Solid-state synthesis strategy of ZnO nanoparticles for the rapid detection of hazardous Cl₂

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Abstract

In the present study, rapid and highly efficient solid-state synthesis strategy has been successfully employed for the synthesis of zinc oxide nanoparticles (ZnO NPs). Herein, prepared ZnO NPs are characterized and used for the fabrication of highly sensitive, selective, and accountable gas sensors. Structural elucidation, surface composition, and morphological investigations of as-synthesized ZnO NPs respectively, are carried out using X-ray diffraction, Raman spectroscopy, energy dispersive X-ray spectroscopy, scanning electron microscopy, transmission electron microscopy, and selected area electron diffraction measurement techniques. The gas sensing properties of ZnO NPs studied at various operating temperatures and towards

different oxidizing and reducing gases demonstrated the ability of ZnO to detect hazardous chlorine (Cl_2) gas (optimum @ 200°C) with rapid response and recovery times. In addition, ZnO sensor film has detected the low 5 ppm concentration of Cl_2 with reasonable response of 199% with outstanding repeatability and stability in response. The variation of ZnO response with respect to different Cl_2 concentrations has systematically been investigated and explored. Finally, the plausible sensing mechanism of ZnO with Cl_2 gas molecules has been proposed using energy band model diagram.

Keywords: Solid-state synthesis; ZnO NPs; Microstructure; Gas sensor; Cl_2 sensor

1. Introduction

An apprehension for hygienic environment needs strict regulations on the emission of toxic and hazardous gases from the automobiles and industries [1, 2]. Chlorine (Cl_2) gas is an extremely hazardous halogen gas with a stinky smell whose extensively use in various processes including bleaching of pulp in paper mills, producing pharmaceutical drugs, treatment of sewage effluents, and as a disinfecting agent is practically unavoidable. Toxic Cl_2 gas is a very destructive air pollutant and exposure to few parts-per-million (ppm) is harmful to human beings and the environment too. It causes distress in respiration as it communicates with the mucous membrane of the lungs and otherwise can be a serious problem after a few breaths at 1000 ppm [2-6] and have an irritation to eyes and skins at its high concentration. As a result, from the perspective of both the human health and environment concern, the detection of Cl_2 gas at low ppm levels is essential. The increased concern associated to the inauspicious belongings of air pollutants on the environment and humans has resulted in the development of low cost gas sensor devices, which detect toxic and hazardous gases at low concentration range for

monitoring the emission of gases from the automobile/industries and for the protection of human and environmental surroundings [1, 2].

In recent years, nanostructured metal oxides such as, zinc oxide (ZnO) [7], iron oxide [8], tin oxide (SnO₂) [9], indium oxide [10], titanium oxide [11], cobalt oxide [12], nickel oxide [13], and tungsten oxide [14] with semiconducting properties have attracted much more attention of researchers for fabricating low-cost chemical gas sensors with enhanced response to hazardous gases [7-14]. Among different metal oxides, ZnO is a versatile II–VI type semiconductor with wide bandgap (3.37eV) and has been broadly used in a variety of applications such as solar cells [15], photocatalysts [16], luminescent materials [17], and field effect transistors [18] etc., due to its intrinsic properties e.g. low cost, less toxicity, optimal conductivity, availability of various morphologies, and remarkable stability. Till today in order to meet the demand for precise applications, different 1D and 3D ZnO nanostructures including tubes [19], rods [20], wires [21], cups [22], rings [23], dandelions [24], stars [25], and flowers [26] etc., obtained through different synthesis methods such as hydrothermal decomposition, microwave irradiation, seedless aqueous route, hydrothermal method, microwave synthesis, microwave-assisted hydrothermal route, solution process and microwave-assisted route, etc., are reported. However, the synthesis procedures mentioned above work with high energy exploitation, additives, rigid environmental conditions, sophisticated equipment and synthetic procedures, which makes them too complicated to scale-up the desired production. For the large scale synthesis of metal oxide nanostructures, unsophisticated and eco-friendly synthetic procedures would be more appropriate. Therefore, rapid synthesis routes for the metal oxide nanostructures in ambient conditions are challenging and remain extremely advantageous. Considering large scale synthesis, we report here a rapid and highly efficient solid-state synthesis route for the formation of ZnO

