Reduced Graphene Oxide-ZnO Nanotubes Based Binary Hybrid Structure as Room Temperature Ethanol Sensor

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Abstract— **In this paper, we report a highly sensitive and fast responsive room temperature ethanol sensor based on rGO-ZnO nanotubes (NTs) hybrid structure. ZnO NTs were grown on Indium doped Tin Oxide (ITO) substrate using a two-step process, consisting of electro-deposition (for ZnO nanorods deposition) and electrochemical etching (for etching of ZnO nanorods to form nanotubes). After that, rGO layer was deposited on top of the ZnO NTs employing a programmed dip coating technique. Subsequently, detailed structural and morphological characterizations were carried out using FESEM (Field Emission Scanning Electron Microscopy), Raman spectroscopy and XPS (X-Ray photo electron Spectroscopy) techniques to confirm the formation of hybrid structure. After that, alcohol (i.e. ethanol, methanol, 2-propanol) sensing properties of the device were investigated in the concentration range of 1-700 ppm at different temperatures (27–175°C). ~70% response magnitude, (towards ethanol) was observed at room temperature. Moreover, fast response time and recovery time were also noticed (response time: ~56 s and recovery time: ~202 s at 100 ppm concentration of ethanol). Such sensing performance is attributed to the synergistic hybridization of ZnO NTs and rGO, which offer an extremely large number of gas adsorption/desorption sites and high carrier mobility.**

Keywords- rGO-ZnO nanotubes; hybrid structure; room temperature ethanol sensor; fast response time/recovery time.

I. INTRODUCTION

Metal oxide based nanostructures have widely been used in the development of solid-state gas sensors in different application arena, such as environmental gas/volatile organic compound monitoring, food processing, detection of toxic, flammable and explosive gases etc. [1]. However, the high operating temperature of such sensors inevitably increases the power consumption, cost and hampers the long-term stability [2]. Therefore, in recent years, the development of room temperature gas sensors has attracted serious attention around the globe. The room temperature sensing performance can be achieved by (i) decreasing the activation, energy of sensing surface and (ii) enhancing the carrier transport kinetics of the sensor [1]-[4]. In this context, nanotube structure having high surface to volume ratio (which decrease the activation energy of the sensing layer) proved its promising candidature as a room temperature sensing layer [4]. On the other hand, the high mobility and intrinsic defects of rGO, make it as an essential material to improve the transport kinetics of the sensor [1]. Now, hybridization of nanotube and rGO facilitates room temperature sensing performance as well as fast transport kinetics. Several metal oxide based (i.e. TiO_2, SnO_2, WO_3 etc.) nanotubes structure have already been reported for room temperature volatile organic compound sensor [1], [3]. However, these sensors exhibited sluggish response time and recovery time (in minutes) towards ethanol. Therefore, to obtain room temperature fast responsive ethanol sensor, ZnO NTs and rGO layer were hybridized in this work.

The sensing performance of the rGO-ZnO NTs structure was carried out in the concentration range of 1-700 ppm, targeting ethanol, methanol and 2-propanol. Alcohol (i.e. ethanol, methanol, 2-propanol) sensing properties of the device were investigated in the concentration range of 1-700 ppm at different temperatures (27–175°C). ~70% response magnitude, (towards ethanol) was observed at room temperature. Moreover, fast response time and recovery time were also noticed (response time: ~56 s and recovery time: ~202 s at 100 ppm concentration of ethanol). Such sensing performance is attributed to the synergistic hybridization ZnO NTs and rGO, which offers extremely large amount gas adsorption/desorption sites and high carrier mobility. The formation of hybrid junction between rGO and ZnO NTs possibly enhance the sensitivity as well as response kinetics towards ethanol.

The rest of the paper is structured as follows. In Section 2, device fabrication and measurement procedure are discussed. In Section 3, the morphological and surface characterization outcomes, sensing performance of the rGO-ZnO NTs based hybrid device are discussed and correlated with the possible physical phenomenon. Finally, we conclude the work in Section 4.

