PREPARATION AND CHARACTERIZATION OF METAL OXIDE NANOPowDERS BY MICROWave- ASSISTED COMBUSTION METHOD FOR GAS SENSING DEVICES

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Nanotechnology has become a very prevalent research area in recent years. It is a subjected investigation of the effect on functional materials, devices and systems when the critical sized is scaled down to nanometer length (1 to 100 nm). It is now a common theme that is prevalent over all physical and materials sciences and is of great significance in both science and technology known as nanotechnology. It covers many conventional areas of physics, chemistry, biology and medicine and becomes an interdisciplinary subject. Presently, the most significant aspects of nanotechnology are focused in basic sciences and mainly within physics and chemistry. With development of nanotechnology, it is worthwhile and promising to expect its research and applications on applied sciences, including biology, nanomedicine and other potential areas. The research and development in nanomaterials involved three viewpoints: synthesis of nanomaterials, characterization of their properties and realization of their applications. A large research interests in nanotechnology and nanoscale materials are inspired by the enormous economical, technological and scientific advantages of several areas: (a) With the exponential growth of the processing speed of semiconducting chips, the crucial components that virtually enable all modern technology, the fabrication technique is quickly approaching its limit of functions and demands new technology and new materials science on the nanometer scale, (b) Novel nanoscale materials and devices hold great promising potentials in energy, environmental and biomedical applications. They have supreme properties for more efficient use of energy source, effective treatment of environmental hazards, rapid and accurate detection and diagnosis of human sicknesses and improved treatment of such diseases, (c) When a material is prepared as nanoparticle, its properties can be extremely different from those of the bulk materials. Many of the evolutions in this field arise from the requirements of the increasing integration density with nanometer scale structures. Those requirements have driven scientists to develop advanced fabrication processes in nanotechnology. There are two kinds of methods for manufacturing nanoscale building blocks which can be divided as top to down and bottom to up. In the top to down approach, lithography methods are used to facilitate the
device fabrication. Processing speeds and critical structure size are limited with this processing method. For the bottom to up method: nanostructures are grown at spatially defined positions and then automatically followed by device fabrication around the grown nanostructures.

In the present work, we have studied the metal oxide nanopowders such as ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ by microwave-assisted combustion method. The microwave-assisted combustion method has an advantage that the better nanosized particles can be obtained compared with other techniques. The nanocrystalline ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ powders have been prepared under various organic fuels like urea, glycine, carbohydrazide and citric acid at different temperatures. The preparative conditions have been optimized to get nanopowders. The organic fuels and the preparation temperatures have great influence in modifying the structural, optical and electrical properties of nanopowder. However to the best of our knowledge no detailed investigations have been reported for the preparation of ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ nanopowders with the influence of these organic fuels (urea, glycine, carbohydrazide and citric acid) in microwave-assisted combustion method.

The principal aim of this thesis is to prepare ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ oxide nanopowders by the microwave-assisted combustion method and to characterize their optoelectronic, structural and morphological properties and to study their suitability for developing gas sensors.

Despite the literature available on several properties of ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ oxide powders prepared by different techniques, there is lack of complete information concerning the microstructure, electrical, optical and semiconducting properties. Therefore, the present investigation has been carried out on ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ oxide nanopowders prepared with various organic fuels and these powders are heat treated at different temperatures.

The objectives of present work are as follows:

➢ To prepare ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ nanopowders by microwave-assisted combustion method.
To prepare ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ nanopowders with improved structural and electronic properties by optimizing the preparation conditions like various organic fuels (urea, glycine, carbohydrazide and citric acid) and different heat treated temperatures.

To study and interpret the results based on the measurement of maximum combustion temperature ($T_{\text{measured}}$) and the amount of gases produced during the combustion reaction for various fuel-to-oxidizer.

To study the structural, compositional, surface morphological and optical properties of the prepared nanopowders.

To fabricate gas sensors based on ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ oxide nanopowders and study their sensitivity and usefulness for developing efficient ethanol gas sensors.

