Synthesis and characterization of Perovskite type nanomaterials and their Novel applications

Summary of the Dissertation

Submitted for the Award of the Degree of

Master of Philosophy

in

Physics

by

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(Enrolment No.- 484/16)
Under the supervision

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प्रज्ञा शील करुणा
ESTABLISHED 1996

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2020

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The first chapter is focused on the basic introduction of nanoscience and nanotechnology including different potential market areas for nanotechnology, sensors, perovskites and literature review which accumulate a comparative study on various perovskite structures and their different sensing properties at international and national level and motivation. Graphical abstract of first chapter is depicted in **Figure 1.** Nanoscience is mainly concerned with the fundamental understanding of the phenomena, and the study of materials and systems and their properties lying in the nanoscale of 1~100 nm, whereas nanotechnology covers the vast and diverse range of applications of nanoscience and explains the merger of nanoscience with technology. The critical aspect of molecular nanoscience is the design and assembly of well-defined molecular architectures, which laid a milestone in the way of possibilities for fundamental research and applications. In nanoscience, there is not only the small size that is dealing with but also the quantum effect, which is size-dependent and significantly different from macroscopic properties of materials. Most of the nanomaterials are crystalline in nature and show unprecedented changes in chemical, physical, mechanical, magnetic properties etc., when reduced from bulk to nano scale. When the magnitude of the diameter of a particle is same as the wavelength of electron wave function, quantum confinement effect is observed. For a cubical box with discrete energy levels are shown in **Figure B;** and **Figure C** shows the density of electron states as function of different dimensions. **Figure D** shows the two synthesis approaches for producing nanomaterial. There are large numbers of pathway that have been formulated to synthesize different nanomaterial of various dimensions in gaseous or liquid phase. With the development of two synthesis technologies that are "top-down" and "bottom-up", finally there are opening of two convergence approaches of nano-based products for practical purpose, both to interact with outer world and to tailor the nano-scale device. Currently, environmental pollution has become a severe problem for the whole world and its prevention is very challenging for mankind. Many sensors have been designed and fabricated to detect the levels of various toxic gasses in order to avoid tragedies. From the literature, it is observed that presently available sensors have two major shortcomings; first, low sensitivity and second, high operating temperature [1]. The need for reliable, cheap and user-friendly gas sensors for the detection of CO_2 gas has motivated us to prepare nanomaterial through a suitable synthesis technique which is efficient, cost-effective.

1. Reason for detection of CO_2 gas

The burning of fossil fuels from the industries, motor vehicle and volcanic eruption are the resources of major environment pollutant like carbon monoxide and carbon dioxide. The continuous increase in the concentration of CO_2 in the natural environment has raised the temperature of the earth causing global warming which is further liable for the melting of glaciers and rising sea levels. Also, the excessive presence of CO_2 in the ambient environment causes suffocation and creates unconsciousness in human beings. Therefore, precise measurement and control of CO and CO_2 are necessary.

2. Requirement for CO_2 sensor

The need for reliable, cheap and user-friendly gas sensors for the detection of CO_2 is industrially important and has led to a considerable expansion in the field of sensor research and development. Several types of CO_2 sensors such as chemical sensors, the resistive and conductive type sensors using semiconductors and sensors based on metal-polymer complexes have been investigated by different research groups in various parts of the world. Therefore, great attention has been recently paid to the development of new ‘architect- material’ at the nano-scale.

3. Importance of structure

Tubular shape and cross-linked structure have a major effect on the gas-sensing properties of polycrystalline materials and their full characterization should be the first step in the study of materials.

4. Perovskite

Perovskite has a remarkable distinct appearance. And due to the single structure along with the proficient chemical manipulation are able to illustrate completely different operations along with an incredibly wide range of phase [2]. Perovskite-type oxides are the materials that follow the structure ABO_3, where A and B represent the alkaline earth metal and transition metal, respectively, as shown in **Figure E**. Among the multifunctional ternary structures, usually, the phases which are recognized by A_2BX_4 and ABX_3, represent the spinel and perovskite structures, respectively. In the sensor technology, metal oxides are widely used for good sensing behavior but these materials have a high operating temperature (200-400℃) [3]. Thus, perovskite sensors which may be operated at room temperature with fast recovery and response times are highly desirable.

5. Barium titanate

The first piezoelectric perovskite ceramic transducer was developed with iso-structure using mineral perovskite is Barium titanate ($BaTiO_3$) [4]. On and above the room temperature, $BaTiO_3$ is stable and porous in nature. This property helps to keep more concentration on different sensors like the ceramic gas sensor. Because, the functional mechanism of sensor is adsorption; where gas molecules are being functionally adsorbed.

