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GREEN SYNTHESIS OF ZnO NANOPARTICLES USING SUGARCANE JUICE FOR LPG SENSING APPLICATIONS

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Abstract:

In the present work, we have successfully synthesized ZnO nanoparticles (NPs) by *sugarcane stem* using green synthesis method. Structural, morphological and optical characteristics of ZnO NPs are examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible spectroscopy (UV–Vis). XRD reveals hexagonal wurtzite structure with average crystallite size of 30 nm. SEM images depict the uniformly distributed spherical nanoparticles. The optical measurements showed band gap is 3.15 eV. Synthesized ZnO NPs are investigated for its LPG gas sensing study together with operating temperature, response/recovery time and gas uptake capacity. The detail examination of LPG sensing study demonstrates the operating temperature 220ºC with gas response of 91%, with fast response/recovery times 90/70 sec. respectively. In addition, the LPG gas uptake capacity remained sensible up to 9,000 ppm. Ultimately, we conclude that the green synthesis route, to fabricate sensor devices is encouraging as it is cost-effective, eco-friendly and simple.

Keywords: Green synthesis; ZnO; XRD; UV-Vis; SEM; Gas Sensor.

1. Introduction:

Nanomaterials display a wide range of unique physicochemical properties that are well-known to originate from the high surface area and nanoscale size of their constitutional components, called nanoparticles (NPs) [1]. NPs are a wide range of materials with dimensions below 100 nm, which can be used in various applications, such as medical, pharmaceutical, manufacturing and materials, environmental, electronics, energy collection, and mechanical industries, due to their multiple properties [2–5]. Wherein, metal oxide NPs have gained great attention among researchers for nano-device applications [6]. Among a large variety of metal oxides, zinc oxide (ZnO) NPs has superficially secured a special place in scientific and technological domains. ZnO is an n-type semiconductor having special features such as wide and direct band-gap (3.37 eV), large exaction binding energy (60 meV), high electron mobility, chemical/thermal stability, and good transparency. Hence it have various front-line applications in the field of solar cells, gas sensors, field emission devices, capacitors, coatings, sunscreen lotion, cosmetic and medicated creams [7-9].

Over the years, a wide number of physical, chemical and hybrid synthetic methods have been developed and employed to obtain ZnO NPs.[10-15]. Usually, these preparation methods face several limitations, such as the high cost of equipment, usage/emission of highly toxic and hazardous materials, impurities, high temperature/pressure conditions, and additional use of capping agents, stabilizers [16]. To overcome these limitations, green chemistry procedures gaining importance as they are safe and eco-friendly methods, inexpensive, do not produce toxic by-products, and produce clean nanomaterials.

Hence the main emphasis of researchers is developing simple and green methods for synthesizing ZnO NPs [17]. According to the literature, several types of fruit and plants extracts has been used for the synthesis of ZnO NPs such as *Tabernaemontana divaricata, Citrus maxima (Pomelo), Aristolochia indica, Echinacea spp.,* Mentha longifolia, *Salvadora oleoides, Boswellia ovalifoliolata, Limonia acidissima, Cochlospermum religiosum,* and *Conyza canadensis* for various application including photo catalytic properties, antimicrobial activity, gas sensor etc., [18-29].

In the present work, we herein report, a simple, cost-effective and environment sustainable green approach for the synthesis of ZnO NPs using *sugarcane stem* extract for LPG sensing application. As synthesized, ZnO NPs are characterized for their structural, morphological and optical properties and further employed for detailed investigation of operating temperature, response/recovery time and uptake capacity for LPG gas sensing applications.

