

**SYNTHESIS AND CHARACTERIZATION OF CALCIUM  
CARBONATE NANOPARTICLES** ★

THISS27 Wsy



**By**

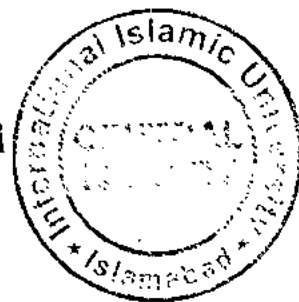
**Aisha kanwal**  
**(202-FBAS/MSPHY/F13)**

**Supervisor**

**Dr. Shamaila Sajjad**

**Co-Supervisor**

**Dr. Sajjad Ahmed Khan Leghari**



**DEPARTMENT OF PHYSICS**  
**FACULTY OF BASIC AND APPLIED SCIENCES,**  
**INTERNATIONAL ISLAMIC UNIVERSITY,**  
**ISLAMABAD**  
**(2015)**

MS  
620.5  
A1S

1. Nanoparticles



# **SYNTHESIS AND CHARACTERIZATION OF CALCIUM CARBONATE NANOPARTICLES**



**By**

**Aisha Kanwal**

**(202-FBAS/MSPHY/F13)**

**DEPARTMENT OF PHYSICS  
FACULTY OF BASIC AND APPLIED SCIENCES,  
INTERNATIONAL ISLAMIC UNIVERSITY,  
ISLAMABAD  
(2015)**


**INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD**  
**FACULTY OF BASIC AND APPLIED SCIENCES**  
**DEPARTMENT OF PHYSICS**  
**SYNTHESIS AND CHARACTERIZATION OF CALCIUM**  
**CARBONATE NANOPARTICLES**


By

**AISHA KANWAL**

**(Registration No. 202-FBAS/MSPHY/F13)**

A thesis submitted to  
**Department of Physics**  
For the award of the degree of  
**MS Physics**

Signature:   
**Dr. Ghazala Sajjad**  
Chairperson  
Department of Physics (FC of Physics)  
(Chairman, Department of Physics)  
International Islamic University  
Islamabad

Signature:   
(Dean FBAS, IIU, Islamabad)

**INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD**  
**FACULTY OF BASIC AND APPLIED SCIENCES**  
**DEPARTMENT OF PHYSICS**

Dated:25-08-2015

**FINAL APPROVAL**

It is certified that the work presented in this thesis entitled "SYNTHESIS AND CHARACTERIZATION OF CALCIUM CARBONATE NANOPARTICLES" by MS. AISHA KANWAL bearing Registration No. 202-FBAS/MSPHY/F13 is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

**COMMITTEE**

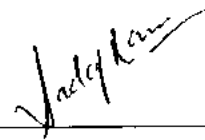
**External Examiner**

DR. TARIQ MAHMOOD  
Associate Professor  
National Centre For physics  
Islamabad



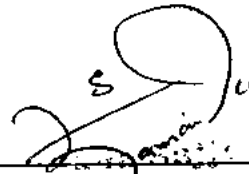
**Internal Examiner**

DR. SADAF JAMIL  
Assistant Professor  
Department of Physics, FBAS, IIUI



**Supervisor**

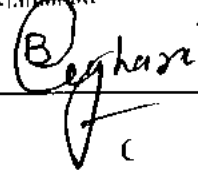
DR. SHAMAILA SAJJAD  
Assistant Professor,  
Department of Physics, FBAS, IIUI



**CO-supervisor**

DR. SAJJAD AHMED KHAN LEGHARI  
Principle Scientist, PAEC, Islamabad

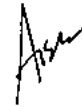
Supervisor  
Department of Physics (PC, FBAS)  
International Islamic University  
Islamabad



A thesis submitted to  
**Department of Physics**  
International Islamic University Islamabad  
As a partial fulfillment for the award of the degree of  
**MS in Physics**

## **Declaration**

I hereby declare that this thesis work, neither as a whole nor a part of it has been copied out from any source. Further, work presented in this dissertation has not been submitted in support of any application for any other degree or qualification to any other university or institute and is considerable under the plagiarism rules of Higher Education Commission (HEC), Pakistan.



**AISHA KANWAL**

**(202-FBAS/MSPHY/F13)**

## DEDICATION

**To**

*My loving Parents*

*And*

*Siblings*



## **Acknowledgement**

In the name of Allah, the Most Gracious and the Most Merciful Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisor, Dr Shamaila Sajjad, for her supervision and constant support. Her invaluable help of constructive comments and suggestions throughout the experimental and thesis works have contributed to the success of this research. Not forgotten, my appreciation to my co-supervisor, Dr. Sajjad Ahmed Khan Leghari for his support and knowledge regarding this topic.

I am most grateful to the collaborators PIEAS and my home institute IIUI for lending me their expertise and intuition to my scientific and technical problems.

I cannot forget my best friend Sana Tabasum who went through hard times together, cheered me on, and celebrated each accomplishment.

Last but not least, I offer my heartiest gratitude to all my family members, especially, Father, Mother, Sister and Brothers for their cooperation, moral support, patience, trust and prayers for my health and success.

**AISHA KANWAL**

# Table of Contents

## **Chapter No. 1 Introduction**

- 1.1. Nanotechnology
- 1.2. Nano materials
- 1.3. Nano particles
- 1.4. Calcium Carbonate
- 1.5. Polymorphs of Calcium Carbonate
- 1.6. Availability of Calcium Carbonate
- 1.7. Sources of Calcium Carbonate
- 1.8. Effect of process condition on physiochemical properties of Calcium Carbonate
- 1.9. Effect of additives on morphology and surface of Calcium Carbonate
- 1.10. Utilization of Calcium Carbonate nanoparticles
- 1.11. Properties of Calcium Carbonate

## **Chapter No. 2 Literature Review**

## **Chapter No. 3 Synthesis and Characterization Techniques**

- 3.1. Instrumentation
- 3.2. Materials
- 3.3. Synthesis of Nanoparticles
- 3.4. Synthesis of Calcium Carbonate Nanoparticles
- 3.5. Characterization techniques

## **Chapter No.4 Result and Discussion**

- 4.1. X-ray diffraction (XRD)
- 4.2. Scanning electron microscope (SEM)
- 4.3. Fourier transmission infrared spectroscopy (FT-IR)
- 4.4. Energy dispersive X-ray analyzer (EDX)

## **Conclusion**

## **References**

## List of Figures

**Figure 1.1:** Multidisciplinary Fields of Nanotechnology

**Figure 1.2:** Comparison of nanomaterial sizes

**Figure 1.3:** Dimensionally classified Nanomaterials

**Figure 1.4:** SEM images of Calcite and Aragonite

**Figure 1.5:** Application of Calcium Carbonate

**Figure 3.1:** Schematic diagram for synthesis of  $\text{CaCO}_3$  Nanoparticles In the presence of  $\text{H}_2\text{SO}_4$

**Figure 3.2:** Schematic diagram for synthesis of  $\text{CaCO}_3$  Nanoparticles In the presence of Urea

**Figure 3.3:** Schematic diagram for synthesis of  $\text{CaCO}_3$  Nanoparticles In the presence of CTAB

**Figure 3.4:** Schematic diagram for synthesis of  $\text{CaCO}_3$  Nanoparticles In the presence of SDS

**Figure 3.5:** Diffraction of X-rays from crystal planes

**Figure 3.6:** X-ray diffraction scheme

**Figure 3.7:** Schematic diagram of an SEM set-up

**Figure 3.8:** Schematic setup of FTIR Spectroscopy

**Figure 3.9:** EDX spectrum, transfer of electron from high energy shell to low energy shell

**Figure 4.1 (a):** XRD scan of unprocessed egg shell

**Figure 4.1 (b):** XRD scan of egg shell in the presence of CTAB

**Figure 4.1 (c):** XRD scan of egg shell in the presence of Urea

**Figure 4.1 (d):** XRD scan of egg shell in the presence of SDS

**Figure 4.1 (e):** XRD scan of egg shell in the presence of  $\text{H}_2\text{SO}_4$

**Figure 4.2:** XRD scan of egg shell bulk (Un-processed), In the presence of CTAB,  $\text{H}_2\text{SO}_4$ , SDS and Urea

**Figure 4.3:** FTIR spectra of (a) Egg shell bulk (Un-processed) (b) In the presence of CTAB(c) In the presence of  $H_2SO_4$  (d) In the presence of SDS (e) In the presence of Urea

**Figure 4.4(a):** SEM images of un-processed egg shell

**Figure 4.4(b):** SEM of Egg Shell  $CaCO_3$  in the presence of  $H_2SO_4$

**Figure 4.4(c):** SEM of Egg Shell  $CaCO_3$  in the presence of SDS

**Figure 4.4(d):** SEM of Egg Shell  $CaCO_3$  in the presence of CTAB

**Figure 4.4(e):** SEM of Egg Shell  $CaCO_3$  in the presence of Urea

**Figure 4.5:** EDX spectrum for of un-processed egg shell

**Figure 4.6:** EDX spectrum for of egg shell in the presence of SDS

**Figure 4.7:** EDX spectrum for of egg shell in the presence of CTAB

**Figure 4.8:** EDX spectrum for of egg shell in the presence of Urea

## **List of Tables**

**Table 1.1:** Difference between Nanomaterials and Bulk material

**Table 1.2:** The availability of three polymorphs of  $\text{CaCO}_3$

**Table 3.1:** List of Chemicals Used in the experiment

**Table 4.1:** Wave numbers of functional groups

**Table 4.2:** Integrative analysis of un processed egg shell

**Table 4.3:** Integrative analysis of egg shell in the presence of SDS

**Table 4.4:** Integrative analysis of egg shell in the presence of CTAB

**Table 4.5:** Integrative analysis of egg shell in the presence of Urea

## **List of abbreviation**

EDX	Energy dispersive X-ray analyzer
XRD	X-ray diffraction
SEM	Scanning electron microscope
TEM	Transmission electron microscope
FTIR	Fourier transmission infrared spectroscopy
PDDA	Polydiallyldimethylammonium chloride
CTAB	Cetyltrimethylammonium bromide
EDTA	Ethylenediaminetetraacetic Acid
ACC	Amorphous calcium carbonate
PAA	Polyacrylic acid
PEG	Polyethylene glycol
SDS	Sodium Dodecyl Sulphate
MEG	Mono ethylene glycol
BSE	Backscattered electrons
SE	Secondary electrons

## Abstract

In present study the effect of additives on the morphology and particle size of calcium carbonate were examined. The existent work used wet chemical method for the preparation of calcium carbonate nano particles from the egg shell as natural source. The CTAB, Urea, sulphuric acid and SDS were used as additives.

The processed and un-processed egg shell calcium carbonate nano particles are characterized by different characterization techniques including Energy dispersive X-ray analyzer (EDX), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transmission infrared spectroscopy (FTIR) and all these techniques showed different aspects of synthesized product.

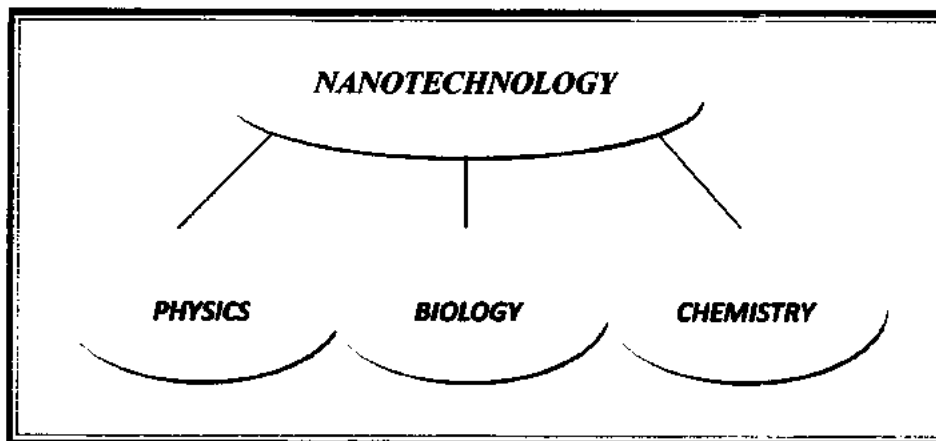
The results are compared for un-processed and processed egg shell calcium carbonate in the presence of CTAB, Urea, sulphuric acid and SDS. The XRD patterns determine the that calcium carbonate nano particle are well crystalline and particle size reduces in the presence of Urea and the sized is found to be less then 20nm where as in bulk it is 20nm..The SEM images reveals that the un processed egg shell has the cubic like morphology and the processed egg shell in the presence of  $H_2SO_4$  showed that it has changed to rod like shape. FTIR results also confirmed the formation of calcium carbonate nano particles.

## Chapter No.1

### Introduction

#### 1.1 Nanotechnology

Nanotechnology is a versatile field. It involves many disciplines like applied physics, interface and collide science, device physics, chemistry, biology, material science, mechanical and electrical engineering etc [1]. Nanotechnology clings to all other sciences at nanoscale. This newly emerging discipline utilized laws and rules from all other sciences yet there is a operating boundary between them at atomic scale [2].



**Figure 1.1:** Multidisciplinary Fields of Nanotechnology [2]

Nanotechnology includes the major physical properties and phenomena of nanostructures which make it different from bulk material. Nanotechnology is feasible to increase both qualitatively and quantitatively. Nanotechnology exhibit high surface reactivity due to large surface to volume ratio [3].

##### 1.1.1 Nanoscale

It is hard to imagine the infinitesimal of nanotechnology, but this technology has the ability to bring revolution in field of science [4]. Nanotechnology is a technology on an atomic or



molecular scale that has potential to manipulate, exploit and control the properties of material at atomic scale .The scale of atom and molecules are of the range of nano scale [5]. The nanometer scale range from 1nm to 100nm in at least one dimension [6].

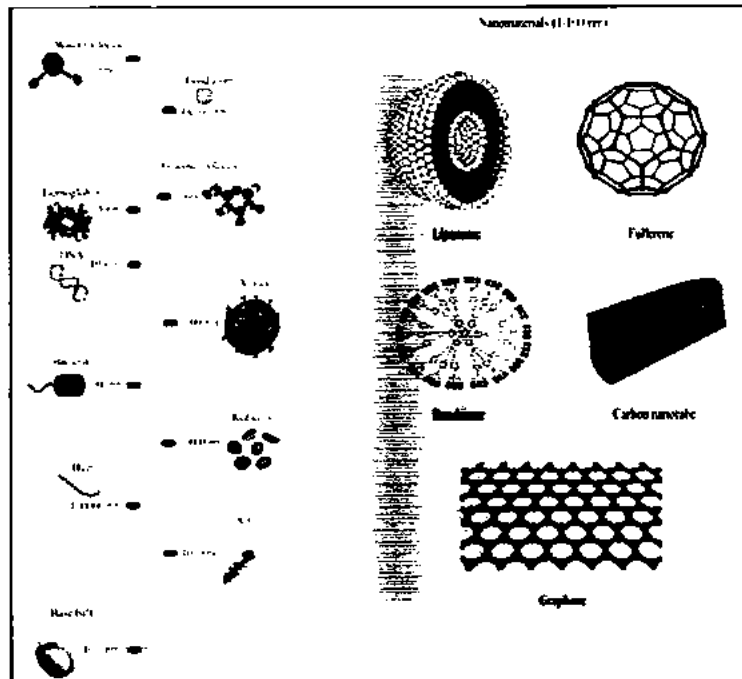


Figure 1.2: Comparison of nanomaterial sizes [7]

## 1.2 Nanomaterials

Nanomaterials are the foundation of nanotechnology [8, 9]. Some Nanomaterials occur naturally but some can be fabricated according to requirement. When the material is brought from bulk to atomic level there is drastic change in its properties .This change is majorly due to increase in surface area as compared to volume [10, 11].

There is a famous quote from Wolfgang Pauli that was expressed long ago, it says:

**“God made the bulk, the surface was invented by the Devil”.**

### 1.2.1 Categories Of Nanomaterials

To understand the importance and diversity of nanomaterials it is essential to classify them. The classification is on the basis of dimensions [12]

- i. 0 dimensional (0-D)
- ii. 1 dimensional (1-D)
- iii. 2 dimensional (2-D)

### 1.3.1 Nanomaterials V/S Bulk Material:

Nanomaterials	Bulk Materials
High surface-volume ratio	Small surface effect
Less number of defects	More number of defects
Range=1nm-100nm(very small)	Range= Greater than $10^5$ nm(very large)
Size dependent properties	Constant Properties

**Table 1.1:** Difference between Nanomaterials and Bulk material [20]

## 1.4 Calcium Carbonate

Calcium carbonate is composed of calcium, oxygen and carbon [7]. Calcium carbonate is a chemical compound with formula  $\text{CaCO}_3$  [21]. Calcium carbonate is one of the most naturally occurring mineral on the earth [22-24]. 71% of calcium carbonate on the earth crust exists as marble or limestone [25]. In nature calcium carbonate accumulates as the major element of the rocks as the minerals in the form of stalactites and of stalagmites. It also exists in the form of skeleton of shell of plants and animals [26].

The connection between these natural resources is calcium carbonate cycle. Calcium carbonate is among most versatile material that is introduced to the mankind [27].

## 1.5 Polymorphs of Calcium Carbonate

Calcium Carbonate has three polymorphs. They are named as follow:

- Calcite
- Vaterite
- Aragonite

The three polymorphs are different from each other due to their morphologies. The morphology can be controlled thermodynamically and kinetically [28-30]. The chemical properties of three forms are same but the other properties like homogeneity, thickness, color are different in calcite, vaterite and aragonite [27].

### 1.5.1 Calcite

The most stable form of calcium Carbonate is calcite .It is configure at an ambient atmospheric pressure And temperature [31].Calcite has a rhombohedral shape [32].

### 1.5.2 Vaterite

The least stable form of calcium carbonate is vaterite. It is expected that vaterite can be used in different purposes because it has a certain feature like high surface area, high dispersion, high solubility, and low specific gravity compared to the other two polymorphs of calcium carbonate [31, 33, 34]. Vaterite is a Strong candidate for a drug delivery system due to its, large surface area, large porosity, and it can decompose fastly under relatively mild conditions [35, 36].Vaterite shows the hexagonal structures [32].

### 1.5.3 Aragonite

Aragonite is stable at high temperature. High temperature basically favors the fabrication of the aragonite [37]. It is the least occurring form of calcium carbonate created artificially or in laboratory. As aragonite is less dense than calcite so this property makes it very useful in biomedical materials and it can be resolved and replaced by the bones [38, 39]. Aragonite has both needle like and octagonal structures[32].

