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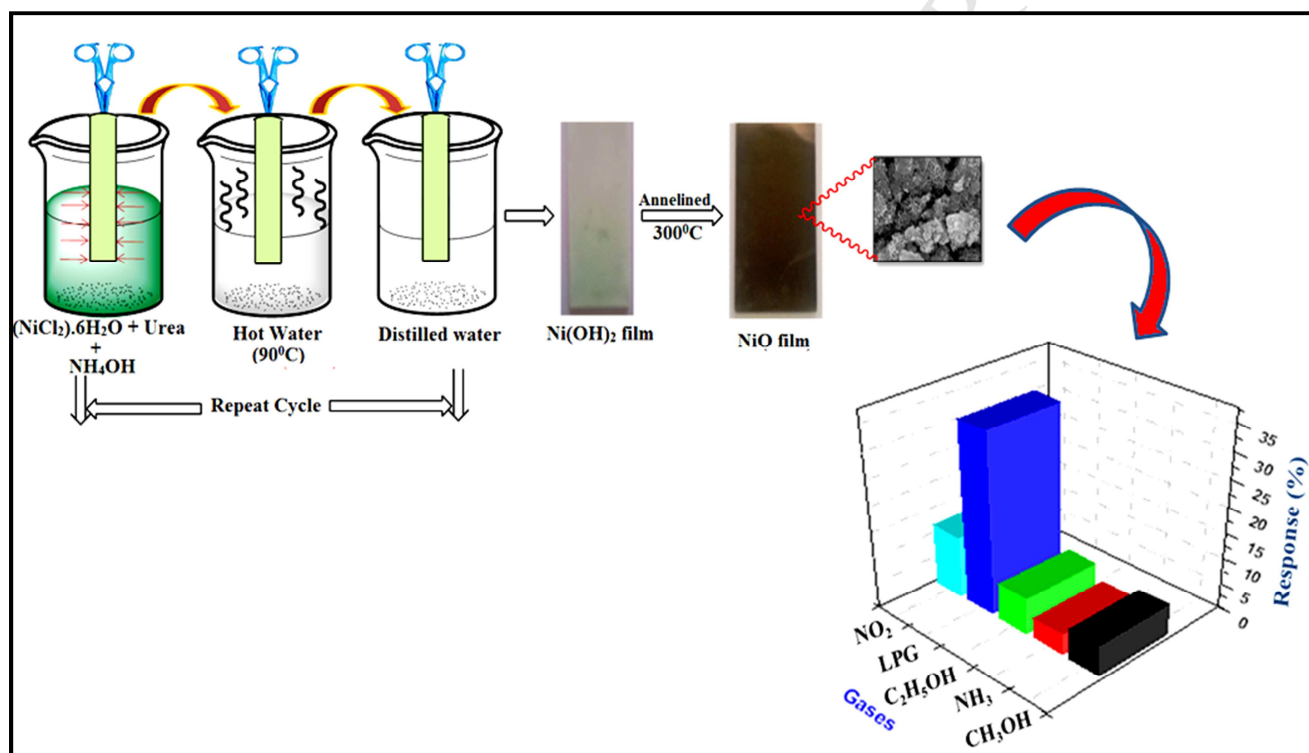
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Graphical abstract

Solution-processed Nickel Oxide films and their Liquefied Petroleum Gas Sensing Activity

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Solution-processed nickel oxide films and their liquefied petroleum gas sensing activity

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Abstract

Present article demonstrates the facial synthesis of nickel oxide (NiO) films *via* an easy and cost-effective successive ionic layer adsorption and reaction (SILAR) method onto glass substrate using nickel (II) chloride as precursor and their gas sensing activity towards different target gases. Structural elucidation and elemental composition analysis measurements were conducted using X-ray diffraction, Raman and energy dispersive X-ray techniques, respectively. Platelet-type morphology was confirmed from the plane-view images recorded on field-emission scanning electron and transmission electron microscopes at different magnifications. Chemo-resistive performance of NiO films was carried out towards hazardous and explosive gases such as ammonia, methanol, ethanol, liquefied petroleum gas (LPG) and nitrogen dioxide as a function of working temperature and gas concentration. Amongst diverse gases, NiO sensor film

exhibits better response of 72% to 5000 ppm LPG at lower operating temperature (180 °C). Effect of LPG concentration on gas response of the NiO film was systematically investigated and explored. Also, the synergistic interaction between LPG molecules and NiO nanoplates was studied and explored using potential barrier model.

Keywords: Nickel oxide; SILAR, Gas Sensing properties; Response-recovery; Modeling

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1. Introduction

The importance of gas sensor as the low-cost and environmentally friendly technology is prompting researchers to seriously consider industrial and domestic safety [1, 2]. Liquefied petroleum gas (LPG) is one of the perilous combustible gases because leaks can lead to serious accidents. Therefore, development of sensing materials detecting hazardous LPG gas at low ppm level is essential. Alternatively, nitrogen dioxide (NO₂) above its 100 ppm level can cause death due to asphyxiation from fluid in the lungs and 25 and 30 ppm levels of ammonium (NH₃) are respectively detected simply by smelling and reasonable for feeling uncomfortable for human beings. The comprehension of these goals is unfeasible without taking the importance of the materials like transition metals/metal oxides into account, so the focus on the preparation and deposition methods is vital. These methods can be either physical or chemical in the form of powders or thin layers (on an appropriate substrate). Metal oxide chemical bath deposited thin films composed of nanoparticles such as ZnO, SnO₂, Fe₂O₃, In₂O₃, TiO₂ etc., are attractive for the development of gas sensing devices owing to their obvious advantages such as low production-cost as well as conservable thermal and chemical stabilities [2-13]. In addition, transition metal oxide nanostructures with altered surface morphologies can be excellent for the manufacture of the gas sensor devices. It is accepted that the conductivity of transition metal oxide nanostructures can be tuned with the surface desorption and adsorption of gas molecules. This change is mainly caused by the electronic transfer that occurs upon the adsorption of gas molecules over the surface of film. Conductivity changes robustly depending upon the shape and the size of the nanostructures used [5-7]. Among various transition metal oxides, nickel oxide