2. Experimental and Characterization Technique

2.1 Green synthesis of ZnO NPs using sugarcane stem

The schematic representation of the ZnO NPs by green synthesis using *sugarcane stem* is shown in Figure 1. Initially, fresh *sugarcane stem* is collected from agriculture field and cut into small pieces by sharp blade. Further it is washed with distilled water and dry in sunlight for two hour. Thereafter, 10 gm of dried *sugarcane stem* dipped in to 1M zinc acetate solution for specific period of 24 hrs to 48 hrs. Zinc acetate solution is absorbed by the *sugarcane stem* wherein complex reaction is occurred. Then solution is filtered and separated *sugarcane stem* dried under infrared lamp for 3-4 hours. Subsequently *sugarcane stem* is sintered at 800 ^{o}C for 3 hrs and crushed in to powder form. As prepared powder is used to prepare sensor matrix in the form of thick film by screen printing on glass substrate is reported in our earlier work [30].

Figure 1: Experimental Scheme of the ZnO NPs by green synthesis using *sugarcane stem*

The prepared films are further used for structural and morphological characterizations. The structural and surface characterization is carried out using XRD, SEM and UV analysis. X-ray diffraction pattern is recorded with a Bruker AXS Germany (Model D8 Advanced) having CuKα (λ= 1.54 Å) incident radiation. The surface morphology and elemental analysis is visualized by means of Scanning Electron Microscope (FE-SEM Hitachi S-4800) with EDAX. UV–Visible absorption spectra is obtained by a Shimadzu UV-3600 spectrophotometer.

The electrical and gas sensing characteristics are monitored using a home built static gas sensing system reported in our earlier work [30]. The sensor matrix in the form of thick film is typically 1 cm x 1.5 cm in dimension, which is placed on the heating plate in the test chamber where it is preheated at the required temperature using a temperature controller to remove the humidity effect. The two probe dc measurement technique is used to measure the electrical resistance of film in air atmosphere and in the presence of test gas. Silver paste contacts are applied at the edges of the film separated by 1 cm, as top electrodes whose ohmic nature is tested within ± 10 V. The desired gas concentration inside the system is achieved by injecting a known volume of the LPG gas. Measurement of the voltage across the reference resistance is followed by measurement of sensor resistance in air and gas (LPG) atmosphere as a function of temperature. The change in resistance of the sensor, due to the presence of LPG gas, is noted in Gas response (%), calculated using classical relations,

$$\text{Gas response (\%)} = [\ R_g - R_a\ ] / R_a * 100 \quad = (\Delta R / R_a * 100) \qquad (1)$$

where R_g and R_a are the resistances measured in gas and air, respectively.

3. Results and Discussion

3.1. X-ray, SEM and UV analysis

Figure 2 (a) shows the X-Ray diffractogram of ZnO NPs obtained from *sugarcane stem* by green synthesis. Peak positions indexed to (100), (002), (101), (102), (110) (103), (112) and (201) observed at 2θ values such as 31.98^{o}, 34.67^{o}, 36.48^{o}, 47.71^{o}, 56.79^{o}, 63.08^{o}, 68.21^{o}, 69.24^{o}, respectively. All the reflections are observed commonly in ZnO, which support the formation of hexagonal wurtzite type structure of ZnO films [JCPDS (76-0704)]. As the width of the peak increases the size of particle decreases, which is attributed to the nano size of the present material [31]. The average crystallite size of as synthesized ZnO NPs are calculated from the full-width half maximum (FWHM) of all the obtained peaks using the Debye–Scherrer formula and it is found to be 30 nm.

