Synthesis and characterization of doped ZnO nano-material for removing hazardous impurity of Arsenic in water

Dissertation

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January, 2021

Dedicated

To

My Loving Parents

And

My Teachers

DECLEARATION

I declare that the dissertation entitled **"Synthesis and characterization of doped ZnO nano-material for removing hazardous impurity of Arsenic in water"** has been prepared by me under supervision of Dr. Khem B. Thapa, Assistant Professor, Department of Physics, School of Physical & Decision Sciences, Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow-226025, U.P., India. No part of this dissertation has formed the basis for the award of any degree, diploma or fellowship previously. Further, I declare that the material embodied in the present work is based on original research work and the indebtedness to others has been duly in acknowledged at relevant places. This is also declared that the dissertation is essentially free from any kinds of plagiarism.

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CERTIFICATE

This is to certify that the dissertation titled , **"Synthesis and characterization of doped ZnO nano-material for removing hazardous impurity of Arsenic in water"** submitted by **Ms. Varsha Gautam** is an original research work and has not been previously submitted in part or full for the award of any degree or diploma to this or any other university.

This dissertation submitted to Babasaheb Bhimrao Ambedkar University Lucknow, satisfies all the requirement as stipulated in the Master of Philosophy (M.Phil.)/Doctor of Philosophy (Ph.D.) regulations amended in 2019 and it is fit for submission and evaluation for the award of Master of Philosophy of the University.

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ABSTRACT

Undoped ZnO and copper doped ZnO nanomaterials were prepared by co-precipitation method technique. The doped copper metal in the ZnO nanomaterials may be enhanced the efficiency of photocatalytic process to remove pollutants from earth's water. The nano-catalysis system based on the photocatalytic may be counterpart of the existing techniques for the removal of trace pollutants/impurities. The solar photocatalysis and artificial ultraviolet light photocatalytic activities are the ability to water treatment at room temperature and ambient pressure.

The modifications in structure, morphology, band gap of the copper doped ZnO nanomaterials due to the doping of the copper were investigated through XRD, FE-SEM/EDAX, and UV–Visible characterization respectively. The analysis of XRD pattern revealed the comprehend of the dopants copper into ZnO lattice. The XRD patterns show that all the synthesized nanomaterials are a nano-crystalline phase with hexagonal Wurtzite and tripod type structure. The analysis of FE-SEM indicated that the copper doping affects the surface morphology of ZnO nanomaterials. The compositional study performed by EDAX confirmed the presence of Zn, O, and Cu. The optical study revealed that the energy band gap decreased with doping of copper into ZnO nanomaterials. The enhanced physical properties revealed that the synthesis 2% copper doped ZnO nanomaterials may be fruitful to remove hazardous arsenic impurity from water application. The Cu(2%):ZnO nanomaterials is more better than the Cu(1.08%):ZnO nanomaterials in the reported paper [V. Vaino, et al., *Applied Catalysis B: Environmental* 18**, (2018),** p.no.30634-9] because the large amount of the copper in the ZnO semiconductor has the low energy bang gap. The low band gap may be more useful for solar photo catalysis and artificial ultraviolet (UV)-light photocatalytic activity.

PREFACE

The dissertation entitled, *"Synthesis and characterization of doped ZnO nano-material for removing hazardous impurity of Arsenic in water"* under the supervision of Dr. Khem B. Thapa, Assistant Professor, Department of Physics, Babasaheb Bhimrao Ambedkar University Lucknow is reported the obtained experimental research results, which was carried out in the Condensed Matter Physics Laboratory, Department of Physics, Babasaheb Bhimrao Ambedkar University (A Central University) , Lucknow in between 2019-2020.

In this present M.Phil. dissertation work, the dissertation is divided into four chapters.

Chapter-1: In this chapter, the introduction starts with the water problems throughout the world. All the water contaminants are listed with their impact on human life. The arsenic impurity in the water, which is found in most states of India especially Uttar Pradesh, Bihar and West Bengal, is very hazardous for human life. This chapter also contains the literature survey to study on the the metal oxide nanomaterials (especially ZnO & Cu:ZnO nanomaterials) by low cost method like co-precipitation method and the literature survey showed that the ZnO & Cu:ZnO nanomaterials are fruitful to remove the arsenic impurity from earth's water.

Chapter-2: This chapter contains the various methods of synthesis to synthesize the metal oxide nanomaterials. Among the methods, the Co-precipitation method is the best, very simple process and low cost method which can be done at room temperature and ambient pressure. Characterization techniques are also described in this chapter. These characterization techniques are used to analysis the properties of synthesized nanomaterials for the nano-catalytic system. We have discussed some characterization techniques of SEM/FESEM, EDX, XRD, UV-visible spectrometer for analysing the elemental composition, morphology, structure information, shape, size as well as chemical and physical property of the synthesis metal oxide nanomaterials and such analysis of the synthesis nanomaterials is useful and important to support for removable of the hazardous water contaminants.

Chapter-3: In this chapter, we have reported the results and discussion of the synthesis and characterization of the ZnO nanomaterials and copper doped ZnO (Cu:ZnO) nanomaterials. It contains two parts: first part gives the synthesis and characterization of pure ZnO nanomaterials where three samples (A, B and C) are prepared at different annealing temperatures. These A, B and C samples of pure ZnO nanomaterials are analyzed the elemental composition, morphology, structure information, shape, size of the synthesis pure ZnO nanomaterials; second part gives the synthesis and characterization of the Cu(1%):ZnO nanomaterials and Cu(2%):ZnO nanomaterials. The pure ZnO nanomaterials, Cu(1%):ZnO nanomaterials and Cu(2%):ZnO nanomaterials were synthesized successfully by co-precipitation method. The synthesized pure ZnO nanomaterials, Cu(1%):ZnO nanomaterials and Cu(2%):ZnO nanomaterials were characterized by SEM/FESEM, EDX, XRD, UV-visible spectrometer. Generally the SEM/FESEM is used to analysis the surface morphology. The EDX characterization is used to analysis the elemental composition of the nanomaterials. The XRD characterization is used to analysis the crystalline structure and particle size. The UV-Visible spectrometer is used to calculate the optical band gap. The analysis results of all pure ZnO nanomaterials and copper doped ZnO nanomaterials are compared. On the basis of elemental composition, morphology, structure, shape, size as well as energy band gap properties of the synthesized copper doped ZnO nanomaterials is proposed for the removable of the hazardous water contaminants.

Chapter-4: The general conclusion and future scope are given in this chapter where the pure ZnO nanomaterials, Cu(1%):ZnO nanomaterials and Cu(2%):ZnO nanomaterials was synthesized by low cost co-precipitation method; and the elemental composition, morphology, structure, shape, size as well as energy band gap properties were analyzed by SEM/FESEM, EDX, XRD, UV-visible spectrometer. The Cu(2%):ZnO nanomaterials may be fruitful for nano-catalysis system and such nano-catalysis based on the copper doped ZnO nanomaterials having the good photocatalytic activity may be counterpart of the existing techniques for the removal of trace pollutants/impurities.

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Introduction

Water pollution is most captivating problem in the world because there is impossible to living on the earth without drinking water. Scientifically it has been proved that humans without the water can survive for a maximum of four days only. Neither the animals nor the birds around us can survive without the water even trees also. Why is the world worrying so much for the water? The reasons behind it is, while the earth surface, being covered by 70 percent water of earth, only 03 percent water on the planet is potable water. It means the world is not having adequate drinking water. Hence, lots of peoples across the world are living now days with scarcity of the water than they require to be in the world's most prosperous towns or farming heartland. According to United Nation; approximate 1 billion people of the world are living less the access potable water. Under the age of 5 more than 900 children die from water born diseases (diarrhoea) every day because of lousy water and sanitation **[1].**

In the whole world, one fourth part of the earth's population i.e. estimated 1.8 billion public in the next few years will appear towards a water scarcity-with the possibility of intense shortages. According to report by Washington D.C.-based World Resources Institute's (W.R.I.) Aqueduct Water Risk Atlas, there are total seventeen countries including twelve from the North Africa and Middle East facing from the lack of the drinking water **[2]**. The two nations in Asia-Bharat and Pakistan are also facing from the lack of the drinking water. The rest hotspots are Botswana in Africa, San Marino in Europe and Turkmenistan in Central Asia.

Potable Water is the basic need of life. The presence of fresh potable water is important for life portative activities such as drinking, cooking, cleaning, farming, etc. The beauty of the nature is that it has its own mechanism for water recycling to give us with a good enough quantity of potable water with consumable purity level. Human activities are created the imbalance between natural source of water and purifying process, this imbalance is the reason of shortage of fresh water among the human beings **[3]**. Throughout the world, the potable water is a big problem due to the reason behind climate change, people growth, and modernization in urban lives. According to World Health Organization report 2019, the maximum population of the world is going to face the water problem with stress water by 2025. India is going to become a water stressed country by 2022. The water pollution will be infected about 67 million Indian peoples in 20 states, which is a big health risk in India **[4].**

1.1 Recycling of Wastewater

The problem of the potable water can be solved somehow purify the wastewater by removing the wastewater ingredients for the waste water. In the waste water, the impurities iron, manganese, arsenic, chloride, fluorides, sulphates etc. are found. So, it is required the removing these impurities as wastewater ingredients and recycled the waste water as the potable water **[5].** Maximum natural resources of potable water are found to be infected with different poisonous materials F, As, Pb, Cu, Cr, Hg, Sb etc. The man-made sources of organic pollution are home waste, commercial wastes and pesticides, etc. The pathogenic microorganisms are algae, bacteria, protozoan or viruses which are usually found in the man-made sources of organic pollution. Due to presence of the some radioactive materials, the man-made pollutions are created more problems in ground water than upper surface of water. Therefore, combine information of all types of pollutant with their sources and effects are given below in the tabulated form of list **[6].**

Table 1.1: List of different water contaminants with their origins and unfavourable effect.

Water Pollutants	**Source of Pollutants**	**Effect of Pollutants**	**Nanomaterials**	**Ref.**
Agricultural Pollutants	Farming Chemicals	Directly affect the potable ground water	TiO_2, ZnO etc.	**[7,8]**
Sediments and suspended solids	Farmland, destruction, tapping operations	Harm fish spawning, influence oceanic environment of insects and fishes	TiO_2, Al_2O_3, SiO_2 and ZnO etc.	**[9,10]**
Pathogens	Viruses and bacteria	Water born diseases	ZnO, Ag, TiO_2, CNT etc.	**[11,12]**

Commercial Pollutants	Municipal pollutants water	Created pollutants in water as well as air	nano-zeolites, metal organic frameworks and carbon-based nanomaterials etc.	**[13,14]**
Radioactive Pollutants	Different isotopes	Bones, teeth, skin and can cause	MnO_2 – based NPs, TiO_2 as photo catalysts etc.	**[15,16]**
Nutrients Pollutants	Plant debris, fertilizer	Effect on eutrophication	CBNs, SWCNTs MWCNTs, C_{60} etc.	**[17,18]**
Macroscopic Pollutants	Marine debris	Plastic Pollutants	Titanate nano ribbon (TNR) membrane, zirconia nano fibrous (ZNF) membranes, titanium dioxide (TiO2) etc.	**[19,20]**
Sewage and contaminated water	Domestic wastewater	Water borne diseases	ZnO TiO_2, Ag etc.	**[7,21]**
Organic Pollutants	Detergents, insecticides, Herbicides	Aquatic life problems, Cacogenic	TiO_2, Fe_3O_4, ZrO_2 etc.	**[22,23]**
Inorganic Pollutants	Heavy metals and Minerals acids	Illness in people	TiO_2, Fe_2O_3, ZrO_2, NiO, $MnFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$ etc.	**[22,24]**

As discussed in the above table 1.1, the inorganic pollutants in ground water are the main atmospheric problems. Now, the inorganic chemicals, carcinogenic organic and infectious pathogens have polluted a day's water. Almost water contaminants are caused from anthropogenic activities like sewage and cosmos activities like volcanic eruption and etc. **[25].** Generally, these inorganic pollutants are found due to two main reasons: the first reason is lack information about chemicals of disposal; and second reason is unsuccessfulness to destroy the anthropogenic pollutant from nature. Consequently the inorganic pollutions arise in the environment. The inorganic pollutants include nitrates, nitrites, fluorides, arsenic, lead, mercury, chromium, cadmium, and aluminum etc. **[25, 26]**

1.2 Arsenic as a Hazardous Ingredient in Water

According the Report of World Health Organization (W.H.O.) on 15 February 2018, the biggest problem in human health life is the consumed Arsenic metal (As) through the infected groundwater, which originates from contaminated groundwater. Inorganic pollutants mainly contain Arsenic that exists naturally at peak in the ground water in the main territories Chile, China, Bangladesh, USA and India **[27]** and it has been observed that these territories have faced many challenges and problems in human health due to presence of Arsenic in the potable water. There are some health problems that are given below as:

- Skin lesions,
- Skin cancer,
- Bladder diseases,
- Lungs and cardiovascular diseases,
- Reduced intellectual function in children etc.