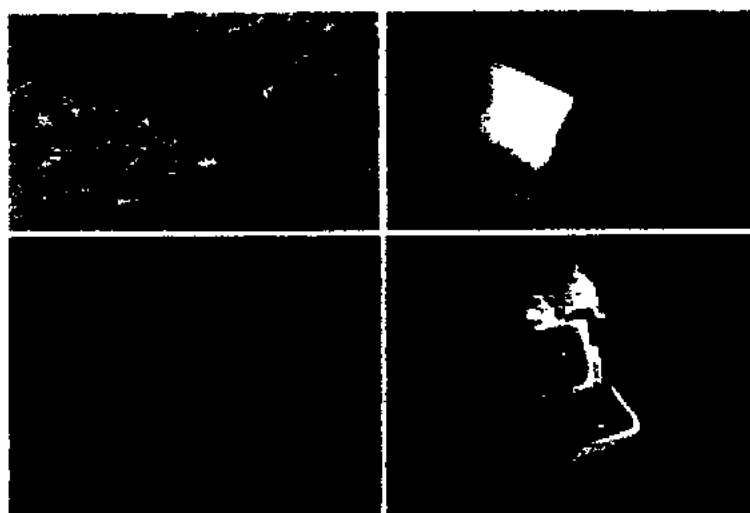


Figure 1.4: SEM images of Calcite and Aragonite [37]

At higher temperature the aragonite was formed and this attributed to decrease in super saturation conditions [37].

## 1.6 Availability of Calcium Carbonate Crystals

Polymorphs	Biological	Non-Biological
Calcite	Very Common	Very Common
Aragonite	Very Common	Rare
Vaterite	Rare	Very Rare
Non Crystalline CaCO <sub>3</sub>	Rare	Non-Existent

Table 1.2: The availability of three polymorphs of CaCO<sub>3</sub> [40]

## 1.7 Sources of Calcium carbonate

Nature has pure Calcium Carbonate resources like carbonate rocks that has a high percentage of calcium carbonate; Corals Pearls and Cockle shell etc [41-44]. Calcium carbonate has a special position among the biological minerals as it is the major element of bones and shells. In both materials inorganic minerals linked with biopolymers [45]. Some natural biological and geological calcium carbonate resources are as follow:

### 1.7.1 Marble

Marble is the largest ore body for carbonate minerals in the world which contains dolomite and calcite as major rock forming minerals.

### 1.7.2 Egg Shells

Eggshell is in category of natural bio-ceramic composite which has combination of both inorganic and organic that has the extraordinary characteristics. Calcium carbonate in the form of calcite is the main constituent of eggshell about 94% by weight. The other components of the eggshell are magnesium carbonate, calcium Phosphate and proteins. The interactions between the inorganic and organic components within the structure of the eggshell occur at the nanometer scale, affecting the mechanical performance of the eggshell. The unique properties of eggshell make it very useful in the bone tissue engineering.

The eggshells have variety of applications. It has been observed that eggshells are used in paper printing.

### **1.7.3 Cockle Shells**

Cockle Shells commonly known as *Anadara Granosa* is considered to be most important source of calcium carbonate. Due to its low cost and easy availability it fulfills the increasing demand of biomaterials [27].

## **1.8 Effect of Process Conditions on Physiochemical Properties of Calcium carbonate**

The technological importance of polymorphism is due to dependence of properties of material like solubility, density, optical properties and morphology on the structure. For many years the focus area of researchers is the controllable polymorphism of calcium carbonate nanoparticles but the parameters like particle size and particle size distribution remain the key challenges. Synthesis of  $\text{CaCO}_3$  in aqueous solution can be plate like or cube like crystals of calcite, aragonite or needle like vaterite can be of spherical shape, but the shape of synthesized particles depends upon reaction condition.

### **1.8.1 Super saturation**

At higher super saturation, there will be the formation of calcite [46, 47]. Low super saturation favors aragonite formation [48].

### **1.8.2 Temperature**

It has been observed that low temperature is suitable for calcite formation on other hand aragonite dominate at higher temperatures [49].

### **1.8.3 Aging Time**

One of the essential factors in the polymorphism of calcium carbonate is aging time. Long aging increases the size of the particle re-crystallization of aragonite to calcite [50]

### **1.8.4 pH**

pH is one of the important factor in morphosynthesis of calcium carbonate. There will be the formation of aragonite when the pH is between 10 to 12 [25,50]. At low temperature  $7^\circ\text{C}$  and pH less than 11, calcite was formed and pure aragonite was obtained at high temperature  $58^\circ\text{C}$  and pH less than 10 [25].

## **1.9 Effect of Additives On Morphology And Surface Of Calcium carbonate**

The presence of the additives is often critical for fabricating the crystals with different and unusual morphologies[51]. Synthesis of different polymorphs of  $\text{CaCO}_3$  and Nano- $\text{CaCO}_3$  have been carried out by the use of additives and by presence of different agents such as lysozyme, alcohols(ethanol, isopropanol, and diethyleneglycol), Polyacrylamide [52]. From industrial point of view the presence of additives affect the morphologies of the  $\text{CaCO}_3$  and also transforming from one polymorph to another [30].

## **1.10 Utilization of Calcium Carbonate Nano Particles**

Calcium carbonate is not only important from natural process perspective it is equally important system in industry [35]. Calcium Carbonate is considered as a striking model mineral in the laboratory, because its morphology and characterization of its crystals has been subjected to control in biomineralization process [53].

### **1.10.1 Filler Materials**

It has been observed that as filler material calcium carbonate can contribute extremely useful properties like pigments, coatings, paper, plastics lubricants and paints [54]. In paper industry calcium carbonate is used as filler to improve certain things like brightness, water resistance and the ink retention. The two properties surface area and porosity of nano calcium carbonate particles absorbs more oil in inks and prevents print rub from occurring [55]. Maximum brightness of paper by ideal light scattering was attained with a blend Aluminum magnesium silicate compound and precipitated calcium carbonate (PCC) [56]. Water resistance is increases by the presence of surface modified calcium carbonate [57].

The rheological and mechanical properties of many plastics such as poly L-Lactic acid (PLLA) [58], Polypropylene (PP) [59], polyvinylchloride(PVC)[60,61] and high density polyethylene(HDPE) enhances in the presence of calcium carbonate [62]. The performance of nanoparticles was found to be better than micronized particles because of better dispersion inside a matrix. It has been observe that nanosized calcium carbonate is suitable for outdoors insulators due to low value of dielectric constant  $\epsilon \approx 8.19$  [63].

### 1.10.2 Biomedical

Calcium carbonate is non-toxic and compatible towards human body and that makes it useful for drug delivery purposes. This effect is studied in numerous studies. The preferred particles for such applications are of porous spherical shaped particles [54]. Polymeric shells can be synthesized by using calcium carbonate particles as templates which can encapsulate drugs. The drug consisting of  $\text{CaCO}_3$  templates can be dissolved at ordinary conditions such as pH of 2–3 or complexing agent. As a result, the capsules could be designed to provide sustained release of drugs such as daunorubicin (DNR) and Dox [64].

The calcium carbonate particles in biomedicine are used for bone substitution and in the treatment of by using the material that is based on the aragonite [65]. ACC may be used as drug carrier in the pharmaceutical industry due to its high solubility [66]. Calcium alienate beads could be fabricated by calcium carbonate and it is used for the immobilization of cells like bacteria, fungi and yeast in fermentation process [67, 68].

### 1.10.3 Food Industry

Calcium carbonate has wide range of uses in food industry such as enzyme supports, biosensors and catalysis [54].  $\text{CaCO}_3$  nanoparticles have been used as an enzyme immobilization matrix for the construction of xanthine biosensors [69]. The fish freshness can be estimated by Xanthine. The Biosensor provided a rapid response, high sensitivity, good stability and was successful in avoiding interference of coexisting substances.

### 1.10.4 Environmental

A Calcium carbonate particle becomes an attractive candidate for the low cost and reliable biosensors and other environmental application due to high porosity and surface area [54]. In flue-gas desulfurization applications  $\text{CaCO}_3$  is the most common reagent, it prevents harmful

SO<sub>2</sub> emissions from coal and other fossil fuel exhausts [70].

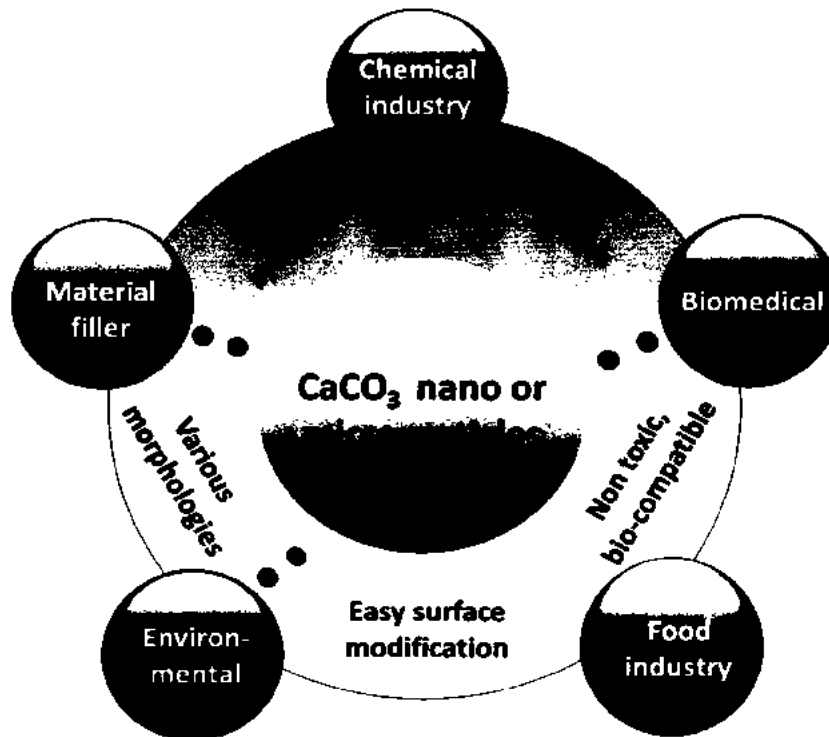


Figure 1.5: Application of Calcium carbonate [54]

## 1.11 Properties of Calcium carbonate

Some of the properties of calcium carbonate are as follow:

### 1.11.1 Odor

Calcium carbonate is odorless.

### 1.11.2 Color

The color of calcite crystal or powder is white, an aragonite crystal appears to be white and vaterite is colorless.



**1.11.3 Solubility**

Practically it is insoluble in water, but it is soluble in acids.

**1.11.4 Density**

The density of calcium carbonate is found to be  $2.8 \text{ g/cm}^3$ .

**1.11.5 Decomposition**

It decomposes into the calcium oxide and carbon dioxide at  $825^{\circ}\text{C}$ . When it decomposes it emits irritating vapors.

**1.11.6 Corrosivity**

It is non corrosive.

**1.11.7 Molecular Weight**

The molecular weight for calcium carbonate is  $100.0869 \text{ g/mol}$  [21].

## **OBJECTIVES**

The particular objectives of this study are to:

- To determine the formation of calcium carbonate nanoparticles by applying different chemical routes.
- To determine the effect of different additives on the morphology and particle size of calcium carbonate experimentally.
- Egg shell is used as natural calcium carbonate source.
- To compare the results of synthesized nanoparticles with the standard calcium carbonate

Following techniques were used to study the synthesized product:

- XRD: To determine the crystallinity and confirmation of calcium carbonate
- FTIR: To determine the vibration mode of formed calcium carbonate.
- SEM: To study the morphological structure of synthesized calcium carbonate.
- EDS: To study the composition

**CHAPTER No.2****Literature Review**

Calcium carbonate and their modified surface has been the focus area of research in science and engineering to execute in different fields of life. Also at the present time under experimental study of nanoscale particles, a number of researches on calcium carbonate nanoparticles has been accomplished and also has been published in various literature of scientific world.

Calcium carbonate with different morphologies, particle sizes and forms were successfully fabricated by Q. Zhang et al. (2010) using p-amino benzene sulphonic acid and L-Lysine (L-Lys). The p-amino benzene sulphonic acid was used for the purpose of controlled morphology of the calcium carbonate nanoparticles. The method adopted by the author for synthesis of the Calcium carbonate particles with controlled morphology was Gas Diffusion method.

The author observed that concentration of p-amino benzene sulphonic acid strongly effect the shape. The author showed that shape could be like spherical lens type or pancake etc [71].

T. A. Hassan et al. (2011) carried out a experiment for size reduction of particles. The main aim of his study was to reduce the size of the particle by mechano chemical method followed by sonochemical method. The eggshells were crushed by wet ball mill. The grounded particles were then irradiated by sonication. An energy dispersive X-ray analyzer (EDX), X-ray diffraction (XRD), Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to analyze the final product. They determined that there was a change in shape and size of the synthesized calcium carbonate particles. The author reported that the particles size was visibly reduced and the BET result showed high surface area. They revealed that these prepared nanoparticles could be used in many advanced application [72].

A. Tavangar et al. (2011) formed the calcium carbonate nanofibrous from eggshell that were in 3D. The adopted the method of femtosecond laser ablation. The formed product was analyzed by using), X-ray diffraction (XRD), Scanning electron microscope (SEM) and transmission electron microscope (TEM). The results showed that by the use of controlled laser pulse repetition, nanostructures can be made with different densities of nanofibrous and author revealed that 3D nanofibrous can be used in different medical application [73].

The presence of surface modifier agents, organic and inorganic additives will have visible effect on the morphology and shape of nanoparticles. The same work is done is by K. Nurul Islam et al. (2011) compared the calcium carbonate from cockle shell and commercial calcium carbonate.  $\text{CaCO}_3$  from cockle shell were grounded by pestle to reduced the size of the particles. The grounded particles were dried for 7 days at  $50^\circ\text{C}$  to remove any moisture.

Author then compared both the powder that is Commercial  $\text{CaCO}_3$  and the from the cockle shell. Both powders were analyzed by variable pressure scanning electron microscope (VPSEM), an energy dispersive X-ray analyzer (EDX), and Fourier transmission infrared spectroscopy (FT-IR). The results showed that cockle shell calcium carbonate contained more carbon and calcium where as commercial calcium carbonate contained more oxygen.

The analysis also showed that cockle shell had aragonite structure and commercial calcium carbonate had calcite or cubic like structure [74].

M. E. Hoque et al. (2013) reported the experimental condition to prepared calcium carbonate particles from cockle shell using Chemical Wet Method. They took dilute sulphuric acid ( $\text{H}_2\text{SO}_4$ ) for washing of cockle shells. These washed calcium carbonate based shells were dried in an oven for 3 days. The dried shells were then crushed by rotor mill which was operated at 100W, 230V and 50/60Hz.

Author analyzed the final product by using an energy dispersive X-ray analyzer (EDX), X-ray diffraction (XRD), Scanning electron microscope (SEM) and Fourier transmission infrared spectroscopy (FT-IR). They revealed that the synthesized sample of calcium carbonate from cockle shell had a rod like crystals which is the shape of aragonite. So the calcium carbonate present in cockle shell is of aragonite form. The Fourier transmission infrared spectroscopy (FT-IR) results showed that characteristics peaks are at  $861.93\text{cm}^{-1}$  [27].

Cetyltrimethylammonium bromide (CTAB) is a surface-active agent .It has ability to dissolve in water. Cetyltrimethylammonium bromide (CTAB) is usually used because it is important for the pore formation, Scattering and self assembly [75].

N. Wang at el. (2013) studied that the morphology and particle size of calcium carbonate nanoparticles can be controlled by controlling the ratio of water to surfactant content.

Author found that size of calcium carbonate particle was sensitive to surfactant content. The decreased value of water to surfactant content reduced the size of particle very rapidly and it reduced from 75-15 nm [76].

The particles were studied in detail by X-ray diffraction (XRD), Scanning electron microscope (SEM) and transmission electron microscope(TEM).The results revealed that spherical calcium carbonate nanoparticles was obtained by choosing the ratio of water to surfactant from 3.40 to 22.63 [76].

Calcium carbonate nanoparticles have been synthesized in various shapes each with unique properties and each published in different literatures of Science and Technology.

E. Altay at el. (2007) performed the Sol Precipitated technique to form the calcium carbonate at different ranges of mixing and aging temperatures. They used polydiallyldimethylammonium chloride (PDDA), Cetyltrimethylammonium bromide (CTAB), ethylenediaminetetraacetic (ETDA) as additives .PDDA is among the polycationic electrolyte. It has ability to interact with solid surface and ions in solution. Before this the effect of PDDA on the polymorphs of calcium carbonate has not been studied. At lower temperature CTAB does not affect the morphism of calcium carbonate [30].EDTA presences reduces the amount of fee ions and it retards the nucleation.

Author observed the morphology of calcium carbonate particles in the presence of these additives. He showed that these additives degrade the aragonite formation. X-ray diffraction (XRD), Scanning electron microscope (SEM) was used for the analysis of calcium carbonate particles. The results showed that only EDTA had the most prominent effect on the morphology of calcium carbonate [77].

By the mean of wet chemical method the calcium carbonate particles were made by Z. Sadowski at el. (2010) they studied the influence of chemical and physical properties on the size of particles. They did so by dissolving calcium chloride ( $\text{CaCl}_2$ ) with polyethylene glycol (PEG) solution. The mixture was then added in potassium carbonate solution ( $\text{K}_2\text{CO}_3$ ) water solution in four different molar ratios. Calcium carbonate precipitates was filtered off, washed with water and finally dried in vacuum. Their conclusion was stirring speed and mixing time had a great effect on precipitated calcium carbonate.

They also observed that the concentration of the PEG influences the size of particle. Size of particles appeared to increase when there is interaction between bio-surfactants and precipitated particles [59].

The presences of additives in different concentrations have a crucial effect on the morphology and size of the particles of calcium carbonate. The same effort was done by E. M. Flaten et al. (2009) by wet chemical method using mono ethylene glycol (MEG).

Mono ethylene glycol (MEG) was found to influence the morphology, polymorphism and transformation from one form to another. The characterization of the synthesized particles was done by scanning electron microscope (SEM). Author presented that high amount of MEG produced the Vaterite polymorph of Calcium Carbonate. At different temperatures, the two step transformation occurred. Firstly the structure would change from cube to calcite and then to spherical. The size of the particles reduced by the higher concentration of mono ethylene glycol (MEG) [56].

H. Tang et al. (2009) prepared the peanut shape calcium carbonate aggregates via facile precipitation reaction. The reaction was between  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  in the presence of ethanol as solvent and magnesium ions. The solution was stirred for 1 minute and then it was place under static condition for 24 hours at room temperature. The final product was filtered off, washed with distilled water and then dried.

The prepared product was evaluated by X-ray diffraction (XRD), Scanning electron microscope (SEM) and induced couple plasma atomic emission spectroscopy(ICP-AES). Author found that there would be phase transition and it occurred in two steps .From amorphous calcium carbonate (ACC) to calcite and then from calcite to aragonite. The author revealed that proper concentration of magnesium ions and ethanol solvent produced the unusual peanut like aggregate calcium carbonate [24].

Amorphous calcium carbonate were made by H. S. Lee et al. (2005).They did so by mixing ethanolic  $\text{CaCl}_2$  and ammonium carbonate. Ethanol is one of the common industrial solvents with negligible toxicity. Ammonium has ability to maintain the reaction medium in neutral or weak basic condition. Author reported that ethanol prevents the dissolution of amorphous calcium carbonate (ACC).The phase transition on was from ACC to vaterite or calcite. X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FT-IR) and Raman spectroscopy were used for the analysis of synthesized product. Particles obtained can be converted into calcite by giving proper temperature [23].

