



Room-temperature chemiresistive g-C₃N₄/Ag₂ZrO₃ nanocomposite gas sensor for ethanol detection

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ABSTRACT

Designing the efficient ethanol gas sensors with high sensitivity, selectivity, and stability is of great interest in diverse applications. Herein, g-C₃N₄, Ag₂ZrO₃, and g-C₃N₄/Ag₂ZrO₃-based nanomaterials have been synthesized, characterized, and subjected for gas sensor studies against 50 ppm concentration of six different gases namely n-butanol, isopropanol, methanol, xylene, toluene, and ethanol at room temperature. All nanomaterials g-C₃N₄, Ag₂ZrO₃, and g-C₃N₄/Ag₂ZrO₃ have shown higher response values of 15.1, 24.5, and 53.1%, respectively, against ethanol gas compared to other gases. The observation of highest response value of g-C₃N₄/Ag₂ZrO₃ may be due to involvement of cooperative effect of g-C₃N₄ and Ag₂ZrO₃ in the nanocomposite. Further, the elaborated gas sensor studies of g-C₃N₄/Ag₂ZrO₃ showed that the present nanocomposite material has excellent repeatability, quick response/recovery, and good stability for the detection of ethanol gas. By careful modification of this kind of semiconductor, metal oxide-based nanocomposites will afford room-temperature-operable high-performance ethanol gas sensors in near future.

1 Introduction

Ethanol is intensely penetrated into our day today life as one of the volatile organic compounds (VOCs). It is extensively used for medical treatment, alcoholic drinks, food industry, and industrial chemistry process. However, it is important to monitor that long-term exposure of excess ethanol to humans can cause severe injuries for instance irritation of eyes and skin,

coma, and even intoxication which threaten lives [1–4]. Thus, it is extremely needed to build up a highly selective as well as sensitive ethanol gas sensor to prevent potential injuries caused by ethanol. Further, ethanol gas sensors can be used in various applications such as monitoring industrial ethanol gas leakage, measuring the ethanol concentration in the blood by means of breath alcohol checker using the exhaled ethanol gas of human breath, etc. Even

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there have been different approaches that are available for ethanol gas sensing, it is still a great interest to develop chemiresistive-type alternative materials for ethanol gas sensors. Particularly, semiconducting metal oxide-based gas sensors have been greatly paying attention due to their high sensitivity, long-term stability, simple fabrication, and low cost [5–8].

Importantly, the performance of semiconducting metal oxides-based gas sensors is typically reliant on the device working temperature, due to the operating temperature that has an imperative part in controlling the conductivity, electron mobility, and kinetics of surface reactions. In general, conventional metal oxide-based gas sensors are needed higher temperatures like in the range of 150–500 °C for their operation. This minimum thermal energy is required for the gas-sensing measurement to defeat the activation energy barrier in the surface redox reaction of metal oxide and also used to enlarge the free carrier concentration in the metal oxides. Further, the usage of higher operational temperature makes reducing its limits for broader applications by lowering sensor stability, possibility of risks by the explosive and flammable gases, and device energy consumption. Thus, it is also needed to develop alternative materials for the efficient room-temperature operable ethanol gas sensor applications [9–11].

Even there have been a diversity of metal oxides such as WO_3 [12], TiO_2 [13, 14], In_2O_3 [15, 16], ZnO [17–19], SnO_2 [20, 21], etc. are available for ethanol gas-sensing applications, studies on the room-temperature operable ethanol gas sensor materials are limited in the literature. Hence, a rational designing of materials are needed for attaining highly selective as well as sensitive ethanol gas sensors. There are several strategies available for enhancing the sensitivity and selectivity of semiconducting metal oxides for ethanol gas-sensing applications. It includes incorporation of noble metals [22, 23], preparation of binary/ternary metal oxides composites [24, 25], and synthesis of different morphological nanostructures [26–28]. Porous nanomaterials are often used as gas-sensing materials and its structural parameters like grain size, grain agglomeration, pore size, and surface morphology are playing important role in the sensor performance [29, 30]. Among the many strategies used, developing composite materials using metal oxides and graphitic structure materials have been showed very good results for tailoring the sensitivity and selectivity of gas sensors.