(NiO) is a promising metal oxide with a wide band gap of 3.6-4.0 eV and acts as a *p*-type semiconductor, which finds numerous applications in smart windows [8], electrochemical supercapacitors [9-11], as a transparent *p*-type semiconducting layer [12, 13], as an anti-ferromagnetic film [14], and in dye sensitized solar cells (as a photocathode) too [15]. It exhibits anodic electrochemical stability, excellent durability, large spin optical density, and various manufacturing possibilities. Nowadays, plethora of NiO semiconductor nanostructures is a hot topic in the new era of gas sensor research. Different methods have been reported for the synthesis of NiO nanoparticles such as thermal evaporation [16, 17], magnetron sputtering [18-19], electrodeposition [20], sol-gel [21], chemical bath deposition (CBD) [10], successive ionic layer adsorption and reaction (SILAR) method, spray pyrolysis [22], surfactant mediated synthesis [23], polymer matrix-assisted synthesis [24], thermal decompositions [25], microemulsion [26], etc. Of these, SILAR is one of the prominent methods because of its simplicity and inexpensive way of deposition of variety of metal oxides in the form of thin films. In this method, a uniform thin film of nanoparticles is obtained through layer-by-layer approach on the substrate surface. Advantages of this method include simple operation, cheap, highly efficient and thickness controllability of the deposited film [27] etc. The gas sensing performance can be improved by understanding the influence of size, porosity, and morphology of the nanostructure [3-5]. Nanoparticles, on account of their sizes, exhibit novel material properties that are significantly different from those of their bulk counterparts. NiO nanoparticles of equal dimensions and good dispersion are desirable for many applications e.g. in designing ceramic, magnetic, electro-chromic, and heterogeneous catalytic [24-29] etc. Gunjekar *et al.* [30] reported LPG sensor-based on chemical bath deposited NiO thin films operating at 698 K with a response of 36.5% and in a second report, Nalage *et al.* [31] developed sol-gel-based NiO thin film sensor with 23.3% response for the detection of NO₂ gas at 200 °C. Recently, Dalavi *et al.* [32] reported nanoporous network of NiO using CBD method and applied for NH₃ gas with 13% response at 250 °C. In short, depending upon the nature of conductivity i.e. *n/p*-type, type of nanostructure, porosity and crystal structure of thin/thick metal oxide/polymer films and type of gas used for detection have strong influence of sensor application.

Herein, we demonstrate the synthesis of NiO films by a facile SILAR method approach at room temperature (25°C) without the necessity of any surfactant and later used for the detection of hazardous LPG at lower temperature. As-deposited NiO film was characterized for its structural,

morphological, and surface related properties and then studied its sensing properties, which shows an excellent response of 72% towards 5000 ppm exposure of LPG gas. The obtained results of NiO sensor film for LPG constitute a significant improvement of reports in literature [30-32].

2. Experimental details

2.1. Synthesis of NiO film

Analytical reagent grade (AR) chemicals such as $(\text{NiCl}_2) \cdot 6\text{H}_2\text{O}$, and ammonia (NH_4OH) were used for synthesis of nickel oxide. Before the deposition of NiO thin films, glass slides were cleaned with detergent and double distilled water, then boiled in chromic acid (0.5 M) for 15 min, and then were washed with double-distilled water and ultrasonicated for 15 min. Finally, these slides were degreased in AR grade acetone and used for deposition. To obtain good quality NiO thin film; adsorption, reaction and rinsing time durations were controlled correctly and carefully. The film was deposited as a complete film layer with experimental conditions-like pH , concentration and temperature of cationic and anionic precursor solutions. One cycle of $\text{Ni}(\text{OH})_2$ film was composed of combination of two half cycles; first half was immersion of glass slide in nickel precursor solution maintained at $\text{pH} \approx 12$ for 25 s followed rinsing in water 20 s and second half was in hot water maintained at 90°C for 20 s. It was observed that NiO film deposited onto glass slide using SILAR method was gray in appearance, uniform and well-adherent to the glass substrate. Additionally, we performed the same kind of synthesis with 30 cycles to visualize the film. Moreover, it would be pointed out that the initial growth of $\text{Ni}(\text{OH})_2$ was limited, however, as the nucleation rate was considerably high. The deposited films of $\text{Ni}(\text{OH})_2$ were annealed at 573K for 1 h in order to form NiO, which was qualitatively confirmed as the surface appearance was changed from faint greenish to dark black (Fig.1).