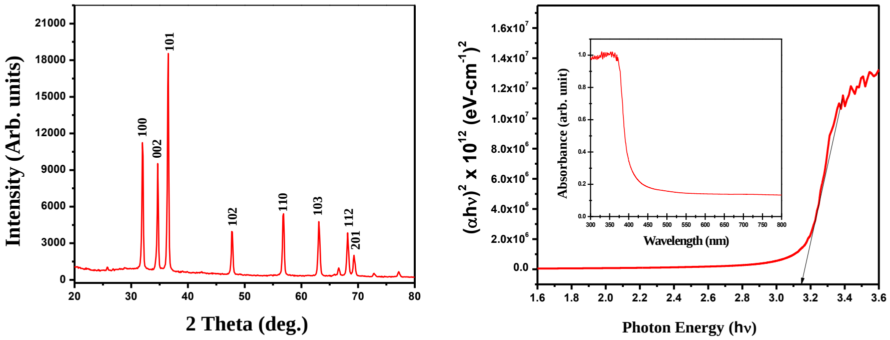
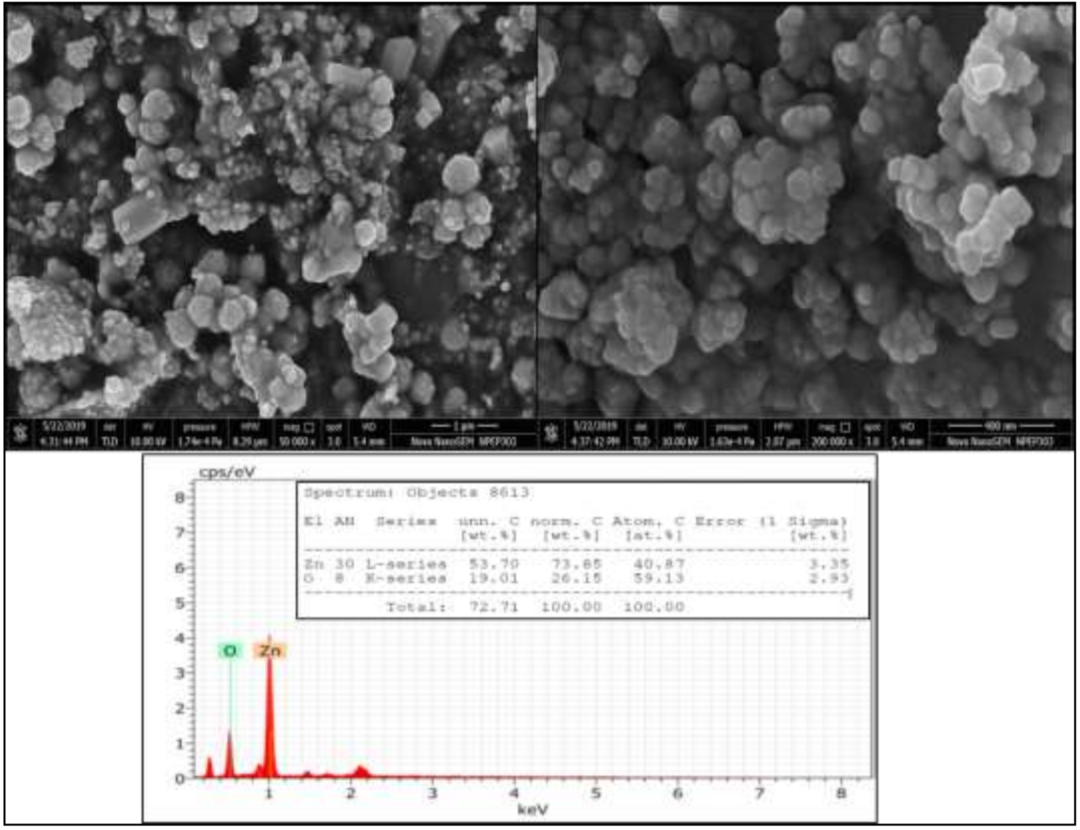


Figure 2: (a) The X-ray diffraction pattern of ZnO NR. (b) UV-Visible Spectra of Tauc’s plot and absorption spectra (inset) for ZnO NR.

The optical study is performed to evaluate the optical properties of the ZnO NPs as shown in Figure 2 (b). The band gap of the samples are estimated by extrapolation of the linear relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$). The direct band gap (Eg) values are determined from the intercept of $(\alpha h\nu)^2$ vs ($h\nu$) curve. The band gap obtained using the variation showed the value 3.15 eV which is in good agreement with the reported value of ZnO [32]. Moreover, the absorption peak at 360 nm as shown in figure 2(b) (inset) which is blue shifted. Thus, a strong blue shift in the absorption spectra gives the predication that ZnO must be smaller than the bohr radius of exciton [33], which confirms the formation of ZnO particle in nanoscale.