Nanoparticles of amorphous calcium carbonate were prepared by M. M. M.G. P. G. Mantilaka et al. (2014) by carbonation route in which poly (acrylic acid) PAA is mainly used. The source used

to form amorphous calcium carbonate was impure marble. The author reported that temperature for proposed method was 40°C and pH was 4.5. The size of the synthesized amorphous calcium carbonate particles were in the range of 21-53nm. The author showed that concentration of PAA greatly affect the morphology of particles. The vaterite shape particles were produced and the prepared particles were sufficient to meet the industrial requirements [78].

Various researches have carried out to synthesize the nanoparticles of calcium carbonate from eggshell.

The researchers used raw eggshells as the source of calcium carbonate and made them compatible to the different application in industry and other field of science and technology. Same work was done by T. A. Hassan et al (2013) who prepared nanoparticles of calcium carbonate via Mechanochemical by and Sonochemical techniques.

S. Yoo et al. (2009) worked on the utilization of calcium carbonate from eggshells. For this purpose they performed an experiment in which the calcium carbonate particles from eggshell were prepared by using vinegar, yeast and high temperature treatments. The author used Fourier transmission infrared spectroscopy (FT-IR) for the analysis of the synthesized product. They revealed that calcium carbonate from eggshells were successfully used in various applications. The author reported that the major use of eggshells calcium carbonate was in coating pigments for inkjet printers. They also determined that eggshell calcium carbonate in pigments enhanced its optical density [79].

A-X. Wang et al. (2014) prepared the calcium carbonate micro crystals. The calcium carbonate was of vaterite type with unusual morphology. The author adopted simple precipitation route to synthesize such particles. They used ethanol and sodium bicarbonate ( $\text{NaHCO}_3$ ) as the major elements. They observed that the polymorph of final product could be controlled by the use of ethanol and sodium bicarbonate. The particles were then studied by X-ray diffraction (XRD), Scanning electron microscope (SEM) and transmission electron microscope (TEM) and Fourier transmission infrared spectroscopy (FT-IR). The results showed that the shape of the synthesized particles were of spica-like hierarchical [80].

The size and shape of resulting material depends upon the preparation method and the reaction conditions. J. Wang et al. (2014) prepared calcium carbonate particles with different shapes and morphologies. They synthesized the particles via precipitation in an octal amine/water self

assembly bilayer system. The author reported that water to octal amine (R) molar ratio of the bilayer system was responsible for the shape and crystal structure of calcium carbonate particles. The prepared particles were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM). The results revealed that the shape of the particle will be hopper like when water to octal amine ratio (R) is 16.0. As the value of R was decreased to 7.2 the particles shifted their morphology to vaterite tabular aggregates and the change in size of particles were also observed [81].

G. Hongxia et al. (2011) prepared the aragonite calcium carbonate particles with multiple morphologies. The adopted method for synthesis was homogeneous precipitation method. The author studied the effect of urea and PVP on the calcium carbonate particles. These synthesized particles were analyzed by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Fourier transmission infrared spectroscopy (FT-IR). The results showed that the presence of PVP affect the morphology of these particles. They found that the morphology of the synthesized particles were complexed, it might be bundle of rods, dumb bell like structure and the prepared particles were almost 100% aragonite [82].

Y. Boyjoo et al. (2014) gave a contribution in nano and micro sized particles of calcium carbonate by CO<sub>2</sub> bubbling method and biomimetic method. They determined that the presence of additives, temperature and agitation time effected the properties of synthesized calcium carbonate particles. The author also showed the importance of the micro and nano sized calcium carbonate particles in biomedical, environmental, and many other areas of daily life.

The author showed that biomimetic method changed the morphology and size of the particles as compared to carbon dioxide bubbling method. The shape of the prepared particles might be rod, like, spherical or flower like etc [54].

Ukrainezyk et al. (2007) performed an experiment to prepare the calcium carbonate particles. They studied the effect of temperature, stirring rate and the mass concentration of Ca(OH)<sub>2</sub> in a semicontinuous process. The particles synthesized by this process were characterized by transmission electron microscope (TEM). The author showed that polymorphs did not change, every time calcite was formed. They revealed that crystal shape and size of particles affected significantly by temperature and conductivity [83].

S. Quhenia et al. (2008) prepared the calcium carbonate nanoparticles via simple wet chemical method. The polyacrylic acid was used as additive. The author studied the effect of PAA on the



morphology of calcium carbonate particles in co-operation of temperature. The prepared particles were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM). They showed that there were visible changes in the synthesized calcium carbonate particles. At temperature 5°C the vaterite was formed. It is largely destabilized at higher temperature. The particle size observed was of 10-12nm [84].

A. S. Kamba et al. (2013) synthesized the calcium carbonate nanocrystals via micro emulsion technique. In this technique high pressure homogenizer was used. In oil in water O/W micro emulsion the particle size was reduced. The particles prepared by this method were analyzed by different characterization techniques. The results revealed that synthesized product had a rod shape morphology and the size of the particles were about 50nm. Author also determined that there would be a change in polymorph at 300-373 °C and at 600-700 °C i.e aragonite began to transform into calcite. The results showed that at low temperature small particles decomposed faster than larger sized particles [85].

W. M. Jung et al. (2000) investigated the size and morphology of calcium carbonate particles by precipitation reaction that was carried out in Cocuetle –Taylor Reactor. Author concluded that due to the presence of excessive reactant the particle size and morphology was noticeably changed at stichiometric reaction conditions the particles were observed with cube like particle and largest mean size. The results revealed that when the concentration of excess species increases the morphology changed to spindle like shape and particle size decreases [86].

B. Aziz et al. (2011) worked on the formation of calcium carbonate with complex shapes by changing some parameters such as stirring rate or time, pH and temperature. Author observed that with greater stirring time the vaterite transformation into calcite. They concluded that both kinetic and equilibrium dependencies became important when energy difference was small between different polymorphs of calcium carbonate [87].

**CHAPTER No.3****Synthesis and Experimental Techniques****3.1 Instrumentation**

- i. Electronic balance
- ii. Beakers
- iii. Hot plate
- iv. Magnetic Stirrer
- v. Electric Stirrer
- vi. Petri Dishes
- vii. Centrifuging Machine
- viii. Drying oven

**3.2 Materials**

Name of Chemicals	Chemical formula
Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>
Ethanol	C <sub>2</sub> H <sub>6</sub> O
Sodium Dodecyl Sulphate	NaC <sub>12</sub> H <sub>25</sub> SO <sub>4</sub>
Cetyltrimethylammonium bromide	C <sub>19</sub> H <sub>42</sub> BrN
Urea	CH <sub>4</sub> N <sub>2</sub> O

**Table 3.1:** List of Chemicals Used in the experiment**3.3 Synthesis of Nanoparticles**

There are two main approaches for the synthesis of nanoparticles

- i. Top down approach
- ii. Bottom up approach

### **3.3.1 Top down Approach**

It is a method in which bulk piece of material is carved into small pieces and that is in the range of nm. Top down approach has four sub techniques i.e lithography, high energy ball milling, gas condensation technique and severe plastic deformation [88].

### **3.3.2 Bottom up Approach**

In Bottom up approach, the structure being built up atom by atom, molecule by molecule and cluster by cluster through covalent bonding [89]. These building blocks are naturally self assembled and can be organized into composed morphology. Bottom up approach has five sub techniques i.e physical deposition method, soft lithography, self assembly, sol gel method and chemical vapor deposition. Sol gel method is preferred because it yields uniform particle size distribution and is easy [88].

## **3.4 Synthesis of Calcium carbonate Nanoparticles**

The entire chemicals used in synthesis were commercially available and were used without further purification.

### **3.4.1 Preparation of Micron Sized Eggshell Powder**

For the preparation of eggshell nanoparticles, firstly it was prepared in micron sized and then by different methods it is made on nanoscale. 500 grams of raw eggshells were first washed by normal tap water to remove grime and dust from the outer surface of shells and inside of the shells. Then shells were soaked in distilled water for 24 hours in a glass beaker. After that the inner membrane was separated then eggshells were collected and dried for 24 hours at room temperature.

After drying the eggshells (in white color) were crushed by using a mortar or pestle for 3-4 hours to reduce the diameter of the particles. The particles size was in micron size. The powdered calcium carbonate was packed in polyethylene plastic bag [27, 42, 72, 74,].

### **3.4.2 Preparation of Nanosized Eggshell Powder**

The nanosized calcium carbonate particles were prepared by the presence of different additives by four different ways.

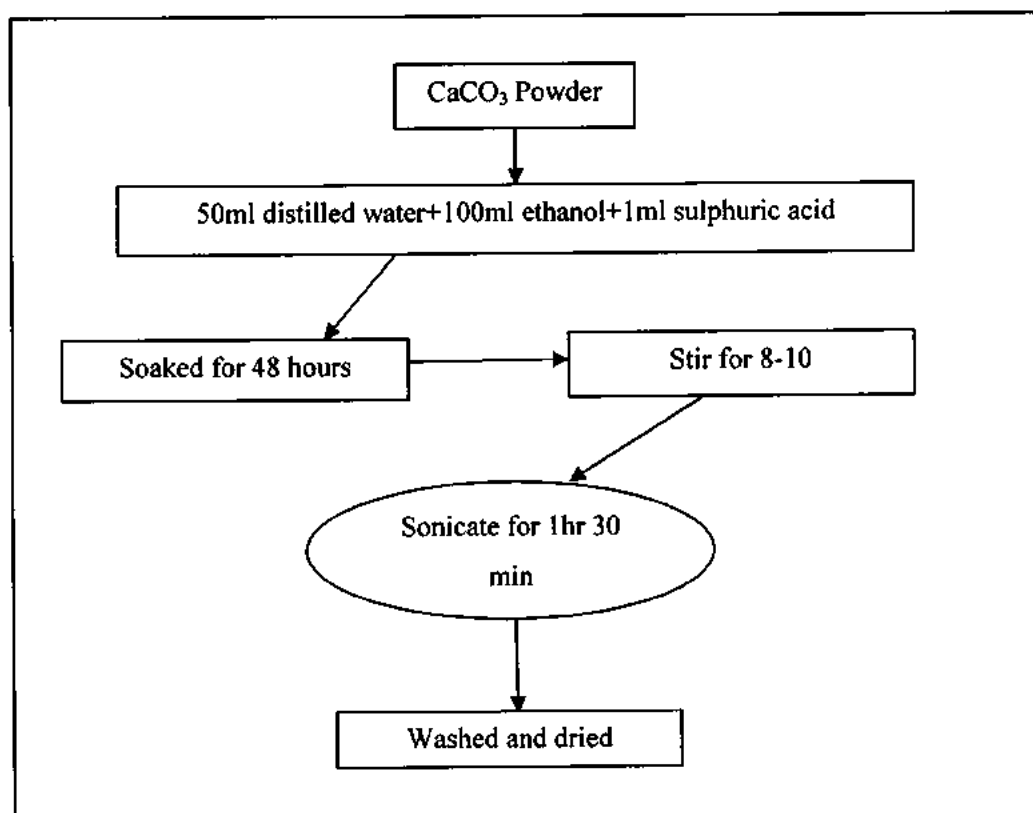
## Chapter3 Synthesis and experimental Techniques

### 3.4.2.1 In the presence of $H_2SO_4$

Five grams of micron sized egg shell powder was taken into a 250ml glass beaker. Slurry was formed by adding 50ml distilled water. Now to prepared calcium carbonate nanoparticles 1ml of sulphuric acid ( $H_2SO_4$ ) and 100ml of ethanol was added into a beaker. This was soaked for 48 hours. The soaked solution was vigorously stirred at 1000 rpm at room temperature for 8-10 hours using a magnetic stirrer bar and hot plate.

The ultrasound irradiation method was adopted to reduce the size of the particles to nanoscale [90, 91]. Sonication is an effective tool for reducing the size of particles without disturbing the crystalline structure [72].

The obtained particles were sonicated or irradiated in a sonication bath for 90 minutes with the high intensity ultrasonic horn. After sonication the particles were collected and washed with distilled water several times. The final product was centrifuged at 15000rpm to separate the eggshell particles from solvents. The particles were then dried in oven at  $50^\circ C$ . These particles were then characterized.



**Figure 3.1:** Schematic diagram for synthesis of  $CaCO_3$  Nanoparticles In the presence of  $H_2SO_4$

### 3.4.2.2 In the presence of Urea

Five grams of calcium carbonate eggshell powder was taken into beaker. A 50ml ethanol was added to the beaker and then stirred for 10-15 minutes. Another solution was made by five gram of urea and 50ml of ethanol [82]. The solution was stirred by using magnetic stirrer for 15 minutes. Both the stirred solutions were then added up and the mixture was again vigorously stirred for 30 minutes at the temperature of 90°C. The stirred solution was left for 2-3 days. The obtained solution was washed with distilled water many times by centrifuge machine. The washed product was dried in an oven and it was then used for further characterization.

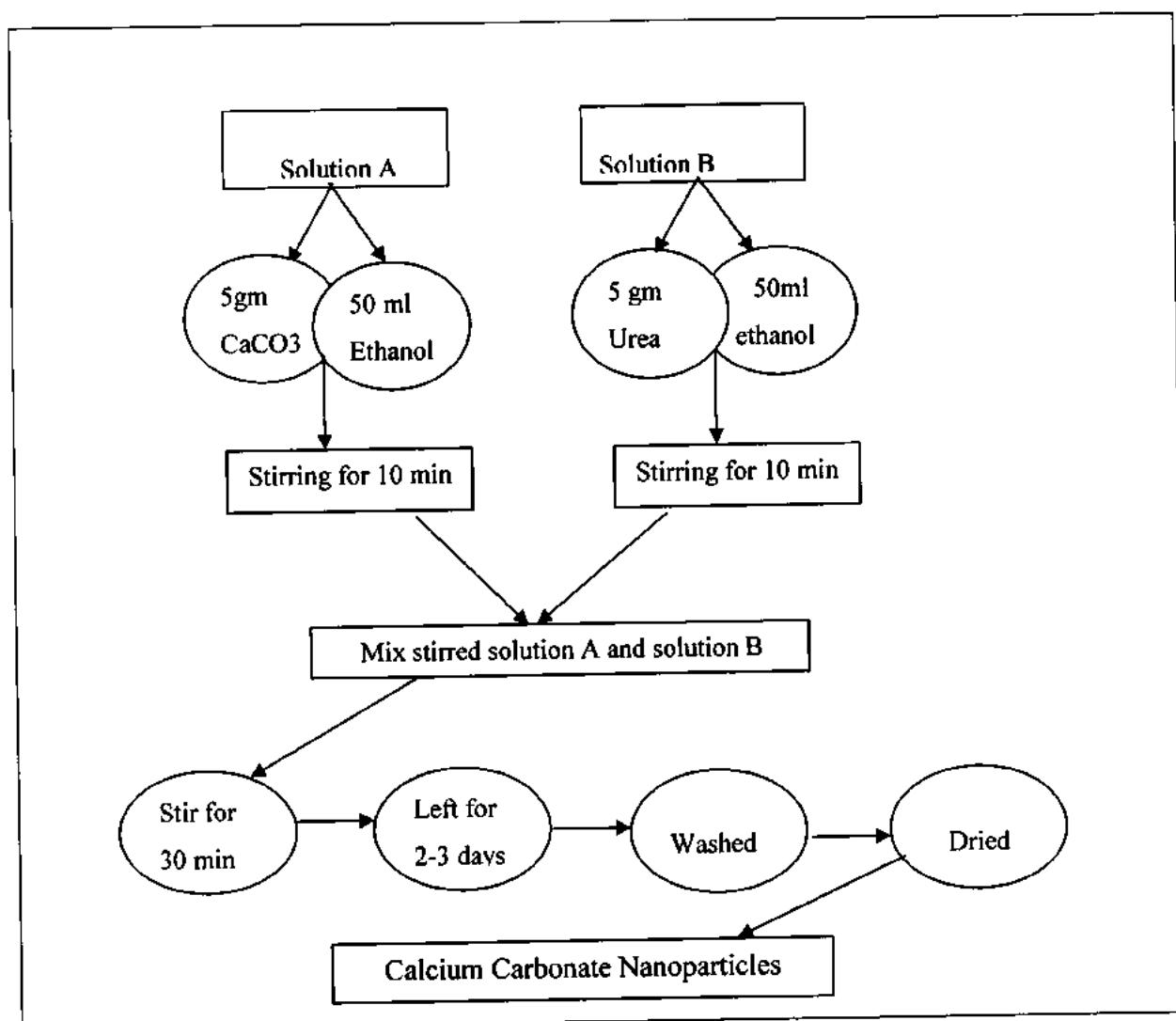


Figure 3.2: Schematic diagram for synthesis of CaCO<sub>3</sub> Nanoparticles In the presence of Urea

### 3.4.2.3 In the presence of Cetyltrimethylammonium Bromide (CTAB)

5 grams of eggshell powder and 5grams of Cetyltrimethylammonium bromide (CTAB) were measured by electronic balance. CTAB was used as a surfactant [30].50ml ethanol and 50ml of distilled water was measured by measuring flask. Eggshell powder and CTAB were added into a ethanol and distilled water. The slurry was stir for 4-5 hours at 1500 rpm with the temperature of 50-70°C by the use of magnetic stirrer and hot plate. The solution was left for 48 hours. After that washing was done for 2 hours by centrifuging machine. The obtained product was dried in an oven for further use and purification.