2.2 Material characteristics

X-ray diffraction (XRD) pattern of NiO film was recorded using Rigaku D/MAX 2500V diffractometer using Cu-K_α radiation (source of X-ray). Wavelength of source was 1.5418 \AA and operating conditions were; 40 kV, 60 mA, 10° - 80° (2θ) scanning angle range and $0.03^\circ/\text{s}$ scanning rate. The microstructure of the NiO sample was analyzed by field-emission scanning

electron microscopy (Model: FESEM, Hitachi S-4200). The atomic concentrations of carbon, oxygen, and nickel were determined by energy dispersive X-ray spectrometer (EDX). The high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SEAD) measurements were carried out by using FEI TECNAI G2 S-TWIN instruments equipped with LaB₆ cathode and a GATAN MS794 P CCD camera. The micrographs were obtained at an acceleration voltage of 200kV.

2.3 Sensor properties

Chemiresistive performance of NiO sensor film, composed of upright-standing nanoplates, was monitored by using home built static gas sensing unit. For the measurement of change in film resistance, two silver contacts separated from each other by 1 cm were drawn on the film and dried at air atmosphere before measurement. Concentration of several gases such as ammonia (NH₃), methanol (CH₃OH), ethanol (C₂H₅OH), nitrogen dioxide (NO₂), and LPG (propane + butane) in the air-tight chamber was achieved by injecting a defined amount by a syringe. All gases used for the study were in the form of canisters with 40000 ppm concentration. The measurement of resistance was carried out in presence of air and gas atmosphere as a function of temperature (in increment of 10° C). Temperature of the sensor was controlled with the help of digital temperature controller of the sensing unit, which can heat from room temperature to 500 °C. For the gas sensing measurements, sensor film was mounted in an air-tight glass chamber with a volume of 500 cm³. The changes in resistances of the NiO sensors due to the presence of LPG and NH₃, CH₃OH, C₂H₅OH, and NO₂ gases were noted and plotted as function of time. The response (%) was calculated using the following relation;

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

where, R_g and R_a are the resistances of NiO film in gas and air, respectively. The gas concentration in ppm was calculated by the following formula:

$$\text{Concentration in ppm of test gas} = [\text{Volume of gas in ml.} \times \text{Conc. of gas in cylinder} / \text{Volume of Chamber}] \quad (2)$$

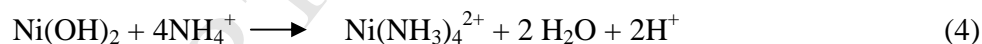
3. Results and discussion

3.1. NiO film formation mechanism

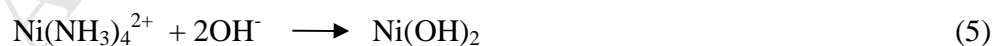
Films of $\text{Ni}(\text{OH})_2$ were initially obtained by immersing ultrasonically cleaned glass slides into separately placed cationic and anionic precursors i.e. NiCl_2 and water. Initially, 0.1 M NiCl_2 was used as a source of nickel and ammonia (NH_4OH) solution (25% extra pure) was added with constant stirring to make it alkaline ($\text{pH} \approx 12$). The growth of a thin film deposition process is of the *ion-by-ion* type by surface coagulation and adsorption of collides at the nucleation sites [32-34]. When aqueous ammonia solution was added to nickel chloride, the ionic product of $\text{Ni}(\text{OH})_2$ exceeds the solubility product and the solution becomes turbid due to formation of $\text{Ni}(\text{OH})_2$ precipitates. We believed that at higher pH, solution attains supersaturation thereby ions find considerably higher energy and fast rate of reaction by losing OH^- ions whereas at lower pH ions are bound and reaction kinetics is relatively slow.



However, excess addition of surplus ammonia solution reduces Ni^{2+} ion by producing the complex with coordination number four. This can be explained by the following reaction;



The triple distilled water provides source of OH^- ions by heating at the temperature near boiling point (90°C). When glass slide is immersed in the above solution, the force of attraction between nickel (complex) ions and the substrate leads to their adsorption on the surface eventually making the film adherent.



3.2. Structural elucidation

The XRD pattern of NiO film, as seen in Fig. 2(a) shows the NiO deposited onto a glass slide was perfectly crystalline and pure. XRD spectrum of NiO showed Bragg reflections at $2\theta = 37.28^\circ$, 43.31° , 62.54° and 75.46° , which were assigned to the scattering from (111), (200), (220) and (311) planes of cubic NiO respectively. All the diffraction peaks agreed closely with JCPDS file no. 47-1049 (cubic nickel oxide (bunsenite, NaCl type structure)). No other noticeable impurity peaks were detected in XRD analysis, suggesting purity in structure and phase of NiO. The presence of sharp diffraction peaks was an indication of the polycrystalline nature of the synthesized NiO [35]. The formation of NiO was also evident from the Raman spectrum (Fig. 2(b)) carried out on thin films of NiO formed by SILAR method. Raman spectrum of NiO illustrates two vibrational bands centered at 550 cm^{-1} and 1095 cm^{-1} , which were due to one phonon (1P) longitudinal optical (LO) and 2LO modes of Ni-O oscillation, respectively [36, 37].