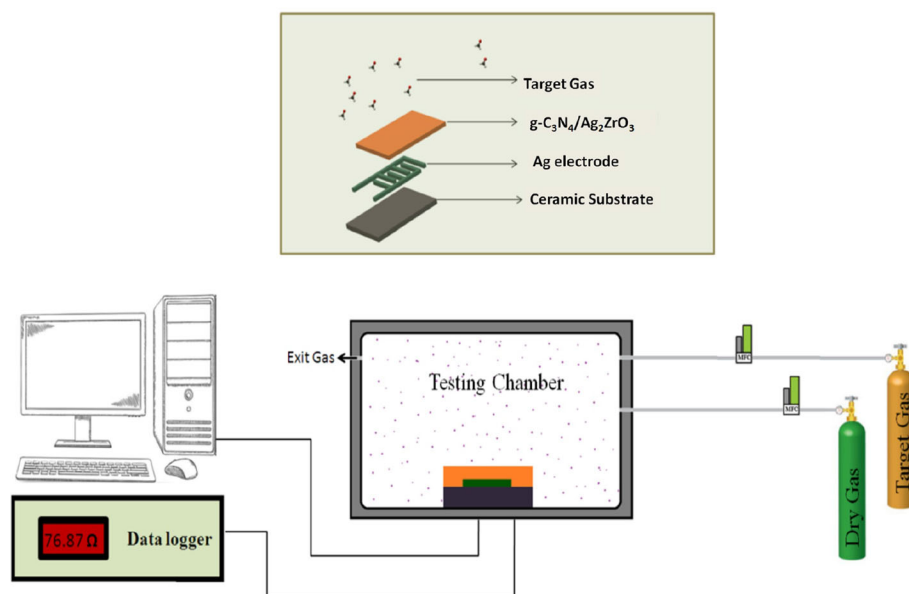
Recent days, researchers have been attracted with graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) due to its numerous advantages like high chemical stability, large specific surface area, easy preparation, and non-toxicity. Further, its medium band gap offers pathway to modulate its electronic structure via doping or chemical functionalization. This kind of tuning the electronic structure is a potential factor in optimizing gas sensor properties [31]. Numerous studies pointing on $\text{g-C}_3\text{N}_4$ -loaded different metal oxide composites have been resulted that $\text{g-C}_3\text{N}_4$ plays a very vital role in the activity of composites. The $\text{g-C}_3\text{N}_4$ nanosheets can offer several grown sites for other semiconducting substrates, which can improve the charge transport and limit the recombination possibility of charge carriers. Hence, $\text{g-C}_3\text{N}_4$ nanosheets ought to be a potential material for the gas-sensing applications [32]. Even there are few reports that are available for the $\text{g-C}_3\text{N}_4$ -based ethanol gas sensors, still it is needed to improve the performance of the nanomaterials in terms of sensitivity, selectivity, operational temperature, and stability for the commercial applications [33, 34]. Thus, the present work was aimed to investigate the impact of $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{-ZrO}_3$ -based nanocomposite for sensing some of the VOCs at room temperature. As this nanocomposite has shown higher ethanol gas-sensing behavior, the material was further subjected to detailed ethanol gas sensor studies to measure the sensor response, sensor efficiency, sensitivity, repeatability, and stability against the different concentrations.

2 Experimental section

2.1 Materials and methods

Melamine (Sigma-Aldrich 99% purity), zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.9% Merck) and silver nitrate (99.9% Merck) were used for synthesis of nanomaterials. All other chemicals were of analytical grade and double-distilled water was used throughout the investigations. All calibrated gases were obtained from Chemix special gases and equipments, India. The XRD analysis for the prepared nanomaterials was conducted by X-ray diffractometry (D2 Phaser, Bruker). UV–visible diffuse reflectance spectra (UV–Vis DRS) were recorded in the wavelength range of 200–800 nm using a Perkin Elmer, Lambda 850 UV/Vis spectrophotometer

Fig. 1 Pictorial representation of gas sensor set-up



equipped with an integrating sphere accessory using BaSO_4 as the reference. JEOL JSM-7610F instrument was used to obtain Field emission scanning electron microscopy (FE-SEM) images of the samples. Transmission electron microscopy (TEM) images were taken with a Hitachi H7650 electron microscope. Surface area of nanomaterials was taken for about 10 mg of the sample for each analysis (Quantachrome Chem BET-3000 analyzer). The gas sensor studies were performed by adopting the same experimental procedure as reported in our previous paper and pictorial representation of gas sensor set-up is shown in Fig. 1 [35].

2.2 Synthesis of graphitic carbon nitride

$\text{g-C}_3\text{N}_4$ was synthesized based on the previous reported procedure [36]. In brief, calcination of melamine (5.0 g) at 550 °C for 4 h under the heating rate of 3.5 °C/min in a high-temperature muffle furnace resulted to yield a yellow solid, which was pulverized into powder, and washed with excess amount of water and ethanol. The obtained sample was further subjected to dry at 80 °C for 12 h, followed by kept to store in a vacuum desiccator.

2.3 Synthesis of Ag_2ZrO_3

Ag_2ZrO_3 was synthesized by following reported procedure [37]. In brief, 100 mL aqueous solution of zirconyl chloride octahydrate (0.355 g) was

ultrasonicated for 30 min, and then 0.071 g AgNO_3 was added followed by ultrasonicated for 30 min. Then, the resulted precipitate was washed with excess amount of water and ethanol and was dried for overnight at room temperature. The obtained sample was kept to store in a vacuum desiccator.

2.4 Synthesis of $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ composite (1:1 weight ratio)

To synthesis $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ composite, 0.355 g of Ag_2ZrO_3 in 100 mL of water was dispersed by ultrasonication for 30 min, and then 0.355 g of $\text{g-C}_3\text{N}_4$ was added in the above solution and continued to ultrasonicate for 30 min. The resultant precipitate was washed with excess amount of water and ethanol and was dried for overnight at room temperature. The product was collected and stored in the vacuum desiccator [38].