This thesis is organized into 10 chapters.

In Chapter I, brief introduction to nanomaterials, methods of nanomaterial synthesis and their applications are presented.

In Chapter II, a brief introduction is given with respect to semiconductor materials. Also the properties and applications of ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ materials are given. Further, this chapter briefly covers the reviews on existing literature.

Chapter III gives the complete experimental details of metal oxides like ZnO, SnO₂, ZnSnO₃ and Zn₂SnO₄ nanopowders by microwave-assisted combustion method using different fuels (urea, glycine, carbohydrazide and citric acid). Further, this chapter briefly described the working principle of microwave oven, how microwaves interact with a material, why this interaction causes an increase in the temperature of the material and also summarized the factors involved in the preparation method.

Chapter IV gives the complete experimental background for the different characterization techniques used in the present investigation. The elaborative details of the characterization techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder x-ray diffractometer (PXRD) with refinement by Rietveld
method, x-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL), four transform infrared spectroscopy (FTIR), laser raman spectroscopy, UV-Vis-NIR spectrophotometer and impedance spectroscopy etc. were discussed. Not only the mechanism of nucleation and growth was identified, but also the synthesis method was developed. The choices of the analytical instruments were fast, economical and sensitive without complex producers. Besides, they were extensive technologies applied on the research and measurement of various domains as well. The improvement of the analytical approaches enhances the progress of science and engineering, including quality and quantity. The analytical methods can be effective to achieve the detailed study on nanomaterials.

Chapter V gives a brief discussion about the maximum combustion temperature produced and calculates the adiabatic flame \( (T_{ad}) \) with the fuel-to-oxidizer molar ratio (\( \psi \)) values of the discussed reactions which has been calculated theoretically according to the thermodynamic concept. A possible reaction mechanism based on thermodynamic formulae, calculations of the fuel-deficient, stoichiometric, fuel-rich condition and experimental results was proposed and explained the effects of the reactant composition on the combustion reaction.

In Chapter VI, we have described in detail the structural, compositional, surface morphological properties of various organic fuels used ZnO nanopowders of as-prepared and treated at different temperatures by microwave-assisted combustion method. Powder X-ray diffraction (PXRD) results completely showed the structural properties of the nanopowders. The PXRD patterns of all the prepared samples confirmed the presence of hexagonal wurtzite phase ZnO and it is further confirmed by the selected area electron diffraction using TEM analysis. The particle size of the samples were estimated using Debye-Scherrer formula and its value is very close to the Rietveld refinements method and further these values are agreed well with the TEM analysis. The chemical states and composition analysis was made using XPS analysis. The peak positions of the respective core line peaks were well agreed with the standard values. The surface morphology of the ZnO powders are analyzed using SEM and TEM micrographs. Optical band gaps obtained from the absorption spectra are presented in this chapter.
Chapter VII elaborates the preparation and optimization of SnO$_2$ nanopowders with various organic fuels and heat treated temperatures are discussed. The structural, surface morphological, compositional of the prepared SnO$_2$ nanopowders are found from PXRD, SEM, TEM, EDS and XPS spectra. The Powder X-ray diffraction patterns for all the prepared samples were tetragonal rutile structure of SnO$_2$ and it was confirmed by the selected area electron diffraction using TEM analysis. The particle size of the SnO$_2$ powders were estimated using Debye-Scherrer formula and its value is close to the Rietveld refinements method and these values are agreed well with the TEM analysis. The chemical states and composition analysis were made using XPS analysis. The peak positions of the respective core line peaks were well agreed with the standard values. Surface morphology of the SnO$_2$ nanopowders has been investigated using SEM and TEM micrographs which revealed the particle size and shape variation with respect to heat treated temperature. In addition, particle size was calculated from the Rietveld refinement method and specific surface area was obtained using the Brunauer-Emmett-Teller (BET) method. Optical studies were carried out using UV-Vis-NIR, PL, Laser Raman and FTIR spectrophotometers. From the optical spectra, the band gap of 3.8 eV was observed in the glycine fuel used as-prepared SnO$_2$ nanopowder and the results are discussed.