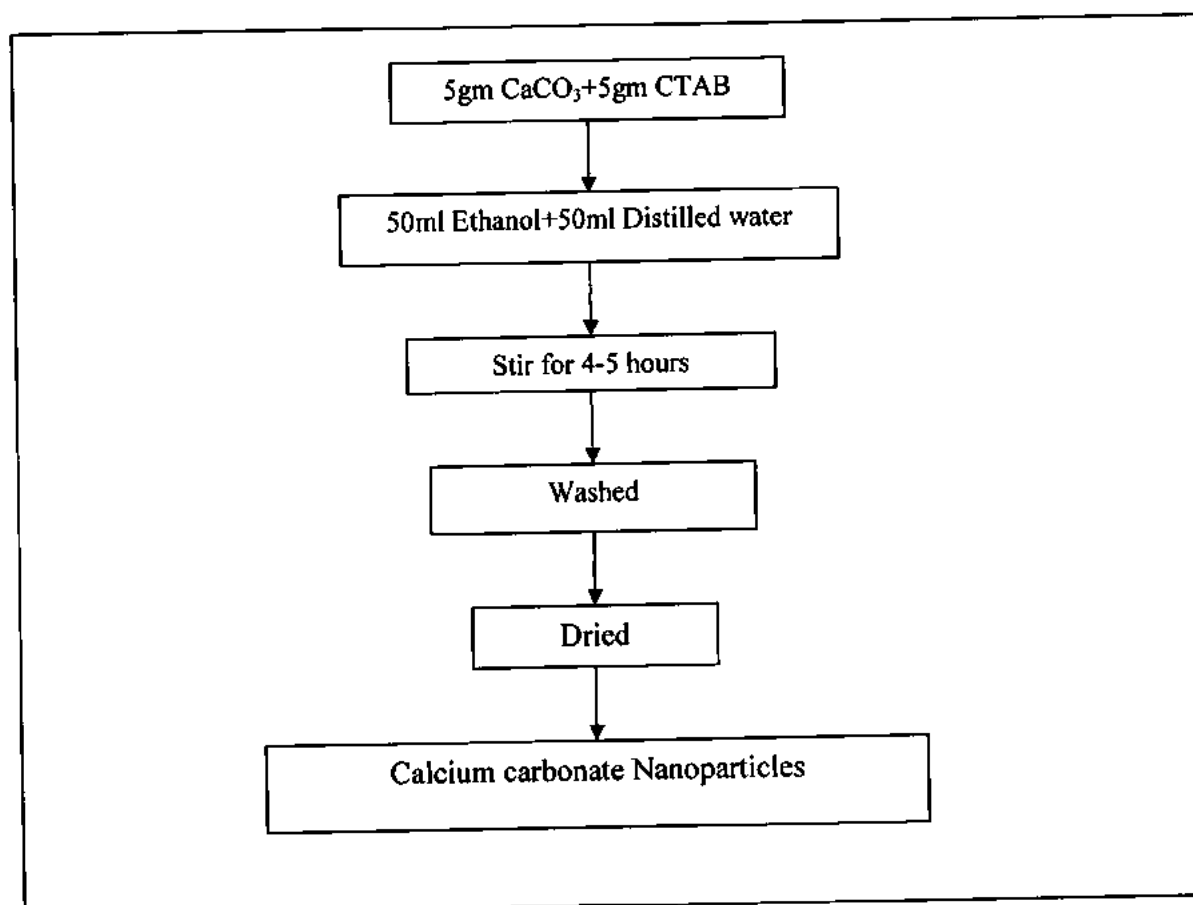


Figure 3.3: Schematic diagram for synthesis of CaCO<sub>3</sub> Nanoparticles In the presence of CTAB

### 3.4.2.4 In the presence of Sodium Dodecyl Sulphate (SDS)

Different methods were adopted for the synthesis and modified the surface of calcium carbonate nanoparticles. In present method 5 grams of egg shell powder were added to 1 gram of sodium Dodecyl sulphate and the mixed to the solvents ethanol and water. Both ethanol and distilled water was taken 50 ml. The mixture was left for vigorously stirring for 90 minutes. Then the obtained solution was washed many times with distilled water. The particles were dried in oven .The dried product was used for characterization and analysis.

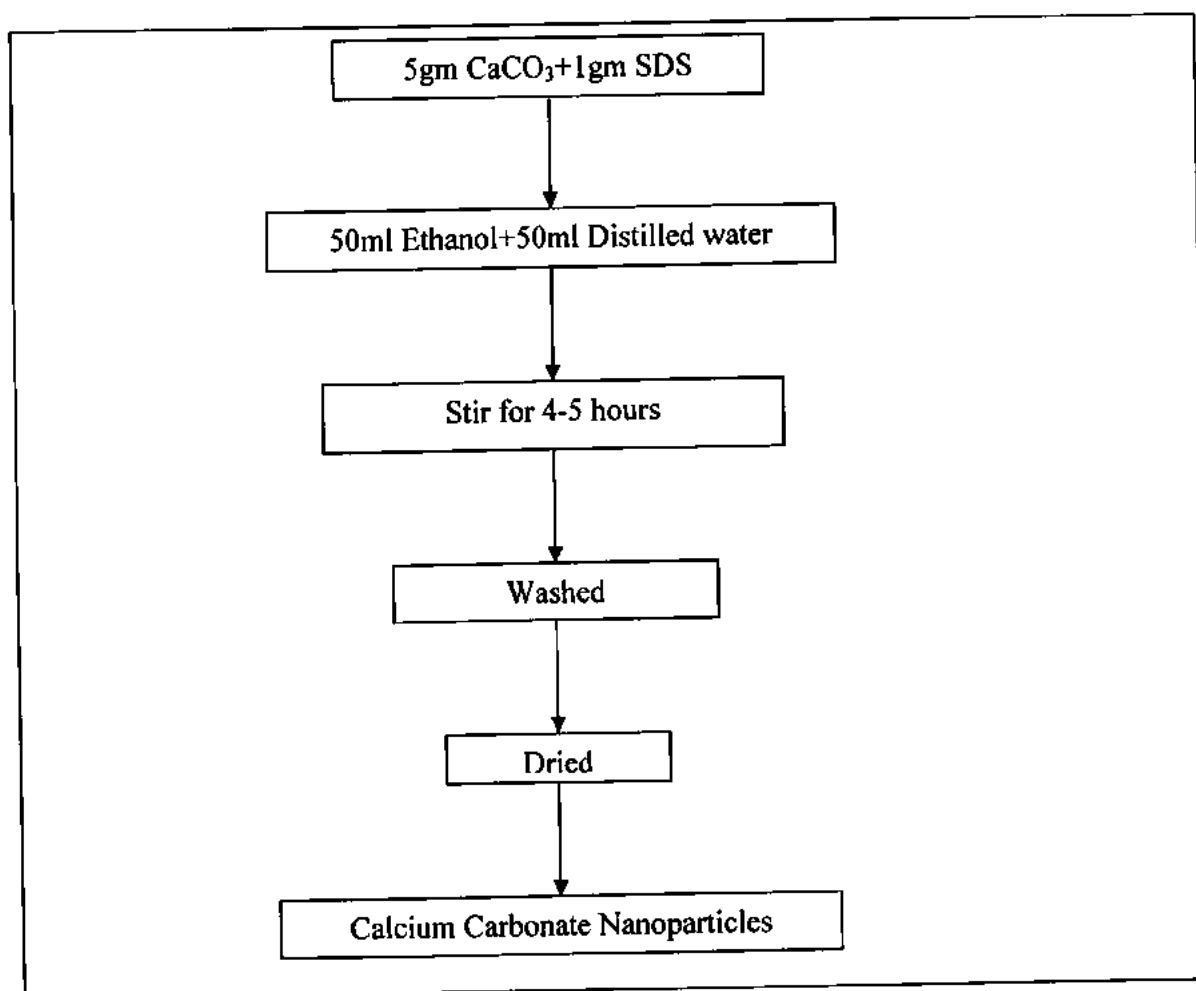


Figure 3.4: Schematic diagram for synthesis of CaCO<sub>3</sub> Nanoparticles In the presence of SDS

### 3.5 Characterization Techniques

The most significant part of materials exploration is the characterization of the created materials that we utilize or examine with a specific end goal to procure more learning about them. The

prepared samples were analyzed by using different characterization techniques as described in section 3.5.1-3.5.4.

### 3.5.1 X-Ray Diffraction

X-Ray diffraction is an instrument which is utilized to examine the fine matter structure. In 1912, Von Laue's found that crystal diffracts x-ray which reveals the crystal structure. At earlier times, it was utilized for the investigation of crystal structure yet with improvement of technology, now it is conceivable to get the data about crystal geometry e.g. cross section constant, measurement of molecule size, chemical analysis and orientation of crystals planes [92].

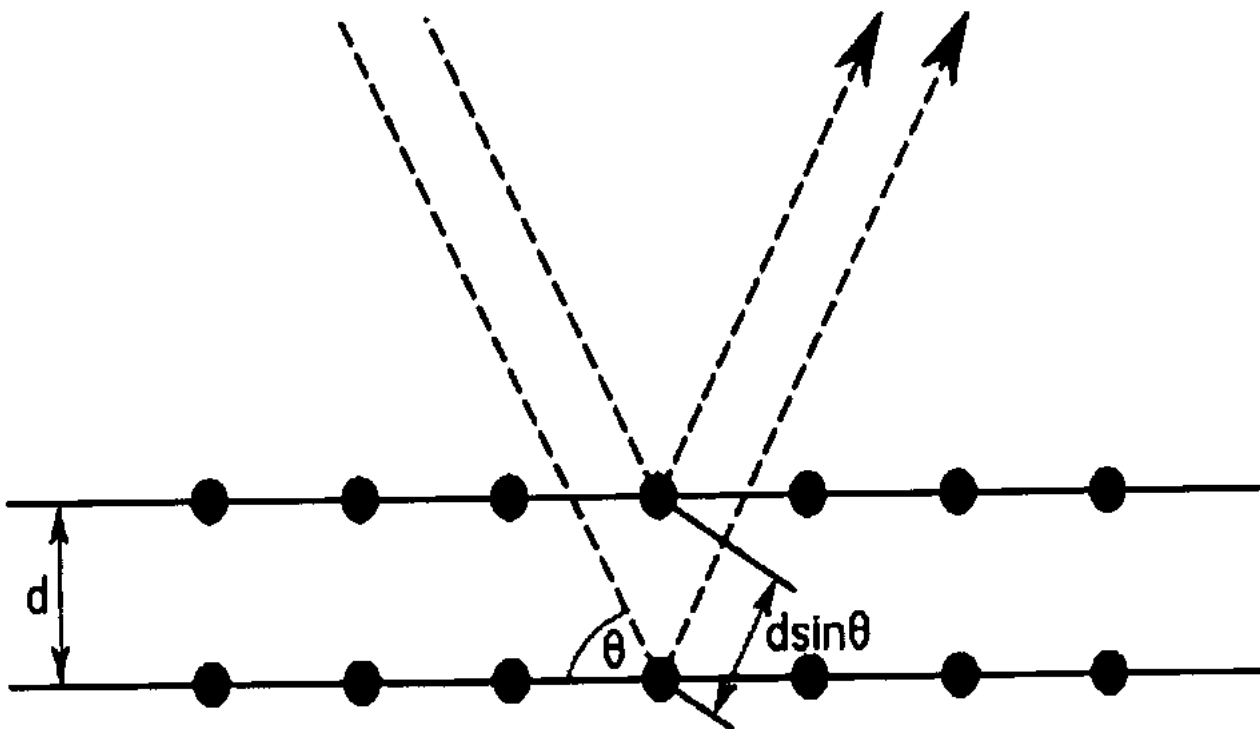


Figure 3.5: Diffraction of X-rays from crystal planes [93]

A collimated light emission beam with wavelength of  $0.7$  to  $2\text{\AA}$  is fallen on to the specimen. Fig 3.5 shows the diffraction of X-rays from crystalline planes of specimen.

#### 3.5.1.1 Bragg's Law

Bragg's law is given as



$$2d\sin\theta = n\lambda \quad (3.1)$$

Where  $n$  has integral values

$d$  = Spacing between atomic planes

$\lambda$  = Wavelength of X-rays [94]

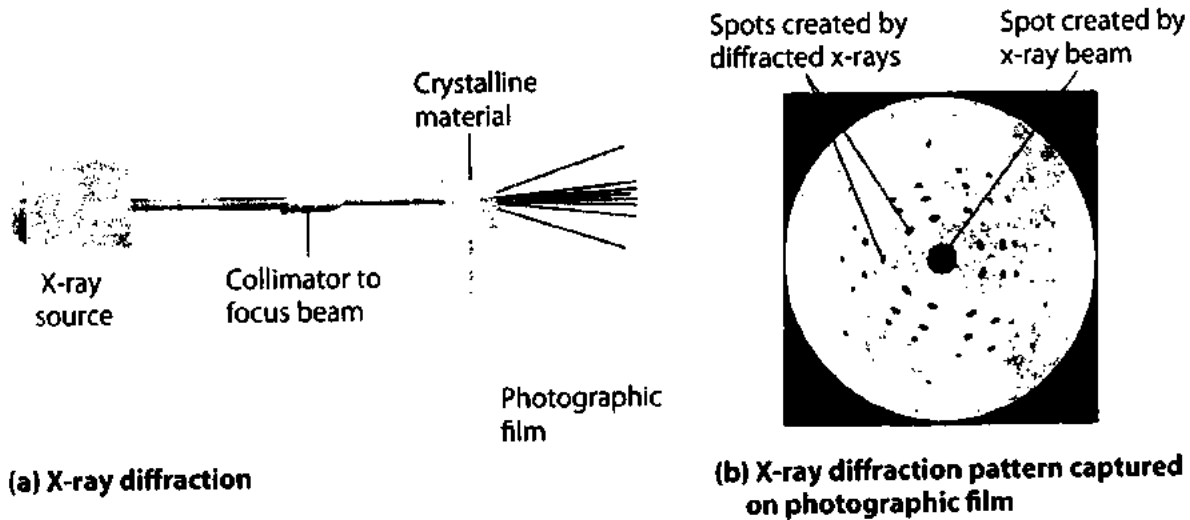


Figure 3.6: X-ray diffraction scheme [95]

X-rays generated by ionization of electrons from K-shell are utilized for the diffraction investigation because of its shorter wavelength when contrasted with those X-ray from L-M shells. The most basic target materials are copper and Molybdenum used to create X-rays with wavelength 1.54 to 0.8 Å [96,97]. The Crystalline size "D" can be ascertained from Scherrer's formula

$$D = 0.9 \lambda / \beta \cos\theta \quad (3.2)$$

Where  $D$  = particle size

$\lambda$  = Wavelength of X-rays

$\theta$  = Bragg's angle

$\beta$  = full width at half maximum (FWHM) [98]

### 3.5.2 Scanning Electron Microscopy

#### 3.5.2.1 Basic Principles:

Scanning electron microscope is most extensively useful tool for the study of the surface of the sample since it offers a superior determination than the optical microscope. It uses electrons radiated from tungsten or Lanthanum hex boride ( $\text{LaB}_6$ ) thermionic emitters for the representation of surface of the specimen. A temperature between 2000-2700 K is accomplished by heating the filament by the use of current. This results in a discharge of thermionic electrons from the tip more over an area around  $100\ \mu\text{m} \times 150\ \mu\text{m}$ . The electrons produced by the electron gun are accelerated toward the sample within the energy range of 0.1-30 keV [99].

An arrangement of lenses centers the electron beam on to the sample where it interfaces with the specimen to a depth of nearly  $1\ \mu\text{m}$ . Figure 3.8 shows the components of a scanning electron microscope [100].

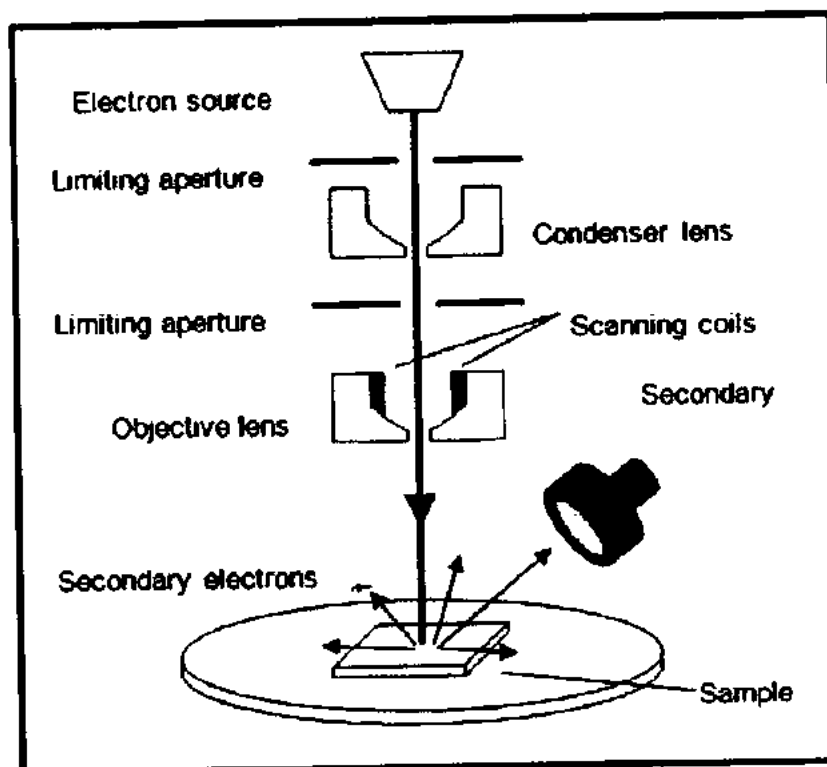


Figure 3.7: Schematic diagram of an SEM set-up [100]

When the electron beam falls on the sample, numerous sorts of signals are generated and any of these can be displayed as an image, numerous sorts of signs are created and any of these can be displayed as an image. The two signals usually used to create SEM images are backscattered electrons (BSE) and secondary electrons (SE). When the electrons interact with the positively

charged nucleus, most of the electrons are scattered at large angles (from  $0^\circ$  to  $180^\circ$ ). These elastically scattered electrons usually called 'backscattered electrons' (BSE) are used for SEM imaging. A few electrons are scattered in-elastically because of the loss in kinetic energy upon their cooperation with orbital shell electrons. The electrons which are incident on sample can knock out loosely bound conduction electrons from the sample. These are secondary electrons (SE) and along with backscattered electrons are widely used for SEM topographical imaging. When a positive voltage is applied to the collector screen in front of detector both SE and BSE signals are collected. Only BSE signal is captured because SEs has a low energy and is being repelled when a negative voltage is applied on the collector screen. Electrons captured by the scintillator/ photomultiplier are then amplified and used to form an image in the SEM [101].

### 3.5.3 Fourier Transforms Infrared (FTIR) Spectroscopy:

All the method of spectroscopy are based on interaction of electromagnetic radiation with a medium or the specifications related to radiations emitted from medium [102]. In electromagnetic radiations, radiations which cover the wave number between  $13300\text{cm}^{-1}$  and  $3.3\text{cm}^{-1}$  are called infrared radiations. Fourier transforms infrared spectroscopy (FTIR) is a technique which is used to detect atomic vibrations [103].

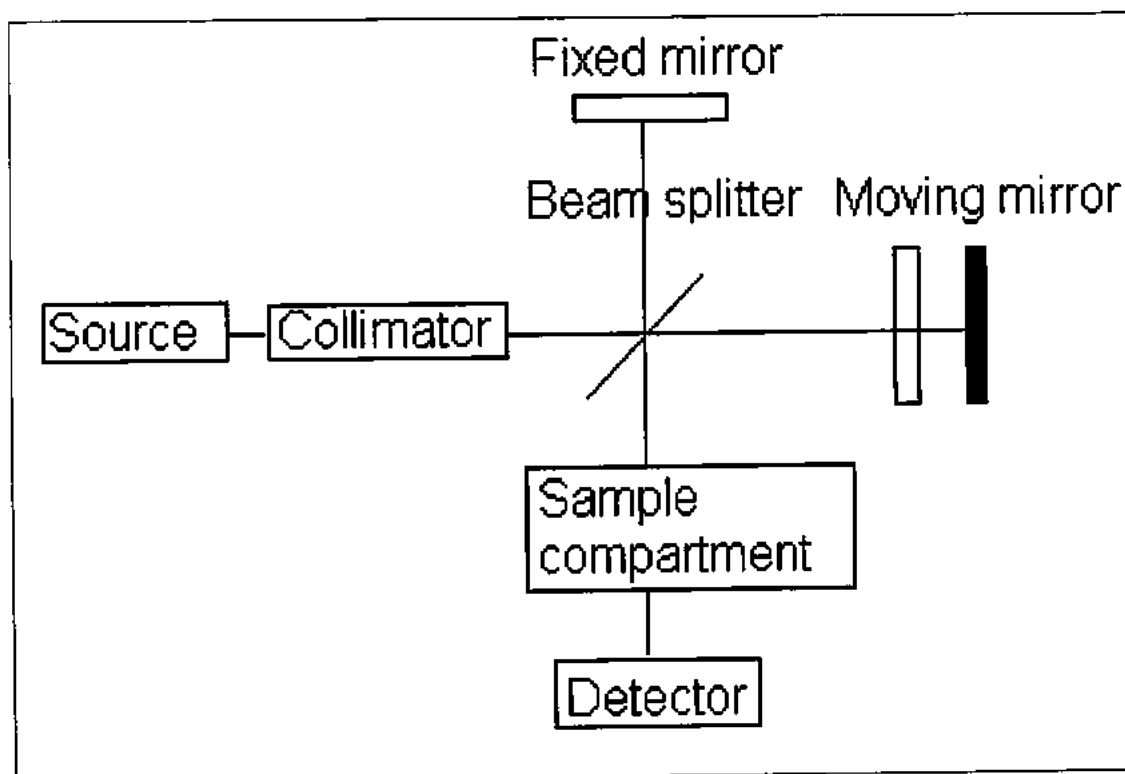
#### 3.5.3.1 Basic Principle

The FTIR basically works according to Michelson interferometer. It is the major part of Fourier transform infrared spectroscopy [104]. FTIR is type of vibrational spectroscopy [105]. The FTIR is composed of laser light source and detector, moving mirrors and the several fixed mirrors.

