

Novel synthesis approach for stable sodium superoxide (NaO_2) nanoparticles for LPG sensing application

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Abstract The synthesis of stable superoxide is still great challenge for the researchers working in the field of materials science. Through this letter, we report the novel and simple synthesis approach for the preparation of stable sodium superoxide (NaO_2) nanoparticles. NaO_2 nanoparticles were prepared by a spray pyrolysis technique, under oxygen rich environment for gas sensing application. The texture characterizations show that as-obtained NaO_2 nanoparticles have high structural purity. Most importantly, NaO_2 nanoparticles exhibits higher sensing response, shorter response time and recovery time, low operating temperature and good stability during sensing of liquefied petroleum gas (LPG). The main accomplishment of present work is that as-fabricated sensor has low operating temperature (423 K), which is below auto-ignition temperature of LPG. The gas sensing mechanism of NaO_2 nanoparticles was discussed without the conventional oxygen bridging mechanism. Through this short communication, LPG sensing application of stable sodium superoxide nanoparticle is explored.

Keywords Nanoparticles · Sodium superoxide · Sensors

Introduction

Gas sensing action is basically run by the adsorption and chemisorption processes occurring on sensing surface. Adsorption diminishes the inequity of attractive forces, which exists at a surface free energy of a heterogeneous system [1, 2]. Thus, solids have the capacity to absorb a certain amount of gas. Generally, oxygen is adsorbed on the surface of solid. The molecular oxygen in the air gets adsorbed on the surface of sensing material and dissociates to produce different superionic species like O_2^- and O^- . These species form a depletion layer among the adsorbed oxygen ions and the sensing materials caused due to transfer of conduction electron. This develops an electric field between adsorbed oxygen species and the sensing surface. But, this discussion is not appropriate for the materials, which itself contains superionic species such as superoxides.

Inspiring from this distinct property of superoxides, we planned to study LPG sensing by sodium superoxide (NaO_2) nanoparticles. To the best of our knowledge, it is unique report on the study of gas sensing by NaO_2 in the literature of materials science.

Experimental

In the present work, NaO_2 nanoparticles were prepared by a spray pyrolysis in oxygen-rich environment. The sodium nitrate (NaNO_3) and hydrogen peroxide (H_2O_2) were used as starting chemicals for the synthesis. The process of spray pyrolysis was initiated by dispersing 1 M NaNO_3 in 20 ml H_2O_2 under probe sonication. This solution was used for spraying under constant oxygen flow on SiO_2 heating

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substrate (673 K). The specifications of spray pyrolysis set-up are described in Ref. [3].

The chemiresistive sensing film of NaO₂ nanoparticles was prepared by doctor blade technique on a chemically cleaned glass substrate of dimensions 25 mm × 25 mm. The highly conducting silver paste was used as Ohmic contacts to determine the film-surface resistance change measurements. The thickness of the deposited electrodes was 12 μm. To check the gas-sensing response, the chemiresistor was loaded into a gas-sensing chamber of specifications mentioned in Ref. [4]. The gas sensing performance of chemiresistor was checked in air as reference gas and sensing response defined as reported in [5]. The measurements of each gas-sensing parameter were carried out 5 times to check reproducibility of gas sensing results. The results show good accuracy level.

Results and discussion

As prepared NaO₂ nanoparticles possess structural purity presented in Fig. 1. The Miller indices associated with diffraction peaks correspond to superoxide nanoparticles according to JCPDS reference card No. 01-077-0207. The inset of Fig. 1 shows FE-SEM image of NaO₂ nanoparticles. The FE-SEM shows that nanoparticles acquire spherical shape and had irregularity in diameters. The analysis of XRD and FE-SEM results indicate that as-prepared NaO₂ nanoparticles exhibit particle sizes in the range 10–35 nm.

The corresponding absorption spectrum of NaO₂ nanoparticles is depicted in Fig. 2. The NaO₂ nanoparticles exhibit an intense peak around 225 nm, which correspond to the presence of quantum confinement effects [6]. The

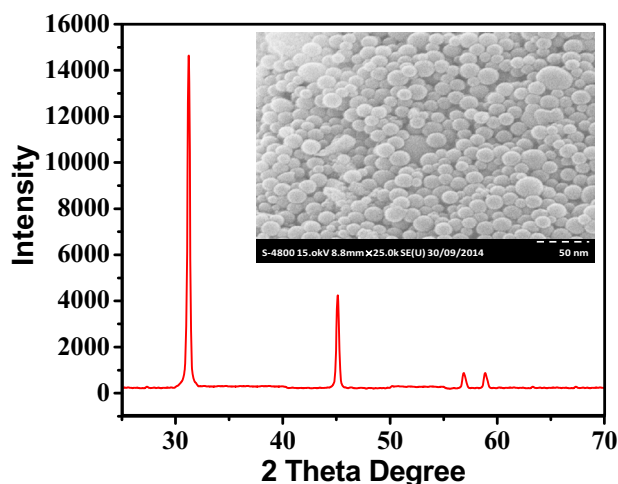


Fig. 1 XRD pattern of sodium superoxide nanoparticles, the inset shows the FE-SEM

