FABRICATION OF A HUMIDITY SENSOR USING CARBONIZED NITRILE BUTADIENE RUBBER (NBR) WASTES

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INTRODUCTION

Humidity sensors are the most widely used type of sensor that affects a wide range of domestic and key industrial processes(1). A wide range of materials have been explored to be used as humidity sensing materials such as ceramics, composites, and polymers. Among these, nanocomposite materials have attracted great attention as promising materials in fabricating humidity sensors with high performance and good stability. In this study resistive humidity sensor based on conductive carbon/ZnO was developed by the controlled heat treatment of Nitrile Butadiene Rubber (NBR) polymer wastes with zinc hydroxide. Herein, $ZnCl_2$ was used to synthesize $Zn(OH)_2$, which was used as the precursor for the formation of ZnO on the carbon surface. ZnO is a promising semiconductor material for sensor application with multifunctional properties such as wide bandgap (3.37eV), the high exciton binding energy (60meV), low cost, non-toxicity, and controlled morphology(2). Herein we report a simple, cost-effective chemical route for the preparation of high-performance humidity sensors with fast response and recovery times. Such a high-performance humidity sensor possesses great potential for application in a wide range of fields where humidity needs to be controlled.

METHODOLOGY

Waste nitrile gloves were collected from laboratories of the Sri Lanka Institute of Nanotechnology, Sri Lanka. Zinc chloride (97%) and sodium hydroxide (98%) of analytical grade were purchased from Sigma Aldrich. Hexane and deionized water were used to wash the waste nitrile glove samples. All chemicals used in this study are analytical grade.

The collected waste nitrile gloves were washed in distilled water and hexane to remove adhered impurities. The samples were sun-dried for 1 day and crushed into small pieces. Zinc hydroxide was synthesized using zinc chloride and sodium hydroxide. An equal amount of Zinc Hydroxide was then mixed with the crushed glove sample and carbonized in an OTS-1200X tube furnace at 700°C in inert air. After maintaining the temperature at 700 °C for one hour, the sample was cooled down to room temperature. The fabricated composite material was applied on a resistive type gold-coated electrode and cured at 140 °C for 8 hours.

RESULTS AND DISCUSSION

Fig.1. (a) shows the XRD spectra representing the carbonized waste nitrile butadiene glove sample with zinc hydroxide. Sample has eleven characteristic diffraction peaks of ZnO at 2θ=31.30°, 36.00°, 47.16°, 56.02°, 62.42°, 66.10°, 69.00°, 72.54°, 76.00°, 81.90°, and 89.00° which correspond to (100), (101), (102), (110), (103), (200), (201), (004), (202), (104), and (203) crystal planes of ZnO, respectively (JCPDS# 36-1451)(3). The spectra show 4 diffraction peaks located at 26.48°, 54.00°, 59.06°, and 77.42° which correspond to (002), (004), (103), and (110) crystal planes of graphitic carbon (JCPDS# 00-008-0415).

The fabricated sensor was further characterized using FTIR and Raman spectroscopy. The Raman spectrum of the sensing material is shown in Fig.1. (b) The spectrum of the material exhibits two peaks at 1325 cm^{-1} and 1592 cm^{-1}. These two peaks are attributed to the D and G bands of the graphitic carbon(4). The ID/IG ratios for the NBR sample without zinc hydroxide (NBR) and the NBR sample with zinc hydroxide (NBR-Z) were 0.900 and 1.009, respectively, and the increased ID/IG ratio for the NBR-Z sample is ascribed to an enhanced structural distortion caused by ZnO doping within the lattice.

The FTIR spectrums of the NBR glove sample before carbonized (a), and carbonized with zinc hydroxide (b) are shown in Fig.2 It has several important peaks that are normally present in the nitrile rubber. The peaks around 2235 cm^{-1} and 968 cm^{-1}confirm the presence of the –CN group and the –C-H stretching vibration of the butadiene double bond in NBR(5). The peaks at 449 cm^{-1} and 413 cm^{-1} correspond to the stretching frequency of Zn-O bonds.

