Comparative Study of Chemo-Bio Synthesized MgO Nano Particles for LPG Sensing

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ABSTRACT

The present work describe the synthesis of MgO nanoparticles in two way i.e., green synthesis using aloe vera plant extract and chemical method by glycine-based solution combustion route. Organic molecules present in aloe vera plant extracts can be used to reduce metal ions to nanoparticles in a one-step green synthesis technique. Effect of different synthesis methods (green and chemical) nano materials was optimized almost equal sensitivity for LPG. Characterizations performed were Transmission electron microscope (TEM) was used to determine the particle size of the prepared sample, X-Ray Diffraction (XRD) for crystalline size and structure, the product nanoparticles analyzed by Fourier Transform-Infrared (FT-IR) spectroscopy, the morphology confirmed by field emission scanning electron microscopy (FE-SEM) and UV-Visible measurement for optical studies. The dynamic gas sensing characteristics were measured for LPG at different ppm levels with altered temperature, the synthesized both materials were coated on preprinted electrode devices using drop drying method and bio method material showed good sensitivity.

Key words: MgO, LPG, green synthesis, chemical synthesis, gas sensing

1. INTRODUCTION

Nanostructured Metal oxides based gas sensors have great devotion for a past few decades due to their potential applications, low cost, easy to synthesis and very high sensitivity for the flammable and lethal gases [1]. In nanostructured metal oxides the conductivity change when interacts with gas molecules. This reaction output gives the materials sensing characteristics it is depending up on the many factors chemical, physical properties of the material, temperature, analyte concentration and humidity [2]. A good catalytic nature, thermal stability along with great mobility of conduction electrons are the basic specifications for MgO based chemical sensors [3]. Conventionally MgO is used as refining process and steel making [4]. The nanostructured MgO having distinctive functional, electrical and optical characteristics this features may leads to find several technological applications like sensors, solar cell and cosmetics. They are used as good catalyst in many applications due to vacancies of oxygen on the MgO surface and boundaries which have the potentiality of charge transfer between substrate and adsorbate [5-6]. MgO is a pre-transition-metal oxide having bit larger band gap compare to other metal oxides, holes nor electrons can simply formed. MgO shows high sensitivity towards various toxic and flammable gases. In conventional processes, synthesis of MgO nano particles are prepared by physical and chemical methods [7-10]. These methods involves expensive chemicals, sophisticated instruments and several limitations for large scale production which involves high temperature, power consumption, time taking process and hazardous to environment; while green method are reasonably cheaper, simpler and eco-friendly. The expansion of safe environmental friendly methods are having great interest in the present scenario [11]. Still green synthesized nano materials were used as only in the field of health –related areas such as anti-bacterial activity. Green method has its own significance than conventional chemical routes in terms of large scale production with less contamination and have in the range of nanoscale with desired morphology, in this green synthesis plant extract act as a reducing and stabilizing agent. Green method can be performed at ambient temperature as these were natural plant extract with non-toxic chemicals [12-14].The present study, involves two different methods i.e., green and chemical synthesized MgO nanoparticles used as a liquefied petroleum gas sensing (LPG) element. The obtained MgO nanoparticles have been studied for different LPG

concentrations at various operating temperatures [15]. There are less papers published on green synthesis of MgO nanoparticles for LPG sensor application.
In present investigation, comparison between the green and chemical method MgO nano particles, got high sensitivity at 1000 ppm of LPG with green and chemical synthesized MgO at 300℃ operating temperature.

2. EXPERIMENT SECTION

2.1 Chemical Method

Chemical combustion method comprises an exothermic reaction between metal nitrate and fuel. In this method magnesium nitrate and glycine have been used as oxidizer and fuel respectively. For the preparation of MgO nano material in chemical route the required amount of $Mg(NO_3)_2$ and $C_2H_5NO_2$ were dissolved in distilled water, all reagents were analytical grade form Sigma Aldrich, USA. The above solution is thoroughly stirred to form a complete dissolution of all reagents. The obtained clear solution is moved on to a hot plate and the temperature is set to 200℃ until it caught fire and powder was formed. The heat treatment was given at 400℃ for 4 h [12].

2.2 Green Method

MgO nanoparticles was prepared by using aloevera plant extract [16]. Aloevera plant extract was added to the metal nitrate ($Mg(NO_3)_2$) in 100 ml of distilled water under constant stirring. Temperature (60℃) applied to the above mixture for a 4 h, after that reaming mixture was placed on a hot plate, water started to boil and evaporated and compound was attained. This precursor annealed in muffle furnace for 4 h at 400 °C.