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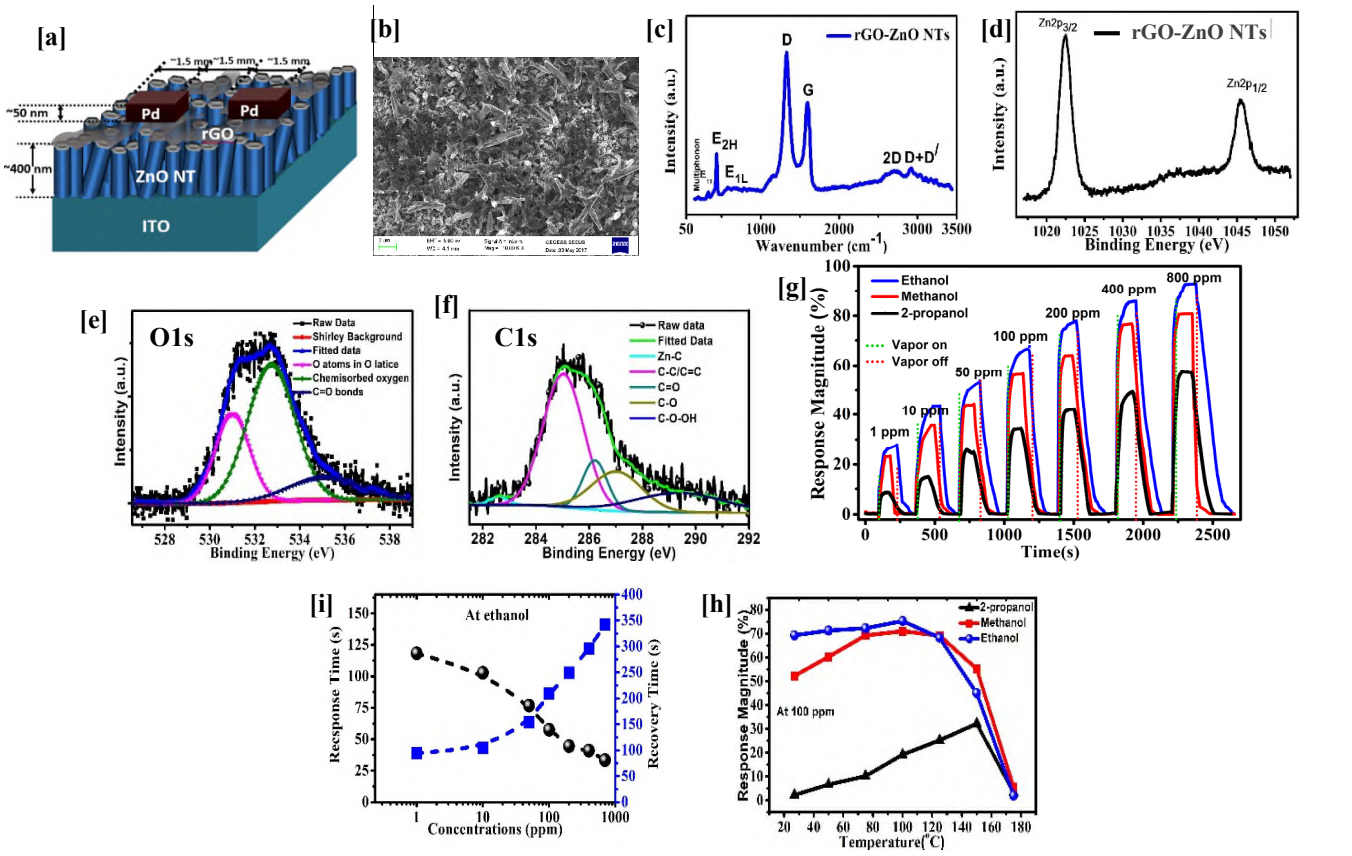