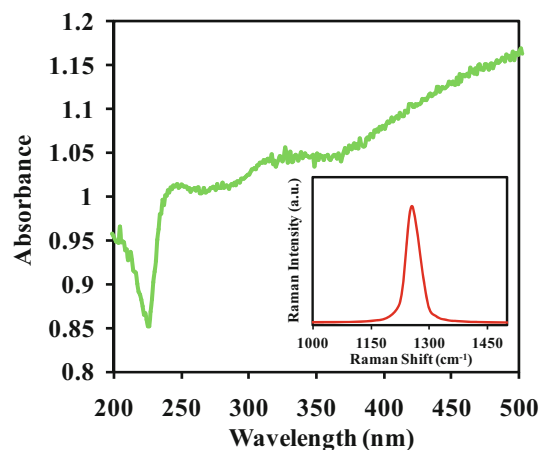


Fig. 2 UV-VIS spectrum of sodium superoxide nanoparticles, the inset shows the Raman spectrum

ultraviolet region from 200 to 400 nm (in term of charge transfer-direct transition) is attributed for ligand-to-metal charge transfer. In the present case, this charge transfer related with Na⁺ ligand field transition. The visible region is assigned to the pair excitation processes most likely contributed by ligand field transitions [7]. Beyond 225 nm, absorbance increases up to 500 nm. Raman spectra of NaO₂ nanoparticles were recorded using the Bruker spectrometer of specification 2 mW laser power at wavelength 523 nm and depicted in inset of Fig. 2. The Raman spectrum shows peak at 1260 cm⁻¹, which is attributed to the single-electron transfer process in sodium superoxide (O₂ + e⁻ → O₂⁻). This superoxide anion O₂⁻ is highly nucleophilic [8].

First, selectivity response of as-fabricated chemiresistor was analyzed towards the oxidizing (CO₂) and reducing (LPG) gasses (Fig. 3a). This performance was checked for different dose concentrations. The selectivity performance of NaO₂ nanoparticles chemiresistor clearly shows that chemiresistor is more selective towards LPG. For every dose, LPG sensing response dominates CO₂ response. Therefore, further study of sensing response of NaO₂ nanoparticles based chemiresistor confined about the LPG.

Figure 3b shows the LPG sensing response of NaO₂ nanoparticles based chemiresistor. The response curve has nearly linear nature, which shows that NaO₂ nanoparticles based chemiresistor has good dependence on concentration of LPG. The resistance of chemiresistor falls in the presence of LPG. This reflects the n-type behavior of chemiresistor [9]. The LPG is composition of CH₄, C₃H₈, C₄H₁₀, etc., and these species are reducing in nature, which have tendency to donate electron to the surface. Hence, resistance of chemiresistor falls in the LPG surrounding.

It is well-known that gas sensing process proceeds in the presence of atmospheric oxygen as an adsorbed oxygen