6. CO_2 sensor working principle

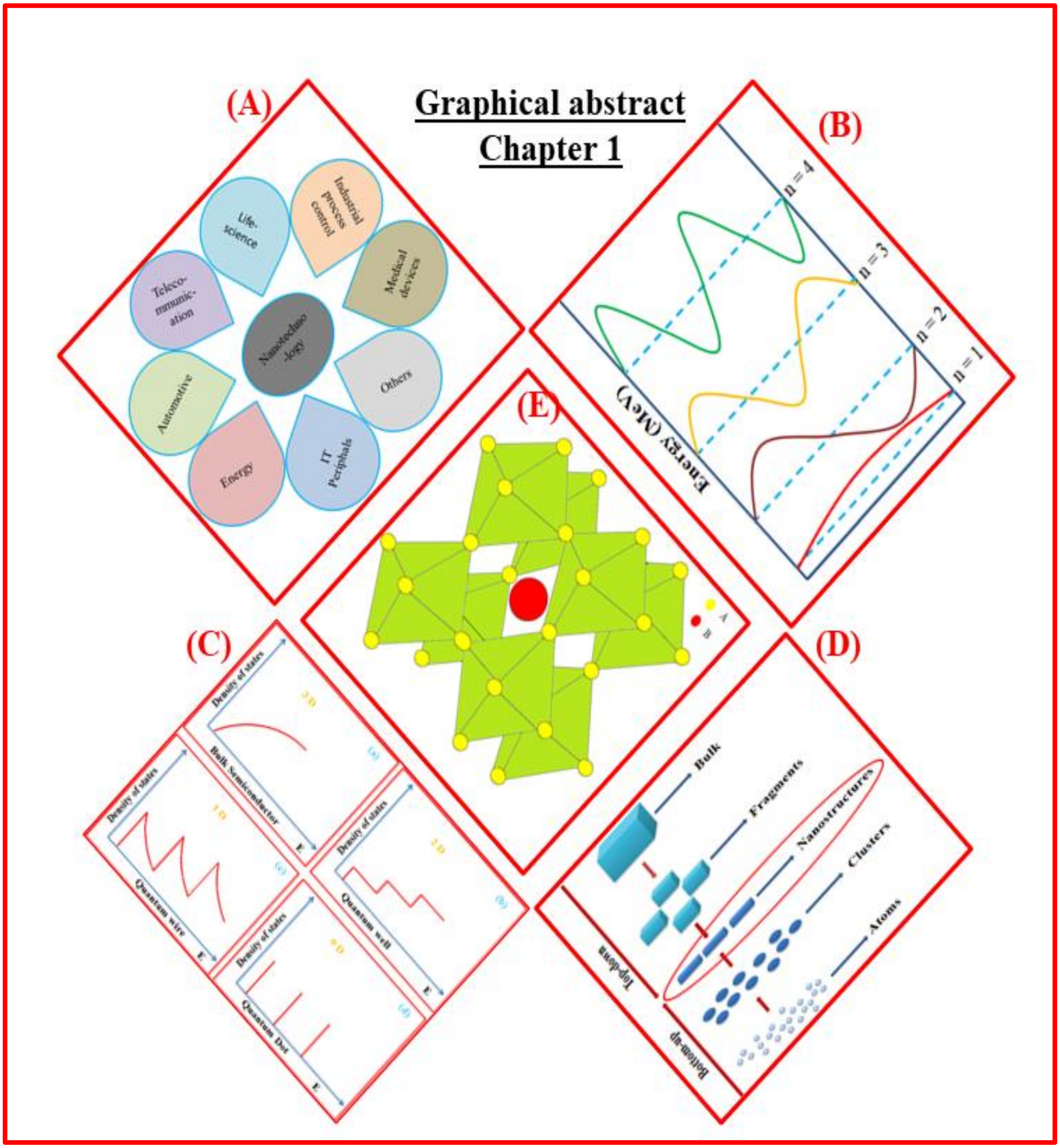
When the film was exposed in air, the O_2 of air was adsorbed on the nano surface and ionized to oxygen ion by trapping the free electron and built a thick space charge layer, which increases the potential barrier. At lower concentration of gas, the CO_2 molecules interact with oxygen species and form a metastable compound CO_3 and release electrons which attenuate the potential barrier and the resistance starts decreasing.