nanoparticles (NPs). At room temperature, by means of a solid-state reaction along with two generally accessible inexpensive reactants such as metal precursor zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) and reactant sodium hydroxide (NaOH), NPs of ZnO can be synthesized promptly [27-31].

The main thrust of the present article is to synthesize the ZnO NPs (in film form) by rapid solid-state route and investigate their gas sensing properties to various target gases at different temperatures. Gas sensing results demonstrate the ability of ZnO films, prepared through simple doctor-blade method, to detect Cl_2 gas with short response time and recovery time at lower operating temperatures. The structural, morphological and gas sensing characterizations of ZnO films are systematically carried out and reported. To the best of our knowledge and literature survey, this is the first ever attempt to study the Cl_2 sensing properties of ZnO films synthesized by solid-state route.

2. Experimental

2.1 Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), and ethanol ($\text{C}_2\text{H}_6\text{O}$). All the used chemicals are of analytical grade and were used as received without further purification. Distilled water was used during the entire experiment.

2.2 Solid-state synthesis of ZnO NPs

In a typical solid-state synthesis route, 5 gm of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.5 gm of NaOH were mixed together into a 25 ml capacity of glass beaker without addition of any other solvent and the desired mixture was stirred for 10-15 min until the formation of white colored thick slurry. Subsequently, resulting product was washed several times by distilled water and separated by means of centrifugation. In order to form a homogeneous paste, the product was again dispersed into distilled water and ethanol. Finally, films were fabricated on glass substrates using

doctor blade technique and annealed at 400°C for 1 h before using them for further investigations. The synthesis scheme of the formation of ZnO NPs by solid-state synthesis method is shown in Fig.1.

2.3 Reaction mechanism

The reaction mechanism, i.e. the interaction of the metal salt and NaOH, of formation of ZnO by solid-state synthesis method is as follows [27]:

When the ions from the reactant NaOH come into contact with the metal salt, the precipitation reaction takes place immediately with the evolution of heat, which further supports for combining the reactants and carrying the reaction forward. Hence, NaOH reacts preliminary with the metal salt and yields the resulting metal hydroxide (Zn(OH)₂), which further decomposes to produce ZnO on air-annealing [27].

2.4 Characterization and gas sensing measurements

The orientation and crystallinity of *as*-prepared samples was investigated by using Rigaku X-ray diffractometer with CuK_α source (λ=1.54 Å) in between 10°-80°. Different chemical bonding and vibrations present in the *as*-prepared samples were analyzed by using Fourier transform infrared spectroscopy (FT-IR, Model: Bruker Tensor 27 Spectrophotometer) and Raman spectroscopy (Model: Hololab series 5000 Raman spectroscopy, Kaiser Optical Systems, Inc.) respectively. Morphology and surface area of the samples were analyzed by using scanning electron microscopy (SEM, Model: JEOL-6300F), high resolution transmission electron microscopy (TEM, Model: FEI TECNAI G2 S-TWIN instruments) and Brunauer-Emmett-Teller technique (BET, Model: Belsorp II, BEL Japan Inc.) measurements, respectively.