FTIR spectrometers belong to third generation infrared spectrometer. FTIR spectrometers have various dominates advantages:

- (1) The signal-to-noise ratio of spectrum is significantly higher than the previous generation infrared spectrometers.
- (2) The accuracy of wave number is high. The error is within the range of  $\pm 0.01\text{ cm}^{-1}$ .
- (3) The scan time of all frequencies is short (approximately 1 s).
- (4) The resolution is extremely high ( $0.1 \sim 0.005\text{ cm}^{-1}$ ).
- (5) The scan range is wide ( $1000 \sim 10\text{ cm}^{-1}$ ).
- (6) The interference from stray light is reduced. Due to these advantages, FTIR Spectrometers have replaced dispersive IR spectrometers.

The FTIR schematic setup is shown in fig.



**Figure 3.8:** Schematic setup of FTIR Spectroscopy [106]

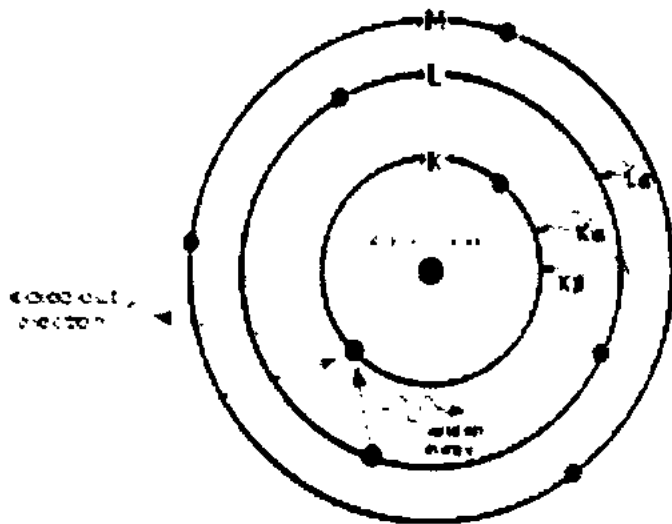
In Michelson interferometer the infrared light is divided into two parts and both waves cover different path differences and that path is referred as optical path difference. The beam splitter is the key part of Michelson interferometer. The beam splitter is often made up of germanium plate coated with KBr. The germanium splitters reflects 50% incident light and at the same time 50% light is transmitted. One splitted part travels toward moving mirror and other part toward the stationary mirror. At this stage both beams reflects from mirror and recombine at beam splitter. When they recombine interference pattern is produced. As the moving mirror moves back and forth, beam brightness changes. The change in intensity of light versus optical path difference is called interferogram [107].

#### 3.5.4 Energy Dispersive X-Ray Analysis (EDX):

The characterization technique which is usually used to identify the elemental composition of the specimen is known as EDX (Energy Dispersive X-Ray Analysis). The EDX technique is basically the integrated part of scanning electron microscope (SEM) [108]. To affirm the composition of

## Chapter3 Synthesis and experimental Techniques

Sample, EDX was used because it is genuinely simple and surely understood technique. In EDX electrons having high energy are move towards the atoms and knock out the electrons orbiting in the inner core shells of atoms, the incident electron takes its place. In this way electron loses its energy which is emitted as x-ray radiations. The energy of the radiated photons depends upon atomic species.



**Figure 3.9:** EDX spectrum, transfer of electron from high energy shell to low energy shell [7]

The perhaps greatest disadvantage of EDX is that the electronic configuration of elements are quite similar ,due to this the energy of emitted x rays are quite same .The second major drawback is that lighter material such as hydrogen is invisible in EDX spectra[7]

An EDX spectrum normally manifests the relation of energy level and peaks and also reveals the type of X-ray. K-Alpha peaks are formed if electron transition is occurred from L-Shell to K-Shell. Similarly if the transition of an electron is between M-Shell to K-Shell then its peak is identified as K-Beta peak [108].

# Chapter No .4

## Results and Discussion

### 4.1 X-Ray Diffraction (XRD)

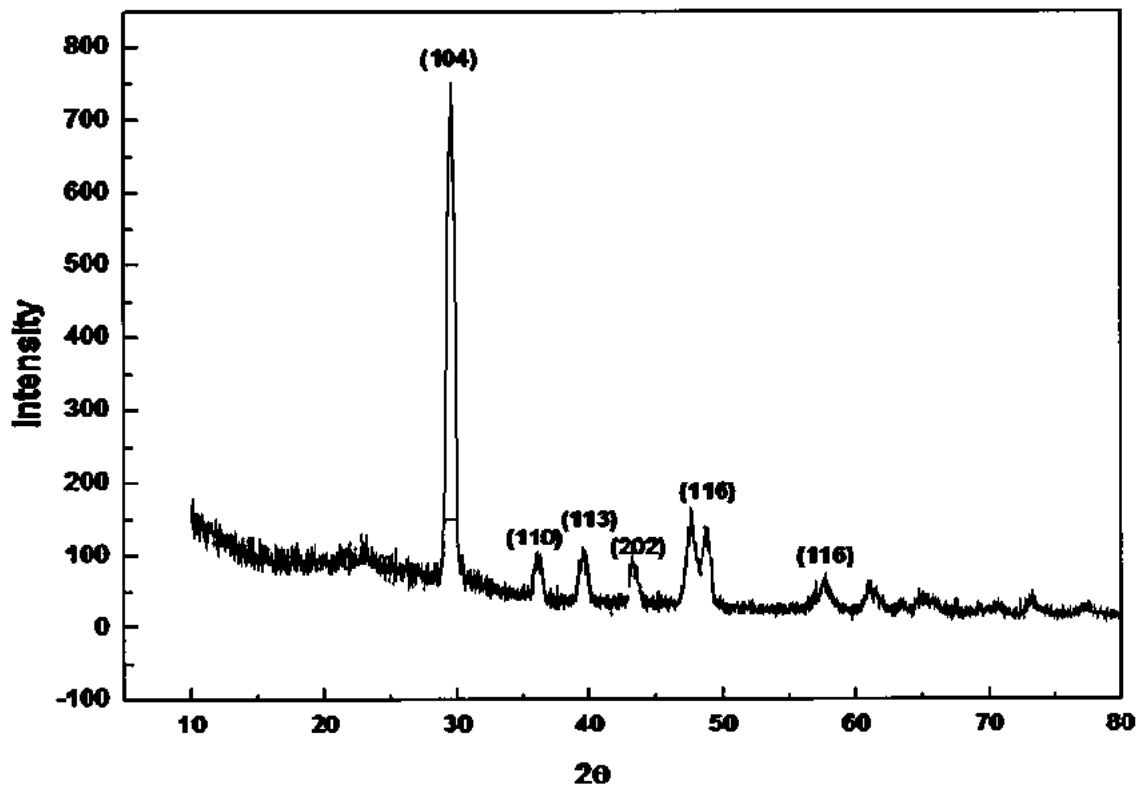


Figure 4.1 (a): XRD scan of unprocessed egg shell

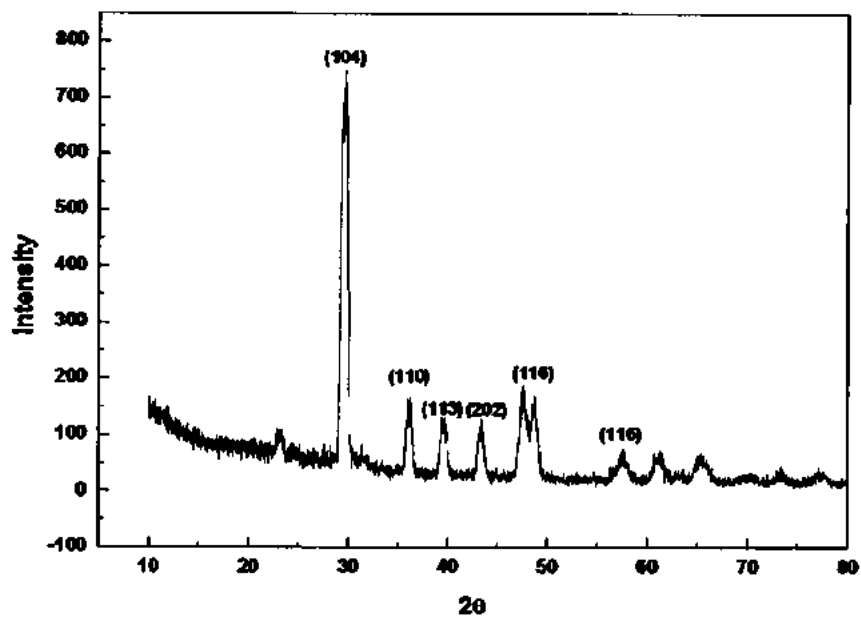


Figure 4.1 (b): XRD scan of egg shell in the presence of CTAB

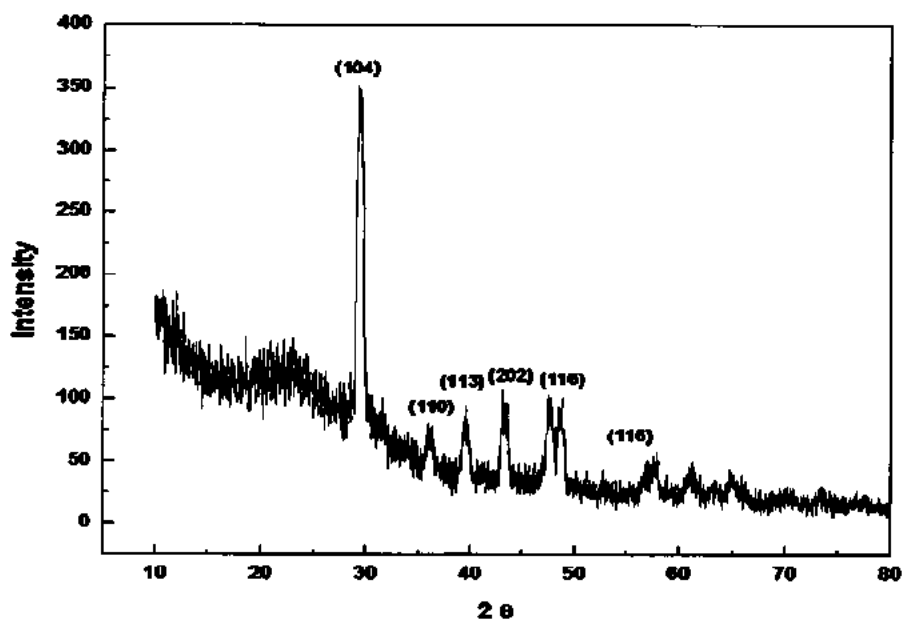


Figure 4.1 (c): XRD scan of egg shell in the presence of Urea

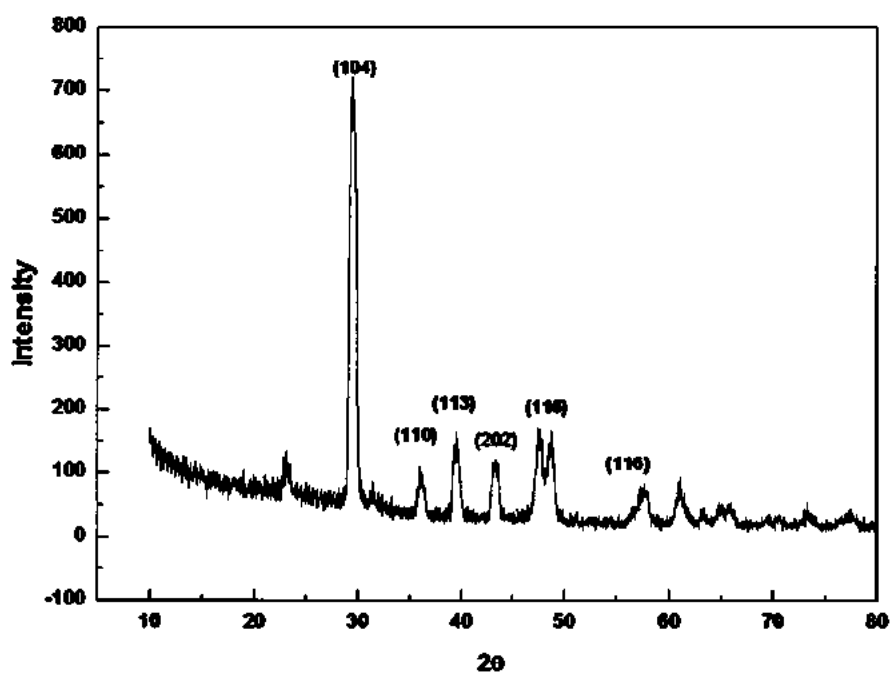


Figure 4.1 (d): XRD scan of egg shell in the presence of SDS

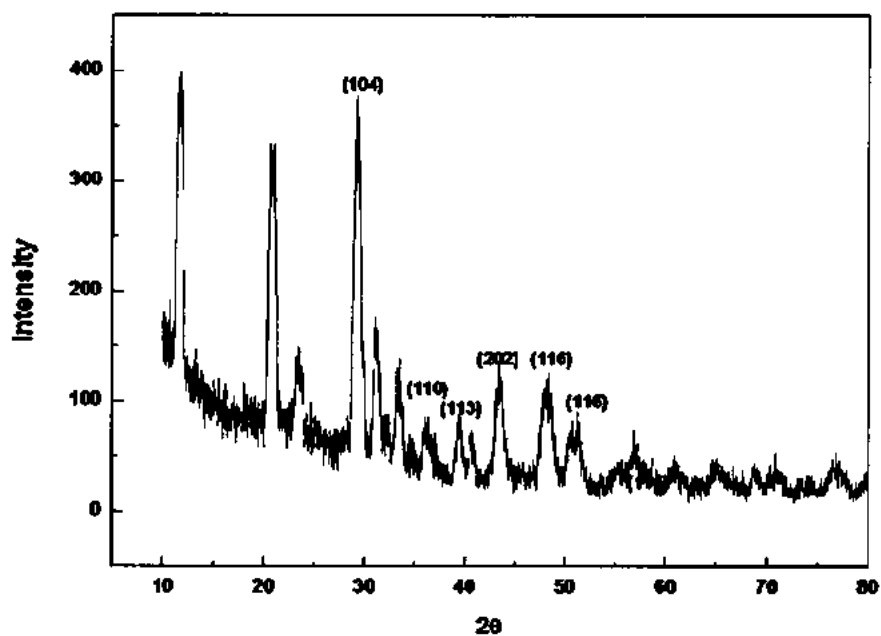
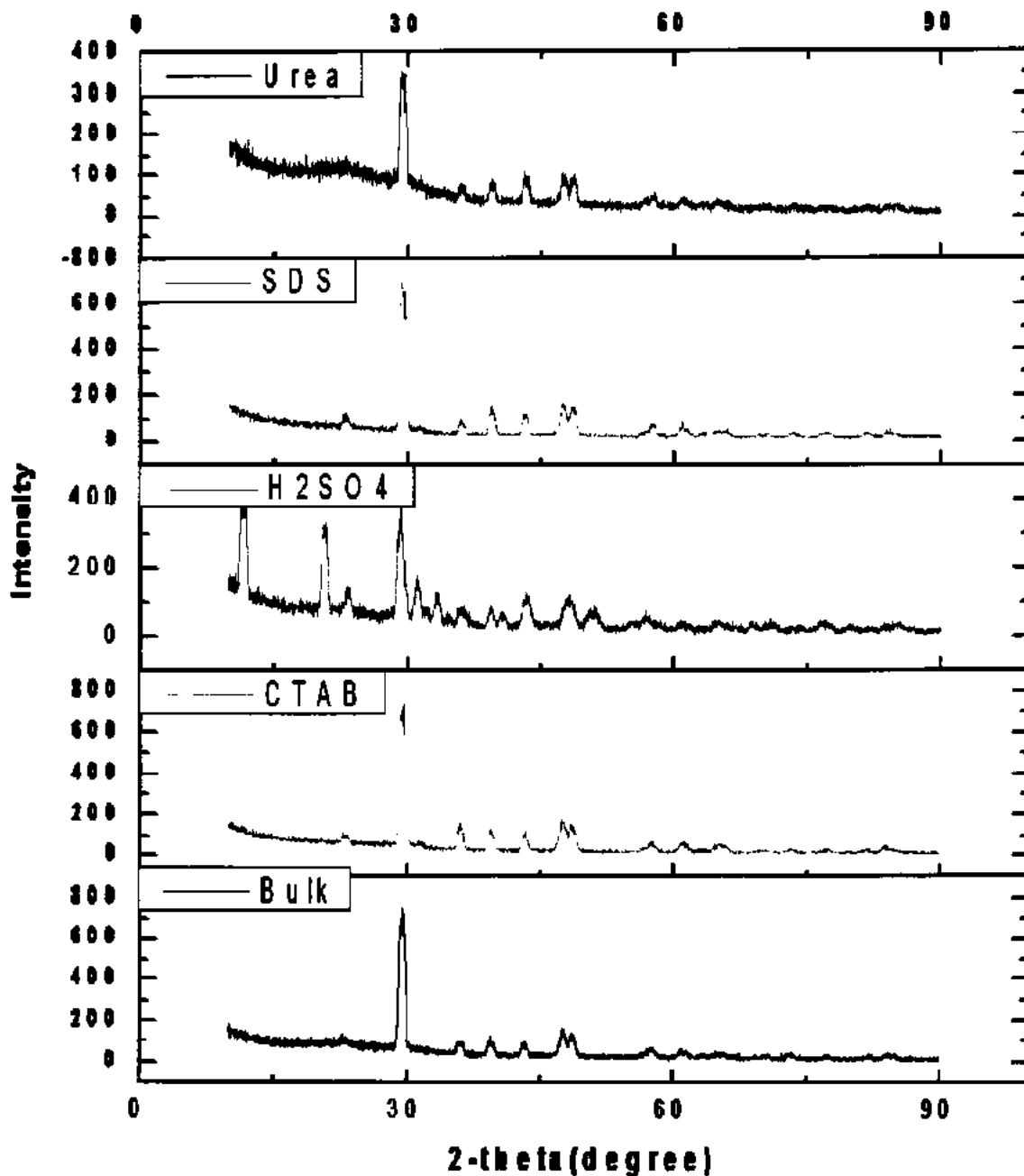