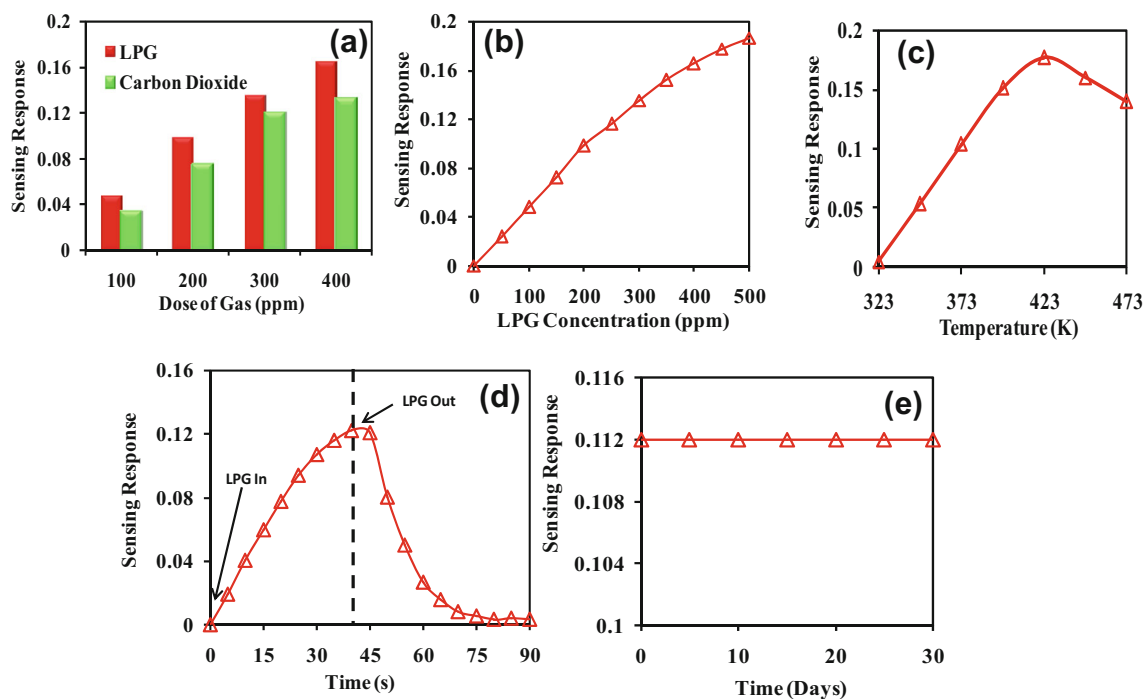
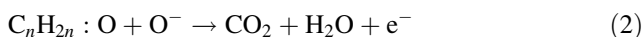
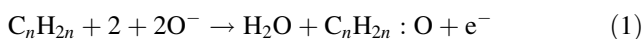


Fig. 3 a Selectivity, b Sensing response, c Operating temperature, d Transient and e Stability response of sodium superoxide nanoparticles towards the LPG

species. But this mechanism is not valid for the materials containing superionic species such as superoxides. This mechanism is first time coined through the present letter; therefore we termed it as “unescorted oxygen bridging mechanism”. As the chemiresistor is exposed to LPG, it interacts with the superionic species present in the NaO_2 nanoparticles and formed H_2O and CO_2 . The reaction between LPG and superionic species are as follows (Eqs. 1 and 2) [10],



The response of as-fabricated chemiresistors towards the 250 ppm LPG as a function of temperature is shown in Fig. 3c. The sensing response curve shows that response value increases up to certain temperature. This temperature is the operating temperature of NaO_2 -based chemiresistor. From the plot, it is examined that chemiresistor possess operating temperature at 423 K. This is one of the most important accomplishments of the present investigation, because sensing of LPG at elevated temperature is risky due to its explosive nature. The sensing response start to decreases from certain temperature, this may be due to desorption of superionic species from sensing surface due to thermal vibrations. Figure 3d shows gas sensing response curves of the NaO_2 nanoparticles under exposure

to 250 ppm of LPG at room temperature. As seen from Fig. 3d, both response and recovery times are much faster to be a practical LPG sensor. The response and recovery time obtained without any heating to facilitate desorption of gas species and UV irradiation procedure. In case of LPG sensing, both approaches are risky due to highly explosive nature that is auto-ignition temperature is very low. Therefore, any electrical device larger than a digital wristwatch has the potential to generate sufficient energy to ignite LPG.

Figure 3e depicts the stability performance of NaO_2 nanoparticles against 250 ppm LPG at room temperature. The sensing response curve is almost linear for the entire month. This shows that chemiresistor is stable against the atmospheric change and responsive towards LPG. Thus, the as-fabricated chemiresistor has authentic performance as practical LPG sensor. The results of the chemiresistor is reproducible, may be due to its stable characteristics against the atmospheric change. The response and recovery time value determined in this work is quite fast than reported in literature [11, 12]. The achievement of the present work is low operating temperature, which is below the auto-ignition temperature of LPG. The obtained operating temperature value is much below than reported in literature of sensor technology [13, 14].



Conclusions

In summary, we successfully demonstrated LPG sensing by NaO₂ nanoparticles synthesized by a spray pyrolysis. The experimental results indicated that the as-fabricated chemiresistor has good selectivity towards the LPG. NaO₂ nanoparticles had n-type behavior and good gas-sensing response and stability against LPG. The main accomplishment of this work is that operating temperature of chemiresistor is below the auto-ignition temperature of LPG. The non-conventional oxygen bridging mechanism effectively employed for LPG detection using NaO₂ nanoparticles. Thus, NaO₂ nanoparticles based chemiresistor is a very promising candidate for LPG sensing with a fast response and recovery time.

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