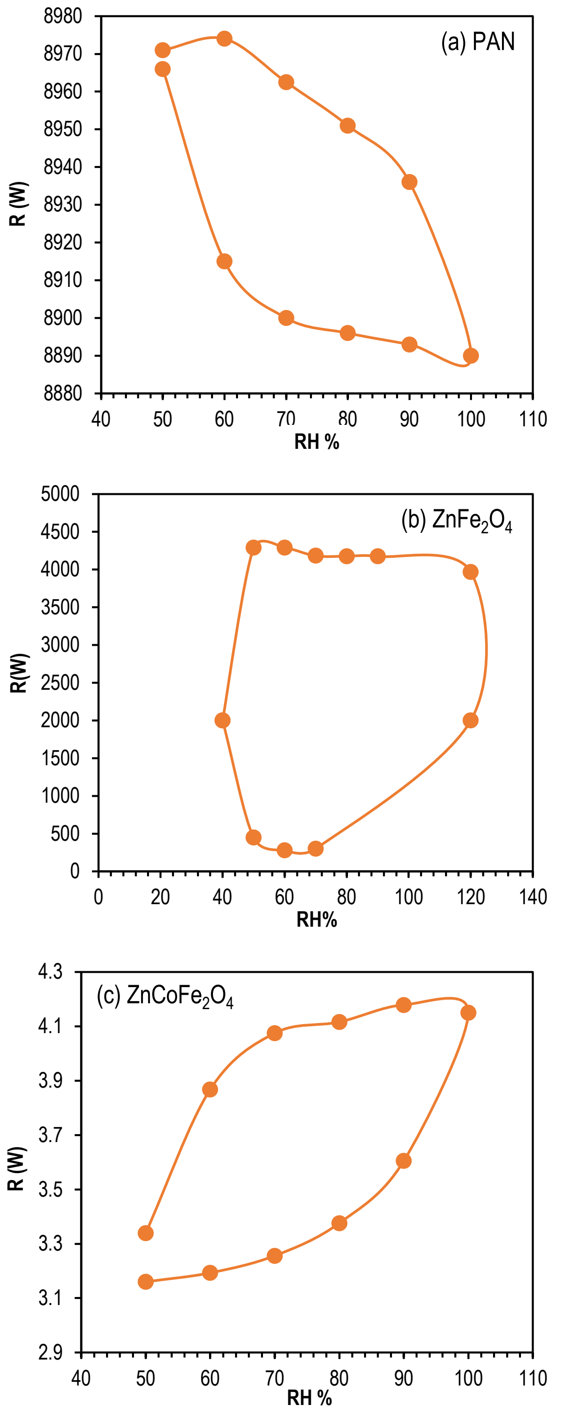

Fig. (6) (a) PAN humidity sensor, (b) PAN@$ZnFe_2O_4$, (c) PAN@$ZnCoFe_2O_4$

4. Conclusions

We successfully synthesized PAN and its composites ($ZnFe_2O_4$ and $ZnCoFe_2O_4$) nanofibers using the electrospinning technique. The FESEM examination confirms the nature of the nanofiber. We created a unique, extremely sensitive humidity sensor based on the nanostructures of PAN, $ZnFe_2O_4$, and $ZnCoFe_2O_4$. The PAN@ferrite nanocomposite showed a broad adsorption/desorption hysteresis loop.

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