Figure 4.1 (e): XRD scan of egg shell in the presence of  $H_2SO_4$





**Figure 4.2:** XRD scan of egg shell bulk (Un-processed), In the presence of CTAB, H<sub>2</sub>SO<sub>4</sub>, SDS and Urea

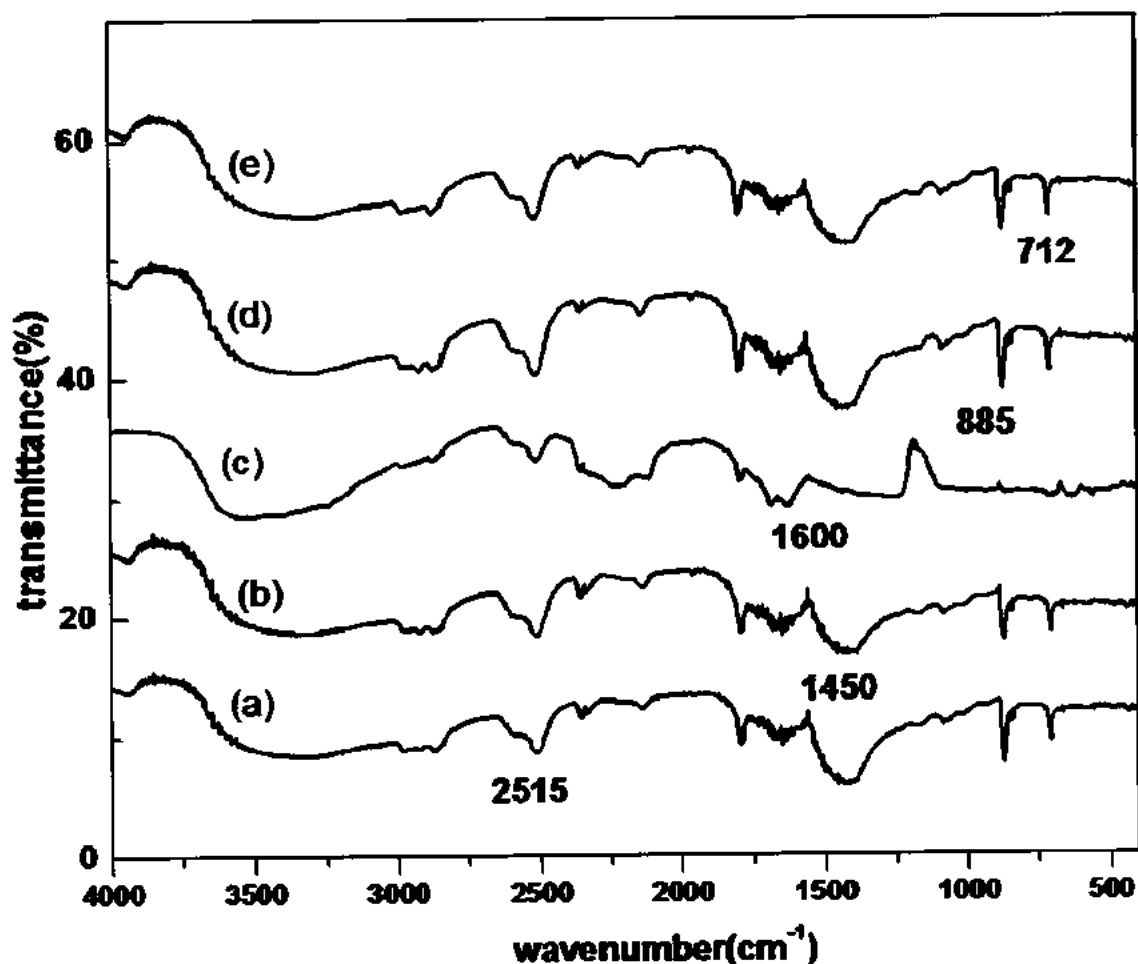
X-ray diffraction measurements were carried out using X-ray diffractometer to study the crystal structure, possible phase changes and other impurities presented in the processed and un-processed egg shell [72]. XRD scan of processed and unprocessed eggshell are displayed in

figure 4.1 (a), (b), (c), (d), (e). The X-ray diffraction pattern lies in the limit of 0 – 80 degrees with several peaks. There were few unidentified peaks noticed in the scans [27]. As seen from all XRD patterns for figure 4.1 (a) unprocessed shell (b) In the presence of CTAB (c) In the presence of Urea (d) In the presence of SDS (e) In the presence of H<sub>2</sub>SO<sub>4</sub> are comprised of peaks at 2θ values of 29.5°, 36°, 40°, 43.1°, 48.5°, 56.5° with the corresponding planes of 104, 110, 113, 202, 116, 211 (PDS No. 83-1762) which is for calcite calcium carbonate [78]. The sharp and strongest peak in figure 4.1(a, b, c, d) showed that egg shell calcium carbonate powder was very well crystalline. The results clearly showed that the characteristic peaks of calcite calcium carbonate there is no change in phase or peak angle but the morphology was changed by the presence of (a) CTAB (b) Urea (c) SDS but did not cause any structural changes to their chemical composition. XRD scans clearly suggest that high level of inorganic calcium carbonate is present in eggshell and no other impurities were observed in figure 4.1 (a, b, c, d) but in figure 4.1 (e) clearly suggest that in which egg shell was processed in the presence of sulphuric acid showed that there were some other peaks which showed that another material is formed along with calcium carbonate but in that the intensity is reduced and peaks broadens which showed that particle size is reduced and found to be 25 nm. The particle size found in bulk calcium carbonate is 30nm, in the presence of CTAB it is 30nm, in the presence of SDS it is 28 nm [72].

Figure 4.2 shows the comparative study of calcium carbonate in the presence of different additives. It can be observed that intensity of the XRD peaks has been decreased for calcium carbonate in the presence of Urea which indicates the reduction of calcite crystal size [73]. The particle size is found to be less than 20 nm.

The obtained XRD pattern of calcite calcium carbonate was also compared with the standard calcite XRD pattern and it is concluded that peaks are exactly in accordance with the standard XRD pattern.

## 4.2 Fourier Transforms Infrared (FTIR) Spectroscopy:



**Figure 4.3:** FTIR spectra of (a) Egg shell bulk (Un-processed) (b) In the presence of CTAB (c) In the presence of  $H_2SO_4$  (d) In the presence of SDS (e) In the presence of Urea

The phase of the eggshell calcium carbonate was further confirmed by FTIR spectroscopy. The FTIR spectrum was produced by the absorption of radiation in the range of  $400-4000\text{cm}^{-1}$  [109].

The FTIR spectra of prepared calcium carbonate nanoparticles by different methods are shown in Fig 4.2. The FTIR spectrum of the calcium carbonate nanoparticles indicated the presence of different organic compounds such as alkynes, alkanes and carboxylic acid [110].

The Fig 4.2 (a), (b), (c), (d), (e) showed that the absorption peak of calcite at  $885\text{cm}^{-1}$  of carbonate group ( $\text{CO}_3^{2-}$ ) and exactly in accordance with commercial calcium carbonate [74].

The Fig 4.2 showed the vibrational band at 1450, 885 and 712 indicate the plane bending of carbonate. The FTIR analysis affirmed the calcium carbonate nanoparticles got from egg shell

had a characteristic peak of carbonate groups. A sharp peak in FTIR scans displayed in Fig (a), (b), (d), (e) was calcite [109].

The band at  $712\text{ cm}^{-1}$  is due to bending of O-C-O, band at  $885\text{ cm}^{-1}$  is due to external plane bending vibrational of  $\text{CO}_3^{2-}$  and anti symmetric stretching vibration of C-O is at  $1412\text{ cm}^{-1}$ .

phase	External plane bending of vibration of O-C-O	Internal plane bending of vibration of $\text{CO}_3^{2-}$	anti symmetric stretching vibration of C-O
Calcite	885	712	1421

**Table 4.1:** Wave numbers of functional groups [27]

In Fig 4.2 (b) in which eggshell is processed in the presence of sulphuric acid showed the deviation from calcite and had different vibrational bonds. So we conclude that all methods (a), (c), (d), (e) carried out for the preparation calcium carbonate nanoparticles confirmed the presence of calcite and is well matched with XRD results.

### 4.3 Scanning Electron Microscopy

#### 4.3.1 SEM of un-processed Egg Shell

The surface morphology of egg shell calcium carbonate nanoparticles was analyzed by scanning electron microscope (SEM). The nano particles of calcium carbonate was in the powdered form and is non-conducting powder, therefore the SEM scans were taken at low vacuum mode to get sharp images. The images are displayed in fig 4.3 (a,b) which confirmed the presence of calcium carbonate in egg shell and that the powder was finally grinded.

Figure 4.3(a) depicts the surface morphology of the egg shell calcium carbonate nanoparticles. The SEM micrographs of the egg shell calcium carbonate showed the cube-like crystals. This is in accordance with the literature cubic like calcium carbonate was also observed in commercial calcium carbonate. The SEM images shows the surface of particles is smooth and belongs to calcite form of calcium carbonate[27,42].

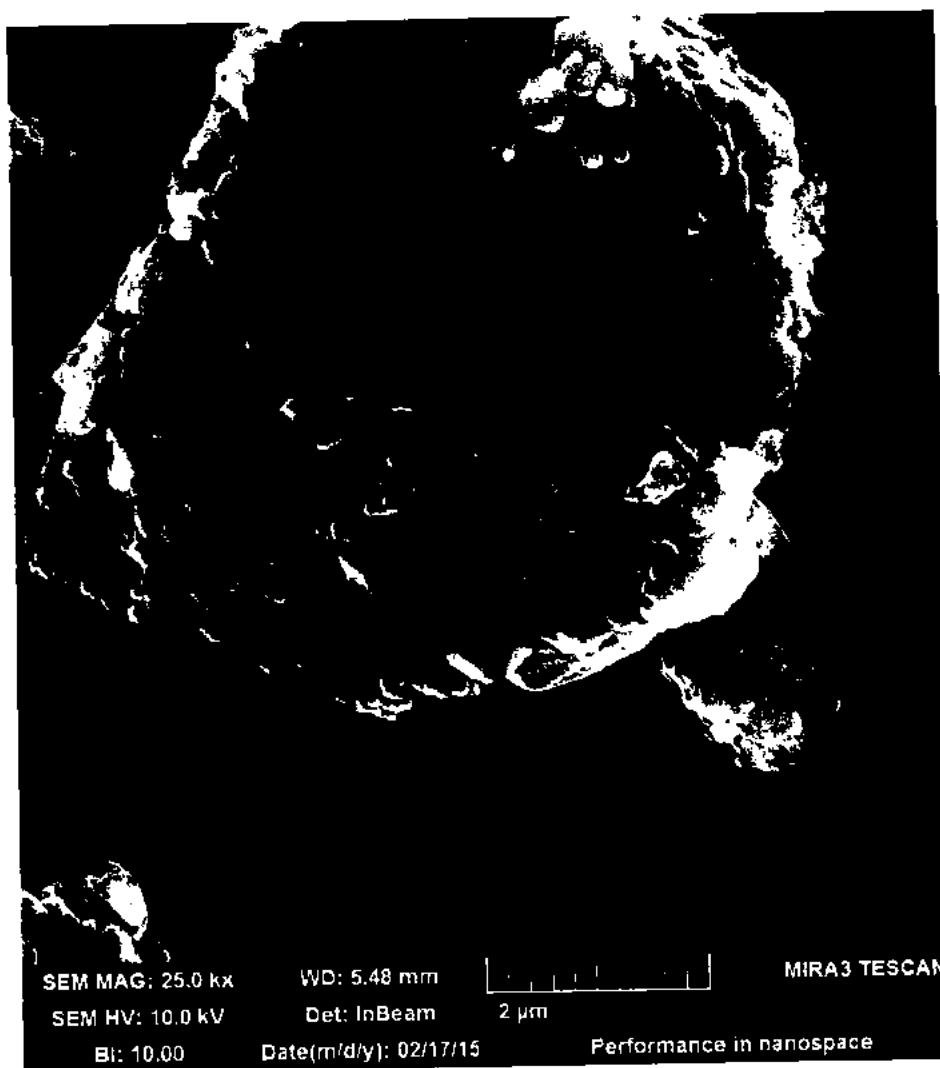
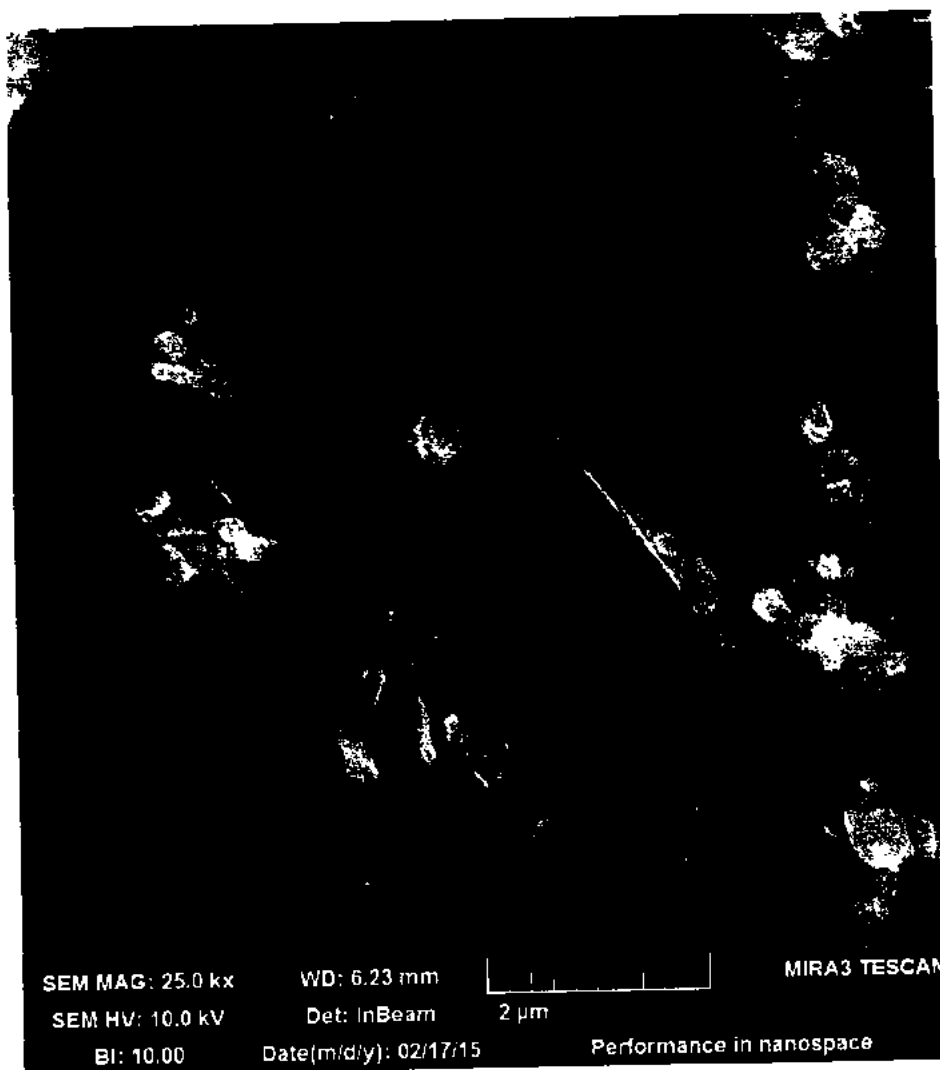


Figure 4.4(a): SEM images of un-processed egg shell

#### 4.3.2 SEM of Egg Shell $\text{CaCO}_3$ in the presence of $\text{H}_2\text{SO}_4$

Fig 4.4 (b) delineates the effect of  $\text{H}_2\text{SO}_4$  as additive on egg shell calcium carbonate nano particles morphology. The Fig 4.4(b) clearly showed that the particle transform from cubic like shape to rod like morphology .The literature showed that rod like crystals Are un stable as compared to the cubic structure. The SEM result reveals that presence of additives has a great effect on morphology.



**Figure 4.4(b): SEM of Egg Shell  $\text{CaCO}_3$  in the presence of  $\text{H}_2\text{SO}_4$**

### 4.3.3 SEM of Egg Shell $\text{CaCO}_3$ in the presence of SDS

The morphology of the calcium carbonate nano particles was examined using Scanning Electron Microscopy (SEM). The SEM micrographs of the calcite  $\text{CaCO}_3$  is shown in the Fig 4.4(c). The SEM results revealed that in the presence of SDS the shape of calcium carbonate transforms. The increasing concentration of SDS caused the particles to agglomerate [111]. The shape of the particles resembled to the calcite. So the surface morphology of eggshell calcium carbonate in the presence of SDS is exactly in accordance with XRD results.