3 Results and discussion

3.1 Structural and surface morphological analysis

The crystalline nature and phase purity of $\text{g-C}_3\text{N}_4$, Ag_2ZrO_3 , and $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ were analyzed using X-ray diffraction pattern (XRD). A peak at 27.5° in the XRD pattern of $\text{g-C}_3\text{N}_4$ (JCPDS: 87-1526) belongs to (002) planes of the interlayer stacking of aromatic

components and tris-triazine units of $g\text{-C}_3\text{N}_4$, which have been also noted in the $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ nanocomposite [39, 40]. All the diffraction peaks of Ag_2ZrO_3 perfectly match with that of previously reported Ag_2ZrO_3 and which corresponds to 2θ values of 27.85° , 32.25° , 46.25° , 54.80° , 57.50° , 67.50° , 74.51° , and 77.10° . The crystalline phases of Ag_2ZrO_3 are compared and resulted in similar with Na_2ZrO_3 and Ag_2SnO_3 , because the structural chemistry of Ag_2ZrO_3 is not well studied in the literature [41–43]. Further, it is also noted that the characteristic peak positions of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ nanocomposite are analogous to those of pure $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 , and there are no other distinguished peaks noted in the recorded XRD pattern (Fig. 2). Further, a peak emerges about 27° , in the synthesized composite

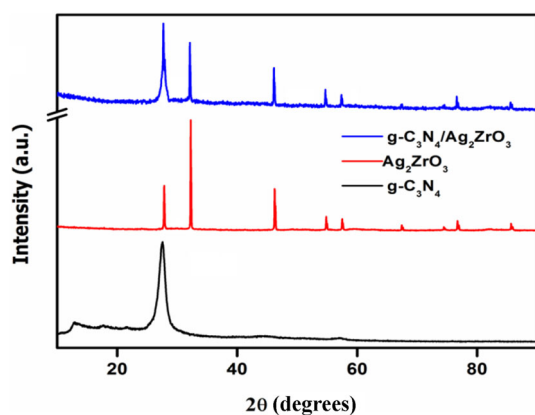
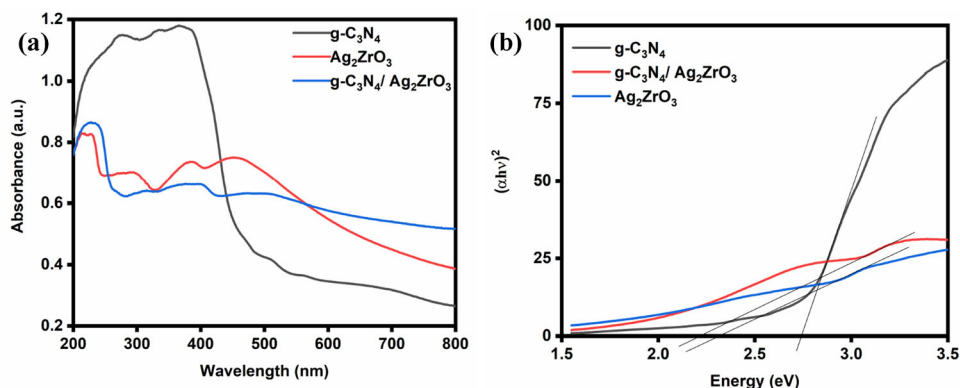


Fig. 2 Powder XRD pattern of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$

Fig. 3 UV–Vis DRS spectra (a) and Tauc plot (b), for $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$



which may be related to the hybridization between $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 .

UV–Vis DRS spectra of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ are displayed in Fig. 3a. To find the band-gap energy of the materials, the following Tauc Eq. (1) was used [36, 44].

$$\alpha h\nu = A(h\nu - E_g)^{n/2}, \quad (1)$$

where α , h , ν , A , and E_g are the absorption coefficient of the nanomaterial, Planck's constant, frequency of light, proportionality constant, and band-gap energy of the materials, respectively. The type of transition in the material could be determined from its n values ($n = 1$ and 4 , respectively, for direct and indirect transitions). By plotting $(\alpha h\nu)^2$ vs. $h\nu$ and extrapolating the graph to the x -axis as in Fig. 3b, E_g values for the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ were obtained as 2.73, 2.33, and 2.22 eV, respectively. The observation of reduction in the E_g values clearly shows the efficient creation of tight chemically bounded interfaces between the $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 phases in $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ nanocomposite.

The FE-SEM images for the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ are given in Fig. 4a–c. $g\text{-C}_3\text{N}_4$ appears as multiple wrinkled-layer stack, whereas Ag_2ZrO_3 and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ seem as regular granules. Furthermore, it is also noted that spherical-shaped Ag_2ZrO_3 nanoparticles were evenly anchored and distributed over the surface of graphitic carbon nitride.

TEM image of Fig. 5a $g\text{-C}_3\text{N}_4$ shows smooth sheet-like structures with sharp edges and crystal clear lattice fringes. TEM image of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ nanocomposite in Fig. 5b shows the homogeneous