In order to calculate the response to different target gases, the change in the value of resistance of the solid-state synthesized ZnO films was measured in the presence of an air ambient and the target gases. The gases used for the study include nitrogen dioxide (NO₂), carbon dioxide (CO₂), ammonia (NH₃), hydrogen sulfide (H₂S), Cl₂, and liquefied petroleum gas (LPG) etc., which were commercially procured in the form of canisters (1000 ppm concentration). As to resistance measurement, two silver contacts (0.1 mm thick) 10 mm apart from each other were drawn on the top surface of the ZnO film using commercially procured silver paste and the sample films i.e. ZnO NPs were mounted in the airtight chamber (250 cm³). Concentration of different gases in the chamber was attained by injecting a known quantity of gases with the help of syringes. Change in the resistance of the ZnO films, due to the presence of target gases, was measured by using the 6-digit Keithley 6514 System Electrometer. Keithley Electrometer was coupled to the computer via RS232 interface to record the resistance change with respect to time. Temperature of the sensor films was controlled by the digital temperature controller of the sensing unit, which can heat from room temperature (30°C) to 500 °C. Recovery of the sensor films was achieved by introducing air into the chamber through opening the outlet of the chamber. The sensor response was calculated by using following relation;

$$\text{Response (\%)} = [(R_a - R_g)/R_a] * 100 \quad (1)$$

where R_a and R_g are the resistances of the sample films in presence of air and gas respectively.

3. Results and discussion

3.1 Structural elucidation

The XRD pattern shown in fig.2 (a) demonstrates the crystallographic structure and phase purity of the solid-state synthesized ZnO film composed of NPs. The XRD pattern clearly shows several strong and sharp diffraction peaks, which indicates the polycrystalline behavior of ZnO.

All the observed prominent diffraction peaks are indexed to the hexagonal Wurtzite structure of ZnO, which accords well with standard JCPDS data card No. 36-1451 of ZnO with $a=b=0.3246$ nm and $c=0.5204$ nm. Furthermore, no other peaks associated with the impurity have been noticed in the diffraction pattern, demonstrating the high purity of the *as*-synthesized ZnO product. An average crystallite size, calculated using well-known Scherrer relation ($D=0.9\lambda/\beta\cos\theta$), is found to be ≈ 38 nm.

The surface chemistry of *as*-synthesized ZnO NPs was investigated by using Raman technique and the observed results are presented in fig.2 (b). Corresponding to the vibrational E_2 (high) phonon mode Raman shift analysis presents a single strong intensity peak at 438 cm^{-1} . The observed E_2 phonon mode is a main characteristic of nanocrystalline Wurtzite hexagonal phase of ZnO [32, 33]. EDX spectrum, shown in fig.2 (c), was recorded in order to recognize the existence of zinc (Zn) and oxygen (O) elements in the solid-state synthesized ZnO product. EDX spectrum evidently shows the presence of Zn and O elements in the *as*-synthesized ZnO NPs, corroborating for the formation ZnO. No other noticeable impurity peaks are observed. The calculated atomic and weight percentages of Zn and O are tabulated in the table (inset of fig.2(c)). In addition, the elemental mapping investigation of *as*-synthesized ZnO NPs (see *supporting fig.1*) has clearly revealed that the existence of Zn and O elements into the synthesized product.

3.2 Morphological analysis

Low- and high- magnification SEM images of the ZnO NPs films are shown in fig. 3 (a) and (b), respectively. SEM images present an aggregate type ZnO NPs which are found to be interconnected well with each other and randomly dispersed on the substrate surface with few additional pores. Such kind of well-connected and porous morphology is preferred for gas

sensing application, because it provides larger surface area to volume ratio and high diffusive paths to target gas molecules for infiltration through the pores, which maximizes the surface reactions and as a result enhances the sensor response [34].