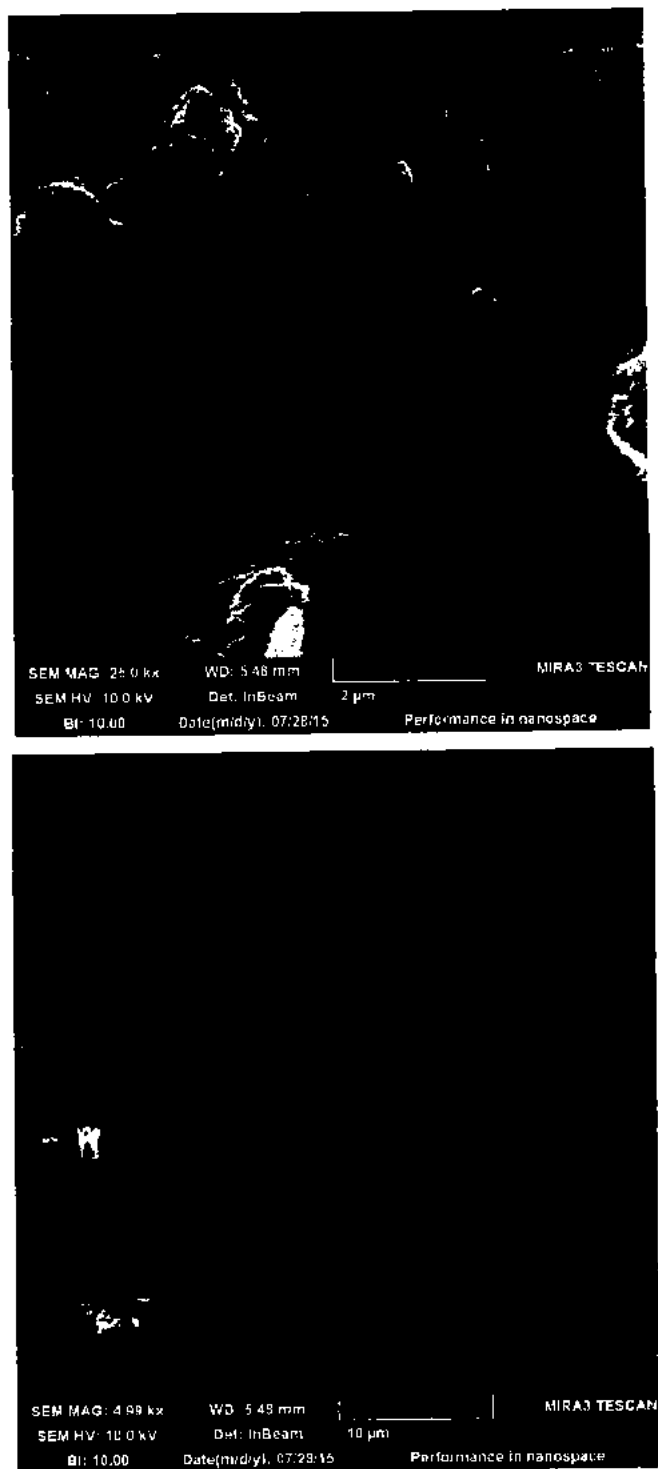
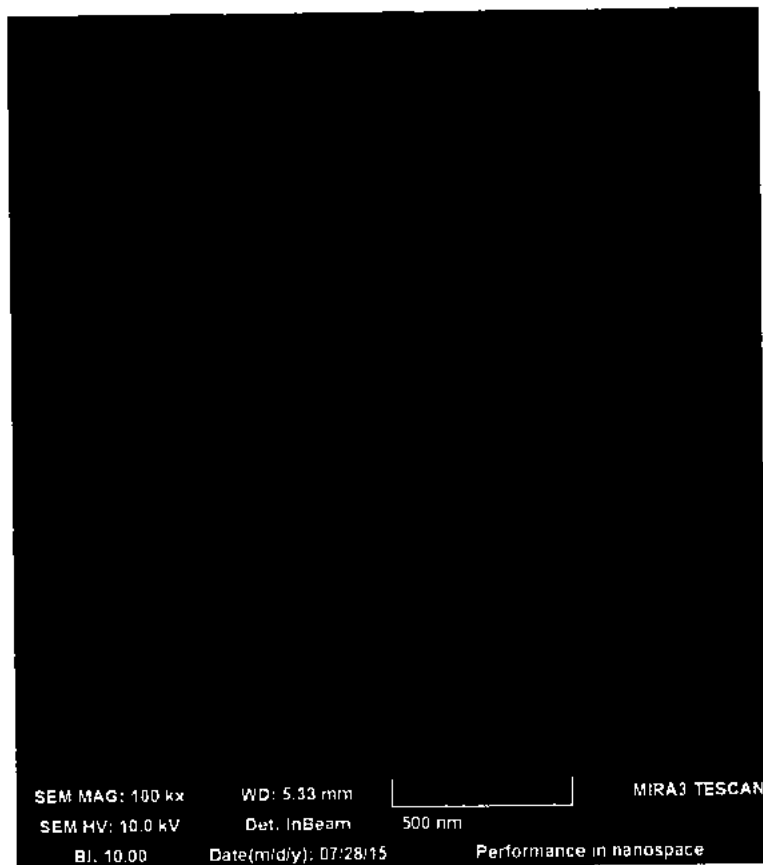


Figure 4.4(c): SEM of Egg Shell  $\text{CaCO}_3$  in the presence of SDS

#### 4.3.4 SEM of Egg Shell $\text{CaCO}_3$ in the presence of CTAB

The SEM images in the presence of CTAB is shown in Fig 4.4 (d). The SEM results indicated that presence of CTAB in the reaction medium causes the calcite crystals to agglomerate. The results showed that it deformed the calcite to the plate like shape. At 30 °C, agglomerations of rhombohedral and plate-like crystals are observed. The agglomerations decreased at 50 °C and crystals possessing various surface and step defects dominated by plate-like and rhombohedral shapes were observed[112]. So presence of CTAB greatly affect the shape of particle.







**Figure 4.4(d): SEM of Egg Shell  $\text{CaCO}_3$  in the presence of SDS**

#### **4.3.5 SEM of Egg Shell $\text{CaCO}_3$ in the presence of Urea**

Fig 4.4(e) illustrates the SEM photographs for the egg shell calcium carbonate processed in the presence of urea at magnification of 50,000 kV and 25,000 kV. It is observed that particle shape is changed from cube to plate like shape. From the images it can be clearly seen that urea has highly change the shape of bulk egg shell calcium carbonate. It is observed that it does not change poly of calcium carbonate but morphology has been changed.

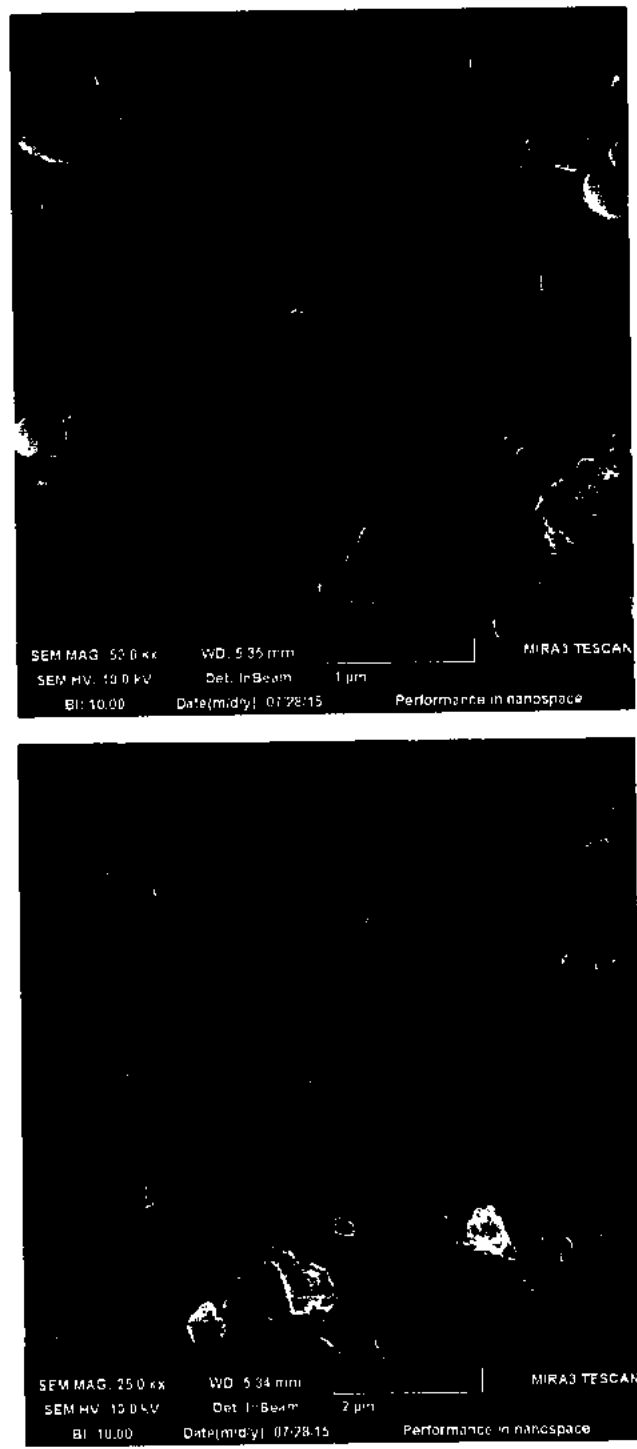


Figure 4.4(e): SEM of Egg Shell  $\text{CaCO}_3$  in the presence of Urea

## 4.4 Energy dispersive X-Ray Analysis

### 4.4.1 EDX of Egg Shell

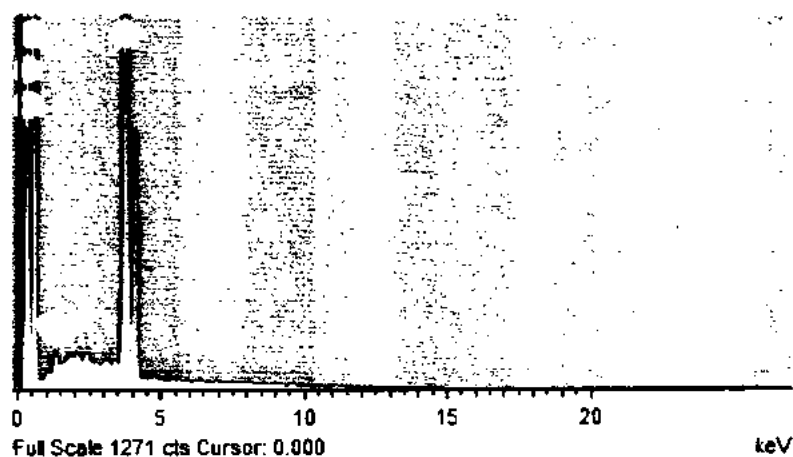


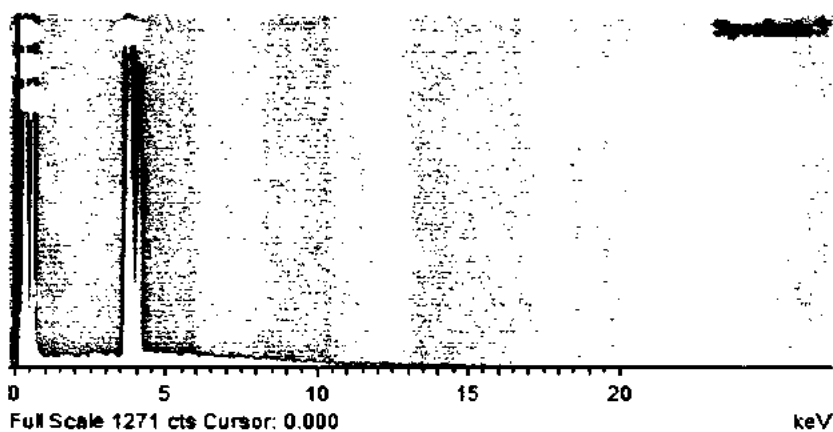
Figure 4.5: EDX spectrum for of un-processed egg shell

Element	Weight%	Atomic%
C K	17.06	26.85
O K	47.82	56.51
Mg K	0.24	0.18
Ca K	34.89	16.46
Totals	100.00	

Table 4.2: Integrative analysis of un processed egg shell

Fig 4.5 indicates the EDX graph for unprocessed egg shell. It shows that the presence of Calcium (Ca),Carbon (C),Oxygen (O) and some traces of magnesium was also present in un processed egg sell powder and that are acceptable because eggshell composed of 94% of Calcium carbonate and 6% of other organic and inorganic substances and magnesium is one of them.

**4.4.2 EDX of Egg Shell in the presence of SDS**



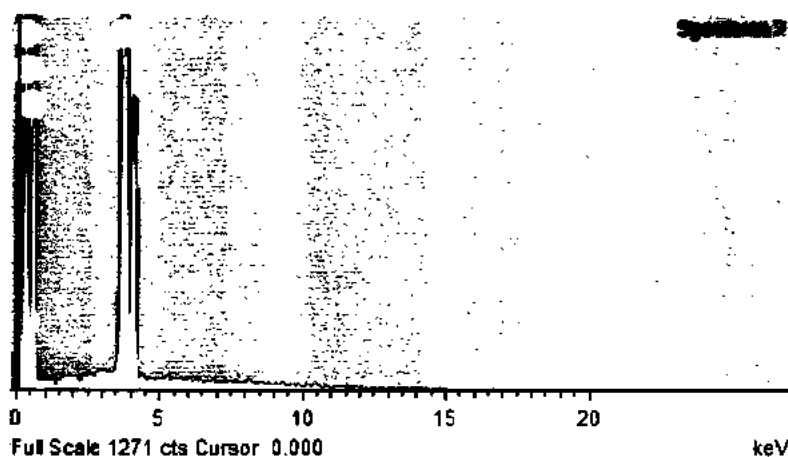
**Figure 4.6:** EDX spectrum for of egg shell in the presence of SDS

Element	Weight%	Atomic%
C K	17.14	26.91
O K	47.82	56.51
Ca K	35.05	16.58
Totals	100.00	

**Table 4.3:** Integrative analysis of egg shell in the presence of SDS

Figure 4.6 indicates the EDX graph for calcium carbonate nanoparticles. It clearly reveals that presence of Calcium (Ca), Carbon (C), Oxygen (O) in as prepared nanoparticles. It showed that in raw egg shell magnesium was present whereas after process that in the presence of additives the impurities has been removed.

#### 4.4.3 EDX of Egg Shell in the presence of CTAB



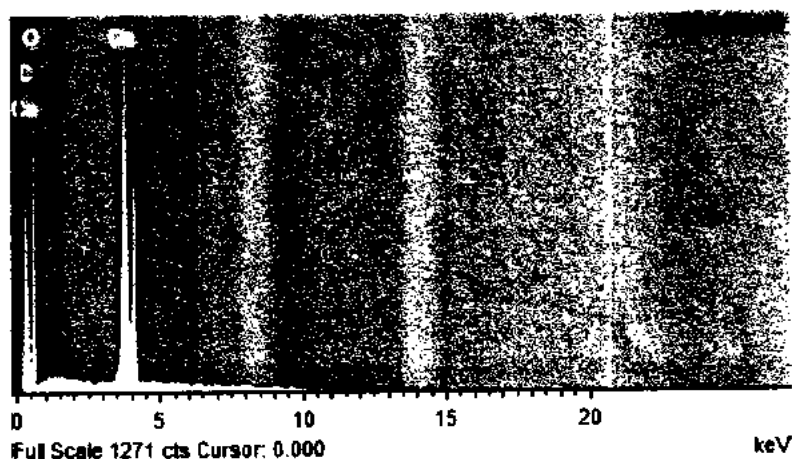
**Figure 4.7:** EDX spectrum for of egg shell in the presence of CTAB

Element	Weight%	Atomic%
C K	22.86	34.07
O K	46.55	52.19
Ca K	30.59	13.73
Totals	100.00	

**Table 4.4:** Integrative analysis of egg shell in the presence of CTAB

Figure 4.7 delineate that the formed nanoparticles of calcium carbonate are well matched with standard calcium carbonate .No other peaks is appeared except Calcium (Ca), Carbon (C), Oxygen (O).

#### 4.4.4 EDX of Egg Shell in the presence of Urea

**Figure 4.8:** EDX spectrum for of egg shell in the presence of Urea

Element	Weight%	Atomic%
C K	15.78	25.03
O K	48.65	58.02
Ca K	35.55	16.95
Totals	100.00	

**Table 4.5:** Integrative analysis of egg shell in the presence of Urea

EDX graph for calcium carbonate nanoparticles is shown in figure 4.8 indicate the presence of Calcium (Ca),Carbon (C),Oxygen (O).The magnesium which was appeared in un processed egg shell has been removed after its processing in the presence of Urea.

## **CONCLUSION**

The findings of this work showed that:

- The calcium carbonate nano particles are successfully synthesized by the mean of wet chemical method.
- The particles size of egg shell calcium carbonate is reduced by the presence of additives.
- XRD results showed that particle size is up to 20nm whereas in bulk it is 30nm. .
- SEM micrographs revealed that cubic like morphology in egg shell calcium carbonate and the rod like morphology in the presence of H<sub>2</sub>SO<sub>4</sub> as additive .The results delineate that presence of additive effect the morphology.
- FTIR results affirm the presence of Ca and CO<sup>-2</sup><sub>3</sub> in calcium carbonate.
- EDX analysis show composition of calcium carbonate and it is composed of Ca, C and O which confirmed the formed particles to be calcium carbonate particles.

## References

- [1] Komiyama, H., Yamaguchi, Y., & Noda, S. (2004). Structuring knowledge on nanomaterials processing. *Chemical engineering science*, 59(22), 5085-5090.
- [2] Wautelet, M. (2001). Scaling laws in the macro-, micro- and nanoworlds. *Eur. J. Phys. European Journal of Physics*, 601-611.
- [3] Mueller, N. C., & Nowack, B. (2010). Nanoparticles for remediation: solving big problems with little particles. *Elements*, 6(6), 395-400.
- [4] Pardo-Guerra, J. P. (2011). Mapping emergence across the Atlantic: Some (tentative) lessons on nanotechnology in Latin America. *Technology in Society*, 33(1), 94-108.
- [5] Uskokovic, V. (2007). Nanotechnologies: What we do not know. *Technology in Society*, 43-61.
- [6] [www.nature.com](http://www.nature.com)
- [7] Wikipedia
- [8] Kelly, A. (1985). Composites in context. *Composites Science and Technology*, 23(3), 171-199.
- [9] Kelly, A., & Zweben, C. (2000). Editors-in-Chief. *Comprehensive Composite Materials*, 1-6, I-I.
- [10] Sahoo, S. K., Praveen, S., & Panda, J. J. (2007). The present and future of nanotechnology in human health care. *Nanomedicine: Nanotechnology, Biology and Medicine*, 3(1), 20-31
- [11] Adams, F. C., & Barbante, C. (2013). Nanoscience, nanotechnology and spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 86, 3-13.
- [12] Amber, S. & Ali, S. (2007-2008). *Engineering and Technology*, 11-20 (2007-2008)
- [13] Pokropivny, V., & Skorokhod, V. (2008). New dimensionality classifications of nanostructures. *Physical E: Low-dimensional Systems and Nanostructures*, 40(7), 2521-2525.
- [14] [www.gitam.edu](http://www.gitam.edu)
- [15] Kodama, R. H. (1999). Magnetic nanoparticles. *Journal of magnetism and magnetic materials*, 200(1), 359-372.
- [16] Luna, C., Serna, C. J., & Vazquez, M. (2003). Multidomain to single-domain transition for uniform Co<sub>80</sub>Ni<sub>20</sub> nanoparticles. *Nanotechnology*, 14(2), 268.
- [17] Fiorani, D. (2005). *Surface effects in magnetic nanoparticles*. Springer Science & Business Media.