Table 1.2: List of states in India that are affected by arsenic in the groundwater **[29]**

Sr. No.	State	Percentage of state population
1	Assam	65%
2	Bihar	60%
3	West Bengal	44%

According to latest report, about 2.34 crore peoples of India, table 1.2, especially north India i.e. Uttar Pradesh (U.P.) are revealed to be found the peak of As metal in ground water. There are several districts of Uttar Pradesh are uncovered to high congregation of As in earth's ground water. The majority districts of the Uttar Pradesh are belonging to the rivers of Ganga, Rapti and Ghaghara. However, the districts Shahjahanpur, Unnao, Chandauli, Varanasi, Balarampur, Mau, Deoria and Siddharthanagar etc. are the moderate risk zones of arsenic (As) contaminated ground water. There are many reasons in these districts for ground water pollution with As, but two main reasons are: one is due to industrial waste spread from these districts with the worst polluted water with As especially Barabankhi, Faizabad, Gorakhpur, Gonda, Kushinagar, Lakhimpur Kheri, Mau, Pratapgarh, Shahjahanpur, Siddharthanagar, Unnao, Varanasi, etc.; and second is a native part of As in the earth's layer that is comprehensively dispersed throughout the atmosphere in the air and earth water [**28-31].** The tube wells and hand pumps are the main sources for drinking water in Uttar Pradesh. The groundwater from tube wells and hand pumps usually spreads the high health risk due to consuming the drinking water with arsenic contamination.

Arsenic is found natuarally component of the earth's crust in both form organic and inorganic. So it is widely obtained in the air and water including heavy metals makes the most water pollutants with enoumorus toxicity and carcinogenicity. Arsenic is also present in both forms with different five oxidation states (-3,-1, 0, +3, +1) and it makes possible of the element to be widely distributed in nature in variety of forms. Arsenate is mostly present in the form of As (+5) in the earth's water, during the oxygenation of water. However, in reducing conditions (less than 200mV), the mostly present in Arsenite or As (+3) form is found in the earth's water **[33].** The inorganic species are the more toxic than the organic species. Large numbers of arsenic containing chemical compounds are present in the environment: they include the inorganic species As (+5) or Arsenate and As (+3) or Arsenite **[34].** Arsenic is universal element in the nature. The reasons of arsenic pollutant in earth's water may be geological as well as manmade. Arsenic is called ***death dealing poison*** since past time because of its have many side effects and murderous.

Arsenic is found in the form of different compounds. Their different compositions are found with oxigen, sulphur, acid and metal:

- Arsenic (As)
- Arsenic Trioxide (As_2O_3)

- Arsenic Pentaoxide (As_2O_5)
- Arsenic Sulphide (As_2S_3)
- Dimethyl Arsenic Acid [DMA - $CH_3)_2AsO(OH)$]
- Monomethyl Arsenic Acid [MMA-$(CH_3)AsO(OH)_2$]
- Lead Arsenate ($PbHAsO_4$)
- Potassium Arsenate (KH_2AsO_4)
- Potassium Arsenite ($KAsO_2HAsO_2$)

The sequence of poisonous arsenic compounds which are present in earth water are Arsenite > Arsenate > Monomethyl Arsenic (MMA) > Dimethyl Arsenic Acid (DMA) **[35-40].** So, that's why arsenite is venomous and very hard to eliminate from earth's water than As (+5) because it is reacted with water and formed a stable compound of H_3AsO_3 **[41].** An example of arsenic compounds that reacts strongly with water. This is an amorphous arsenic compound reaction mechanism**.** The chemical reaction mechanism is given as **[43]:**

$$As_2S_3 + 6H_2O -> 2H_3AsO_3 + 3H_2S \tag{1.1}$$

The Arsenic is found in water in the form of the fairly insoluble, but the arsenic compounds are easily soluble. The HAs_4O^{2-} (aq.) and H_2AsO_4 (aq.) are watery soluble in the form of the H_3AsO_4 (aq.), AsO_4^{3-} (aq.) or H_2AsO^{3-} (aq.) [**43**]. Besides this, there are several applications of Arsenic and Arsenical products, industrial and commercial uses as:

- Alloying agents in the manufacture of transistors
- Lasers
- Metal adhesives
- Processing of glasses
- Semiconductors
- Textiles
- Wood preservatives etc.

The enhancement of pH in the water is indicated the increasing of concentration of soluble Arsenic in the water **[44].** The quantity of arsenic in earth's water, existing seawater, is mainly ranges between 1-2µg. The main source of intake of Arsenic in human bodies is mostly from seafood like fish and the other source of the intake of Arsenic in human bodies is also in the form of the meat of animals. The dietary of arsenic in meal for teenage has been estimated between 16.7µg to 129µg. Arsenic is a needy element, but still biological part did not evidence to demonstrate so far [**45-46].** The fatal amount of arsenic in human bodies is from 1.5 mg/kg of body weight **[47].** These are some over view of the Arsenic which is found in the environment as well as human being, but the consuming of the Arsenic through the water is the main problems for human life. There are several techniques to reduce the Arsenic form conventional to advanced technology, but we here discuss the advanced technology, nanotechnology, to use as the water treatment.

1.3 Role of Nanomaterials in Water Treatment

Over past few years, the revolutionary growth in the field of nano science and nanotechnology has encouraged the scientific circle to investigate the nanomaterials in different shapes and sizes in this massive potential field of research. The special and beneficial properties of novel nano-structured materials, especially having large surface area to volume ratio, can be utilized to bring more efficient and continual solutions to prevail in water treatment [**48].** The nanoparticles used in nanotechnology is of very lesser size say less than 100nm i.e. 01nm-100nm. Nanoparticles have several qualities with fascinating, interconnecting and responding abilities because of its tiny size with high ratio of atoms at surface **[49].** The novel nano-structured materials in the nanotechnology have huge effect in atmospheric protection, for example, water pollution, where useless atoms can be purifying and keep the control on the pollutions **[50,51].** Nano-structured materials are used in very comprehensive areas:

- Radiotherapy, catalysis sensing, electronics, photonics, environmental cleaning, imaging, textile industry **[52-59].**
- Sunscreens, water purification, food supplement, paint, photo catalyst, antibacterial coating **[60-66].**
- Long term multiple colours imaging of cells, insulators, semiconductors **[52, 60, 67-69].**

According to the Baruah et. al. (2019) [**3,70**], the nano-materials are used for water disinfections. These nano-materials are Zinc Oxide (ZnO), Copper Oxide (CuO), Iron

Oxide (Fe_2O_3), Stannous Oxide (SnO), Titanium Oxides (TiO_2), Iron Hydroxide ($Fe(OH)_2$), Nickel Oxide (NiO) etc. The other nano-materials are Zeolites [$M^n_{x/n}Si_{1-x}Al_xO_2$•Yh_2O, where M= Na^+, K^+, Li^+, Ag^+ etc., Si/Al> 1, x < 0.5], Graphene [(Graphene oxide ($C_{140}H_{42}O_{20}$ etc.)], Fullerene (C_{2n} where n=12, 13,14...), Aluminum oxide (Al_2O_3), Cadmium Sulfide (CdS), Cobalt Ferrite ($CoFe_2O_4$), Gold (Au), Iron (Fe), Silica (SiO_2), Zinc Sulphide (ZnS), Zirconia (ZrO_2) etc. and some alloys are also employed for water treatment. Many technologies are used in water treatment to overcome from the problem of polluted earth's water. This process of the water treatment may be made availability of the drinking water and may fulfil the demand of the drinking water in all across the world.

Generally these methods are used to eliminate the pollutant from earth’s water: Coagulation-flocculation, Photocatalytic Oxidation, Adsorption **[71]**. These methods are discussed briefly.

- When certain chemical agent [(e.g. Aluminium Sulphate $Al_2(SO_4)_3.18H_2O$] mixed with waste water, then colloidal and suspended particles are agglomerated and originated insoluble metal hydroxide known as flocks. This process is called coagulation-flocculation process.
- UV irradiation interacts with substance (catalyst-ZnO, TiO_2 etc.) and forms hydroxyl radicals. After this attacks on harmful pollutants, the results is obtained harmless water molecules. There are used some oxidants like O_3, H_2O_2, Cl_2, NH_2Cl etc. when oxidation is done in UV radiation then known as photocatalytic oxidation.
- Adsorption is a surface process in which contaminants are adsorbed on a solid surface by physical forces and sometimes weak chemical bonds. Adsorbents (nanomaterials) have high specific surface and good adsorption capacity and used to remove organic and inorganic contaminants and bacteria etc.

In this dissertation work, we have adopted the adsorption method for eliminating the pollutant from earth’s water. The zinc oxide (ZnO) nanoparticles are mainly used to eliminate the pollutant water, however, the copper doped zinc oxide (Cu:ZnO) nanoparticles is also used to eliminate the pollutant water. Therefore, in the next section, we briefly give the review literature of ZnO and Cu-ZnO nanoparticles to eliminate the pollutant water.

1.4 Literature Review of ZnO nanomaterials:

Generally Co-precipitation, Sonochemical, Sol-Gel, Microwave, Emulsion and Hydrothermal methods are used to synthesize the ZnO nanoparticles **[72].** Besides these methods, there are several others methods are used to synthesize, but one method will have selected so that the methods would be the low cost and high feasibility for synthesis of the considered materials. The Co-precipitation is the best method for synthesis of the ZnO and Cu:ZnO nanoparticles because this method is very cost effective and high feasibility of synthesis ZnO nanomaterials. So, we have discussed as the literature review of synthesis ZnO and Cu:ZnO nanoparticles/nanomaterials by the Co-precipitation method.