2.3 Apparatus

The sensor testing measurement setup reported in our previous work gas sensing characteristics were measured according [12]. The MgO nano material was coated as a layer on the pre-printed copper electrode by drop drying method. This method for preparation of sensing element is very simplicity and can achieve better uniform films. The fabricated sensing element performance measured by calibrated known concentration analytes (LPG) with output current at different operating temperatures. The following $(R_a-R_g)/R_a$ equation is used to determine relative resistance (A_R) [17]. That resistance examined at the atmospheric pressure condition and here R_a represents resistance in the presence of zero air, R_g denoted under the flow of LPG.

3. RESULT AND DISCUSSION

3.1 Characterization

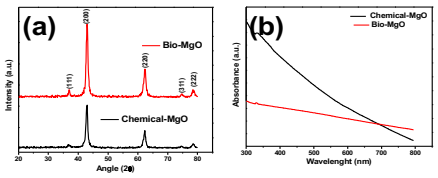

Fig.1 Prepared Chemical and Bio synthesized MgO (a) Powder XRD pattern; (b) UV-Visible spectra

The XRD (Bruker D8 advanced) spectrum of the chemical and biological route synthesized MgO nanoperticles are illustrated in Fig.1 (a). All the peaks corresponded to JCPDS (89-7746) values and no extra peaks was observed. Hence proved that biological and chemical method are capable of synthesize pure nanostructured MgO. Prepared MgO powder XRD peaks broadness indicates the nanocrystallinity of the particles. XRD pattern analysis was done by using the reflection planes corresponding to (111), (200), (220), (311) and (222). The crystalline size of the MgO nano particles was valued as 18.21 nm form the line widening of XRD peaks by using the Williamson-Hall equation [18] i.e., $\beta \cos\theta = 0.9\,\lambda/D + 2\varepsilon \sin\theta$. In order to find out optical properties performed UV-vis analysis (Systronic-2203) of both MgO nanoparticles as shown in Fig.1 (b) the corresponding absorption peak is located for chemical and bio MgO in the area of 300-400 nm. The detail that the peak is not high-pitched in biological method compared with chemical method. Hence, both prepared MgO materials are well dispersed in the aqueous solution.

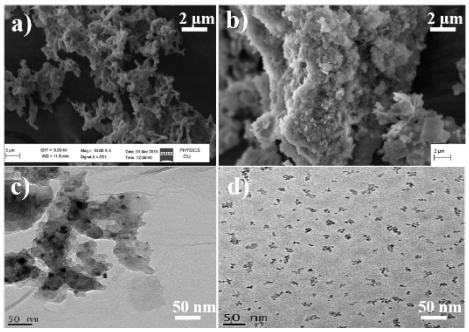

Fig.2 (a and b) FE-SEM micrographs shows the microstructure (a) chemical MgO (b) bio MgO (c and d) High-resolution TEM (HRTEM) image of the

selected area in MgO nano particle (c) chemical MgO (d) bio MgO

FE-SEM (Carls Zeiss-Merlin compact 60- 27) and HR-TEM (JEOL-2010) images for MgO nanoparticles synthesized by both chemical and biological route are shown in Fig.2. These powders of MgO unveiled non-uniform nature and agglomerated with swelling like morphology [19]. In chemical method MgO show porosity when compared to bio route MgO (Fig. 2 (a and b)). Bothe synthesis methods achieved very well grained powder. The TEM images confirms that obtained MgO nanomaterials from both chemical and biological routes were in the nanoscale size of the crystals, characteristically below 35 nm presented in Fig. 2 (c and d). The resulting size of the nanomaterial was a better matching with XRD pattern. In chemical method MgO nanoparticles are lumps like structure and in bio method MgO were more distribution of the particles can be observed.

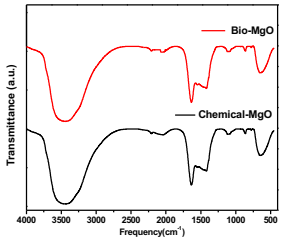

Fig.3 FTIR spectra of the chemical and bio synthesized MgO nanoparticles

The obtained chemical and biological route MgO nanoparticles were characterized by FTIR (PerkinElmer-L160000A), shown in Fig.3 In both method MgO spectra were depict similar peaks. MgO nanoparticles, the found FTIR peaks at 3440 cm^{-1} can be attributed to the physically adsorbed water form air [20]. In spectra FTIR peak at 1451 cm^{-1}depict from the remaining carbonate ions [21]. Peak at 436 $cm^{-1}$was correlated to the Mg-O stretching vibration. In addition, the both chemical and biological synthesized MgO nanoparticles FTIR peak were shown similar results, hence confirmed from the FTIR for both samples MgO formation.