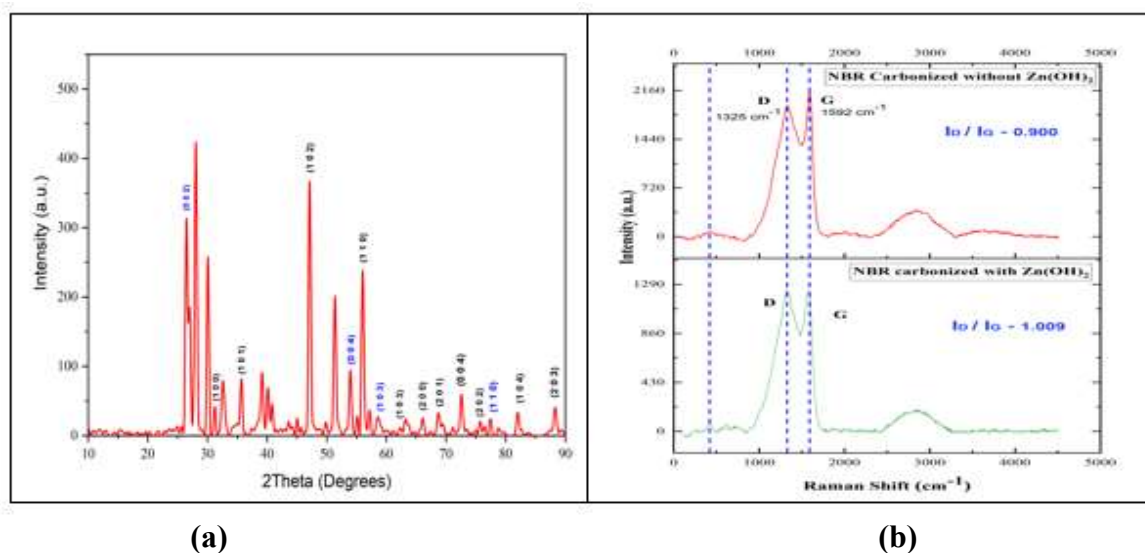**(a)**   **(b)**

Fig.1.a) XRD spectra of carbonized NBR sample with Zinc Hydroxide b) Raman spectrum of carbonized NBR samples
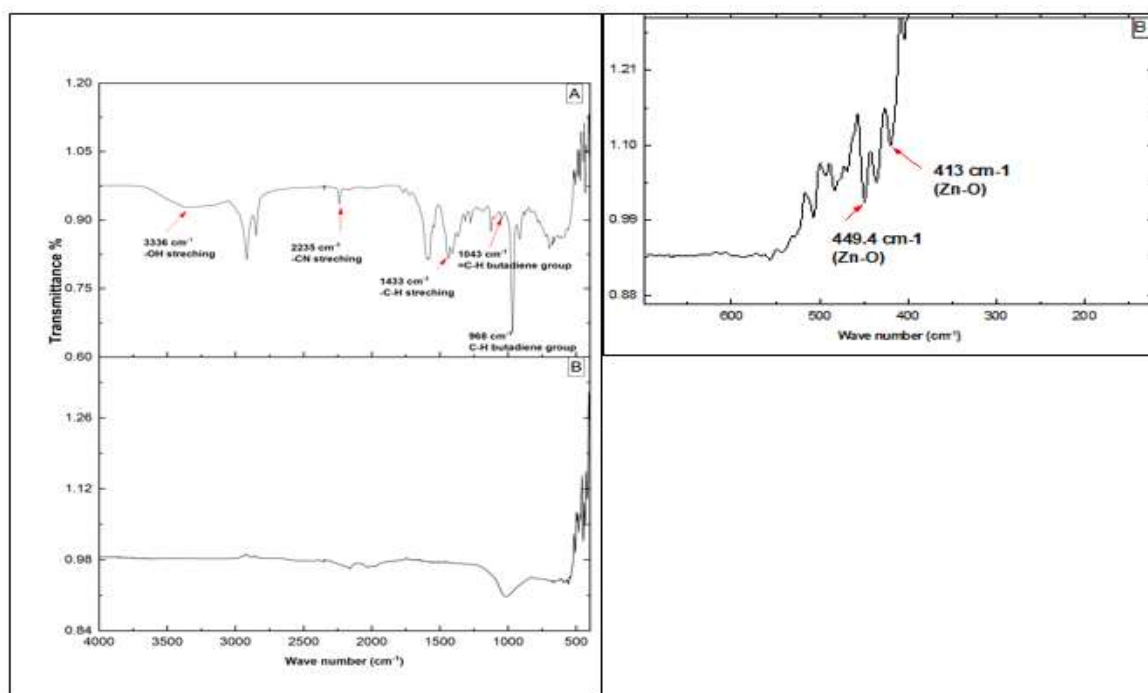

Fig. 2. (A) FTIR spectrum of NBR glove sample before carbonization. (B) After carbonization at 700°C

Sensing performance

The sensing performance of the fabricated sensor is evaluated based on its relative response and recovery, repeatability, linearity, sensitivity, and stability at different humidity levels.

The repeatability of the sensor was tested by changing the relative humidity values between 35% and 65%. The sensor was exposed to the humidity levels for several consecutive cycles and showed excellent repeatability (Fig 3a).

The stability of the fabricated sensors was tested under different relative humidity levels of 15%, 32%, 45%, 60%, and 73% at room temperature. The saturated humidity response would not change significantly for at least 4 hours as presented in Fig. 3(b).