Figure 1. (a) A schematic representation of rGO-ZnO NTs binary hybrid sensor device with requisite dimensions (b) FESEM image of rGO-ZnO NTs (c) Raman spectra of rGO-ZnO NTs (d-f) XPS spectra of rGO-ZnO NTs; (d) Zn ($2p_{3/2}$ and $2p_{1/2}$) and (e) O (1s) peak (f) C1s spectra of rGO-ZnO NFs. (g) Transient response characteristics towards ethanol, methanol, 2-propanol, of rGO-ZnO NTs (green line and red line indicate vapor on and off, respectively), (h) Response time (in black) and recovery time (in blue) as a function of different vapors concentrations (1–700 ppm) for the rGO-ZnO NTs (i) The response magnitude as a function of temperature for rGO-ZnO NTs at 100 ppm concentration of ethanol, methanol, and 2-propanol.

II. EXPERIMENT

In an experiment, ZnO nanotubes were fabricated on an Indium doped Tin-Oxide (ITO) coated glass substrate (from Sigma Aldrich, thickness: 0.9 mm, surface resistivity: ~10 Ω/sq), by a two-step process, consists of (i) electro-deposition of ZnO nanorods, followed by (ii) selective electrochemical etching of those nanorods to form nanotubes [2]. In first step, ITO was connected to the negative polarity, while during etching of ZnO nanorods, positive voltage was applied to ITO. In the first step, aqueous solution of equi-molar (5 mM each) Zinc Nitratehexahydrate ($Zn(NO_3)_2$, $6H_2O$, 99%, MERCK) and Hexamethylenetetramine (HMT) ($(CH_2)_6N_4$, 99%, MERCK) was used to deposit ZnO nanorods. After that, the electro-deposition was carried out for 40 minutes at 78ºC with a bias voltage of -1.8 V [2]. In the second step, electrochemical etching of grown ZnO nanorods was carried out for 1 hours at 65°C, using an aqueous solution of 0.01M Ethylenediamine (EDA) ($C_2H_4(NH_2)_2$, 99.5%, MERCK) with an applied potential of -0.06V. After that, the grown ZnO NTs were annealed in a horizontal tube furnace (heating and cooling rate of 5°C/min) at 350°C for 3 hours. Further, on top of the ZnO NTs layer, rGO layer was deposited employing a programmed dip coating technique. After that, rGO-ZnO NTs hybrid device was again annealed at 300°C for 2 hrs. Subsequently, a planar device structure was fabricated employing rGO-ZnO NTs as the sensing layer and palladium (Pd) as contact electrodes. Sensor device schematic is shown in Figure 1(a).

III. RESULTS AND DISCUSSIONS

FESEM image (top surface) of rGO-ZnO NTs is shown in Figure 1(b). Raman spectroscopy of rGO-ZnO NTs is depicted in Figure 1(c), where the presence of D band (centred at 1334.22 cm^{-1}), G band (centred at 1601.15 cm^{-1}), 2D band (centred at 2705.25 cm^{-1}) and D+D/ (centred at 2921.95 cm^{-1}) validate the existence of rGO [1]. D band attribute to sp^3 defects at the graphene edges and G band signifies E_{2g} phonon [1]. Moreover, the existence of non-polar optical phonon of ZnO, i.e. E(high) band (centred at 432.03 cm^{-1}) and E(low) band (centred at 532.53 cm^{-1}) represents the wurtzite crystal phase of ZnO [2] which further confirms that the wurtzite phase of ZnO unaltered even after deposition of rGO. Further, to observe