- [18] Mao, B., Kang, Z., Wang, E., Tian, C., Zhang, Z., Wang, C., & Li, M. (2007). Template free fabrication of hollow hematite spheres via a one-pot polyoxometalate-assisted hydrolysis process. *Journal of Solid State Chemistry*, 180(2), 489-495.
- [19] Guo, P., Wei, Z., Wang, B., Ding, Y., Li, H., Zhang, G., & Zhao, X. S. (2011). Controlled synthesis, magnetic and sensing properties of hematite nanorods and microcapsules. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 380(1), 234-240.
- [21] Pubchem.ncbi.nlm.nih.gov
- [22] Seo, K. S., Han, C., Wee, J. H., Park, J. K., & Ahn, J. W. (2005). Synthesis of calcium carbonate in a pure ethanol and aqueous ethanol solution as the solvent. *Journal of crystal growth*, 276(3), 680-687.
- [23] Lee, H. S., Ha, T. H., & Kim, K. (2005). Fabrication of unusually stable amorphous calcium carbonate in an ethanol medium. *Materials chemistry and physics*, 93(2), 376-382.
- [24] Tang, H., Yu, J., & Zhao, X. (2009). Controlled synthesis of crystalline calcium carbonate aggregates with unusual morphologies involving the phase transformation from amorphous calcium carbonate. *Materials Research Bulletin*, 44(4), 831-835.
- [25] Tai, C. Y., & Chen, F. B. (1998). Polymorphism of CaCO<sub>3</sub>, precipitated in a constant-composition environment. *AIChE Journal*, 44(8), 1790-1798.
- [26] Petrucci, R. H., and W. S. Harwood (1997) *General Chemistry* (Prentice-Hall, Inc., New Jersey) 776
- [27] Hoque, M. E., Shehryar, M., & Nurul Islam, K. M. (2013). Processing and characterization of cockle shell calcium carbonate (CaCO<sub>3</sub>) bioceramic for potential application in bone tissue engineering. *J Material Sci Eng*, 2(4), 132.
- [28] Dickinson, S. R., & McGrath, K. M. (2003). Switching between kinetic and thermodynamic control: calcium carbonate growth in the presence of a simple alcohol. *Journal of Materials Chemistry*, 13(4), 928-933.
- [29] Jamieson, J. C. (1953). Phase Equilibrium in the System Calcite-Aragonite. *The Journal of Chemical Physics*, 21(8), 1385-1390.
- [30] Altay, E., Shahwan, T., & Tanoğlu, M. (2007). Morphosynthesis of CaCO<sub>3</sub> at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability. *Powder Technology*, 178(3), 194-202.

- [31] Wolf, G., & Günther, C. (2001). Thermophysical investigations of the polymorphous phases of calcium carbonate. *Journal of thermal analysis and calorimetry*, 65(3), 687-698.
- [32] Ogino, T., Suzuki, T., & Sawada, K. (1987). The formation and transformation mechanism of calcium carbonate in water. *Geochimica et Cosmochimica Acta*, 51(10), 2757-2767.
- [33] Svenskaya, Y., Parakhonskiy, B., Haase, A., Atkin, V., Lukyanets, E., Gorin, D., & Antolini, R. (2013). Anticancer drug delivery system based on calcium carbonate particles loaded with a photosensitizer. *Biophysical chemistry*, 182, 11-15.
- [34] Naka, K., Tanaka, Y., & Chujo, Y. (2002). Effect of anionic starburst dendrimers on the crystallization of CaCO<sub>3</sub> in aqueous solution: size control of spherical vaterite particles. *Langmuir*, 18(9), 3655-3658.
- [35] Volodkin, D. V., Petrov, A. I., Prevot, M., & Sukhorukov, G. B. (2004). Matrix polyelectrolyte microcapsules: new system for macromolecule encapsulation. *Langmuir*, 20(8), 3398-3406.
- [36] Schmidt, S., & Volodkin, D. (2013). Microparticulate biomolecules by mild CaCO<sub>3</sub> templating. *Journal of Materials Chemistry B*, 1(9), 1210-1218.
- [37] Tai, C. Y., & Chen, F. B. (1998). Polymorphism of CaCO<sub>3</sub>, precipitated in a constant-composition environment. *AIChE Journal*, 44(8), 1790-1798.
- [38] S. Mann, J. Webb, RJP Williams (Eds.): *Biom mineralization: Chemical and Biochemical Perspectives*. VCH Verlagsgesellschaft, Weinheim, Basel, Cambridge, New York, 1989.
- [39] Stupp, S. I., & Braun, P. V. (1997). Molecular manipulation of microstructures: biomaterials, ceramics, and semiconductors.
- [40] Wolf, G., & Günther, C. (2001). Thermophysical investigations of the polymorphous phases of calcium carbonate. *Journal of thermal analysis and calorimetry*, 65(3), 687-698.
- [41] Kemperl, J., & Maček, J. (2009). Precipitation of calcium carbonate from hydrated lime of variable reactivity, granulation and optical properties. *International Journal of Mineral Processing*, 93(1), 84-88.
- [42] Islam, K. N., Bakar, M. Z. B. A., Ali, M. E., Hussein, M. Z. B., Noordin, M. M., Loqman, M. Y., & Hashim, U. (2013). A Novel methods for the synthesis of calcium carbonate (aragonite) nanoparticles from cockle shells. *Powder Technology*, 235, 70-75.
- [43] Sondi, I., Salopek-Sondi, B., Škapin, S. D., Šegota, S., Jurina, I., & Vukelić, B. (2011). Colloid-chemical processes in the growth and design of the bio-inorganic aragonite structure in

the scleractinian coral *Cladocora caespitosa*. *Journal of colloid and interface science*, 354(1), 181-189.

[44] Wada, N., Nakamura, M., Wang, W., Hiyama, T., Nagai, A., & Yamashita, K. (2010). Controlled deposition of calcite crystals on yttria-stabilized zirconia ceramic electrets. *Crystal Growth & Design*, 11(1), 166-174.

[45] Hunter, G. K. (1996). Interfacial aspects of biomineralization. *Current Opinion in Solid State and Materials Science*, 1(3), 430-435.

[46] Kitamura, M. (2002). Controlling factor of polymorphism in crystallization process. *Journal of Crystal Growth*, 237, 2205-2214.

[47] Schlomach, J., Quarch, K., & Kind, M. (2006). Investigation of precipitation of calcium carbonate at high supersaturations. *Chemical engineering & technology*, 29(2), 215-220.

[48] Kirboga S., & Oner, M., (2013) *Chemical Engineering Transactions*, 32,2119-2124

[49] Flaten, E. M., Seiersten, M., & Andreassen, J. P. (2009). Polymorphism and morphology of calcium carbonate precipitated in mixed solvents of ethylene glycol and water. *Journal of Crystal Growth*, 311(13), 3533-3538.

[50] Hu, Z., & Deng, Y. (2004). Synthesis of needle-like aragonite from calcium chloride and sparingly soluble magnesium carbonate. *Powder technology*, 140(1), 10-16.

[51] Beck, R., & Andreassen, J. P. (2012). Influence of crystallization conditions on crystal morphology and size of CaCO<sub>3</sub> and their effect on pressure filtration. *AIChE Journal*, 58(1), 107-121.

[52] Sadowski, Z., Polowczyk, I., Frąckowiak, A., Koźlecki, T., & Chibowski, S. (2010). Bioinspired synthesis of calcium carbonate colloid particles. *Physicochemical Problems of Mineral Processing*, 44, 205-214.

[53] Naka, K., & Chujo, Y. (2001). Control of crystal nucleation and growth of calcium carbonate by synthetic substrates. *Chemistry of Materials*, 13(10), 3245-3259.

[54] Boyjoo, Y., Pareek, V. K., & Liu, J. (2014). Synthesis of micro and nano-sized calcium carbonate particles and their applications. *Journal of Materials Chemistry A*, 2(35), 14270-14288.

- [55] Koivula, H., Toivakka, M., & Gane, P. (2012). Short time spreading and wetting of offset printing liquids on model calcium carbonate coating structures. *Journal of colloid and interface science*, 369(1), 426-434.
- [56] Juuti, M., Koivunen, K., Silvennoinen, M., Paulapuro, H., & Peiponen, K. E. (2009). Light scattering study from nanoparticle-coated pigments of paper. *Colloids and surfaces A: Physicochemical and engineering aspects*, 352(1), 94-98.
- [57] Hu, Z., Zen, X., Gong, J., & Deng, Y. (2009). Water resistance improvement of paper by super hydrophobic modification with microsized CaCO<sub>3</sub> and fatty acid coating. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 351(1), 65-70.
- [58] Liang, J. Z., Zhou, L., Tang, C. Y., & Tsui, C. P. (2013). Crystalline properties of poly (L-lactic acid) composites filled with nanometer calcium carbonate. *Composites Part B: Engineering*, 45(1), 1646-1650.
- [59] Afshar, A., Massoumi, I., Khosh, R. L., & Bagheri, R. (2010). Fracture behavior dependence on load-bearing capacity of filler in nano-and microcomposites of polypropylene containing calcium carbonate. *Materials & Design*, 31(2), 802-807.
- [60] Chen, C. H., Teng, C. C., Su, S. F., Wu, W. C., & Yang, C. H. (2006). Effects of micro scale calcium carbonate and nanoscale calcium carbonate on the fusion, thermal, and mechanical characterizations of rigid poly (vinyl chloride)/calcium carbonate composites. *Journal of Polymer Science Part B: Polymer Physics*, 44(2), 451-460.
- [61] Kemal, I., Whittle, A., Burford, R., Vodenitcharova, T., & Hoffman, M. (2009). Toughening of unmodified polyvinylchloride through the addition of nanoparticulate calcium carbonate. *Polymer*, 50(16), 4066-4079.
- [62] Sahebian, S., Zebarjad, S. M., Khaki, J. V., & Sajjadi, S. A. (2009). The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE. *Journal of materials processing technology*, 209(3), 1310-1317.
- [63] Momen, G., & Farzaneh, M. (2011). Survey of micro/nano filler use to improve silicone rubber for outdoor insulators. *Rev. Adv. Mater. Sci*, 27(1), 1-13.
- [64] Zhao, Q., Zhang, S., Tong, W., Gao, C., & Shen, J. (2006). Polyelectrolyte microcapsules templated on poly (styrene sulfonate)-doped CaCO<sub>3</sub> particles for loading and sustained release of daunorubicin and doxorubicin. *European polymer journal*, 42(12), 3341-3351.

- [65] Lucas, Giroto, A., Verdier, M. C., Tribut, O., Sangleboeuf, J. C., Allain, H., & Oudadesse, H. (2005). Gentamicin loaded calcium carbonate materials: Comparison of two drug loading modes. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 73(1), 164-170.
- [66] Raz, S., Hamilton, P. C., Wilt, F. H., Weiner, S., & Addadi, L. (2003). The transient phase of amorphous calcium carbonate in sea urchin larval spicules: the involvement of proteins and magnesium ions in its formation and stabilization. *Advanced Functional Materials*, 13(6), 480-486.
- [67] Groboillot, A., Boadi, D. K., Poncelet, D., & Neufeld, R. J. (1994). Immobilization of cells for application in the food industry. *Critical Reviews in Biotechnology*, 14(2), 75-107.
- [68] Chan, L. W., Lee, H. Y., & Heng, P. W. S. (2002). Production of alginate microspheres by internal gelation using an emulsification method. *International journal of pharmaceutics*, 242(1), 259-262.
- [69] Shan, D., Wang, Y., Xue, H., & Cosnier, S. (2009). Sensitive and selective xanthine amperometric sensors based on calcium carbonate nanoparticles. *Sensors and Actuators B: Chemical*, 136(2), 510-515.
- [70] [www.hubmaterials.com](http://www.hubmaterials.com)
- [71] Zhang, Q., Ren, L., Sheng, Y., Ji, Y., & Fu, J. (2010). Control of morphologies and polymorphs of CaCO<sub>3</sub> via multi-additives system. *Materials Chemistry and Physics*, 122(1), 156-163.
- [72] Hassan, T. A., Rangari, V. K., Rana, R. K., & Jeelani, S. (2013). Sonochemical effect on size reduction of CaCO<sub>3</sub> nanoparticles derived from waste eggshells. *Ultrasonics sonochemistry*, 20(5), 1308-1315.
- [73] Tavangar, A., Tan, B., & Venkatakrisnan, K. (2011). Synthesis of three-dimensional calcium carbonate nanofibrous structure from eggshell using femtosecond laser ablation. *Journal of nanobiotechnology*, 9(1).
- [74] Islam, K. N., Bakar, M. Z. B. A., Noordin, M. M., Hussein, M. Z. B., Rahman, N. S. B. A., & Ali, M. E. (2011). Characterisation of calcium carbonate and its polymorphs from cockle shells (*Anadara granosa*). *Powder Technology*, 213(1), 188-191.
- [75] Wang, Y., Cheng, R., Wen, Z., & Zhao, L. (2012). Facile preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with cetyltrimethylammonium bromide (CTAB) assistant and a study of its adsorption capacity. *Chemical Engineering Journal*, 181, 823-827.

- [76] Wang, N., Wang, X., Yang, L., & Chen, H. (2013). Morphology and size control of nanocalcium carbonate crystallised in reverse micelle system with cationic surfactant cetyltrimethylammonium bromide. *Micro & Nano Letters, IET*, 8(2), 94-98.
- [77] Westin, K. J., & Rasmuson, Å. C. (2005). Nucleation of calcium carbonate in presence of citric acid, DTPA, EDTA and pyromellitic acid. *Journal of colloid and interface science*, 282(2), 370-379.
- [78] Mantilaka, M. M. M. G. P. G., Rajapakse, R. M. G., Karunaratne, D. G. G. P., & Pitawala, H. M. T. G. A. (2014). Preparation of amorphous calcium carbonate nanoparticles from impure dolomitic marble with the aid of poly (acrylic acid) as a stabilizer. *Advanced Powder Technology*, 25(2), 591-598.
- [79] Yoo, S., Hsieh, J. S., Zou, P., & Kokoszka, J. (2009). Utilization of calcium carbonate particles from eggshell waste as coating pigments for ink-jet printing paper. *Bioresource technology*, 100(24), 6416-6421.
- [80] Wang, A. X., Chu, D. Q., Wang, L. M., Mao, B. G., Sun, H. M., Ma, Z. C., ... & Wang, L. X. (2014). Preparation and characterization of novel spica-like hierarchical vaterite calcium carbonate and a hydrophilic poly (vinylidene fluoride)/calcium carbonate composite membrane. *CrystEngComm*, 16(24), 5198-5205.
- [81] Wang, J., White, W. B., & Adair, J. H. (2014). Synthesis of Calcium Carbonate Particles in Octylamine/Water Bilayer Systems. *KONA Powder and Particle Journal*, 31(0), 156-162.
- [82] Guo, H., Qin, Z., Qian, P., Yu, P., Cui, S., & Wang, W. (2011). Crystallization of aragonite  $\text{CaCO}_3$  with complex structures. *Advanced Powder Technology*, 22(6), 777-783.
- [83] Ukrainczyk, M., Kontrec, J., Babić-Ivančić, V., Brecević, L., & Kralj, D. (2007). Experimental design approach to calcium carbonate precipitation in a semi continuous process. *Powder technology*, 171(3), 192-199.
- [84] Ouhenia, S., Chateigner, D., Belkhir, M. A., Guilmeau, E., & Krauss, C. (2008). Synthesis of calcium carbonate polymorphs in the presence of polyacrylic acid. *Journal of Crystal Growth*, 310(11), 2832-2841.
- [85] Kamba, A. S., Ismail, M., Ibrahim, T. A. T., & Zakaria, Z. A. B. (2013). Synthesis and characterisation of calcium carbonate aragonite nanocrystals from cockle shell powder (anadara granosa). *Journal of Nanomaterials*, 2013, 5.

- [86] Jung, W. M., Kang, S. H., Kim, W. S., & Choi, C. K. (2000). Particle morphology of calcium carbonate precipitated by gas-liquid reaction in a Couette-Taylor reactor. *Chemical Engineering Science*, 55(4), 733-747.
- [87] Aziz, B., Gebauer, D., & Hedin, N. (2011). Kinetic control of particle-mediated calcium carbonate crystallization. *CrystEngComm*, 13(14), 4641-4645.
- [88] Sanchez, F., & Sobolev, K. (2010). Nanotechnology in concrete—a review. *Construction and Building Materials*, 24(11), 2060-2071.
- [89] Iqbal, P., Preece, J. A., & Mendes, P. M. (2012). Nanotechnology: The “Top-Down” and “Bottom-Up” Approaches. *Supramolecular Chemistry: From Molecules to Nanomaterials*.
- [90] B. Barber, S. Putterman, *Physics. Rev. Letter.* 69, 1182–1184 (1992)
- [91] Suslick, K., (1994). *Proc. First Intl. Conf. Mechanochemistry*, Cambridge Interscience, Cambridge, 1, 43–49
- [92] Cullity, B. (1956). *Elements of X-Ray Diffraction*. American Journal of Physics Am. J. Phys., 394-394.
- [93] Myers, H. (2002). *Introductory Solid State Physics*.
- [94] Kacher, J., Landon, C., Adams, B. L., & Fullwood, D. (2009). Bragg's Law diffraction simulations for electron backscatter diffraction analysis. *Ultramicroscopy*, 109(9), 1148-1156.
- [95] *Principals of General Chemistry*
- [96] Bryan, R. (2003). *Fundamentals of crystallography*, 2nd edition. Edited by C. Giacovazzo. IUCr Texts on Crystallography 7. Oxford: IUCr/Oxford University Press, 2002.
- [97] Warren, B. E. (1969). *X-ray Diffraction*. Courier Corporation.
- [98] Alexander, L., & Klug, H. P. (1950). Determination of Crystallite Size with the X-Ray Spectrometer. *Journal of Applied Physics*, 21(2), 137-142.
- [99] Lawes, G. (1987). *Scanning electron microscopy and X-ray microanalysis*.
- [100] Kalantar-Zadeh, K., & Fry, B. (2007). *Nanotechnology-Enabled Sensors*.
- [101] [www.che.utoledo.edu](http://www.che.utoledo.edu)
- [102] RUS, E. N. *Innovative materials and cutting edge technological processes*.
- [103] Brock, S. L. (2004). *Nanostructures and Nanomaterials: Synthesis, Properties and Applications* by Guozhang Cao (University of Washington). Imperial College Press (distributed by World Scientific): London. 2004. *Journal of the American Chemical Society*, 126(44).

- [104] Martin, A. E. (1980). Infrared interferometric spectrometers. *NASA STI/Recon Technical Report A, 81*, 23378.
- [105] Ataka, K., & Heberle, J. (2003). Electrochemically induced surface-enhanced infrared difference absorption (SEIDA) spectroscopy of a protein monolayer. *Journal of the American Chemical Society, 125*(17), 4986-4987.
- [106] [www.chemwiki.ucdavis.edu](http://www.chemwiki.ucdavis.edu)
- [107] Smith, B. C. (2011). *Fundamentals of Fourier transform infrared spectroscopy*. CRC press.
- [108] Hassan, N, PhD Thesis (2009), Solid state synthesis and studies of Ni doped superconductor
- [109] Hariharan, M., Varghese, N., Benny, A. S., Cherian, A. B., Sreenivasan, P. V., Paul, J., & ka, a. A. Bio inspired synthesis and characterisation of calcium carbonate nano particles using chitosan as precursor.
- [110] Idrees, M. (2013). Characterization of  $\text{CaCO}_3$  nanoparticles synthesized by reverse microemulsion technique in different concentrations of surfactants. *Iran. J. Chem. Chem. Eng. Vol, 32*(3).
- [111] Shen, Q., Wei, H., Wang, L., Zhou, Y., Zhao, Y., Zhang, Z., ... & Xu, D. (2005). Crystallization and aggregation behaviors of calcium carbonate in the presence of poly (vinylpyrrolidone) and sodium dodecyl sulfate. *The Journal of Physical Chemistry B, 109*(39), 18342-18347.
- [112] Altay, E., Shahwan, T., & Tanoğlu, M. (2007). Morphosynthesis of  $\text{CaCO}_3$  at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability. *Powder Technology, 178*(3), 194-202