Table 1.3: Different precursors for obtaining zinc oxide & its applications:

Sl. No.	**Precursors**	**Conditions for synthesis**	**Particle size & shape**	**Applications**	**Ref.**
			Co-precipitation Method		
1.	a) $Zn(CH_3CO_3)$ b) KOH	a) 20-80^{0}C (temp.) b) 120^{0}C (drying)	a) Particle diameter 160-500 nm; b) BET: 4-16 m^2/g		**[73]**
2	a) $Zn(CH_3CO)_2$, b) $(NH_4)_2C_3$, PEG10000	a) 12h, 100°C (drying) b): 3h, 450 °C (Calcination)	a) Zincite structure b) Spherical particles (D ~ 30 nm)	Photocatalyst in photo catalytic degradation	**[74]**

3	a) $Zn(NO_3)_2$	a) 2h, 600°C (Calcinations) b) 240 h, 320 °C (Aging)	a) Wurtize structure; b) Particles diameter: 50nm	Gas sensor	**[75]**
4	a) $Zn(NO_3)_2$, b) NaOH	a) 2 h, 100 °C (Drying)	a) Spherical size = 40 nm		**[76]**
5	a) $ZnSO_4$, b) NH_4HC_3, c) ethanol	a) 100°C (Drying: overnight), b) 300–500 °C (Calcinations)	a) Wurtize structure; b) Crystalline size 9-20 nm; c) Particle size D: ~12 nm d) *BET*: 30–74 m^2/g		**[77]**
6	a) $Zn(CH_3COO_2)$ b) NH_3 aq.	a) 85 °C (Temperature) b) 10h, 6°C (Drying)	a) Hexagonal structure, b) Shape of rods c) Flower-like particles d) L: 150 nm, D: 200 nm		**[78]**
7	a) Micro-sized ZnO powder, b) NH_4HCO_3	a) 2h,25 °C Reaction b) 80 °C (Drying)	a) Hexagonal Wurtize structure b) Flower-like c) Rod-like shape		**[79]**

		c) 1h,350°C (Calcination)	d): D:15−25 nm e) BET: 50−70 m^2/g		
8	a) $ZnSO_4$, b) NH_4OH, c) NH_4HCO_3	a) 30 min, 60 °C in Reaction time b) 12 h, 100 °C (Drying) c) 2 h, 400 °C (Calcinations)	a) Hexagonal structure b) Flake-like morphology c) D: 0.1−1 μm, L: 60 nm		**[80]**
9	a) $Zn(CH_3CO)_2$, b) NaOH	a) Reaction 30 min at 75 °C b) Drying: overnight at room temperature	a) Hexagonal structure b) Flower shape c) L:>800nm;	Antimicrobial activity	**[81]**

The above literature review shows that the co-precipation method is the best for low cost and most feasible method for ZnO nanomaterials with different shapes and sizes. Now, we discuss the ZnO nanomaterials for arsenic removal in the pollutant water.

1.5. Nanomaterials for Arsenic Removal

Arsenic contamination of waters is found common in both toxic and carcinogenic. For arsenic removal in the water, the coagulation, filtration, membrane separation, ion exchange, etc. technologies have been engaged as adsorption method to simple and stable operation. These methods are to easy handle, without added reagents, compacted facilities, and lower cost. Although, these methods for water purification are needed for industrial innovation and gaining more attention worldwide. The nanotechnology is well known to play a vital role for providing fresh and cheap water to encounter personal demands. The nanoparticles and nano-based adsorbents are very efficient to remove the arsenic in the water. Therefore, we have considered ZnO nanoparticles and transition metal doped ZnO nanoparticles for removal of arsenic in the polluted water. Besides this, ZnO nanoparticles have the good photo catalytic properties for removal of arsenic in the polluted water [**80-81**].

1.5.1. ZnO Nanomaterials

Due to wacky qualities like non-poisonous, stability, cheap, high photosensitivity and easily availability etc., the nanoparticles of ZnO materials are broadly synthesized across the world **[82].** Generally ZnO material is replaced with in TiO_2 material, because both have same band gap energy about 3.2eV as well as same photocatalytic process **[83].** The band energy gap of the both materials is same due to the difference of energies between conduction band (CB) and valence band (VB) are similar to each others **[84].** The nanoparticles of ZnO materials have more abilities to adsorb higher arsenic in the earth's water than the nanoparticles of TiO_2 material **[85].** The TiO_2 material is a semiconductor which is not used in water treatment because it is not economical in compare to ZnO material. So,the nanoparticles of TiO_2 material are not possible used at industrial level. Therefore, the ZnO material by co-precipitation method may be probable the replacement of TiO_2 due to the cheapest of synthesised ZnO material **[86].**

The nanomaterials of the Zinc oxide (ZnO) are the excellent and eminent materials for water disinfection applications. ZnO is a non-toxic and low cost material with good thermal stability. The ZnO has a stable Wurtzite structure with lattice parameter values of 'a' is 0.325nm and 'b' is 0.521nm. The zinc oxide shows strongly resist microorganism's property **[87].** Even the very less quantity of zinc oxide appears strong impact in the water disinfection applications. So that's why it is mostly used in the polluted water for disinfection. Zinc oxide is considered as the best antibacterial material due to its stableness in difficult process conditions, and it is also considered as a healthy material for humans as well as animals **[88].**

In addition to this, the zinc oxides have various applications in different areas such as:

- Sunscreens,
- Coatings,

- Absorbent paints of ultra violet light
- Industries of rubber, Pharmaceuticals and food.

The direct and wide band gap of ZnO has special qualities, which is more important in photo catalyst process enhancement in UV-visible region **[89].** Zinc oxide has several functional properties due to its wacky qualities. After study of the several research papers on zinc oxide materials, the zinc oxide has wacky physical and chemical properties of the high stability, electrochemical-coupling coefficient, and light absorption in UV-visible region; and the ZnO having these properties is considered as the multi active materials **[90-91].** Zinc oxide has found in lots of structure with different shape and size along the one dimension, two dimensions and three dimensions. Due to such rich variety of the ZnO structure properties with different methods, its may be useful in a wide range of applications. The ZnO in one-dimension structure exists in the form of nanorods, helix etc. The zinc oxide in two-dimensional structures exists in the form of nanoplates, nanosheet and nanopellets. The ZnO in three-dimensional structure exists in the form of flower shape and snowflakes etc. Generally the nanowires, nanoplates and nanorods have been considered for the antibacterial activity due to the different structure as the key factors of the nanomaterials of ZnO **[92].** As discussed earlier that the different shapes and sizes of the nanomaterials have been used for the potential applications. Now, the transition metal doped ZnO materials have also been used due to variable properties of the doped ZnO materials.

1.5.2. Transition Metals Doped ZnO Nanomaterials

To enhance the photo catalytic activity of the ZnO materials, there are many ways to synthesize ZnO doping especially transition metals. In the literature survey, it has been proposed the cationic dopant (Cu^{2+},Ni^{2+},Co^{2+}), anionic dopant, and rare earth dopant in the ZnO materials for enhancement of the photo catalytic activities. The dopant ZnO nanomaterials make dopant active inside the lattice structure level in the visible region of the light, which decreases the costs of the water treatment. The dopant ZnO with the impurities of the transition metals creates the new energy levels having new photo catalyst properties for the water treatment **[94-95].**

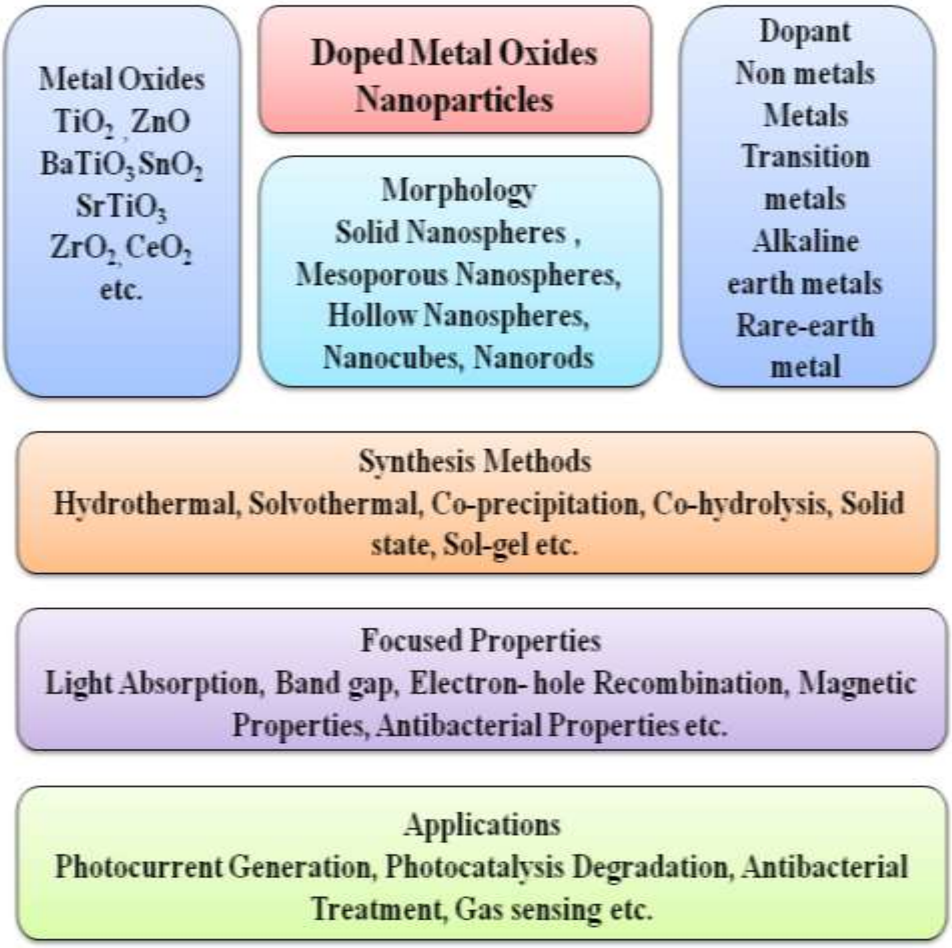


Figure 1.1: Review of the synthesis, properties, and application of doped metal oxide nanoparticles [93].

The photo catalytic activities were examined through the photo degradation of Methylene Blue (MB) in the solar light. It has been observed that, after two hours solar lighting, the solution rest congregation of the MB with different dopant was had Mn =19%, Fe= 63%, Co= 52%, Ni =37%, Cu:ZnO =7%, and ZnO = 81% in the samples. The impact of copper dopant in the samples was found the most significant and degrade within two hours **[96-97].** As (+3) to As (+5) could be oxidized the polluted earth's water. Elimination of the Arsenic by oxidizing As (+3) to As (+5) was reported in many papers and revieved articles. It is significant to get satisfaction of the Arsenic removal form the pollutant water. Adsorption of the Arsenic is mainly dependent upon two factors: first is pH and second is the sample of Arsenic with As (+5) to As (+3) removals at pH value is less than 7 **[40]**. The hydroxyl ion (OH−) as the water molecule absorbent reacts with hole (h+) to produce the hydroxyl radicals (•OH). The dispersed oxygen adsorbed on ZnO upper layer of surface can be changed into the superoxide radical by the induced electron during the photo-catalytic process **[98].** The review of the synthesis, properties, and application of doped metal oxide nanoparticles are shown in the schematic diagram in figure 1.1.

In the photocatalytic oxidation of As (+3) by TiO_2 or ZnO can be oxidized by •OH radicals or directly by h_{VB^+} .The chemical mechanism of photo catalysis oxidation is given below:

$$\mathrm{As(III)} + \cdot\mathrm{OH} \rightarrow \mathrm{As(IV)} + \mathrm{OH}^{-} \tag{1.2}$$

$$\mathrm{As(IV)} + \cdot\mathrm{OH} \rightarrow \mathrm{As(V)} + \mathrm{OH}^{-} \tag{1.3}$$

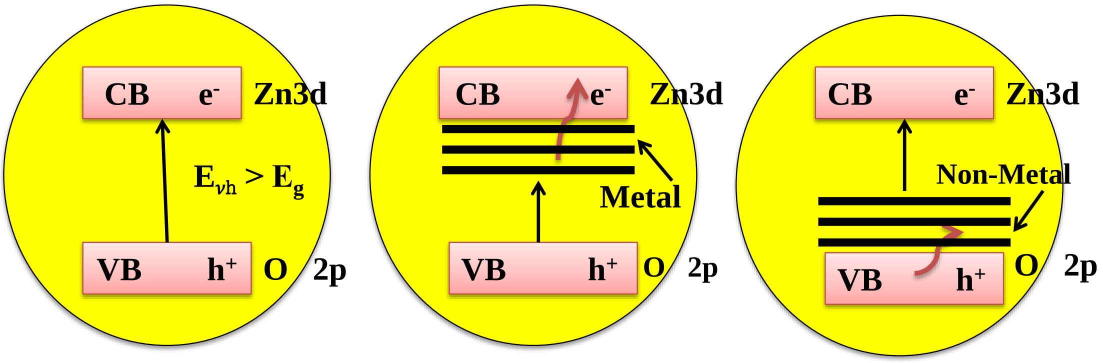
$$\mathrm{As(III)} + h_{VB^+} \rightarrow \mathrm{As(IV)} \tag{1.4}$$

$$\mathrm{As(IV)} + h_{VB^+} \rightarrow \mathrm{As(V)} \tag{1.5}$$

$$\mathrm{As(IV)} + \mathrm{O_2} \rightarrow \mathrm{As(V)} + \mathrm{O_2^{\cdot -}} \tag{1.6}$$

1.5.2.1. Cu doped ZnO Nanomaterials

Doping of copper in ZnO (Cu:ZnO) materials is the fruitful to reform the photo catalyst process.