Low- and high-magnification TEM images are shown in fig.3 (c) and (d), respectively. It is clearly seen that the aggregated-type ZnO NPs have an average diameter of 37.5 (± 2.5) nm. These NPs are homogeneously connected to each other. HRTEM image of single ZnO particle, shown in fig.3 (e), demonstrates the ordered lattice fringes, which sustains the polycrystalline behavior of solid state synthesized ZnO. The interplanar lattice spacing of the two adjacent equivalent fringes, which corresponds to the (100) plane of Wurtzite ZnO, is found to be 0.32 nm. Presence of several concentric diffraction rings composed of white dotted arrays is clearly seen from the selected area electron diffraction (SAED) pattern (fig.3 (f)) of ZnO; indicating polycrystalline nature of as-synthesized ZnO, consistent to the results in accordance with the XRD study. The nitrogen (N₂) adsorption-desorption isotherm of ZnO NPs, shown in *supporting fig.2 (a)*, demonstrates a characteristic IV-type isotherm behavior (H₃-type hysteresis loop) with 18.57 m²g⁻¹ specific surface area and the average pore-diameter estimated from BJH plot (shown in the *supporting fig.2 (b)*) is found to be 38 nm, indicating mesoporous behavior of solid state synthesized ZnO NPs.

3.3 Gas sensing study

It is known that the operating temperature of the sensor films extensively influences the adsorption/desorption process and surface states of the sensing materials, as a result it plays a crucial role in establishing the gas sensing properties [34, 35]. Therefore, in order to find out the optimal operating temperature and selectivity condition, the gas sensing performance of solid-state synthesized ZnO films was carried out at different operating temperatures and in presence

of various target gases. Fig. 4 (a) demonstrates the selectivity study of ZnO films towards various target gases at fixed 200 ppm concentration @ 200°C, in which NO₂, CO₂, NH₃, H₂S, Cl₂, and LPG etc., were used. It was observed that, after the interaction of reducing gases (such as NH₃, H₂S, and LPG: *electron donating in nature*), sample resistance is decreased. While on the other hand, upon exposure to oxidizing gases (such as CO₂, NO₂, and Cl₂: *electron accepting in nature*), the sample resistance is increased, indicating *n*-type behavior of the *as*-synthesized ZnO. In *n*-type semiconducting materials, the conductivity/resistivity changes are mainly caused by the adsorption/desorption of gas molecules on the surface of sensing material. When the interaction of reducing gases like NH₃, H₂S, and LPG with the *n*-type ZnO sensor film takes place then the majority carrier (electrons) density of ZnO gets increases, owing to the electron donating nature of reducing gases, which results in increase in the conductivity and consequently decreasing the electrical resistance value of ZnO sensor film.

Selectivity bar chart, shown in Fig. 4(a), clearly demonstrates that the ZnO films have exhibited obvious response to Cl₂ and much less response to other test gases under the same 200 ppm concentration, indicating the excellent selectivity to Cl₂ as compared to the other test gases, suggesting that the *as*-synthesized ZnO NPs acts a promising gas sensing material for developing high performance Cl₂ sensors. Response of ZnO NPs as a function of operating temperatures at fixed 80 ppm concentration of Cl₂ is shown in fig. 4(b), which clearly demonstrates that the ZnO NPs reveal a maximum response of 542 % to 80 ppm Cl₂ @ 200°C. In the present case, at lower temperature (< 200°C), Cl₂ gas molecules are too inactive to react with the adsorbed oxygen species at the surface of the ZnO NPs, resulting lower response value. Whereas the higher temperature (> 200°C) restrains the gas adsorption, which leads to a decrease in exploitation rate of the sensing material and, hence, exhibits a lower response value. But at 200°C, the high