As shown in Fig. 3(c) the sensor showed a response time of 13s while the relative humidity changed from 35 %RH to 65 %RH. The recovery time was 12s while the relative humidity changed from 65 %RH to 35 %RH. The response of the fabricated sensor was calculated by equation 1(6) and the sensor has a response of 8.28%.

$$\text{Response} = (R_{14\%} - R_{85\%})/R_{85\%} *100 \%\text{...}(1)$$

Additionally, the sensor showed a good linear relationship between relative humidity and the resistance of the sensor. Resistance of the sensor increased from 6.52 kΩ to 7.06 kΩ with the reduction of relative humidity from 85% to 14% as Fig. 3(d).

The sensitivity of the sensor, which is the change in resistance (ΔR) of the sensing element per unit change in RH ($\Delta \%RH$), was calculated using equation 2(7) and the sensitivity of the tested sensor was 7.6 ohms.

$$\text{Sensitivity} = \Delta R/\Delta \%RH \text{ …………………………………… } (2)$$
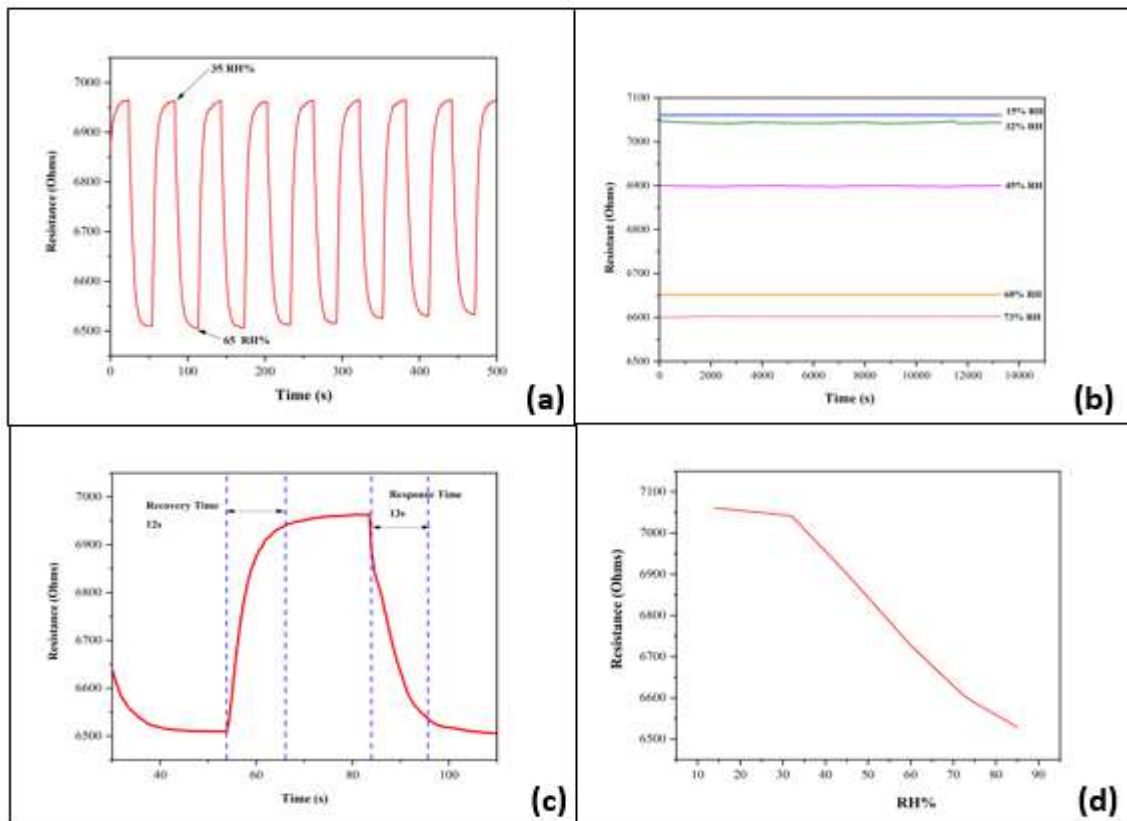

Fig. 3. Carbon/ZnO humidity sensor (a) Repeatability, (b) Stability, (c) Response/recovery time, (d) Relationship between R and RH.

CONCLUSION

In conclusion, a conductive carbon/ZnO modified humidity sensor with high performance was successfully fabricated using prepared by a simple thermal treatment of NBR wastes. The response and recovery times were determined as 13 s and 12 s with 7.6 Ω sensitivity. The present investigation shows that carbon/ZnO nanocomposite has the potential in humidity sensors as an effective way of utilizing NBR wastes into a value-added product.

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