O_2 (ads) + e^- → O^{2-} (ads) + O^- …………..(1)

When interacting with CO_2

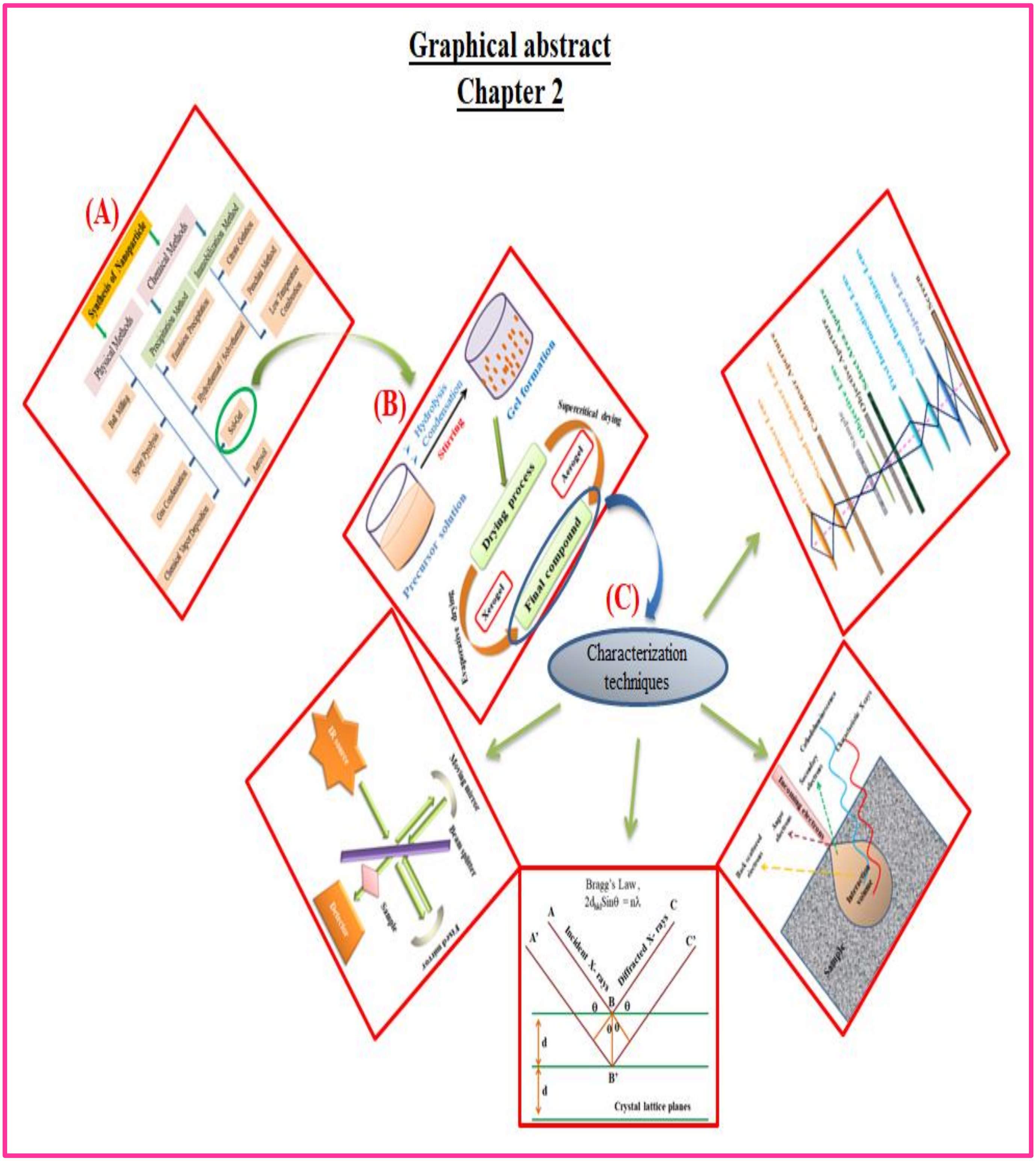
$CO_2 + O^- \rightarrow CO_3 + e^-$ …………(2)

Figure 1


Graphical abstract
Chapter 1
(A)
Industrial process control
Life-science
Medical devices
Teleco-mmunic-ation
Nanotechno-logy
Others
Automotive
Energy
IT Periphals
(B)
n = 4
n = 3
n = 2
n = 1
Energy (MeV)
(E)
A
B
(C)
Density of states
3 D
(a)
Bulk Semiconductor
E
Density of states
1 D
(c)
Quantum wire
E
Density of states
2 D
(b)
Quantum well
E
Density of states
0 D
(d)
Quantum Dot
E
(D)
Bulk
Fragments
Nanostructures
Clusters
Atoms
Top-down
Bottom-up