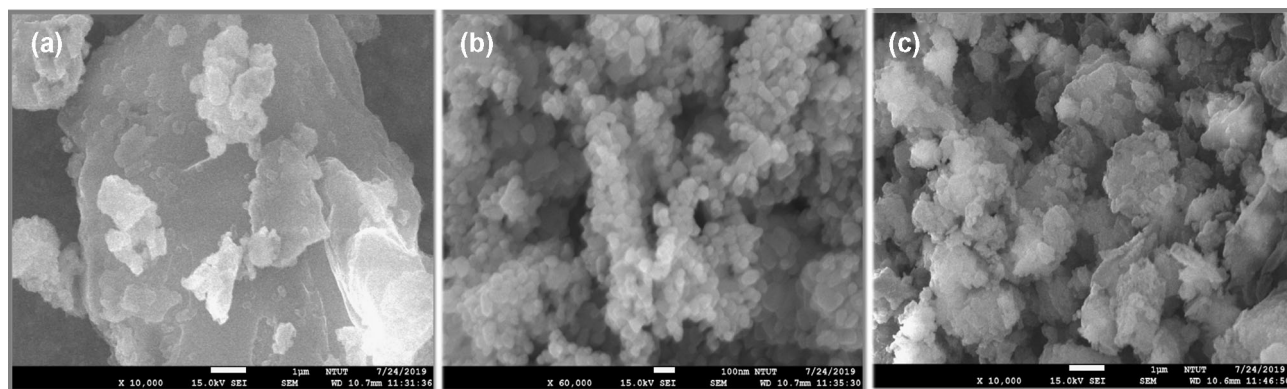
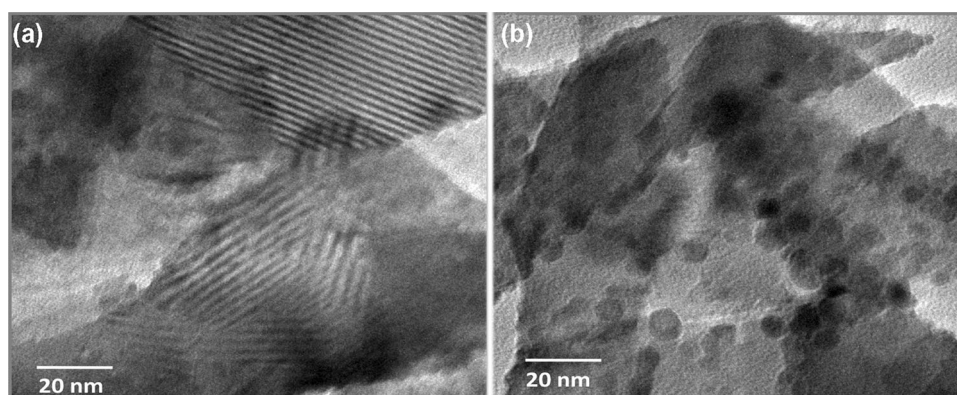


Fig. 4 FE-SEM images of (a) $g\text{-C}_3\text{N}_4$, (b) Ag_2ZrO_3 and (c) $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$

Fig. 5 TEM images of (a) $g\text{-C}_3\text{N}_4$ and (b) $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$



dispersion of the spherical Ag_2ZrO_3 nanoparticles on the entire surface of $g\text{-C}_3\text{N}_4$ nanosheets.

The specific surface area and pore size of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ were studied using nitrogen adsorption–desorption analysis (Fig. 6). The Brunauer–Emmett–Teller (BET)-specific surface area of the $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ was measured to be about $136\text{ m}^2/\text{g}$ which is considerably higher than $g\text{-C}_3\text{N}_4$ ($12.41\text{ m}^2/\text{g}$) and Ag_2ZrO_3 ($31.19\text{ m}^2/\text{g}$). The higher surface area may be due to good interaction between their counter parts leading to the formation of the aggregated pores among them. This provided more reaction sites, which in turn enhanced the electron–hole charge separation causing improvement in the sensor efficiency as compared to $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 . Further, pore size is also decreased for $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ (17.99 \AA) compared to $g\text{-C}_3\text{N}_4$ (76.92 \AA) and Ag_2ZrO_3 (28.18 \AA).

3.2 Gas sensor studies

Preliminarily, gas sensor studies were tested for the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ against

50 ppm concentration of six different gases namely n-butanol, isopropanol, methanol, xylene, toluene, and ethanol at room temperature. Depends on the variation in the chemiresistance behavior of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ in the absence and presence of six different gases, the following parameters have been calculated by using Eqs. (2) and (3) [35, 36].

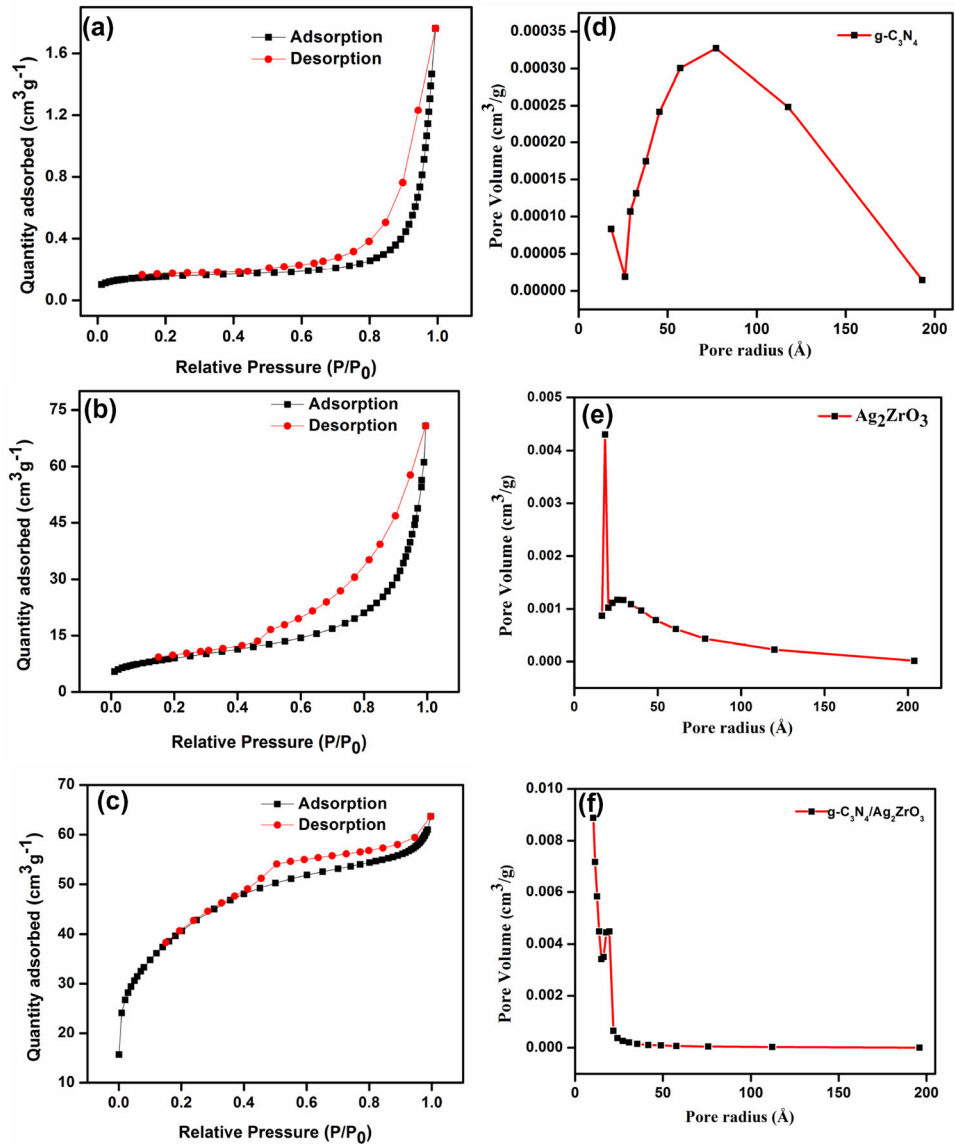
$$\text{Gas sensor response (\%)} = [(R_a - R_g)/R_a] \times 100, \quad (2)$$