3.3. Surface appearance

The microstructure of NiO film was analyzed from digital photo-image obtained using FESEM (Fig.3 (a), (b) and (c) at $1\text{ }\mu\text{m}$, 600 nm and 300 nm). FESEM image confirmed mixed and irregular platelet-type surface morphology of NiO. Such porous-type morphology could be beneficial for gas sensing application due to offerings of large specific surface area to effect elevated response of the target gas (herein LPG). It was interesting to see particles in agglomerated form that could be detrimental in gaining the expected responsively; however, because of high surface area sufficient amounts of active sites for gas adsorption could present. We believe that gas circulation occurred more readily due to nanoplate-type morphology and porous structure, which might promote the reaction between film surface and gas molecules by resulting higher response [38]. The EDX analysis (Fig. 3(d)) was carried out to identify the presence of nickel and oxygen in chemically deposited NiO film with reference peak at 0 keV . EDX spectrum clearly presents the existence of Ni and O elements in the deposited film with stoichiometry of 54:46 (Ni:O). The HRTEM image (Fig.4 (a)) and TEM image (Fig.4 (b&c)) confirmed NiO NPs with size ranging $4\text{--}8\text{ nm}$ in the near surface of copper grew. The high

resolution TEM (Fig. 4(a)) proved lattice arrangement and pure crystallinity. SEAD pattern (Fig. 4 (d)) demonstrates NiO NPs were perfectly crystalline in nature with peaks (111), (200), (220) and (311).

3.4. Gas sensing studies

Gas sensing characteristics of SILAR deposited NiO sensor films were studied towards various oxidizing and reducing gases such as NH_3 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, LPG and NO_2 using the above described two-probe home built gas sensor unit. It is well-known that the sensing material exhibits a maximum response towards a target gas at a particular temperature - termed *optimized temperature*. So, by setting the temperature one can exploit the sensor for the particular gas recognition. Therefore, initially sensing performance of NiO film was carried out with respect to temperature to 5000 ppm LPG as a target gas and the equivalent results are displayed in Fig. 5(a). The NiO film sensor demonstrated a maximum response of 72% to 5000 ppm LPG gas at 180 °C. LPG gas molecules should have adequate thermal excitation energies to respond to adsorbed oxygen species at 180 °C; therefore, at this temperature NiO sensor reached maximum value of its response. Hence, for further sensing study 180 °C was used as optimized value of temperature. Selectivity is an essential constraint of gas sensor and it is the ability of sensor response to target gas in the presence of other test gases. Fig. 5(b) shows selectivity bar chart of NiO sensor for each gas having 500 ppm concentration and operating at 180 °C. Selectivity study clearly demonstrates that the sensor material based on NiO was quite sensitive and selective towards LPG gas (35% response to 500 ppm). Upon the interaction of oxidizing gases (herein NO_2), *electron accepting in nature*, the resistance value of NiO sensor found to be decreasing. In contrast, for reducing gases (NH_3 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and LPG), *electron donating in nature*, is found to be increasing. Therefore, the response value for NO_2 shown towards the opposite direction than that of reducing gases in the selectivity bar chart is due its characteristic features. Higher response to LPG is due to the more rate of interaction of LPG molecules with NiO sensor surface as compared to other target gases. In addition various gases have diverse energies for reaction to take place on the sensor surface. Besides, much lower responses were obtained for NH_3 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and NO_2 gases compared to LPG gas, indicating that the NiO sensor has a better selectivity to LPG. It is well-known that, diverse gases possess diverse energies for adsorption, desorption and reaction on the surface of metal oxide. In present case,

rate of reaction between LPG molecules and surface of NiO could be greater; hence sensor exhibited utmost selectivity to LPG compared to other trial gases. Moreover, selective coefficient (K) was calculated using the following relation [36] and obtained results are tabulated in Table 1.

$$K=S_A/S_B \quad (7)$$

where S_A =Response to LPG and S_B = Response to other test gases.

Larger value of 'K' for target gas signifies that the sensor has excellent proficiency to discriminate target gas from the assortment of gases [38, 39]. Plot of response vs. time for NiO film upon 5000 ppm exposure of LPG is shown in Fig. 5(c). SILAR-deposited NiO film demonstrated a response of 72% to 5000 ppm exposure of LPG with fast response (94 s) and recovery time (92 s). The porous morphology of NiO as visualized by FESEM could provide a high surface area to interact LPG molecules resulting in better response. It was observed that upon interaction of LPG gas with NiO film, resistance of sensing film increased drastically at the beginning and continued to increase gradually before attaining a constant value. Recovery of sensor was achieved by opening the outlet of the test chamber. The variation of response with different LPG concentration for NiO film is illustrated in Fig. 5(d). It was observed that with increase in concentration of LPG from 100 to 5000 ppm, the response increased gradually and above 5000 ppm concentration, sensor presented a stable response of 72%. The plot of response for different LPG concentrations for NiO sensor film is shown in Fig. 5 (d). The low gas concentration implies a lower surface coverage, resulting in a lower surface reaction between the adsorbed oxygen species at surface of film and the gas molecules, hence lower response was observed. Furthermore, the higher response can be attributed to the larger surface coverage as a larger surface offers more possibility for reaction between gas molecules and adsorbed oxygen species at the film surface. High response can be expected, if the amount of adsorbed LPG is larger and reaction between the adsorbed LPG and oxygen species is more favorable. But at a certain stage, upon increasing the LPG concentration, the surface reaction does not increase and eventually saturation takes place and sensor exhibits stable response. The repeatability in response of NiO sensor film was studied (to 5000 ppm LPG) and the equivalent results are presented in Fig. 5 (e), which demonstrates a relatively equivalent response to all the LPG exposures. For the practical application of gas sensors; stability is one of the decisive parameters. Stability measurements of the NiO sensor film towards 5000 ppm exposure of LPG for 30 days

at an interval of 5 days were carried out and displayed in Fig. 5 (f). Initially, NiO sensor film approved a good response of 72%, while it dropped to 66% after 30 days with excellent stability of 91%. It is familiar that, the general disadvantage of inorganic material based gas sensors is its shrinkage in response value due to the aging induced effects [40]. Based on the gas sensing results, it was concluded that the SILAR-deposited NiO was potential candidate for detecting LPG at lower temperature.