Chapter 2

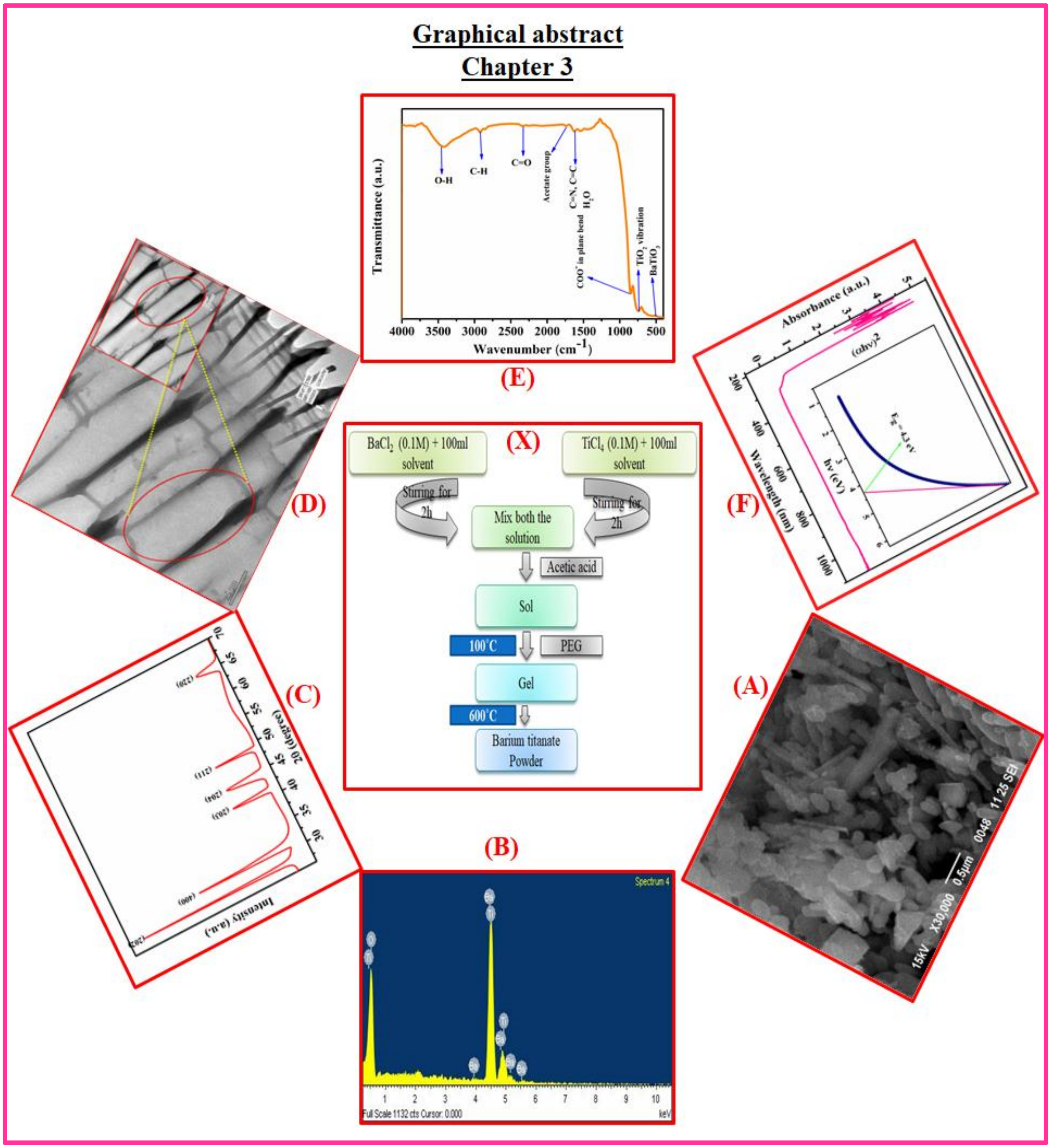
Figure 2



Graphical abstract of second chapter is depicted in **Figure 2.** This chapter includes various synthesis methods utilized for fabricating nanomaterials (**Figure A**). Among all these types, sol-gel is researcher friendly because of low cost, can be applied by minimum instrument facility and also at room temperature (**Figure B**). This chapter also focused on various characterization techniques (**Figure C**), which helps us to characterize the synthesized material. We can study various characteristics with the help of XRD, SEM, TEM, UV-Vis, and FTIR spectrometer.