molecular activity and the exchange rate of adsorbed oxygen species at the surface contributed significantly together, resulting a higher response value [35]. Therefore, the optimum working temperature of ZnO sensor films was fixed to be 200°C and applied to all further measurements. The response of ZnO NPs as a function of time to 10, 100, and 200 ppm Cl₂ @ 200°C is shown in fig. 4(c). The response values for 10, 100, and 200 ppm Cl₂ are found to 282, 714, and 1278 %, respectively. Fig.4 (d) demonstrates the response behavior of the *as*-synthesized ZnO NPs to 5-200 ppm concentrations of Cl₂ @ 200°C, which proves that the response value of ZnO NPs is increased with increasing concentration of Cl₂. The low concentration implies a lower surface coverage of Cl₂ gas molecules, ensuing in lower surface reactions hence lower the response. While, a higher response at high concentration is due to the higher surface coverage of Cl₂ gas molecules, consequently increases the surface reactions. It appears that, the ZnO NPs sensor has exhibited an excellent response values for various Cl₂ concentrations. Intriguingly, the sensor film detects a low 5 ppm Cl₂ concentration with a remarkable response value of 199%. The plot of resistance as a function of time of ZnO sensor films to 10 ppm exposure of Cl₂ is shown in fig. 4(e). The rapid increase in resistance value is evidenced upon the interaction of Cl₂ with ZnO sensor film with a reasonable response value of 282 % as well as a quick response time (6 s) and recovery time (64 s).

3.4 Gas sensing mechanism

The generally accepted gas sensing mechanism for a typical *n*-type semiconductor is related to the change in the resistance value of the sensing material, which is primarily originated due to the adsorption-desorption process of target gas molecules on the top of the surface of the sensing material [8]. The representative gas sensing mechanism of ZnO in presence of air

atmosphere and the Cl_2 gas has been proposed based on the energy band diagram demonstrated in fig. 5.

Basically, ZnO is *n*-type semiconductor, which contains electrons as a majority charge carrier. When the solid-state synthesized ZnO sensor film is exposed to the fresh air, the oxygen molecules from the air adsorb on the top of the ZnO film surface by capturing electrons from the conduction band of the ZnO, leading to the formation of surface adsorbed oxygen species (herein O^-) and hence decreases the concentration of electrons in ZnO. The oxygen absorbed on the surface of the materials influences the resistance value of the oxide-based sensor films. Commonly, the adsorbed oxygen is temperature dependent; having O_2^- character below 100°C , O^- in between $100\text{--}300^\circ\text{C}$, and O^{2-} above 300°C [35]. In present study O^- is dominant because the optimized sensing temperature of the ZnO sensor film is 200°C . Before exposing to Cl_2 , the resistance value of the ZnO sensor film has been stabilized and the results are presented in *supporting Fig.3 (a)*. It is observed that, in presence of Cl_2 , resistance of the ZnO film is increased rapidly with respect to time and a plateau region is achieved in a few seconds, signifying the quick response to Cl_2 . For the recovery of the sensor, outlet of the chamber was opened and fresh air was allowed to pass through the chamber, as a result Cl_2 could desorb and the sensor reached to its initial value of resistance. Upon the interaction of Cl_2 with the ZnO film, the previously adsorbed O^- species take part in the reaction, as a result adsorbed oxygen species get replaced by forming Cl_2 gases species consequently because of the electron accepting nature of Cl_2 the resistance value of the ZnO is increased.

The plot of response as a function of time upon 5 ppm exposure of Cl_2 is shown in fig.6 (a). The ZnO film sensor has exhibited a sensible response of 199 % toward 5 ppm Cl_2 @ 200°C with quick response (8 s) and recovery time (50 s), signifying potential use of ZnO NPs film to

detect a lower concentration of Cl_2 . The plot of response as a function of time, shown in *supporting fig.3 (b)*, of ZnO NPs has revealed that the sensor film has demonstrated a reasonable response of 1278% to 200 ppm Cl_2 . Response repeatability and stability are considered as the decisive parameters for the practical application of gas sensors. The response repeatability study of ZnO sensor film was measured by repeating the response measurement for three times to fixed 100 ppm concentration of Cl_2 and the corresponding results are illustrated in *fig. 6 (b)*, which suggests a quite comparable response to all the measurements. The comparison of different sensing parameters of solid state synthesized ZnO is tabulated in table 1. It was observed that with increasing concentration of Cl_2 gas, response time was found to decreasing while recovery time increasing.