$$\text{Gas sensor response (in times)} = R_a/R_g, \quad (3)$$

where R_a and R_g are the resistance value of the sensors in air and test gas, respectively.

By monitoring the alteration in the chemiresistance of the sensor in the presence of air and exposed gas, sensor response (%) for the chosen nanomaterials against six different gases was plotted in Fig. 7, and it shows that all the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ -based sensors more selectively distinguish ethanol gas in comparison to other gases. Particularly, $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 display moderate sensor response values of 15.1% and 24.5% against ethanol

Fig. 6 BET surface area of (a) $g\text{-C}_3\text{N}_4$, (b) Ag_2ZrO_3 and (c) $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$; Pore size distribution curve of (d) $g\text{-C}_3\text{N}_4$, (e) Ag_2ZrO_3 and (f) $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$



gas, respectively, while $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ shows highest sensor response value of 53.1% for ethanol compare to other gases, possibly due to the involvement of cooperative effect of $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 in the gas-sensing mechanism. With reference to literature, there are a limited number of reports only obtainable for the room-temperature-operable ethanol gas sensors. It could be seen from Table 1 that the present $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ -based ethanol sensor shows a significant sensor response value even at room temperature.

To explain gas-sensing mechanism of investigated nanomaterials, involvement of gas adsorption-induced charge transfer could be utilized. It is well-

known fact that the adsorption of molecular oxygen species on the surface of metal oxide-based gas sensor occurs upon exposing to air [17, 18, 21, 49]. The adsorbed oxygen species obtain electrons from the conduction band of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ and become as chemisorbed ions (O_2^- , O^- , and O^{2-}) due to the high electron affinity of oxygen, through the Eqs. (4–7). Thus, depletion layer is produced on the outer surface of the sensing layer due to the decrease in the electron density by chemisorbed species [13, 20, 21, 50, 51]. According to Eqs. (8–13), the reducing gas molecules like ethanol adsorb on the surface of the sensor and undergo reaction with the chemisorbed oxygen ions resulting liberation of

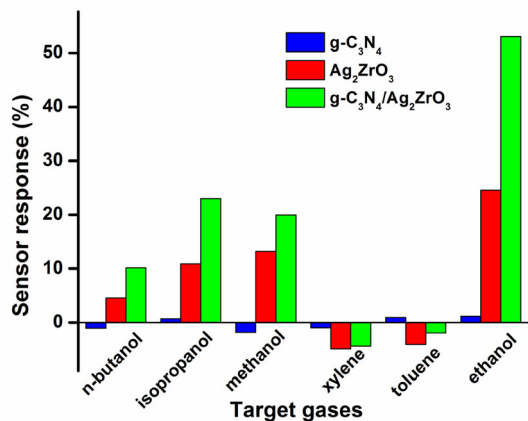


Fig. 7 Sensor responses (%) of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ against 50 ppm concentration of six different gases such as *n*-butanol, isopropanol, methanol, xylene, toluene, and ethanol at room temperature

electrons back to the surface of the sensing layer. The observed high selectivity of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ against ethanol gas may be dependent on the structural and electronic properties of the prepared nanomaterials. As shown in Fig. 8, the gas-sensing mechanism is stoutly reliant on the accessibility of active sites on the surface of gas sensor.