Pure ZnO **Metal doped ZnO** **Non-metal ZnO**

Figure 1.2: Shows the band gap difference among in pure ZnO, Metal doped ZnO and Non-metal doped ZnO **[101].**

The Cu:ZnO nano-material are fabricated through different synthesis methods to command the band gap of Zinc Oxide. Sol-gel [**99-100**], co-precipitation **[101]** as well as hydrothermal synthesis **[102]** are used in synthesis of Cu:ZnO in photo catalyst process. The Cu:ZnO nanomaterials with 40nm particle size synthesized by co-precipitation method **[103]** and decreasing band gap with increase the ratio of copper. The schematic diagram of the band gap difference among in pure ZnO, Metal doped ZnO and Nonmetal doped ZnO are shown in figure 1.2 **[101].**

The literature survey of the synthesis copper doped ZnO through co-precipitation method has been described for different ways as per requirements. In this method, ZnO & Cu:ZnO were synthesized and done the X-Ray Diffraction (XRD), Ultra-Violet Visible (UV-VIS) spectroscopy characterizations, which are used to identify the optical behaviour of nanomaterials. Due to copper concentration in the ZnO lattice, the value of band gap fall from 3.15eV to 2.92eV **[104]**. They had repoerted that this characterizations of the ZnO & Cu:ZnO nanomaterials are useful for Arsenic removal from water disinfections. Another paper reported impact of copper in ZnO lattice which is also synthesis via co-precipitation method and synthesized nanomaterials characterized by XRD which shows that particle size decreased due to the concentration of copper doping and also discussed to use in various applications like optoelectronics devices **[105].** There are many transition dopants of Mn, Co, Ni, Cu etc., which may be used to enhance the photo catalytic activity **[106].** Co-precipitation synthesis is very desirable method for ZnO and Cu:ZnO nanomaterials because of Wacky qualities of low cost and easy process **[107].**

On the basis of previous studies, there are many parameters of band gap, particle size and shape etc. that govern the photocatalytic process. There are lots of studies on photocatalytic systems for potential applications and reported by varying the significance of the parameters of the nanomaterials [**109].** Photo catalyst process is mainly dependent upon the following factors with respect to the removal of Wastewater ingredients from the pollutant water:

(a) Band gap energy,

(b) Particle size,

(c) pH

1.6 Objective of the dissertation

In this dissertation work, the ZnO nanomaterials are synthesized by low cost method and pre-synthesized ZnO nanomaterials are doped with the cationic, anionic etc. The doped cationic metals in the ZnO nanomaterials may enhance the efficiency of photocatalytic process to remove pollutants from earth's water because the nano-catalysis system based on the photocatalytic may be counterpart of the existing techniques for the removal of trace pollutants/impurities. The solar photo catalysis and artificial ultraviolet light photocatalytic activities may be the ability to water treatment at room temperature and ambient pressure.

As discussed earlier that the photocatalytic process is a technology in which this method is beneficial in water treatment to remove the impurities especially Arsenic ingredient. Therefore, the objective of the dissertation is to examine the XRD, UV-VIS, SEM and EDX characterizations to support the photocatalytic process of different cationic dopant of transition metals like Cu^{2+}, Ni^{2+}, and Co^{2+} within ZnO nanomaterials as the oxidation of Arsenic.

The semiconductor of ZnO nanomaterials have used to synthesis by co-precipitation method, which is one of the best, simplest and low cost method because this method is taken less time, economical, uncomplicated and easy process etc. Therefore, in this dissertation work, we use the co-precipitation method for synthesis ZnO nanomaterials and Cu(x%):ZnO nanomaterials where x is the weight percentage ratio of copper. ZnO nanomaterials is characterize by XRD, SEM and EDX and Cu(x%):ZnO nanomaterials are characterize by XRD, SEM/FESEM, EDX and UV-Visible Spectroscopy.

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CHAPTER-2

Synthesis Methods & Characterization Techniques

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Synthesis Methods & Characterization Techniques

2.1. Synthesis Methods

Now days, the public demand of the materials to be low cost and high feasibility. So, it is only possible by changing the structure of the materials with specific processing of the materials. The changed structure with the certain processing belongs to the Materials Science and Engineering by the materials Scientists. Materials scientists are worked on managing the research to generate ideal materials with good qualities with the high functionality and economical materials than the conventional one. Many ways has been discovered to improve the outcome of the materials by changing structures from micro materials to nanomaterials. Bulk material can be converted into the micro materials/nanomaterials by breaking into tiny particles called ***top-down approach*** while materials are fabricated from the atoms to the micro materials/nanomaterials called ***bottom-up approach***. The process of top-down and bottom-up approaches are represents in figure 2.1.

These two approaches are significant to adopt in the synthesis of the micro materials/nanomaterials having different shapes and sizes **[1]**. The detailed explanation of the top-down and the bottom-up approaches are given below:

2.1.1. Top-Down Approach

In top-down technique, cutting away material from the bulk structure that is similar to a sculptor creates the nano-sized feature or pattern of the materials. Mechanical method is the top-down technique and this technique is the cheapest method to synthesis of nano-structured materials from bulk materials. Ball milling process, top-down technique is the basic methods of synthesis of the micromaterials/nanomaterials. Grinding crushing steps are led in the ball milling process. Another technique is the most popular technique called lithographic patterning technique. In this lithographic patterning approach, the short wavelength light source is used to create the desired micro material/nanomaterials structures.

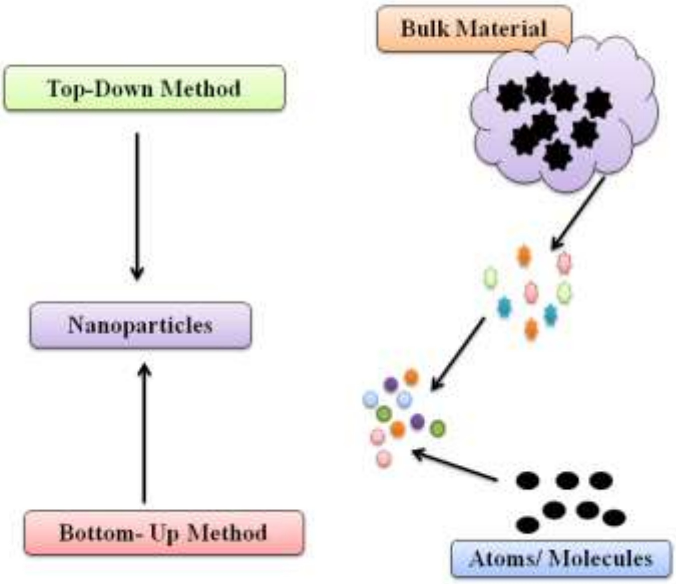

Figure 2.1: Schematic diagram of the top-down and bottom-up approaches [Source: Copy Right Permission from M. Rafique et al., (2017) [**4**]].

Its main advantage is to make the patterns as well as the objects that are created at the desired place; and no further assembling is required. The lithography patterning technique is a highly matured and advanced field in the nanoscience and nanotechnology **[2].** The big issue in this method is created the defects in the structure of material. The others top-down techniques are also used to the desired micro material/nanomaterials structures are:

- High-energy wet ball milling,
- Electron beam lithography,
- Atomic force manipulation,
- Gas-phase condensation,
- Aerosol method,
- Laser ablation method,
- Spray-Pyrolysis method,

The top-down techniques are very expensive methods for synthesizing of micro material/nanomaterials structures. Therefore, the desired micro material/ nanomaterials structures through these methods make the high cost of the materials.

2.1.2 Bottom-Up Approach

All wet-chemical methods are based on bottom–up approach and these chemical methods are Sol-Gel, Sonochemical, Hydrothermal, Co-precipitation, Microwave and Hydrolysis methods [**3**]. In these methods, the nanomaterials are fabricated by atoms-atoms, molecules- molecules and clusters-clusters addition. The selection of synthesis methods decides the size, morphology and crystal structure of the nanoparticles that is needed to the expected characteristics of the nanomaterials **[5]**. The large amount of nanomaterials is synthesized/fabricated through these wet-chemical approaches, but the synthesis of uniform sized nanomaterials particles is very tough to obtain through the wet-chemical methods. But the controlled particle of nanomaterials can be stnthesized in the unique size and shape easily through the wet chemical methods. Although the nanomaterials of the different shapes of nano-rods, nanowires, and nanotubes etc. are found by changing the conditions of reaction mechanisms [**6]**.

Here, we have briefly described some wet-chemical methods of Co-precipitation, Sol-Gel and Hydrothermal method, and these methods are very fruitful in the synthesis of metal oxides because these are low cost and high feasible methods for synthesis of metal oxides nanomaterials compared to other methods. Now next section, we discuss the wet-chemical methods of Co-precipitation, Sol-Gel and Hydrothermal method for synthesis of the nanomaterials.

2.1.2.1. Co-Precipitation Method

The co-precipitation is known for the controlled precipitation method, which is a basic route of wet-chemical method for synthesis of the nanomaterials. In this method, the precursors are an inorganic salt that is decomposed in distilled ionized (DI) water as a solvent to get homogeneous solution. Generally metal oxides are synthesized by this method in open atmosphere; and metal sulphides may also be synthesized in inert atmosphere. Metal oxides synthesis flowchart is given below in figure 2.2 [7].

In this method, the insoluble products are found under the high saturation condition. The nucleation growth of the materials is produced the large number of small particles which are agglomerated to each other. The size, shape and morphology of the products in the Co-precipitation method are affected by Ostwald ripening and agglomeration processes. In the next step, the super saturation condition is the necessary condition to produce precipitation in the wet-chemical method. Besides this, the pH, temperature and concentration of solution are the factors which influence the shape, size and morphology of the nanomaterials **[8]**. After precipitation, the next step is filtration and then washing of the products. In the last, calcinations process is used to change hydroxides into oxides having a finite crystal structures. NaOH, NH_3, NH_4OH, and Na_2CO_3 are used as the precipitating medium in this process. The surfactants work as the avoiding agglomeration and use to control the particle size of the nanomaterials that is fabricated by this method [9].

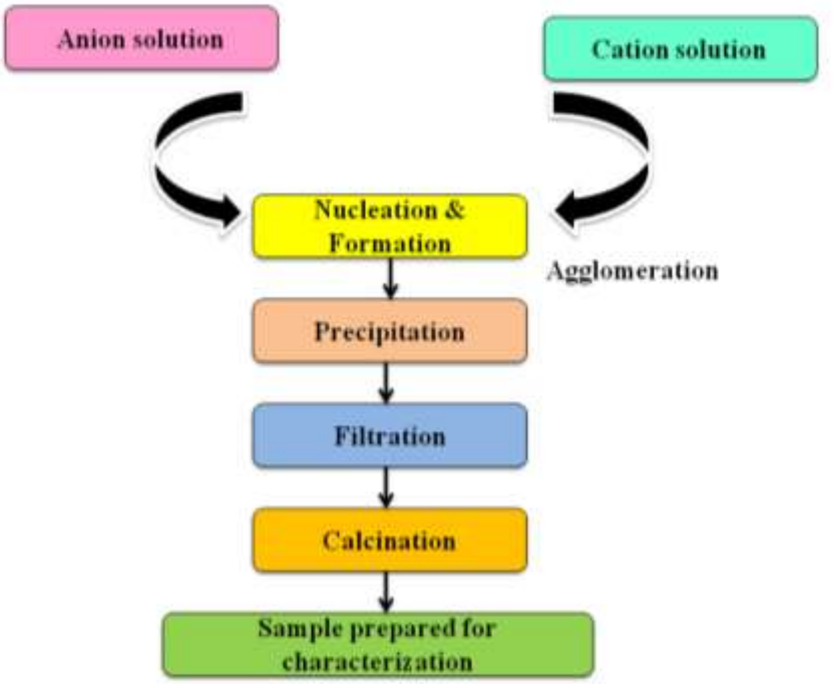

Figure 2.2: Various steps of Co-precipitation method through a flowchart [Source: https://en.wikipedia.org/wiki/Coprecipitation].