morphological properties of rGO-ZnO NTs surface, XPS characterization was carried out. As revealed from Zn (2p) peak (Figure 1(d)) that the doublet spectral line of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ were observed at 1022.35 eV and 1045.24 eV, respectively [1]. Gaussian fitting of O1s spectra for rGO-ZnO NTs (depicted in Figure 1(e)) revealed that the amount of chemisorbed oxygen vacancies dominates the lattice oxygen content of rGO-ZnO NT surface. Moreover, the presence of C-C/C=C, C-O, C=O and C-O-OH peaks in C1s spectra (Figure 1 (f)) confirms the existence of rGO on ZnO NTs surface [5][6]. The sensing performance of rGO-ZnO NTs hybrid structure was investigated in the resistive mode with three different alcohol vapors (ethanol, methanol and 2-propanol) in the concentration range of 1–700 ppm at different temperatures (27–175°C). For each ppm, the gas/vapor was exposed for ~380 sec. The developed sensor offered higher response magnitude towards ethanol followed by methanol and 2-propanol. However, the optimum operating temperature of the device towards ethanol and methanol was found to be ~100°C and ~150°C for 2-propanol (Figure. 1(i)). Moreover, stable transient response characteristics towards ethanol was observed and depicted in Figure 1(g). The operating temperature for Figure 1(g) was ~27°C (i.e. room temperature). It is evident from Figure 1(g), that the sensor showed appreciably high response magnitude towards ethanol (e.g. 17.37 % at 1 ppm, 70.19 % at 100 ppm and 97.82 % at 700 ppm) at room temperature (RT). The response times and recovery times for rGO-ZnO NTs sensor towards ethanol are depicted in Figure 1(h) (in a concentration range of 1–700 ppm). For example, rGO-ZnO NTs sensor offered ~56 s response time and ~202 s recovery time at 100 ppm concentration of ethanol. Such high response magnitude and fast response and recovery kinetics at room temperature are far better than our previous report on pristine ZnO nanotube based ethanol sensor [7]. Such enhancement in sensing results is attributed to the incorporation of rGO on top of the ZnO NTs layer. ZnO NTs radially offers higher amount of gas adsorption/desorption sites (as target gas can adsorbed on the both inner and outer walls). On the other hand, high carrier mobility of rGO increase the carrier transport from the gas-interaction sites to the collecting electrode(s), which improves the response and recovery kinetics of the sensor [5]. To the exposure of air, oxygen molecules are adsorbed on the inner and outer wall of ZnO NTs and oxygen vacant sites of rGO layer, which inevitably increase the adsorb oxygen ions (which are active sites for gas interaction). Moreover, exchange of electrons and holes between ZnO NTs and rGO space charge regions are formed on hybrid surface which also penetrate towards the core from the outer surface of the NT wall. This phenomenon increases the barrier potential of the hybrid structure [4]. On the other hand, with the exposure of ethanol vapour, adsorbed oxygen species on the hybrid surface, oxidize the ethanol, which eventually reduces barrier potential at the surface. Therefore, the sensor resistance decreased dramatically [7].

IV. CONCLUSION

Room temperature ethanol sensing performance of the rGO-ZnO NTs binary hybrid structure is reported in this paper. Hexagonal ZnO NTs were fabricated on the ITO substrate employing two-step process; (i) electro-deposition for ZnO hexagonal nanorods growth, followed by (ii) electro-chemical etching of ZnO nanorods to form nanotubes. The existence of rGO layer was authenticated by FESEM, Raman and XPS characterizations. The sensing characteristics of the sensor was experimented in the concentration range of 1-700 ppm towards ethanol, metanol and 2-propanol. The sensor showed promising sensing characteristics towards ethanol with a response magnitude of 70.19 % at 100 ppm and 97.82 % at 700 ppm at room temperature. However, optimum temperature of this sensor was found to be ~100°C towards ethanol. Moreover, the response time and recovery time were also found to be faster than that of earlier reported room temperature ethanol sensor. Large amount of gas-interaction sites of ZnO NTs along with high carrier mobility of rGO layer possibly offered such improved response characteristics.

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