(i) In the presence of air,



(ii) In the presence of gas,

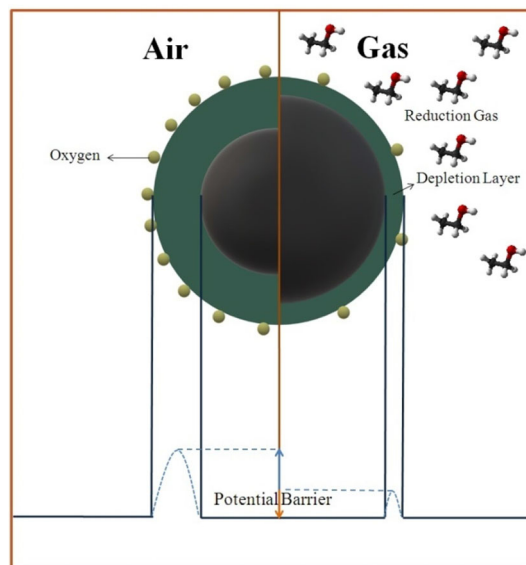


Fig. 8 Mechanism of gas sensing by the semiconducting metal oxide through formation of depletion layer

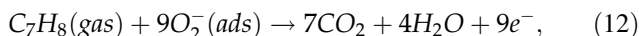
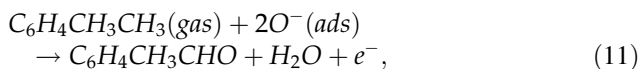
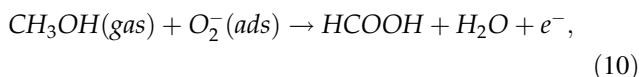
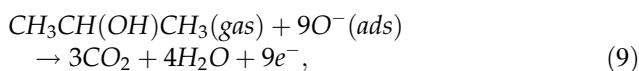
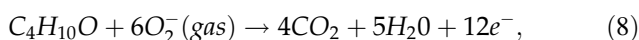


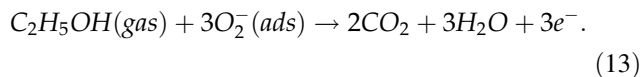
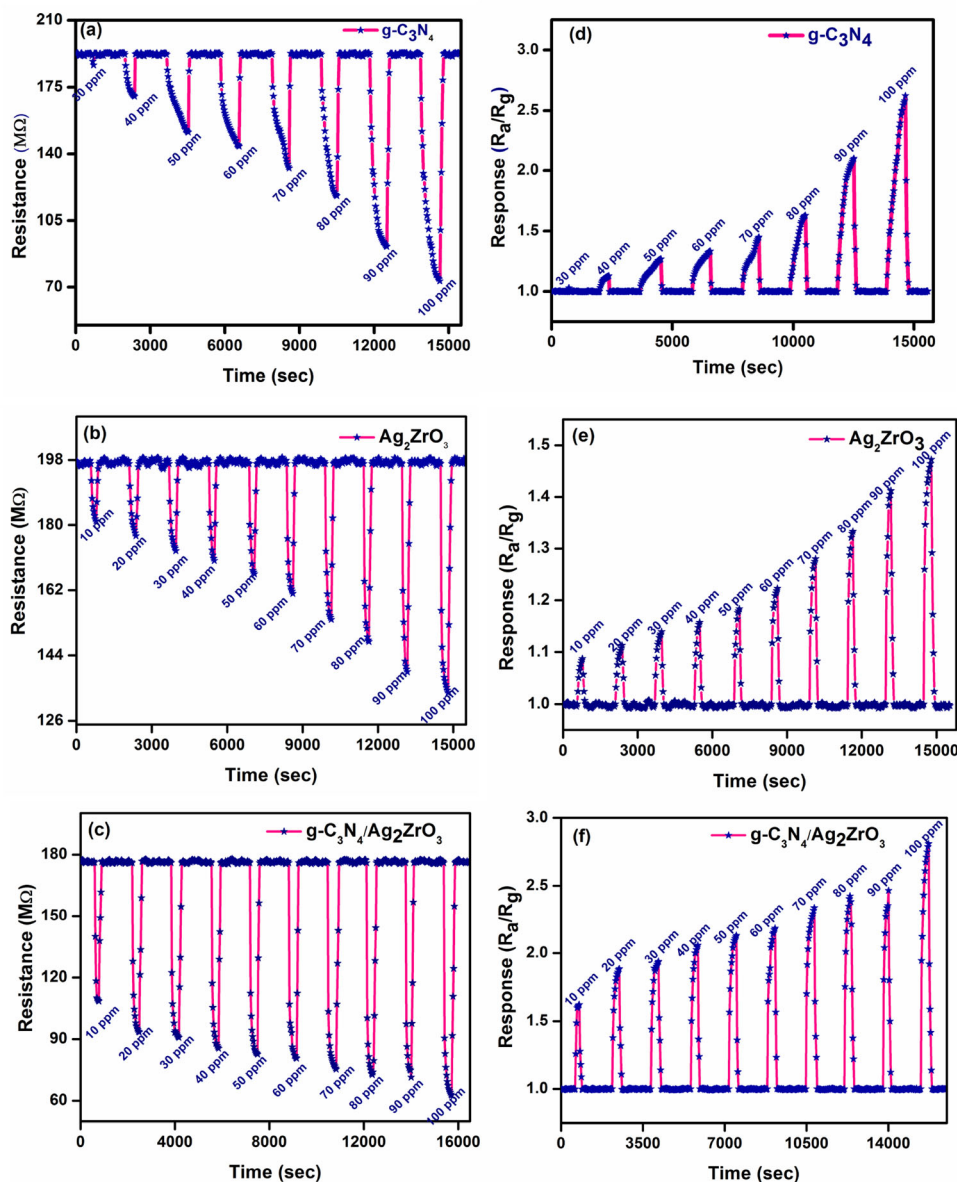
Table 1 Comparison of ethanol gas sensor performance for some $g\text{-C}_3\text{N}_4$ -based nanomaterials