It is renowned that, the response and recovery times of the sensor films are primarily depends on how quick the gas diffusion and reaction among the target gas molecules and the sensor element takes place. This can provide increase to a superior free volume and effortless diffusion of gas molecules (herein Cl_2) in and out of the sensing material (herein ZnO) [36]. The shrinkage in response time of ZnO sensor film with increasing Cl_2 concentration might be owing to the large accessibility of vacant sites on the films for gas adsorption of gas as noticeable from SEM micrograph. On the other hand, rising recovery time is due to the gas reaction species which left behind subsequent to gas interaction ensuing decrease in desorption rate [37].

Stability study of ZnO sensor film was measured for 20 days at a fixed concentration of 80 ppm Cl_2 @ 200°C and the equivalent results are depicted in *fig. 6 (c)*. Initially the ZnO NPs film sensor has exhibited a maximum response of 542% to 80 ppm Cl_2 , while after 20 days a slight decrease in response value of 532% is obtained. Such slight decrease in response is mainly

due to the aging induced effect [8]. The stability performance of ZnO film clearly shows that the response of the sensor retained well, demonstrating the superior stability of the sensor.

Based on the gas sensing results it is concluded that the solid state synthesized ZnO sensor film exhibits superior Cl₂ sensing properties at lower temperature with fast response and recovery time values. Furthermore, ZnO film is able to detect a lower 5 ppm concentration of hazardous Cl₂ with superior response. Thus, the observed sensing properties of ZnO NPs film make it suitable candidate for the detection of hazardous Cl₂ at different fields.

4. Conclusions

In summary, ZnO NPs of the diameter of 35-40 nm are successfully synthesized *via* a rapid solid-state synthesis method and their chemoresistive performance towards various oxidizing and reducing gases has been studied and explored systematically. The gas sensing results demonstrate high response, excellent selectivity, outstanding repeatability in response, and long term stability to hazardous Cl₂ @ 200°C of ZnO NPs when used in sensor application. Film of ZnO NPs showed a reasonable response of 1278% to 200 ppm Cl₂ @ 200°C with fast response and recovery times. Moreover, ZnO sensor films show the potential to detect as low as 5 ppm Cl₂ concentration with reasonable response of 199%. We believe that the solid-state synthesized ZnO NPs film has a potential in the fabrication of low cost and high performance Cl₂ gas sensors and can be applied for other sensors too, which is a topic of ongoing research.

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Figure captions

Fig.1. Synthesis scheme of formation of ZnO NPs.

Fig.2. (a) XRD, (b) Raman, and (c) EDX spectrum of ZnO NPs.

Fig.3. Low- and high-magnification SEM (a, b) and TEM (c, d) images of ZnO NPs; (e) HRTEM and SAED pattern of ZnO NPs.

Fig.4. (a) Selectivity study of ZnO towards various gases, (b) Plot of variation of response of ZnO sensor with respect to different temperatures, (c) Plot of response as a function of time to 10, 100, and 200 ppm Cl_2 @200°C, (d) Variation of response of ZnO sensor film to various concentrations of Cl_2 , and (e) Plot of variation of resistance as a function of time upon 10 ppm exposure of Cl_2 .

Fig.5. Schematic of sensing mechanism of ZnO sample.

Fig.6. (a) Plot of response of ZnO sensor film to 5 ppm Cl_2 , (b) Response repeatability, and (c) Stability study of ZnO sensor film.

Table caption

Table 1: Comparison of different sensing parameters of ZnO sensor film

Table 1

Sample	Operating temp. (°C)	Concentration of Cl ₂ gas (ppm)	Response (%)	Response time (sec)	Recovery time (sec)
ZnO	200	5	199	8	50
		10	282	6	64
		100	714	5	82
		150	1098	5	94
		200	1278	3	97

Figures

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Graphical abstract

Solid-state synthesis strategy of ZnO nanoparticles for the rapid detection of hazardous Cl_2

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