3.5. LPG sensing mechanism

It is eminent that the sensing mechanism of metal oxide semiconductor-based gas sensors is primarily based on a change in the electrical resistance owing to gas adsorption and desorption on the surface of the sensor film. It was observed that upon exposure to LPG gas molecules SILAR-deposited NiO sensor film revealed abrupt increase in its resistance value. Here, the sensing mechanism of NiO with LPG gas was enlightened through the potential barrier model [Fig. 6]. When the sensing material (herein NiO) is exposed to air, it naturally adsorbs oxygen from air. Adsorbed oxygen on the surface of the film is temperature dependent. Oxygen could adsorb on metal oxide surface i.e. NiO through following ways [41]:



Below 100 °C, it has O_2^- nature, in between 100-300 °C having O^- character and above 300 °C, it has O^{2-} nature [42]. In present case, O^- was more reactive because optimized temperature of NiO sensor was 180 °C. The adsorbed oxygen at grain boundary might trap electrons from the NiO by forming a barrier for electron transport [Fig. 6]. After interacting reducing LPG gas (electron donating in nature) molecules with *p*-type NiO electrons to the valence band of NiO were dominant, hence the conductivity was decreased, resulting in increased resistance value. Sudden increase in the resistance value on exposure to LPG is ascribed to an increase in the height of potential barrier [43]. As the sensor exposed to air, LPG gas molecules was removed and recovery of sensor was achieved.

4. Conclusions

In summary, we have investigated gas sensing properties of SILAR-deposited NiO films towards various oxidizing and reducing gases with respect to temperature. Structure, morphology and phase purity studies are initially screened and then applied in gas sensor studied by employing various oxidizing and reducing gases. Gas sensing results corroborated that the NiO sensor film was quite sensitive and selective towards LPG gas at operating temperature of 180 °C. NiO sensor film exhibited fast response time of 94 s and short recovery time of 92 s with a good response of 72% upon 5000 ppm exposure of LPG. Furthermore, NiO sensor is able to detect LPG concentration as low as 100 ppm concentration with response of 10%, which suggesting its potential in discriminating detection of LPG among a variety of gases.

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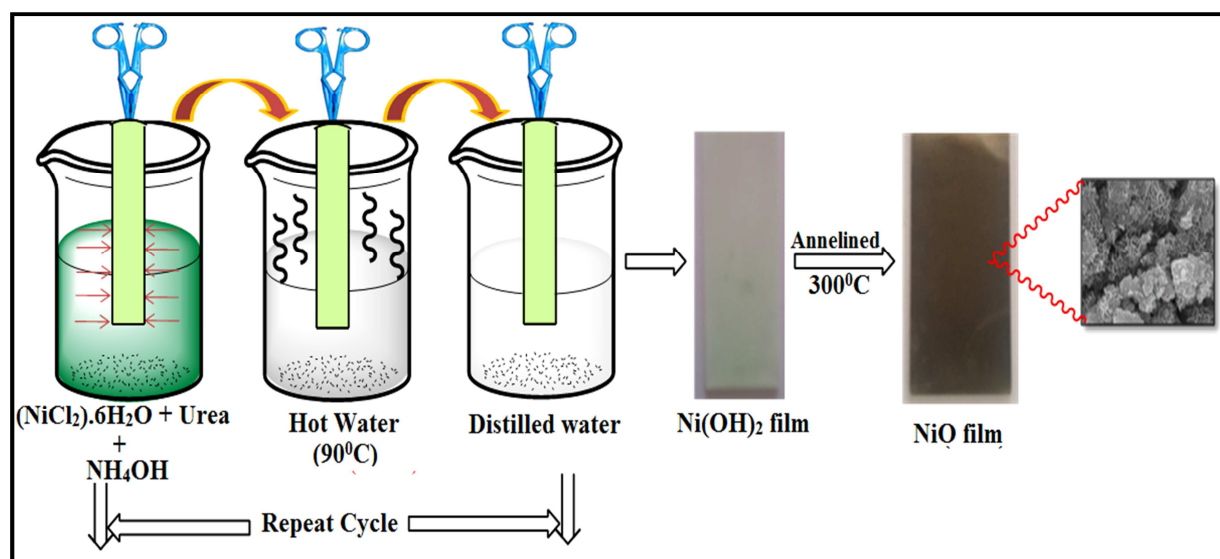


Fig.1: Schematic representation of the formation of NiO film.