Chapter 3

Figure 3



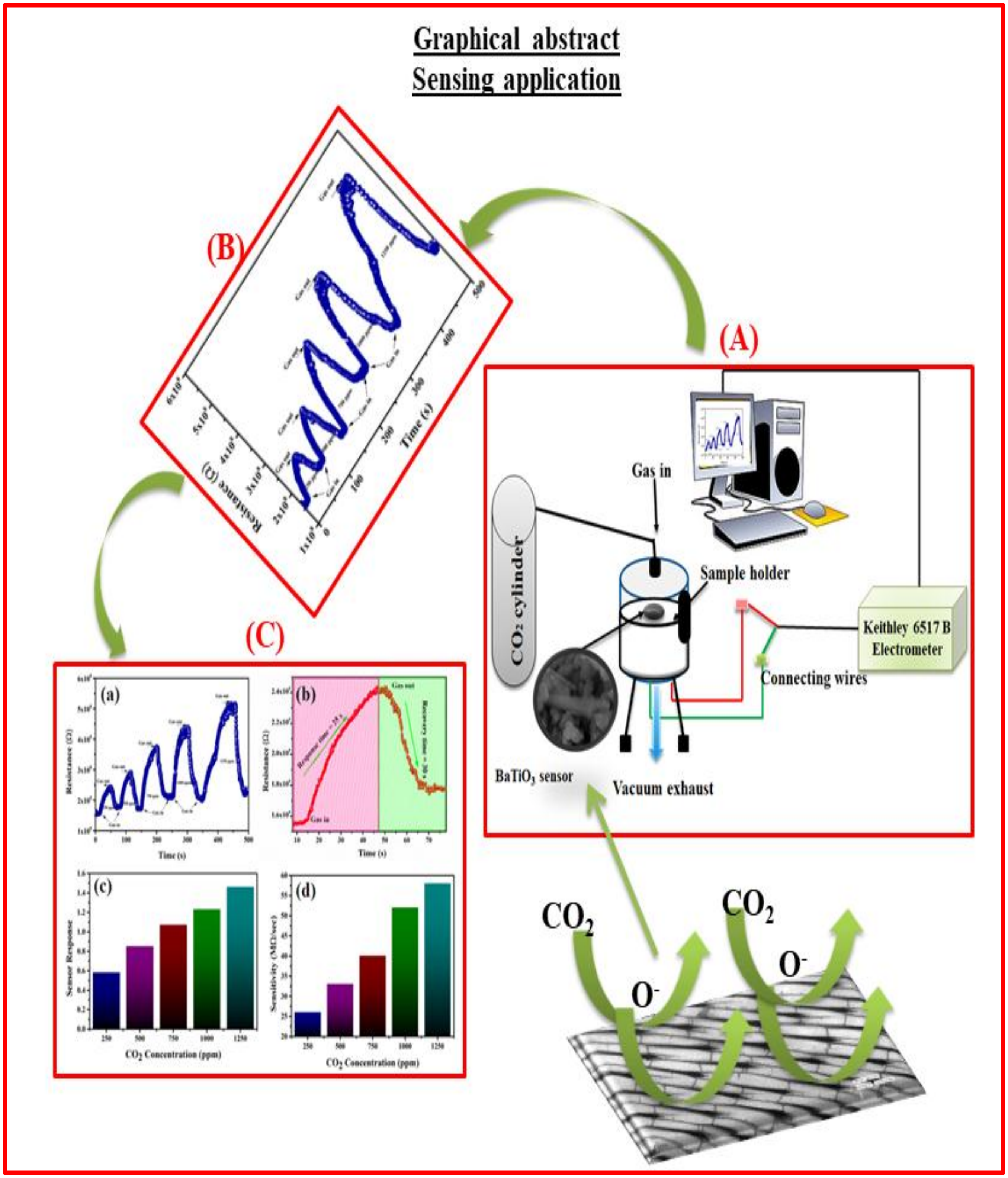
Graphical abstract of second chapter is depicted in **Figure 3.** We have done the synthesis of Barium titanate successfully using sol-gel route. **Figure X** represents the flow diagram of synthesis mechanism. To deposit invariable thickness of thin film, among different type of techniques sol-gel spin coating method is the best method of coating and depositing uniform thickness of thin film. We have studied the surface morphology of the synthesized material by SEM operating at 20kV and EDX. The morphology was observed by SEM analysis (**Figure A**). SEM images characterize tubular configuration with porous nature of the nanomaterial. The EDX record confirms the development of barium titanate, consisting of Ba 24.07%, Ti 22.78%, O 53.15% in the sample (**Figure B**). The crystalline characteristic, formation of phase of the barium titanate was confirmed by XRD analysis. By using Debye Scherer's equation, we have calculated the minimum average crystallite size and it was found to be 9.18 nm. The crystallite size of each peak is also calculated and it was found 15.71 nm the average crystallite size (**Figure C**). The TEM image representation at 500 nm scale express the periodic arrangement of particles in a regular form and the image reveals the unique structure of sugarcane stem like formation. (**Figure D**). The FTIR spectrum reveals the presence of various functional groups (**Figure E**). The peak at 548 cm^{-1} is for the absorption band of $BaTiO_3$ [5]. The synthesized barium titanate optical absorbance spectrum has been shown in **Figure F**. Optical band gap of synthesized BTO was calculated and was found as 4.3 eV.