The strengths of Co-precipitation method are simple and fast method**,** controllered particle size and composition**,** various possibilities to modify the particle surface state and overall homogeneity**,** low temperature**,** energy efficient. This method does not involve and use of any organic solvents, but this method has limitations due to high time consuming**,** not applicable to uncharged species**,** trace impurities also get precipitated with the product and does not work well if the reactants have very different precipitation rate [10].

2.1.2.2. Sol-Gel Method

In Sol-Gel technique, a liquid is changed into a Gel. So that’s why it is called Sol-Gel method. The main advantages of this method are the excess purity and equal nanostructure achievable of the products at very low temperatures. The Sol-Gel technique is very good technique for synthesis of colloidal nanoparticles from liquid phase.

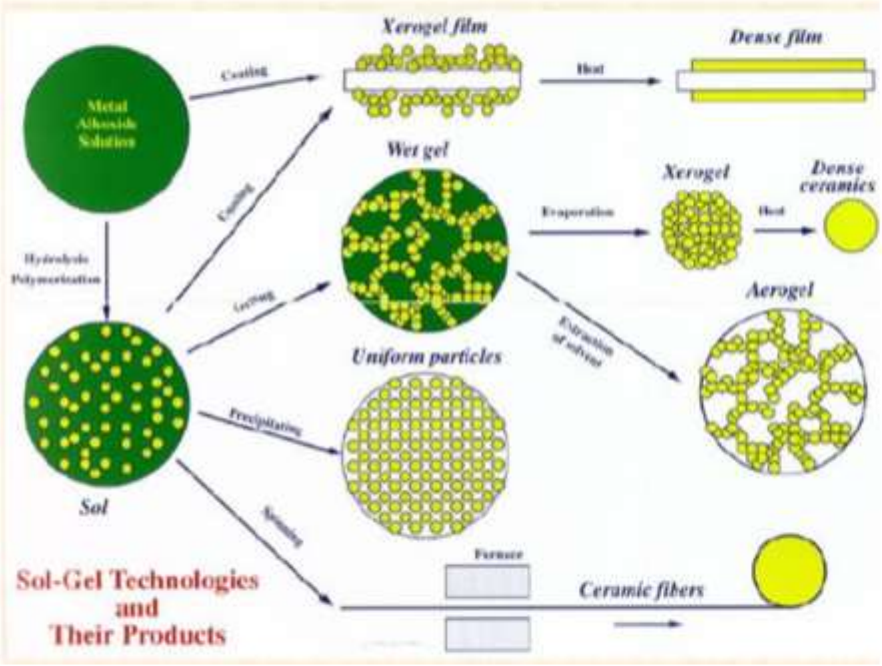

Figure 2.3: Schematic diagram of the Sol-Gel procedure [Source: Copy Right Permission from A. Cannavale “Multifuntional bioinspired sol-gel for architectural glasses” *Building and Environment (Elsevier)(***2010)**].

The Sol form is prepared via hydrolysis and condensation of metal alkoxide precursors. Gel form is typically described as a non-fluid three-dimensional network surrounded by a liquid phase. The Sol–Gel process was observed for the first time in the nineteenth century when silicon based alkoxide began to produce a Gel form upon contact with air. Presently, Sol–Gel processing is the most frequently used technique in materials chemistry. Precursors are the starting materials used to prepare the desired products. The earliest precursors used in Sol–Gel processing were the metal alkoxide. Metal alkoxide were hydrolyzed and condensed to prepare Sol and then Gel forms. The hydrolysis of metal alkoxide is carried out in alcohol solution having a desired amount of water. The general forms of hydrolysis and condensation processes can be described as:

$$\text{Hydrolysis: } MOR + H_2O \rightarrow MOH + ROH$$

$$\text{Condensation: } MOH + XOM \rightarrow MOM + XOH$$

Here, M is a metal; and X is H or R (alkyl group).

Gelation is the process by which the Sol undergoes transition from a liquid solution to a cross-linked Gel, where it can endure elastic stress. After the gelation, the next step is aging of the material. During aging, the structures as well as the properties of the Gel network continuously change till the target density is achieved. Sol–Gel is a versatile technique, which can even be used to synthesize multi-component oxides. This technique can also be used for low temperature syntheses of the nanomaterials [**11-14**]. The whole processes of sol-gel method are shown in figure 2.3.

2.1.2.3. Hydrothermal Method

In Hydrothermal techniques, it is required high-temperature and high pressure to the aqueous solution for producing the crystallized structure [**15**]. Hydrothermal method is based on this premise where the materials are dissolved in water under excessive the temperature as well as the pressure conditions. These dissolved substances are then crystallized to obtain the desired end products in the form of the crystalline. Hydrothermal technique is environmentally benign and it is good control over the particle shape and size. This technique can be used to grow the materials which have high vapour pressures at melting points. Moreover, hydrothermal processing can also be used for producing large and high purity crystals having well controlled compositions.

The cost of instrumentation is so far less in comparison to other advanced techniques. The limitation of the method includes the inability to observe the crystal during its growth **[16]**. The figure 2.4 shows the set-up of Hydrothermal method containing the stainless steel lid, bursting disc, teflon cup and stainless steel shell.

In this chapter, the synthesis of nanoparticles classified into two parts-top to down and bottom-up approaches. Also described of the wet-chemical methods i.e. Co-precipitation, Sol-Gel, Microemulsion, Hydrothermal, Sonochemical and Microwave etc., we have described only three methods briefly having the cost effective and high feasibility of the synthesis of nanomaterials i.e. first was the Co-precipitation method, second was the Sol-Gel and third was the Hydrothermal method. We have selected these methods due to low cost, simple and less time processing etc. compared to others methods.

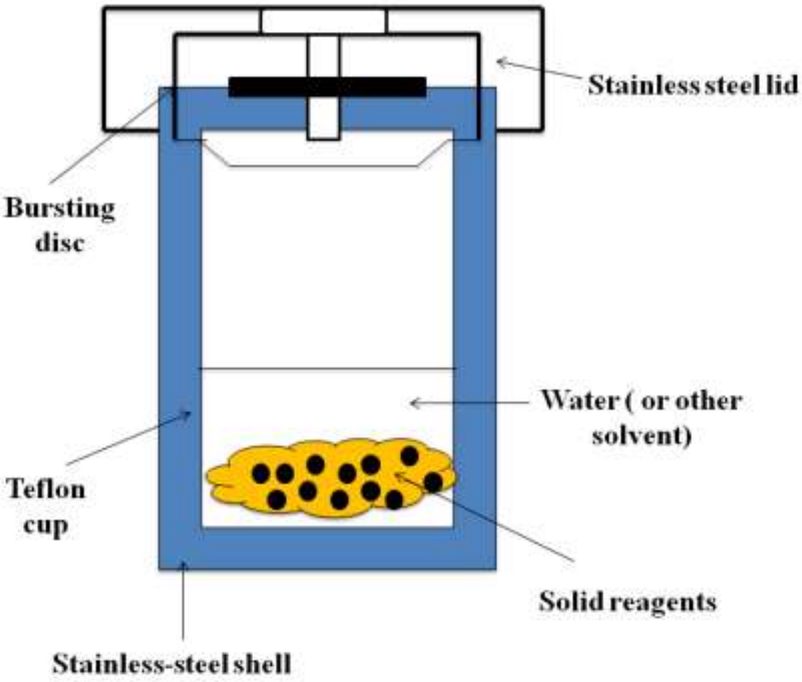

Figure 2.4: Schematic representation of Hydrothermal Experimental setup [Source: https://en.wikipedia.org/wiki/Solvothermal_synthesis]

After the synthesis of the materials, the part of the study is to be the characterizations of the materials. So, we will discuss the characterization techniques in the next section.

2.2 Characterization Techniques

Characterization techniques are used to analysis of the pre-synthesized materials. It is basic process of materials science to investigate the properties of materials based on the internal structures especially shape, size and morphology of the materials. Different–different instruments analyze the materials properties of the elemental composition, morphology, structure information, shape, size as well as chemical and physical property. UV-Visible (UV-VIS) Spectroscopy, X-Ray Diffraction (XRD), and Tunneling Electron Microscopy (TEM) etc. are used to analyze the structural properties. Scanning Electron Microscopy (SEM) / Field Emission Scanning Electron Microscopy (FESEM), X-Ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) etc. are used to observe the surface properties. The table 2.1 gives the summary of the characterization techniques with analyzing properties.

Table 2.1: Some characterization techniques classified are given below **[17].**

Sr. no	**Characterization Techniques**	**Properties to be Analyzed**
1.	X-Ray Diffraction (XRD)	Crystal structure
2.	Energy Dispersive X-ray Spectroscopy (EDX)	Elemental composition
3.	Scanning Electron Microscopy (SEM) / Field Emission Scanning Electron Microscopy (FESEM)	Surface morphology
4.	Atomic Force Microscopy (AFM)	Size (structural properties)
5.	Tunneling Electron Microscopy (TEM)	High resolution image of structure
6.	UV-Visible (UV-VIS) Spectroscopy	Optical properties (e.g. band gap energy)
7.	Fourier Transformation Infra-Red (FTIR) Spectroscopy	Surface composition, functional group
8.	Raman Spectroscopy	Chemical structure and interactions between molecules
9.	X-Ray Photoelectron Spectroscopy (XPS)	Electronic structure

10.	Brunauer–Emmett–Teller (BET)	Specific surface area

In dissertation work, we have focused on the synthesis of the ZnO and Copper doped ZnO for wastewater purification as well as removal of Arsenic from water. There are a number of ways to characterize ZnO and copper doped ZnO nanomaterials. The Scanning Electron Microscopy (SEM) is usually used to investigate the morphology of the materials. The X-ray diffraction (XRD) by using Diffractometer is employed to investigate the structural properties crystal structure of the materials. The composition of the nanomaterials can be analyzed through Energy Dispersive X-ray (EDX) Spectroscopy. The absorption and transmittance spectra are analyzed by UV-VIS spectrophotometer to calculate the optical band gap of the materials. The synthesized ZnO and copper doped ZnO nanomaterials are characterized by different-different instruments to support the photo catalytic process for removable of the pollutants from earth's water, which are described in detailed:

2.2.1. Scanning Electron Microscopy (SEM)

SEM produces highly magnified and resolved images of a material when a highly focused electron beam is scanned on the surfaces of the material. The SEM gives the information of the material having chemical composition and their topology when highly focused electron beam is interacted with atoms of the materials. The two-dimensional scanning beam of the SEM on the surface of the materials is used to the image formation by collecting the secondary and backscattered electrons.

The upper surface area of the sample is scanned by the electron beam where the high energetic electron lies through the electron gun. The secondary and backscattered electrons are the part of electron microscopy. Highly energetic electron falls on sample, and the interaction between the arrangements of the atoms with beam of electrons is used to investigate the surface of sample. The image of sample's morphology is visualized on the computer screen through the secondary and backscattered electrons **[18]**. Power supply, vacuum system, cooling system and vibration free floor, ambient electric and magnetic fields room's infrastructure are requirement for the SEM.

Electron gun, lenses, scanning coils, detectors to collect signals (secondary and backscattered electrons as well as X-ray), sample Stage, display/data output devices are the basic components of the SEM. Figure 2.5 represents the se up of SEM.