Figure 3(a-b) shows the SEM images of two magnifications for ZnO NPs obtained through novel green synthesis of *sugarcane stem*. It illustrates the presence of thickly aggregated spherical ZnO NPs spread over many regions. Moreover, the size distribution histogram revealed that green synthesized ZnO NPs are in the range of 20-40 nm which is in good agreement with the X-ray analysis. The elemental composition of ZnO NPs is also confirmed by EDAX analysis as shown in figure 3(c). This spectrum not only confirmed the occurrence of the Zn and O elements but also verified the relative purity of the material synthesized. Precisely, the EDAX analyses showed the elemental composition of Zn with 73.85% and O with 26.15%; however, the theoretical stoichiometric mass% of Zn and O are 80.3% and 19.7% respectively [34]. The deviations in the experimental data seen from that of the theoretical one can be attributed due to the presence of some organic residue and/or other impurity coming from the starting precursor in minute quantities.



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Spectrum: Objects 8613

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
Zn 30 L-series  53.70   73.85   40.87            3.35
O  8  K-series  19.01   26.15   59.13            2.93
-------------------------------------------------------
        Total:  72.71  100.00  100.00
```

Figure 3. (a-b) The SEM Images of green synthesized ZnO NPs at two magnifications, (c) EDAX spectra

3.2. LPG Sensing performance of Green synthesis ZnO NPs(Temperature optimization, response-recovery time and Gas uptake capacity)

Figure 4 (a) depicts the variation of the gas response as a function of temperature in LPG gas atmosphere, with fixed gas concentration of 1000 ppm. It is observed that gas response remains very low initially and increases as a function of temperature in the range of 150-220°C and further decreases with rise in temperature. It possesses a maximum gas response of 91 % at an operating temperature 220°C for LPG gas. The variation in gas response with respect to time (sec) in response to 1000 ppm of LPG for ZnO NPs held at operating temperature 220°C is showed in figure 4 (b). When the sensor is exposed to gas atmosphere, gas response is found to be increase with time which later on remained constant with further increase in time. Upon exposure to air, the reduction in gas response is observed. From the figure, it can be concluded that the response and recovery time of ZnO film for LPG gas is found to be ~90 and 70 sec.

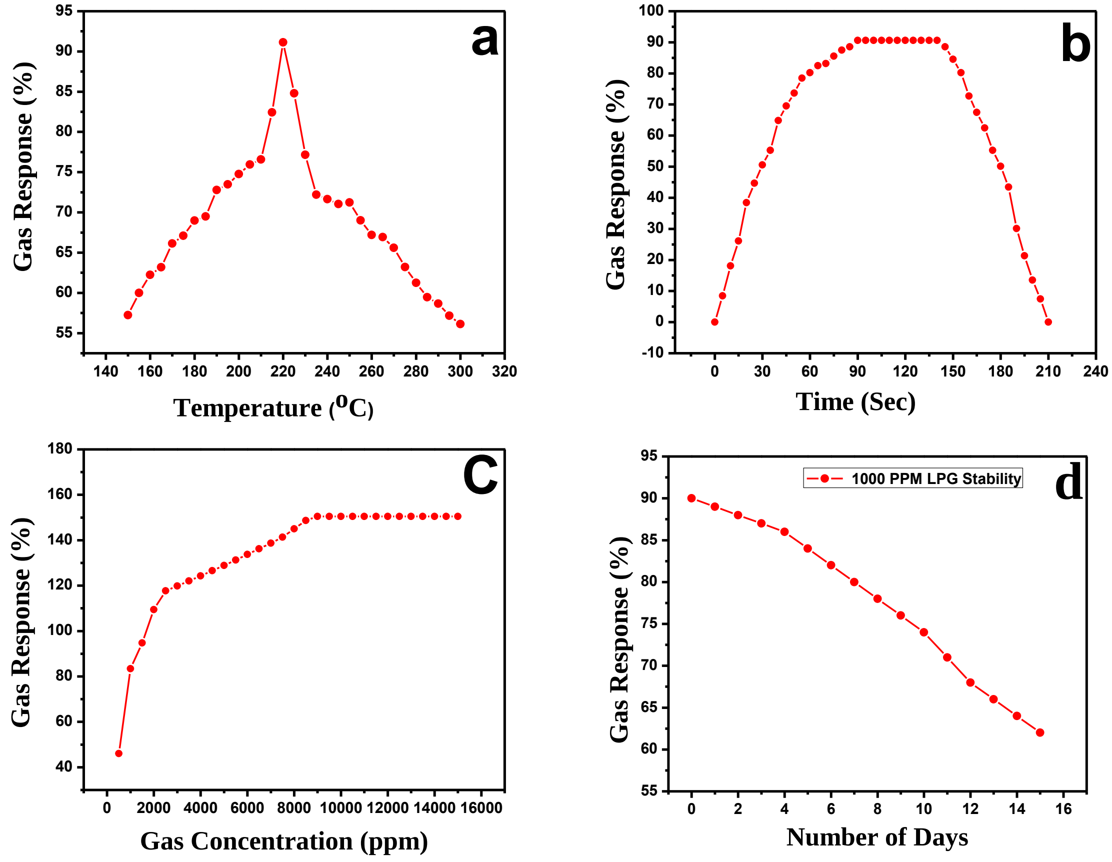