S. no	Sensing material	Conc. in ppm	Operating temperature (°C)	Response
1	$\text{SnO}_2/g\text{-C}_3\text{N}_4$	500	300	240 [33] ^b
2	SnO_2	100	225	17.3 [45] ^a
3	$\alpha\text{-Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$	100	340	7.76 [46] ^a
4	ZnO	350	300	37 [47] ^a
5	$g\text{-C}_3\text{N}_4/\text{ZnO}$	350	100	15.8 [34] ^a
6	$\text{Pt}/\text{ZnO}/g\text{-C}_3\text{N}_4$	250	50	66 [48] ^a
8	$g\text{-C}_3\text{N}_4$	50	RT	15.1 (Present work) ^a
9	Ag_2ZrO_3	50	RT	24.5 (Present work) ^a
10	$g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$	50	RT	53.1 (Present work) ^a

^aResponse (%) = $[(R_a - R_g)/R_a] \times 100$

^bResponse (in times) = R_a/R_g

Fig. 9 Resistance plots (a–c) and response plots (d–f) of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ for sensing the ethanol gas at room temperature



Among the different gases examined, the nano-materials $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ have shown high sensitivity against the ethanol gas and, thus, the gas sensor studies were detailed against ethanol gas in the concentration range of 1–1000 ppm by examining alteration in the resistance value upon alternative exposure of air and ethanol gas. As given in Fig. 9a–c, the resistance value of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ is stable in atmospheric air and gets decreased abruptly upon introduction of ethanol gas and then attains a stable value. Further, the initial

resistance value of sensor is yet again relapsed upon expelling the ethanol gas from the chamber, for the all concentrations investigated.

The fabricated $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ -based gas sensor has considerable reversibility for the sensing the ethanol gas upon a rapid switching between air and gas. By using Eq. (3), sensor response values for the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ were calculated, and the values were plotted against time for the all concentrations investigated (Fig. 9d–f). Upon increasing the concentration of ethanol (1–1000 ppm), $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ exposed a linear enhancement in the sensor response, whereas $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 showed only moderate sensor responses.

The enhancement in the ethanol gas-sensing performance of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ can be explained based on the creation of potential active sites in the $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ sensor with reference to both $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 sensors. Further chemisorbed oxygen anions may liberate trapped electrons back to Ag_2ZrO_3 , and extra electrons may go into Ag_2ZrO_3 from $g\text{-C}_3\text{N}_4$, which may lead to cooperatively improve the detection of ethanol gas upon exposure of ethanol gas on $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ sensor. In addition, there is also possibility of the oxidation of ethanol molecules by $g\text{-C}_3\text{N}_4$ through the formation of hydroxyl species. The enhanced response of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ may lead to stimulate the electron exchange between the sensor material and target gas. Furthermore, the presence of Ag in the Ag_2ZrO_3 may enhance the creation of huge amount of active reaction sites on the surface of $g\text{-C}_3\text{N}_4$. Then, the width of the electron depletion layer is broadened as a result of the adsorbed oxygen molecules, which gain electrons rapidly to generate oxygen ions by means of catalytic action of Ag. Hence, there may be possible to create more number of reaction sites between ethanol gas molecules and chemisorbed oxygen ions at the sensor surface, which leads to the release of electrons back to the surface of the sensing layer.

It could be noted from the response graphs in Fig. 9d–f that the response of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ sensor enhances with the increase of ethanol concentration and its response is relatively higher for $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ than pure $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 . Then, the sensitivity of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ was calculated by making a plot between concentration of ethanol (x) and response (y). $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ displayed high sensitivity value (1.538 ppm^{-1}) in comparison with both $g\text{-C}_3\text{N}_4$ (1.016 ppm^{-1}) and Ag_2ZrO_3 (0.356 ppm^{-1}), and the composite material also has good linearity in gas sensor behavior which is very much needed for the quantitative measurement of ethanol gas (Fig. 10).

The repeatability of the gas sensor response of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ was recorded for five successive response/recovery cycles under the concentration of 50 ppm ethanol gas at room temperature. The observed profile in Fig. 11a displays the similarity and steady repeatability of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ for ethanol gas sensing. The long-term stability of the sensor for over time is an important aspect for its economical usage. The resistance of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ sensor for the detection of 50 ppm concentration of