Figure 2.5: Scanning Electron Microscope (JSM 6490) set-up and microscopy procedure [Source: Copy Right Permission from USIC, BBAU, Lucknow (2020)].

When an electron beam hits the sample, many different types of signals are generated which are eventually used to observe or analyze morphology/ topology of the specimen/material. These signals include secondary electrons, backscattered electrons, Auger electrons, X-rays. The SEM uses for reveal morphology of surface details of the material**,** high-resolution images**;** detect compositional differences and elemental microanalysis (EDX) as well as particle characterization.

There are many advantages of the SEM with high resolution image**,** fast recognition of existing elements and supported with other tools like EDAX; but it has also some limitations with need of typically high vacuum**,** destroy sample for further analysis and size need to cut the specimen etc. **[19].** So, with these limitations of SEM, the researchers are used the SEM to characterize the morphology of the materials. To investigate the shape and size as well as the morphology, the field emission scanning electron microscopy (FESEM) is used for high resolution of the image of the surface morphology.

2.2.1.1 Field Emission Scanning Electron Microscopy (FESEM)

The Field Emission Scanning Electron Microscope (FESEM) is a technique to use as a microscopy which is similar to the set-up of SEM. The difference between FESEM and SEM is only the electron gun, which is led in the system. The FESEM, JSM 7610F, consists the Schottky field Emission electro gun that makes use of electric field emission to lower the work function and increased the thermionic emission of tungsten. The field emission gun produced an electron beam and greater current density or brightness. The FESEM of JSM 7610F is equipped with the Gentle Beam mode that gives high resolution images even the low accelerating voltage from 100V to 3.9 kV without damaging the specimen surface. Figure 2.6 shows the FESEM set up. The FESEM is works on schottky emission effected by high electric field is employed to heated metal surface. A tungsten single crystal (tip radius – few hundred nm) coated with ZrO acting as cathode. ZrO coating reduces the work function to enhance the emission current at low cathode temperature. Thermo electrons are shielded from emitter by applying negative voltage to the suppressor electrode. The advantages of FESEM, electron beam current is highly stable because emitter is placed in ultra high vacuum of the order of 10-7 Pa and it produces larger probe current **[20].**

2.2.2 Energy Dispersive X-ray Spectroscopy (EDS or EDX)

Energy dispersive spectroscopy can be abbreviated as EDS as well as EDX. Occasionally, it is termed energy dispersive X-ray microanalysis (EDXMA). The elemental composition of specimen or sample is investigated by this technique. The sample may be of any form such as, solid powder, solid thin films and liquid sample etc. **[21].**

The SEM set up has also included the EDX with extra detector of X-Ray. EDS or EDX is part of X-ray Fluorescence (XRF) spectroscopy where the ejected X-rays from the sample in response to being interact with electrons/charge particles are analyzed to investigate of a sample when the interactions between EM radiation and sample. The basic principle of the EDX is that every atom has a special atomic structural and it is allowed X-rays characteristic of an elements of atomic structure to be recognized specially when the interactions between EM radiation and sample [**22**]. The electron beam excites an electron in an inner shell and emits electron from the inner shell when generating an electron hole by absorbing the energy. The X-rays energy is released from a sample when filled up the hole with the outer electrons which can be examined through EDS spectrometer. **[23].** Figure 2.7 is shown the basic principle of the EDX for elemental analysis of the sample/material.

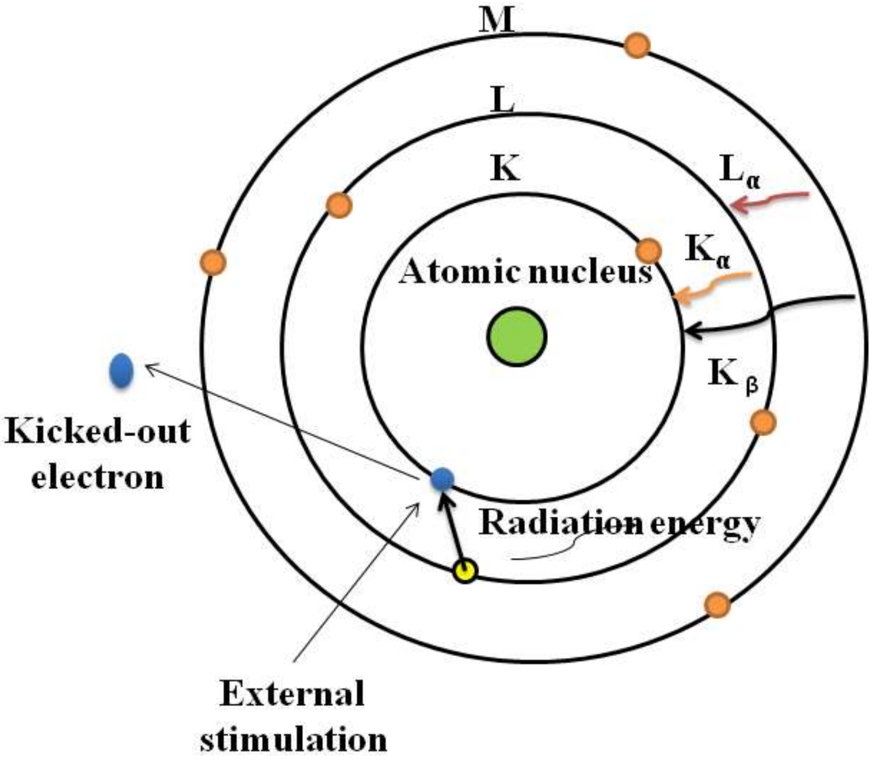

Figure 2.6: Basic principle of EDX for elemental analysis of the sample/material [Source: https://en.wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy].

The EDX is generally used to investigate the composition of elements in the specimen and it is also given the percentage of oxide of the elements in the sample/material **[24, 25].**

2.2.3 UV-Visible Spectroscopy

It is an excellent physical tool where ultraviolet, visible and near infra red wavelength spectrum is considered for investigation of the optical properties of the incident light. To study the optical properties of the incident light with the sample, the Beer-Lambert law is used to calculate the absorption of the light in terms of the length of the sample and concentration of material in the sample. Generally, the wavelength of ultra violet region in the electromagnetic spectrum is 300-400nm, visible region lies in between 400-765nm and Near infra region existing between 765-3200nm. This spectroscopy is used to study the absorption of the liquids, gases as well as solids through radiation [10]. The absorbance of Ultra Violet light or Visible light through compounds gives different-different spectra.

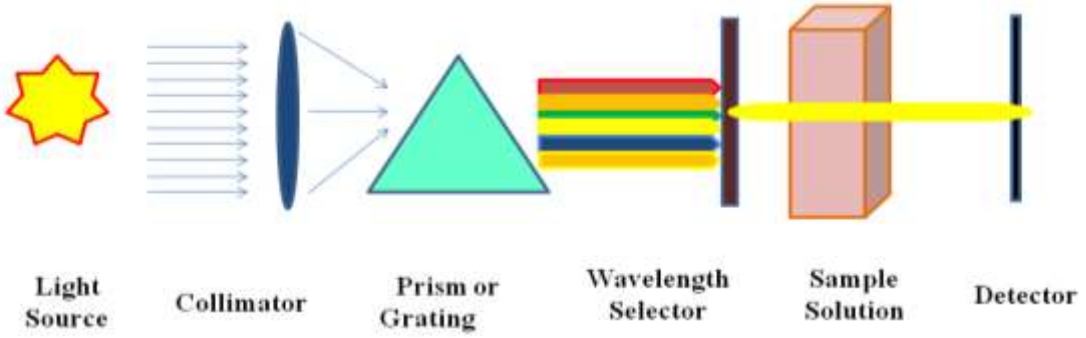

Figure 2.7: UV-Visible spectrometer set-up shown in figure [Source: https://orbitbiotech.com/molecular-analysis-using-uv-visible-spectroscopy-spectroscopy-uv-absorption-reflection-spectra-electromagnetic-radiation]**[27].**

The basic principle of the spectroscopy instrument is collision of light with specimen. When photon energy is falls on specimen, the electrons may be excited from ground state and reached at high energy state. Due to absorbance of light, it shows excitement photons and sometimes it shows de-excitement. After this process, the revealed spectra are observed. It is more significant that the energies difference of ground and higher state is equivalent to the UV-visible radiation **[28].** The working mechanism of UV-visible spectrometer is shown in figure 2.8. The UV-Vis spectroscopy is used to calculate the band gap of compounds using absorption spectra of the UV-Vis spectroscopy which is based on the Tau-plot **[26]**.

2.2.4 X- Ray Diffraction (XRD)

By accidentally, the X-ray was invented by Wilhelm Roentgen and he named it as X-ray and also known as Roentgen rays. After the discovered the X-ray diffraction in crystals by Max von Lau, the X-ray became popular in the crystallographic study of the materials. The wavelength of the X-ray is scaled from 10^{-7} - 10^{-15} m. X-ray diffraction (XRD) characterization is fruitful to analysis the crystalline materials. It gives information about structures of shapes, phases, orientations of crystal, and defects in crystals etc. **[28]**. Crystal structure and inner structures of many solids are investigated by XRD patterns. There are three methods in X-ray diffraction techniques, which are given below:

(a). Laue Method

a) Back-Reflection Laue Method

b) Transmission Laue Method

(b). Rotating crystal Method

(c). Powder Method

The basic principle of the X- ray diffraction (XRD) is based on constructive interference of monochromatic X-ray and a crystalline sample. As the wave incident on the layered of the material, the lattice parameter of the materials is equivalent to the wavelength of the incident X-ray. The diffracted X-ray from different inter planner produces the diffraction. The Diffractometer device obtains XRD pattern, which contains a cathode ray tube, which is a source of X-ray generation and filter. The X-ray generation is used to generate monochromatic light and filters are correlated to focus and directed towards the sample produced constructive interference when condition satisfies the Bragg's law. The difference of path between two rays is found 2d Sinθ and this path difference must be multiple integer of the incident wave's wavelength. Incident rays are interacted with the sample and generated constructive interference and the conditions are given below:

$$n\lambda = 2d_{hkl}\,\mathrm{Sin}\theta_{hkl} \qquad (2.1)$$

where, n = integer; λ = wavelength of the X-rays; d = interplanar spacing generating the diffraction for (hkl) plane and θ =the diffraction angle.

The equation (2.1) is called Bragg's law and the diffraction patterns are shown in figure 2.9.

The Bragg's law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample **[29].** These are some strength of XRD pattern, which are identification of an unknown mineral determination very fast, less time for sample preparation where the time is less than 20 minutes, ease availability of XRD and gives straightforward data interpretation. Figure 2.10 represents the X-ray Diffractometer set-up.

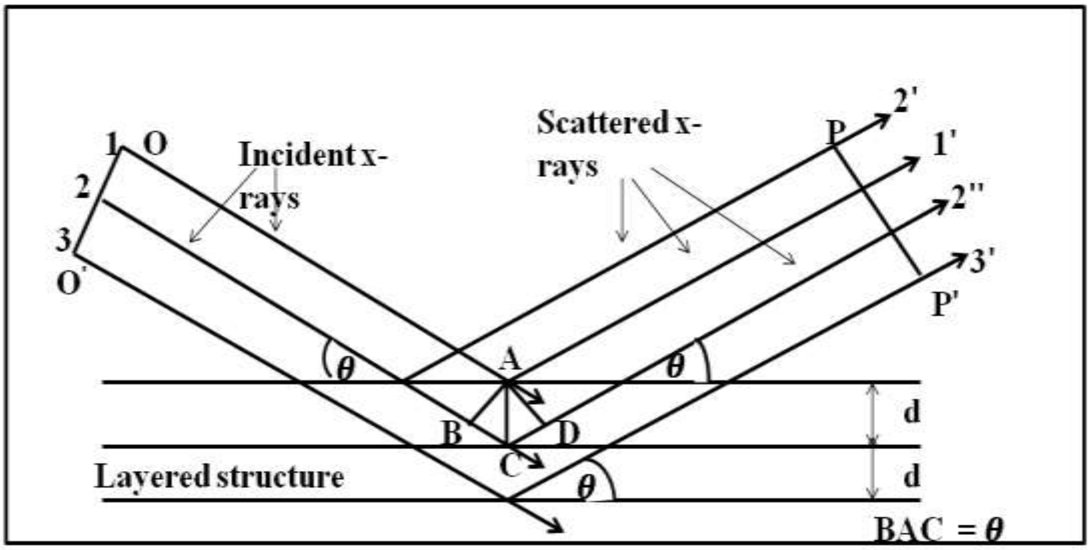

Figure 2.8: X-Ray diffraction from layered structure of the crystals [Source: J. Epp "Characterization using Nondestructive Evaluation Methods" *Electronic and Optical Materials* (Elsevier) (2016)].