3.2 Gas-Sensing Properties of Chemical and Green Synthesized Nano MgO

Sensing characteristics of chemical and biological synthesized MgO was studied against to LPG at different concentrations with operating temperature from room to 300℃. These type of metal oxide can detect gases at higher temperatures. This is due to the generation of electrons by thermal excitations.

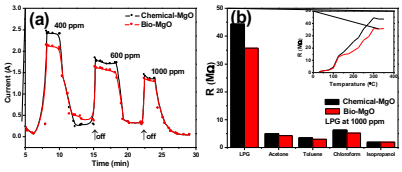

Fig.4 (a)The detailed dynamic LPG sensing response of MgO by chemical and biological route at 300℃ operating temperature; (b) Chemical and bio synthesized MgO response of different compounds at 1000 ppm concentration at 300℃ operating temperature, inset shows operating temperature *vs* sensitivity of both MgO at 1000 ppm LPG

MgO being p-type semiconductors holes are major charge carriers. MgO nanoparticle are exposed to air they absorbs gas molecules, these adsorbed gas molecules arrests electrons and it forms oxide, peroxide and superoxide ions according to the operating temperatures. At the time of generation of oxide ions, space charged layer are formed on the surface, which decreases the charge carrier concentration and decreases the conductivity. When the reaction between the MgO nano material with respect to oxidizing and reducing gases, redox reaction will takes place in between the adsorbed oxygen and analyte gas [22,23].
Fig.4 (a) depicts the dynamic response of MgO which is synthesized by chemical and biological route at 300℃ operating temperature under purging of 400, 600 and 1000 ppm of LPG exposure. At 300℃ extreme response was obtained for 1000 ppm of LPG. Firstly we introduced the synthetic air into the chamber then gas molecules adsorbed onto the surface and with this the current increased because resistance decreased and became saturate for ten minutes then we introduced the 400 ppm concentration of LPG gas which adsorbed onto the sensing material surface and react with the adsorbed oxygen species further resistance increased and current decreased abruptly. After current became saturation then switch off the gas was done. The current increase suddenly then shows a saturating trend for few minutes after that with the increase in concentration up to 600 ppm the current decrease, it means resistance of sensing film increases. Further increase in the concentration up to 1000 ppm leads to more decrease in current. The decrease in current results increase in resistance with this the sensitivity also increases. So it is observed from the figure that resistance increase with increase in LPG ppm, it shows the enhanced response and high sensitivity at 1000 ppm concentration. When compared with chemical

MgO and biological MgO nanoparticles, chemically synthesized MgO nanoparticles was shown bit high sensitivity with green MgO nanoparticles. The result of operating temperature on MgO was shown in inset image Fig.4 (b).High sensitivity was absorbed in both materials at 300℃, hence 300℃ was selected as the optimal operating temperature. Meanwhile, the selectivity of the MgO nanoparticles response to LPG was shown in Fig.4 (b). Further gas analyte comparison for acetone, toluene, chloroform and isopropanol at the 1000 ppm of concentration at 300℃ temperature. Except LPG all compounds were shown very poor response. Hence confirmed that the prepared green and chemical route MgO having accurate specificity to LPG at 1000 ppm in air at 300℃.

CONCLUSIONS

In conclusion, MgO nanoparticles were synthesized by simple two different routes chemical and biological green methods. The obtained MgO nanoparticles were pure, porous and suitable for gas sensor application. Green method shown similar sensing performance, it can be used as eco-friendly, cost-effective and easy procedure as compared to chemical method. Due to more surface area and porous nature gas sensitivity of 38% was detected at 300℃ with 1000 ppm LPG, in the case of chemical synthesis gas response was achieved 45% for similar conditions. Both nanoparticles demonstrated have good sensitivity, response and selectivity to LPG. Further development of LPG detection at trace level are needs to be studied from these economical green synthesis nanomaterials to recommend in direct industrial applications.

ACKNOWLEDGMENT

The author (S.G) is thankful to SERB-DST government of India for the international travel grant and financial support.

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