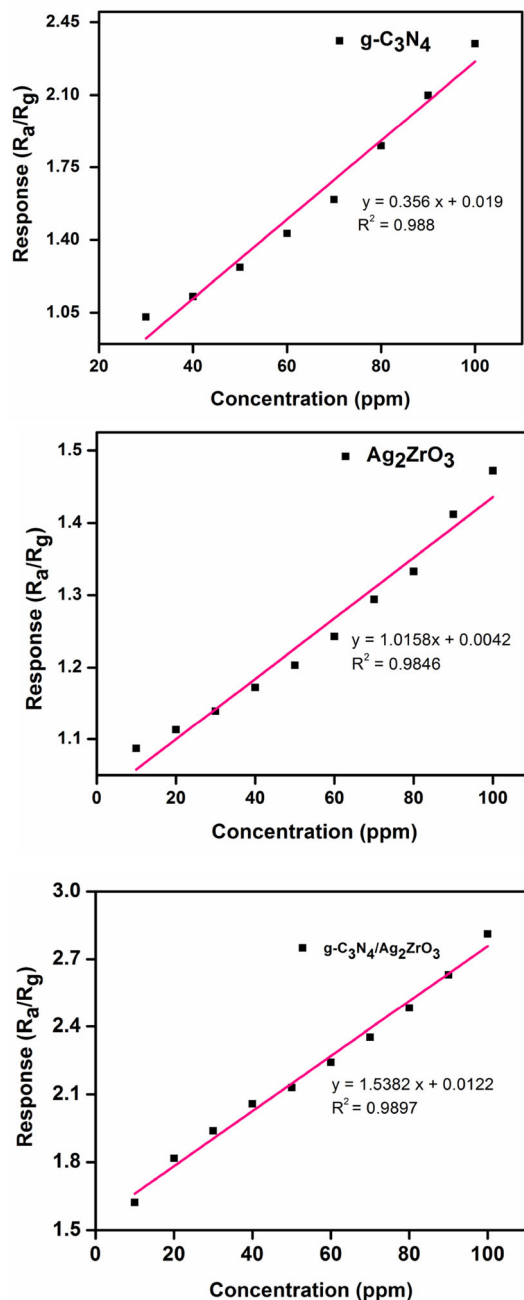


Fig. 10 Sensitivity graphs of $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ -based gas sensors in the concentration range of 10–100 ppm of ethanol

ethanol gas over a time of 24 days is shown in Fig. 11 (b). The obtained results show that $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ sensor has good repeatability and showed nearly constant resistance values as needed for excellent long-term stability. The stability of resistance value of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ in the absence and presence of ethanol gas at 50 ppm is shown in Fig. 11c, and the

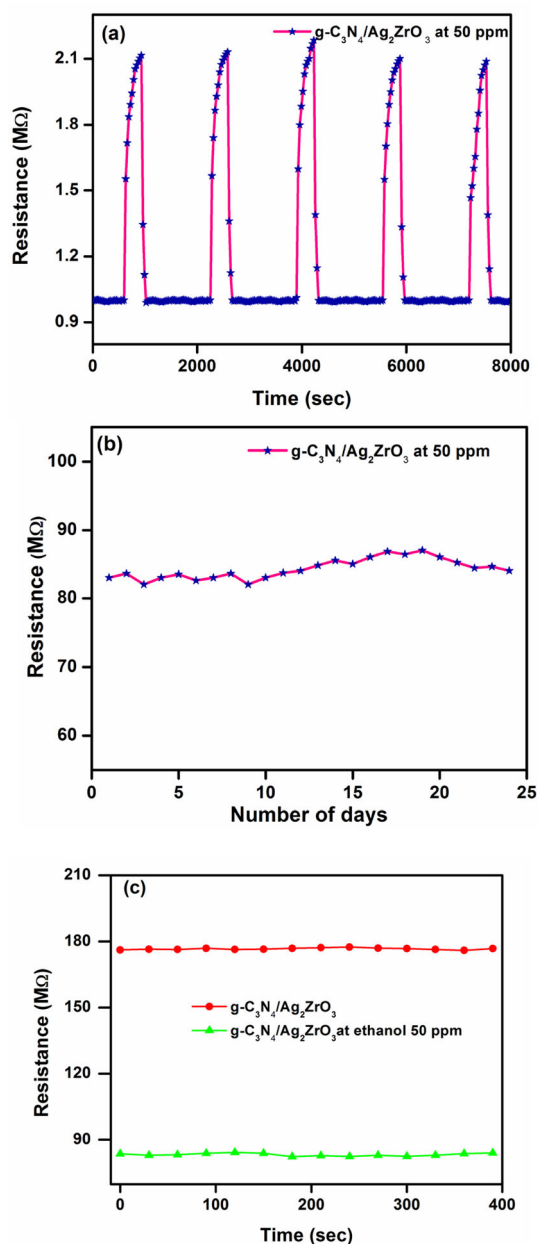


Fig. 11 (a) Repeatability in the sensor response of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ for the five successive cycles at 50 ppm of ethanol gas; (b) Long-term reproducibility of resistance of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ in the presence of ethanol gas at 50 ppm; (c) Stability of the resistance of $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ in air and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ at 50 ppm of ethanol

results show the almost stable resistance value for ethanol gas sensing.

4 Conclusion

In this investigation, $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ was synthesized and characterized by using UV-DRS, XRD, FE-SEM, TEM, and BET. Gas sensor studies for the $g\text{-C}_3\text{N}_4$, Ag_2ZrO_3 , and $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ were analyzed against 50 ppm concentration of six different gases namely against ethanol gas compare to n-butanol, isopropanol, methanol, xylene, and toluene gases at room temperature. Among the six different gases, $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ has shown high sensitivity against ethanol gas, and hence, the gas sensor studies were detailed for ethanol gas sensor. The $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 showed moderate relative sensor response value of 15.1% and 24.5% against ethanol, while $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ showed the highest relative sensor response value of 53.1% for ethanol compared to other gases conceivably due to involvement of cooperative effect of $g\text{-C}_3\text{N}_4$ and Ag_2ZrO_3 . Further, $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{ZrO}_3$ gas sensor showed excellent repeatability, quick response/recovery, and good stability for the detection of ethanol gas. Thus, this kind of modification of chemiresistive semiconductor metal oxide nanocomposite will afford room-temperature-operatable high-performance gas sensors in near future.

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Author contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by SD, SV, and SN. The first draft of the manuscript was written by SD and SV.

Nehru and MS edited the entire draft. SK supervised the whole work and edited the manuscript. All authors read and approved the final manuscript.

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Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare no competing financial interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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