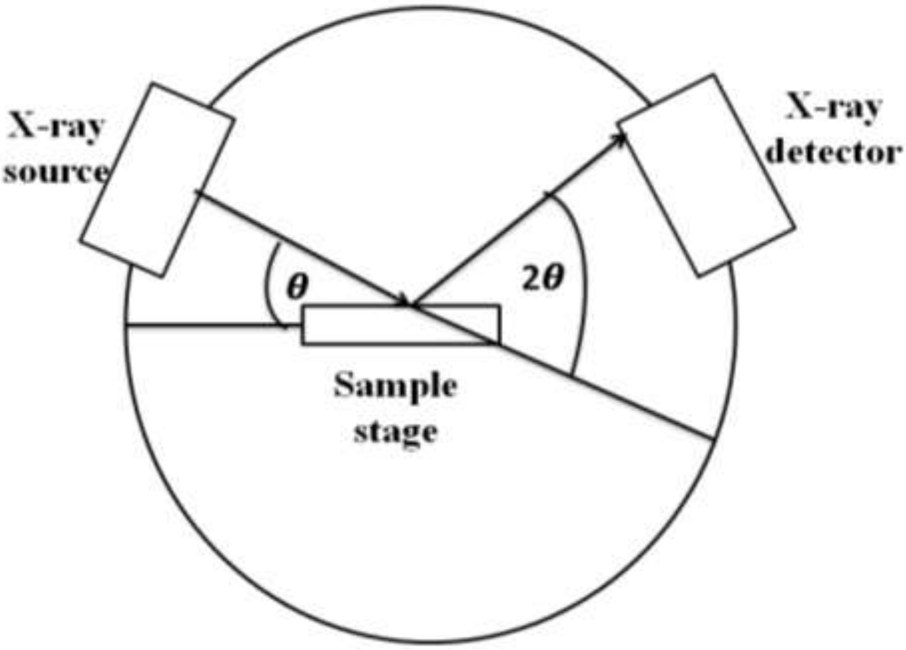

Figure 2.9 X-ray Diffractometer set up [Source: S. Reza et. al., "Evaluating the structural properties of bioactive-loaded nanocarriers with modern analytical tools" *Characterization of Nanoencapsulated Food Ingredients* (2020)]

After the synthesis of nanomaterials of ZnO and Cu:ZnO, the characterization techniques are used to analysis the structural analysis, shape, size, morphology etc. of nanomaterials. There are many characterization techniques to analysis the nanomaterials. However, we need few characterizations only for the requirement of the research work with the photo catalytic process for wastewater purification as well as removal of Arsenic from water especially ZnO and Copper doped ZnO nanomaterials.

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CHAPTER-3

Results and Discussion

CHAPTER-3

Results and Discussion

As discussed in the Chapter-2 of the synthesis and characterization techniques, we have adopted the co-precipitation method for synthesis of the metal oxides due to it is the best and cheapest method. So, zinc oxide (ZnO) nanomaterials and copper doped zinc oxide (Cu:ZnO) nanomaterials are synthesized by the co-precipitation method. For synthesis of the ZnO and copper doped ZnO, dehydrated zinc acetate ($ZnC_4H_6O_4$), aqueous solution of sodium hydroxide [NaOH (aq. Solution)] and dehydrated copper acetate [$Cu(CH_3COO)_2$ are taken as the precursors solutions.

In the first study of pure zinc oxide (ZnO) nanomaterials, three samples (A, B and C) are synthesized with varying the annealing temperatures. In the second study of copper doped zinc oxide (Cu:ZnO) nanomaterials with different weight percentage of copper, two samples have been synthesized: firstly synthesized material is copper with 1% doped ZnO nanomaterials and secondly synthesized material is copper with 2% doped ZnO nanomaterials.

Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) are used to investigate the morphology and structural properties of the pre-synthesized ZnO and copper doped ZnO nanomaterials. Energy Dispersive X-ray (EDX) Spectroscopy is used to analyze the composition of the nano-material. UV-VIS spectrophotometer is used to calculate the optical band gap of the materials by absorption spectra of the copper doped zinc oxide (Cu:ZnO) nanomaterials.

On the basis of the analysis of XRD, UV-VIS, SEM and EDX characterizations of the pre-synthesized pure ZnO and copper doped ZnO nanomaterials, we propose the cationic dopant of copper metals within ZnO nanomaterials for the photocatalytic process. The photocatalytic process of pre-synthesized ZnO and copper doped ZnO nanomaterials are proposed for removal of Arsenic from water.

3.1. Synthesis of Pure ZnO and Copper Doped ZnO (Cu:ZnO) Nanomaterials

We discuss the synthesis process of the pure ZnO and copper doped ZnO nanomaterials by co-precipitation method, which is the best and the cheapest method for synthesis of the zinc oxide and doped zinc oxide nano-materials.

3.1.1 Zinc Oxide (ZnO) Nanomaterials

Synthesis of the pure Zinc Oxide (ZnO) nanomaterials was done by the co-precipitation method, which is simple, best and cheapest method for synthesis of the metal oxide nano-material. For synthesis of Zinc Oxide (ZnO) nanomaterials by the co-precipitation method, 05gm zinc acetate dehydrated ($ZnC_4H_6O_4$) was dissolved in 50ml of deionized (DI) water. A homogenous colorless solution was obtained. Another solution of 2gm of NaOH (aqueous solution) was dissolved in a 25ml of DI water.

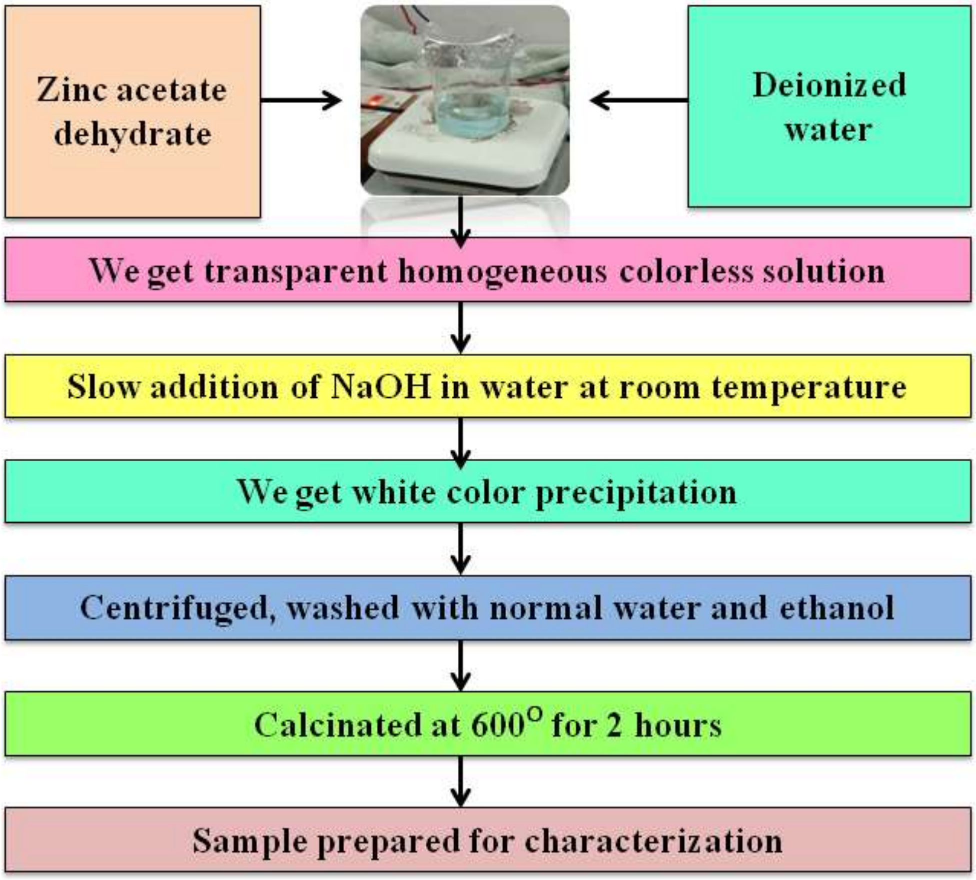


Figure 3.1: Schematic flow chart diagram for synthesis procedure of pure zinc oxide (ZnO) nanomaterials.

After this, the diluted NaOH aqueous solution was gradually added in the homogenous colorless solution. Then a white color precipitation was obtained. Subsequently, the white color precipitation was centrifuged and washed with normal water as well as ethanol. The whole synthesis work was done at room temperature. The filtered and dried the white color precipitation was done the calcination at 600^0C for 02 hours. The whole synthesis process of Zinc oxide nanomaterials is shown in figure 3.1 [**1**]. The pre-synthesized ZnO nano-material is divided into three samples with the different annealing temperatures. XRD, SEM, and EDX characterizations are used to analyze these all pre-synthesized ZnO nano-material.

Now we have synthesized the cationic dopant of copper metals within ZnO nanomaterials with different weight percentage of copper by the co-precipitation method.

3.1.2 Copper Doped Zinc Oxide (Cu:ZnO) Nanomaterials

The pre-synthesized ZnO nanomaterials were doped with different weight percentage of copper for enhancement of the photocatalytic property. The doped copper ZnO nanomaterials have potential application in the removal of the Arsenic from water.

In the coming sections, we synthesize copper doped zinc oxide nanomaterials with the different weight percentage of copper metal [**1**].

3.1.2.1 1%Copper Doped Zinc Oxide (Cu (1%):ZnO) Nanomaterials

The copper doped zinc oxide (Cu:ZnO) was synthesized with the different weight percentage ratio of copper metal by the co-precipitation method. In this method; 4.3466gm by weight of zinc acetate dehydrated ($ZnC_4H_6O_4$) and 0.0403gm copper acetate dehydrated ($Cu(CH_3COO)_2$) was dissolved in 50ml of the DI (distilled water). The obtained solution was gradually added with an aqueous solution of the 02gm of NaOH in 25ml of deionized (DI) water. Subsequently, a white bluish precipitation was obtained and it was centrifuged and washed with normal water as well as ethanol. All the synthesis works were done at room temperature. The dried precipitation was calcinated at 600^0C for 2 hours. Figure 3.2 represents the whole process of 1% copper doped zinc oxide (Cu(1%):ZnO) nanomaterials. After these whole procedures, the outcome compound was to be 1% copper doped zinc oxide (Cu(1%):ZnO) nanomaterials and this pre-synthesis Cu(1%):ZnO nanomaterials is analyzed with the XRD, UV-VIS, SEM and EDX characterizations.