Figure 4. (a) The variation of Gas response (%) with respect to operating temperature at 1000 ppm of LPG gas concentration. (b) Response and Recovery plot at 220°C operating temperature. (c) Variation of Gas response (%) with respect to LPG gas concentration. (d) Long term stability curve of ZnO for 1000 ppm of LPG gas concentration.

Figure 4 (c) shows the variation in gas response with variable LPG gas concentration in the range of 500 ppm to 15,000 ppm. From the figure, it can be concluded that the behavior of gas response as a function of gas concentration shows three main regions. The first region shows sharp initial rise in gas response up to 2500 ppm (high sensitivity region). The second is intermediate region, shows nearly linear increase in gas response, and third region is the saturation region in which the sensor completely saturates. The rate of increase in gas response is relatively larger up to 9000 ppm for LPG. Afterwards, increase in gas concentration, the sensor gets completely saturated. It may be due to the mono/multi-layer adsorption of gas molecules on the surface that could cover the whole surface of the film. The excess gas molecules cannot reach surface active sites of the sensor; hence the gas response at higher concentration not expected to increase further. Therefore it can be concluded that the green synthesized ZnO NPs can monitor the LPG gas up to 9000 ppm concentration respectively. In addition, stability of the gas sensor is very important aspect to assess the long term gas sensing performance. Therefore we have studied the stability curve of ZnO NPs for LPG as shown in Fig. 4(d). It is observed that the gas response of ZnO NPs remains nearly stable up to 15 days which conclude its steady gas response even after its long term exposure.

4. Conclusions

In this study, ZnO NPs are successfully prepared through green synthesis method using *sugarcane stem* extract. Structural, optical and morphological studies are confirmed using XRD, UV and SEM analysis respectively. X-ray analysis confirmed the formation of ZnO hexagonal wurtzite structure with a crystallite size of 30 nm. Uniformly aggregated spherical ZnO NPs is visualized by SEM. The optical characteristics showed the wide band gap 3.15 eV. The organized study of LPG sensing has demonstrated 91% maximum gas responses at operating temperature 220°C. The fast response and recovery time of 90 and 70 sec, proves its possibility to be employed as gas sensor. The maximum gas uptake capacity for LPG remained sensible up to up to 9000 ppm. In summary, we conclude that simple, cost-effective and eco-friendly green synthesized ZnO sensor would be a potential candidate for LPG sensors.

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