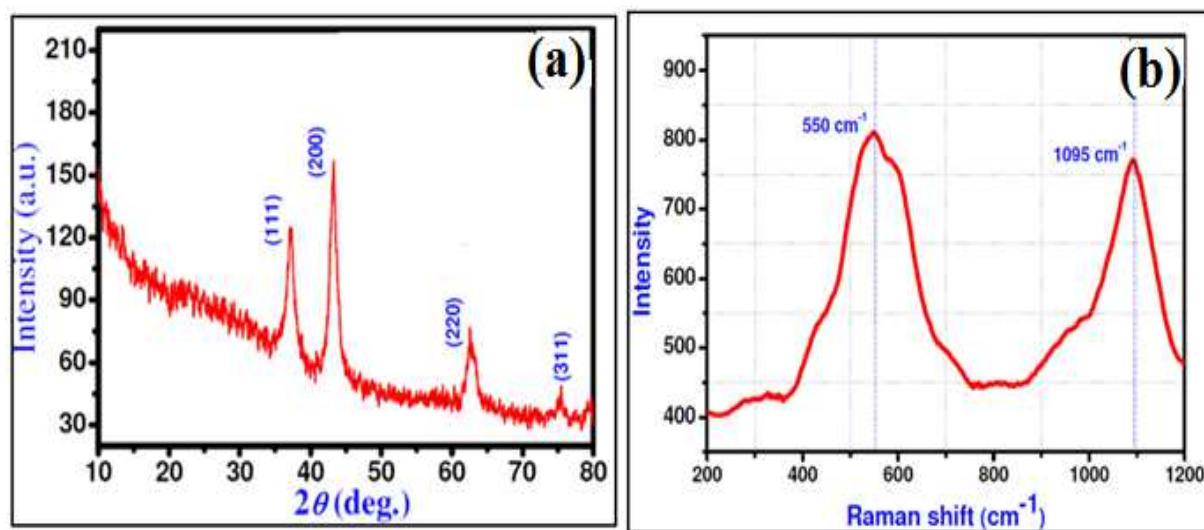


Fig.2: (a) XRD, and (b) Raman spectrum NiO film.

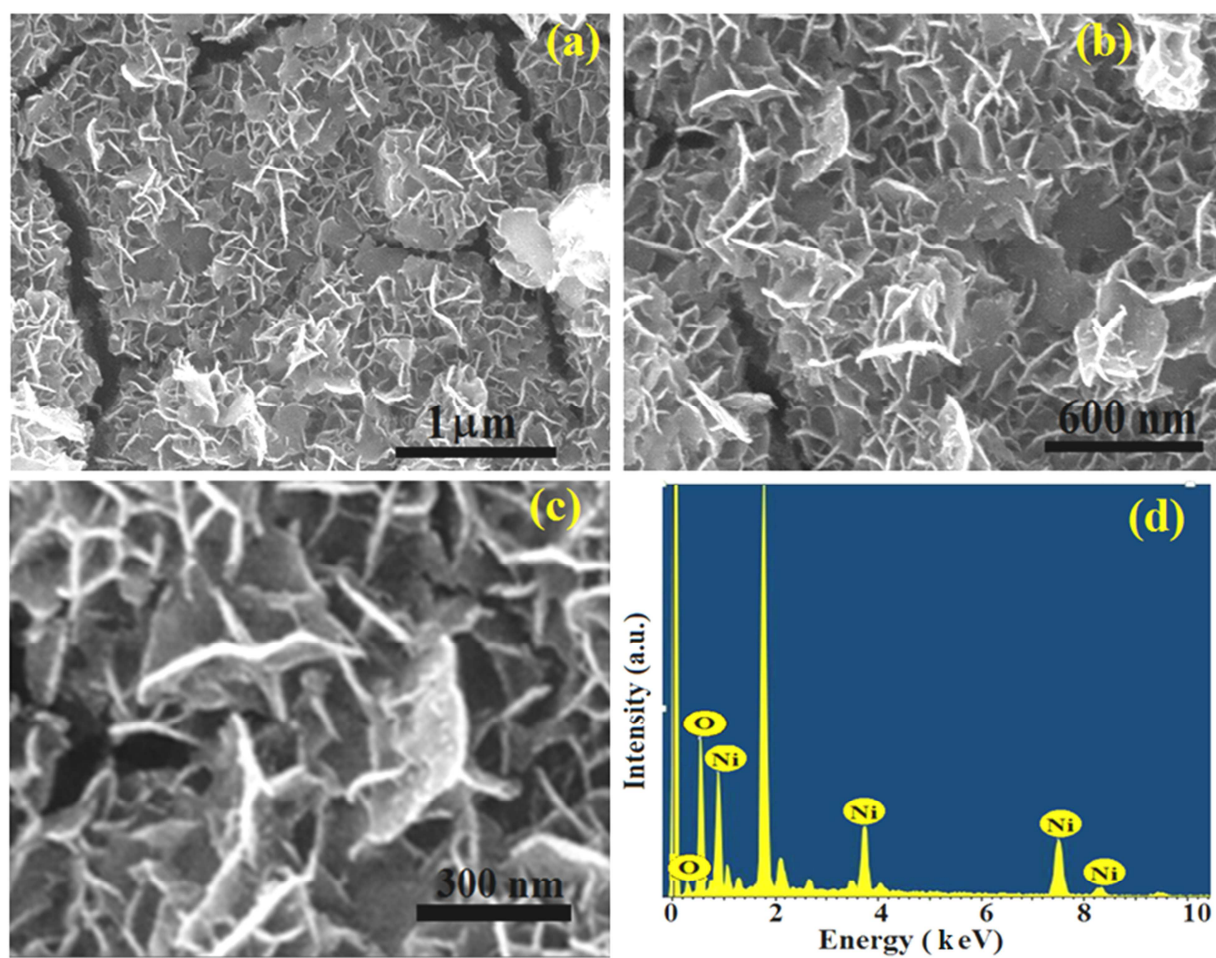


Fig.3: (a, b, c) FESEM images at different magnifications, and (d) elemental composition mapping analysis of NiO film.