Graphical abstract of sensing application is depicted in **Figure 4**, it was described that the synthesized $BaTiO_3$ was used as a room temperature CO_2 sensor, was tested. **Figure A** shows the sensing apparatus where the film was tested as CO_2 sensor. The differences in the resistance of the film with time before and after exposed to different ppm of CO_2 gas in the closed chamber at room temperature has been displayed in **Figure B**.

In the beginning of the experiment, the thin film of $BaTiO_3$ was kept for 15 min inside a vacuum chamber to decrease the effect of surface contaminants and made it more stable. Then the differences in the resistance of the thin film of $BaTiO_3$ exposed to different CO_2 concentrations were observed. When the thin film was exposed to 250 ppm of CO_2 gas, the first sensing curve with first peak was recorded which displays a constant variation in resistance and showed less sensing response , the thin film was exposed to higher concentration of CO_2 gas (500 ppm) and peak of the second sensing curve showed higher sensing response than the earlier one. Again, the film was exposed to highest concentration of CO_2 (1250 ppm) in the chamber and maximum (1.46) sensing response was recorded. But the response and recovery time was found to increasing with the increase in exposure to 1250 ppm of $CO_{2.}$ Similarly, there was an observation of decrease in the sensing response while increasing the concentration of CO_2 inside the chamber. This may be due to fill up of the entire free lattice site on the external surface of the thin film.

The minimum response and recovery time were found as 25 s and 30 s for 250 ppm of CO_2 respectively. The sensor response and sensitivity were also observed at different concentration of CO_2 gas and have been found that it is sensible at 250 ppm of CO_2 gas, as this much concentration of CO_2 is on limelight, especially in metro-cities.

Figure 4


Graphical abstract
Sensing application
(A)
(B)
(C)
Gas in
Sample holder
CO₂ cylinder
Keithley 6517 B Electrometer
Connecting wires
BaTiO₃ sensor
Vacuum exhaust
Resistance (Ω)
Time (s)
(a)
(b)
(c)
(d)
Gas in
Gas out
Sensor Response
Sensitivity (MΩ/sec)
CO₂ Concentration (ppm)
250
500
750
1000
1250
CO₂
O⁻

Chapter 4

This chapter presents all the significant results of whole research work carried out suggestions for future works. Some key conclusions are given underneath:

a) Barium titanate successfully was synthesized using improved sol-gel route and characterized the sample.

b) The crystalline characteristic, formation of phase and minimum crystallite size (9.18 nm) of the barium titanate was confirmed by XRD analysis.

c) The TEM image showed the unique internal structure.

d) The optical band-gap was found to be as 4.3 eV by UV-Vis spectrometer.

e) Further the barium titanate film was fabricated by spin coating method and used for CO_2 sensing application.

f) The maximum sensitivity of the film was found as 58 MΩ/sec at 1250 ppm gas concentration.

g) The sensor response and recovery times were 25s and 30 s respectively.

Scope of future research

Research is the continuous process which never ends. Although best efforts have been put by the author in the present study, still there is a scope for further research and improvement in present work. Future research works that would be productive in further understanding the role of nano-oxides for low-temperature applications, are desirable. These include incorporation of the recovery aspects achieved by the incorporation of catalyst onto the surface of a nano-oxide being used to detect a reducing gas. The application based on surface interaction can be done because of its particle structure, so by testing its toxicity it can be used in biological field also. Theoretical modelling related to the sensing mechanism can also be undertaken for further research.

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