Chapter VIII elaborates the preparation of two oxides, ZnSnO$_3$ and Zn$_2$SnO$_4$, named mostly meta- and ortho-stannate, respectively which are known to exist in the ZnO–SnO$_2$ system. Zinc orthostannate, Zn$_2$SnO$_4$ is the stable phase in the system ZnO–SnO$_2$. Spinel type zinc stannate is a ternary oxide (Zn$^{II}$[Zn$^{II}$Sn$^{IV}$]O$_4$), while the rhombohedral type zinc stannate (ZnSnO$_3$) is unstable and decomposes into Zn$_2$SnO$_4$ and SnO$_2$ at higher temperatures. The interesting properties of both of these ZnSnO$_3$ and Zn$_2$SnO$_4$ are n-type semiconducting material having wide band gap energy (3.6 eV) attracted much attention as new TCO materials. An important example of TCO materials having high electron mobility, high electrical conductivity, and attractive optical properties make it suitable for a wide range of applications. These are promising applications in gas sensing and the special importance of this material is the possibility of its sensor properties i.e detection of combustible gases and humidity such as ethanol detection.
ZnO and SnO$_2$ mixed phase can be detected by XRD for the ZnO–SnO$_2$ composite oxide with atomic ratio of Sn:Zn as 1:1 and 1:2 for treated temperature below 800°C and pure phases are appeared when the sample treated temperature at 800°C for 2 h. Single phase ZnSnO$_3$ and Zn$_2$SnO$_4$ powder materials were successfully synthesized using the microwave-assisted combustion method. The particle size was confirmed using PXRD, SEM and TEM measurements. EDS results showed that all elements in the starting solutions were in the solid films and Sn element is more dominant than Zn on the surfaces. The room-temperature Laser Raman result further confirms that the rhombohedral phase of ZnSnO$_3$ and face-centered cubic spinel structural of Zn$_2$SnO$_4$ structure. The absorption edge corresponding to the band gap energy of ZnSnO$_3$ and Zn$_2$SnO$_4$ is obtained. It is clear that the optical properties of ZnSnO$_3$ and Zn$_2$SnO$_4$ strongly depend on the synthesis condition as well as with fuels. The large band gap energies of the both ZnSnO$_3$ and Zn$_2$SnO$_4$ powders suggest that the materials belong to semiconductors and potential applications in gas-sensing devices. Room-temperature photoluminescence spectrum of ZnSnO$_3$ and Zn$_2$SnO$_4$ nanopowders showed a broad strong green emission at 555 and 562 nm, respectively. And glycine used ZnSnO$_3$ and Zn$_2$SnO$_4$ nanopowders exhibit the respective strong orange emission band centered at 602 and 606 nm, which can be ascribed to a large amount of oxygen vacancies, tin interstitials, oxygen interstitials and tin vacancies during the preparation method. All these results are summarized in this chapter.

In Chapter IX, gas sensing mechanism and sensor testing procedures were explained briefly for the understanding of the chemical adsorption/desorption reaction kinetics. The optimized concentration of ethanol and operating temperature for ZnO, SnO$_2$, ZnSnO$_3$ and Zn$_2$SnO$_4$ sensors are studied and compared briefly. The large surface areas of microwave-assisted combustion method prepared ZnO, SnO$_2$, ZnSnO$_3$ and Zn$_2$SnO$_4$. Zn$_2$SnO$_4$ nanopowders should be in favor of ethanol gas sensor at low temperature. However, to our knowledge, there is still no report about ethanol gas sensing at low temperature using ZnO, SnO$_2$, ZnSnO$_3$ and Zn$_2$SnO$_4$ nano particles. It shows relatively high, quick response to the ethanol vapor and quick recovery time.

Finally, the results of these studies, conclusions drawn and suggestions for future work are presented in Chapter X.