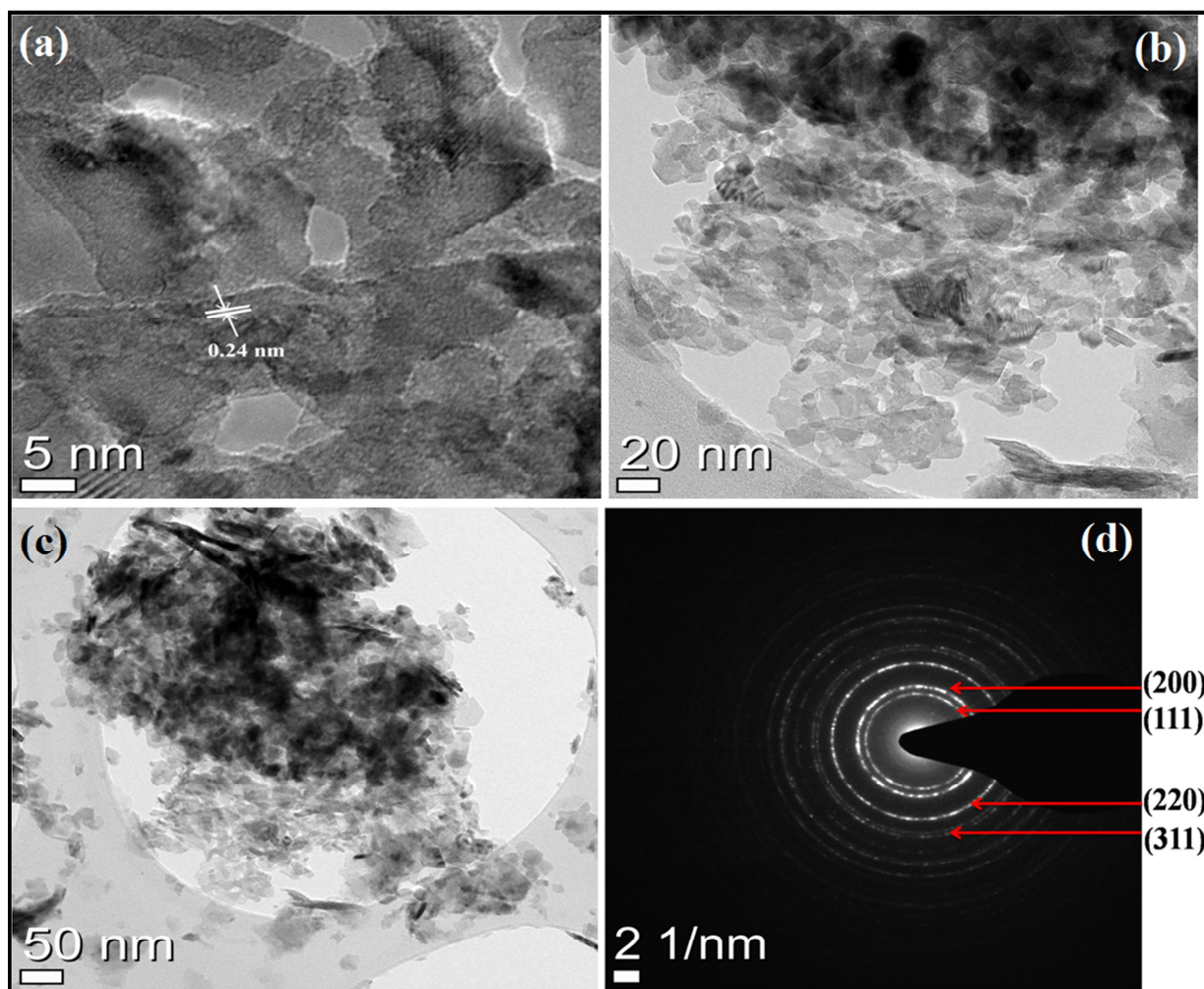


Fig.4: (a) HRTEM, (b, c) TEM images at two different magnifications, and (d) SAED pattern of NiO.

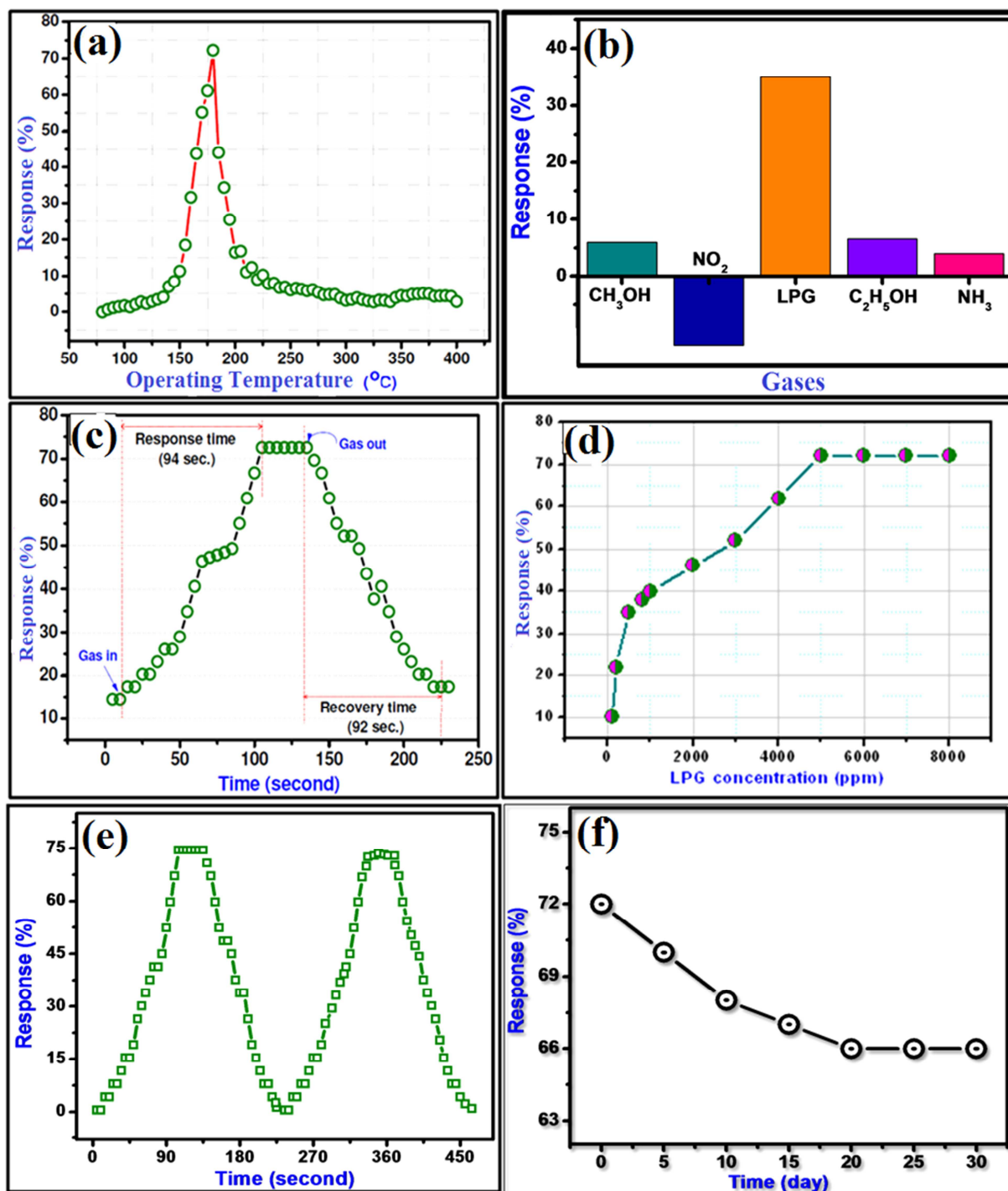


Fig.5: (a) Temperature-dependent response, (b) selectivity study, (c) plot of response as function of time for 5000 ppm LPG, (d) plot of response as a function of different LPG concentration, (e) reproducibility, and (f) stability study of NiO film.

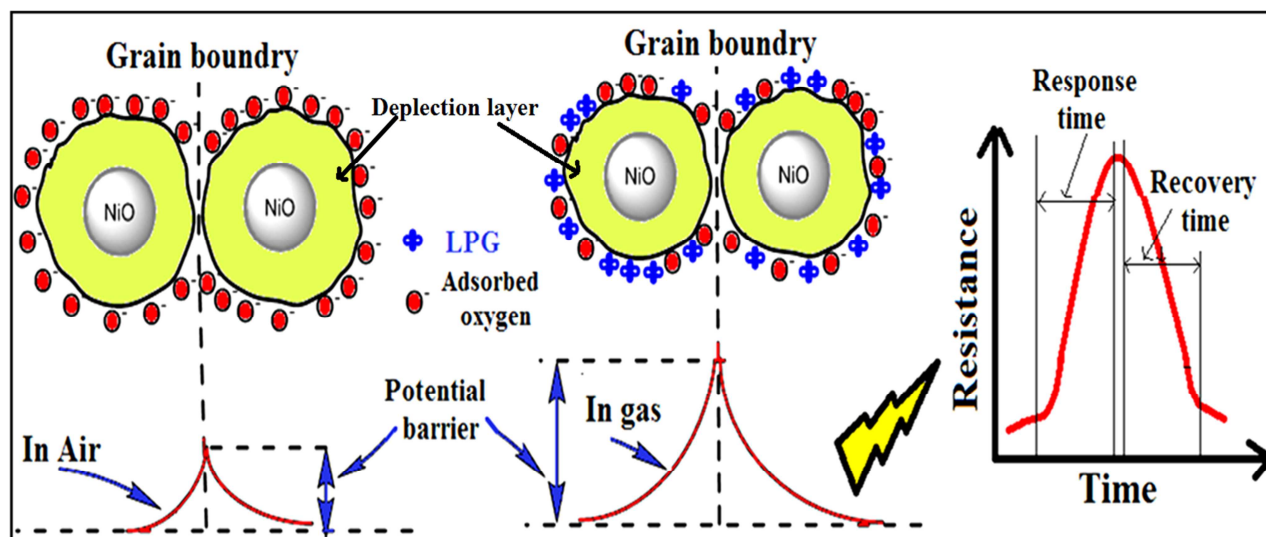


Fig.6: Proposed schematic of interaction of LPG molecules with NiO nanoplates (here Nanoplates are considered as spherical nanocrystallites).

Table 1: 'K' values of NiO sensor for LPG (500 ppm) as target gas.

Gas	NH ₃	C ₂ H ₅ OH	CH ₃ OH	NO ₂
'K' value	8.75	5.35	5.83	2.91

Highlights

- Nickel oxide films are directly grown onto a glass substrate *via* SILAR method
- Films are polycrystalline and are made up of upright standing nanoplates
- Chemoresistive performances toward ammonia, methanol, ethanol, liquefied petroleum gas and nitrogen dioxide gases are tested and reported.
- Good response of 72% to 5000 ppm LPG at 180 °C operating temperature is evidenced.
- Interaction between gas molecules and nickel oxide is proposed through potential barrier model.