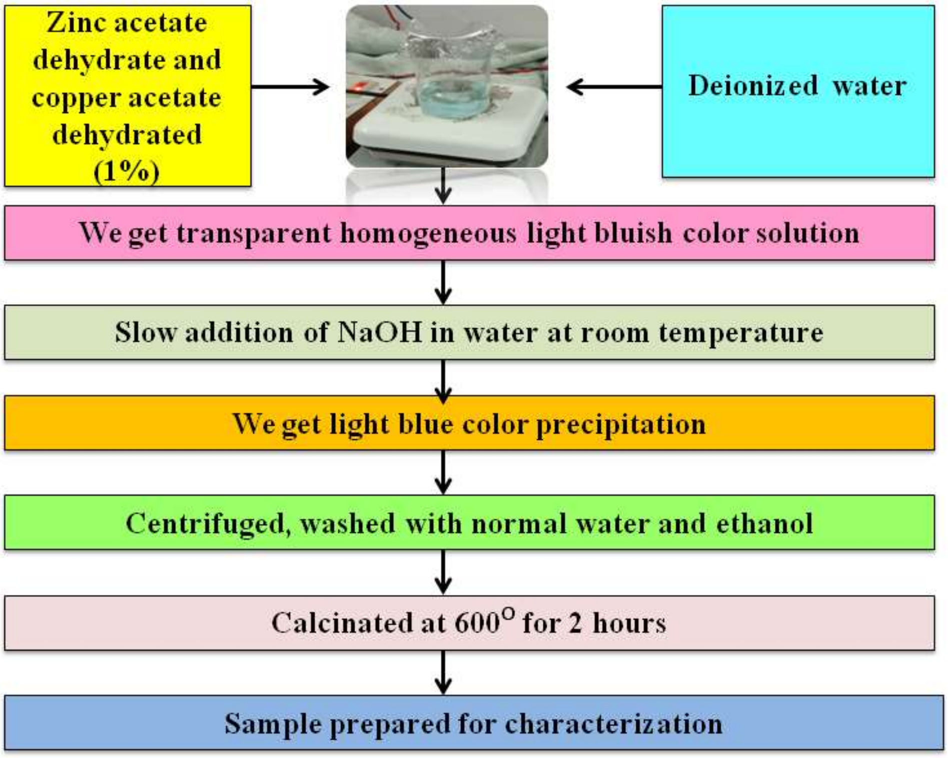


Figure 3.2: Schematic flow chart diagram for synthesis procedure of 1% copper doped zinc oxide (Cu (1%):ZnO) nanomaterials.

3.1.2.2 2%Copper Doped Zinc Oxide (Cu (2%):ZnO) Nanomaterials

Similar procedures were employed for preparing 2% copper doped zinc oxide (Cu(2%):ZnO) nanomaterials by the co-precipitation method. In this process; 4.3023gm of zinc acetate dehydrated ($ZnC_4H_6O_4$) and 0.0799gm copper acetate dehydrated ($Cu(CH_3COO)_2$) was dissolved in 50ml of deionized (DI), and a bluish solution of copper doped zinc oxide (Cu(2%):ZnO) nanomaterials was obtained. The gradually addition of the aqueous solution which was prepared of the 2gm of NaOH (aqueous solution) in 25ml of deionized (DI) water was mixed with the bluish solution of copper doped zinc oxide (Cu(2%):ZnO) nanomaterials. All the synthesis was done at room temperature.

Subsequently, a white bluish precipitation was found and this solution was centrifuged and then wet precipitation was washed by the distilled water as well as ethanol. The dried precipitation was calcinated at 600^0C for 2 hours. The whole process of Cu(2%):ZnO nanomaterials is represented in figure 3.3.

The doped copper transition material with the different weight percentage ratio of copper metal in the pre-synthesized ZnO nanomaterials are used to analyze by XRD, SEM, EDX and UV-Visible characterizations. The UV-Visible spectroscopy is used to study for reducing the band gap of the semiconductor ZnO nanomaterials as well as the enhancement of the photocatalytic property [1].

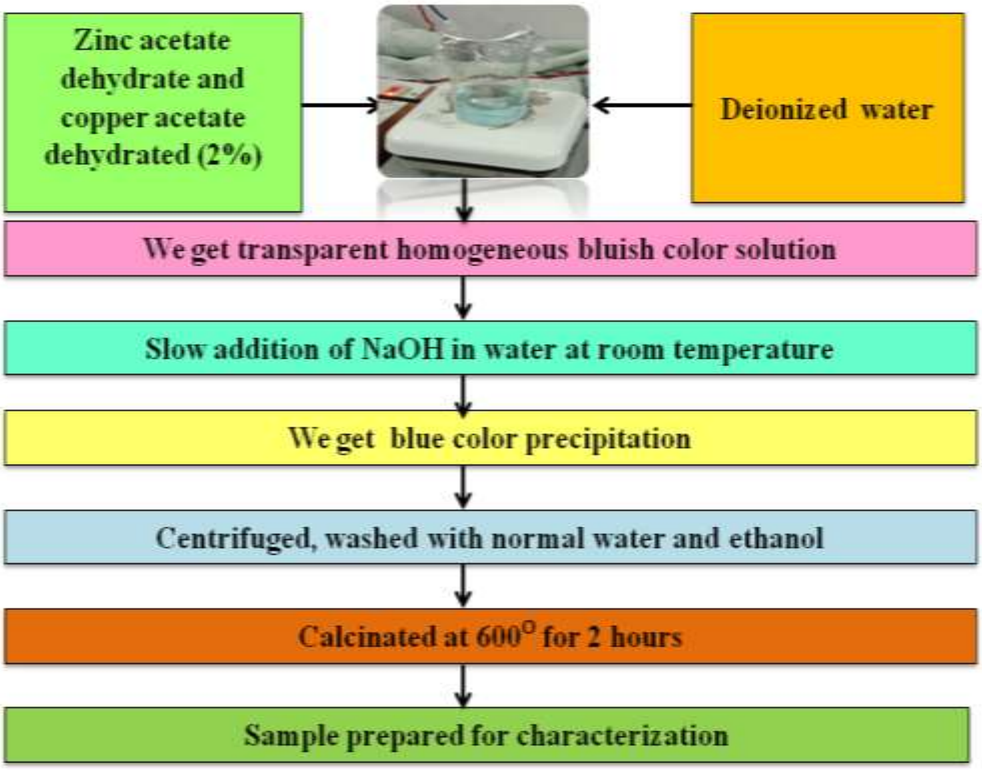


Figure 3.3: Schematic flow chart diagram for synthesis procedure of 2% copper doped zinc oxide (Cu(2%):ZnO) nanomaterials.

In the next section, we discuss and analyze the all the pre-synthesized zinc oxide (ZnO) nanomaterials by the X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) spectroscopy characterizations. However the copper doped zinc oxide (Cu:ZnO) nanomaterials with the different weight percentage ratio of copper metal are analyzed by the X-ray diffraction (XRD), UV-Visible (UV-VIS) spectroscopy, Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) spectroscopy characterizations.

3.2 Characterization of Pure ZnO and Copper Doped Zinc Oxide (Cu:ZnO) nanomaterials

3.2.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is used to analyze the average crystalline size, crystalline structure and lattice parameter of the zinc oxide (ZnO) nanomaterials. The XRD is also used to analyze the structure of copper doped ZnO nanomaterials.

3.2.1.1 X-Ray Diffraction (XRD) of ZnO Nanomaterials

The synthesized ZnO powder by co-precipitation method was characterized the XRD characterization. The XRD characterization was performed by the X-ray Diffractometer (*X'Pert MRD*) in the diffraction ranges of angle $20° \leq 2\theta \leq 80°$, and the source monochromatic CuK$_\alpha$ radiation with wavelength λ = 1.5418A^0. Figure 3.4 shows the XRD patterns of pure ZnO (in green color), calcinated ZnO at 600^{0}C (in red color) and 800^{0}C (in blue color) in the open atmosphere [**2**].

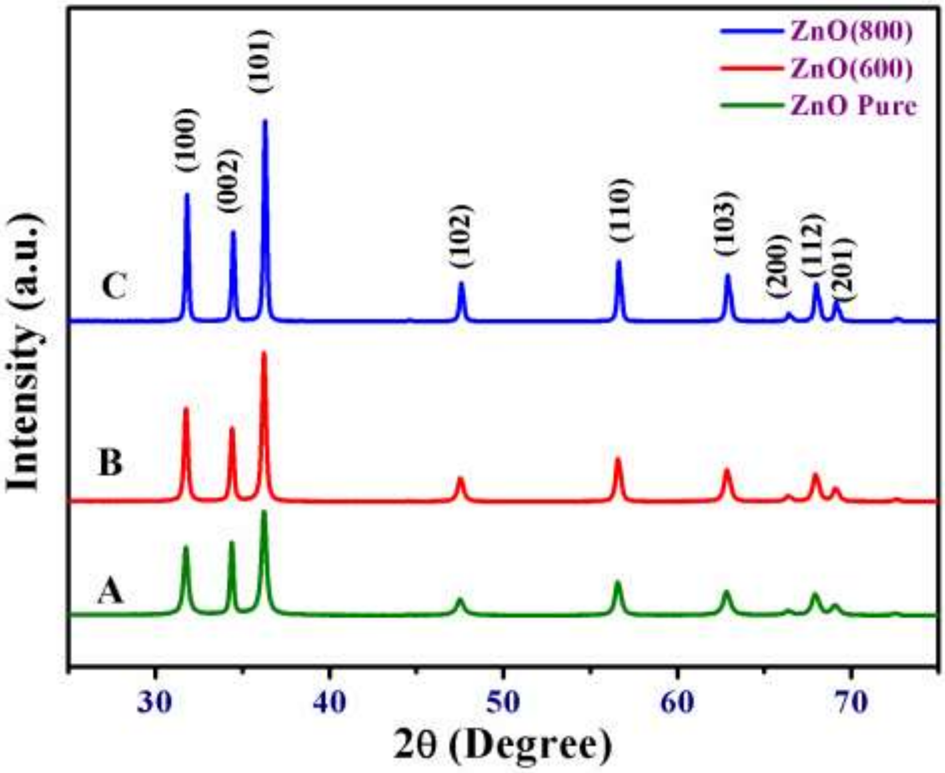


Figure 3.4: XRD patterns of (a) room temperature (A sample) (b) 600^{o}C (B sample) and (c) 800^{o}C (C sample) of pure ZnO nanomaterials [**2**].

The diffraction peaks of ZnO nanomaterials correspond to the indices (100), (002), (101), (102), (110), (103), (112) and (201) planes. The XRD patterns of ZnO nanoparticles (NPs) were calcinated at different temperatures confirm that all peaks shows the Wurtzite structure of ZnO as shown in JCPDS card no. 36-1451. The $2\boldsymbol{\theta}$ values are located at 31.7518^{o}, 34.4014^{o} and 36.2366° for strong peaks of the crystal planes (100), (002) and (101) lines are shown in the figure 3.4 (a), (b), and (c) respectively. There is no identified the other impurity peaks in crystalline material of the ZnO. However, the diffraction peaks become stronger and sharper when the calcination temperatures increase. Such properties are also improved crystalline nature of the material.

The average crystallite size, pure ZnO and calcinated at 600^{0}C ZnO nanomaterials, is found same i.e. 28.15nm and the average crystalline size of the calcinated at 800^{0}C ZnO nanomaterials is found 22.54nm which were calculated by Debye Scherer formula as the precursor of zinc acetate dehydrated. After study the all possess of ZnO nanomaterials, lattice parameters of the pure ZnO nanomaterials are calculated and found a=0.3248nm and c=0.5205nm [3].

3.2.1.2 X-Ray Diffraction (XRD) of Copper doped ZnO Nanomaterials

The Diffractometer (*D8 Advance Bruker*) was used to characterize the copper doped zinc oxide samples. The obtained results of XRD pattern of undoped ZnO nanomaterials and copper doped ZnO nanomaterials are shown in figure 3.5 (a,b). The range of diffraction angle ($2\boldsymbol{\theta}$) is taken from 20^{0} to 80^{0}. The figure 3.5 show the peaks (indices) at 31.79° (100), 34.51° (002), 36.33° (101), 47.52° (102), 56.61° (110), 62.82° (103), 66.40° (200), 67.98° (112), 69.12° (201) ,72.60° (004) and 76.98° (202) for Cu doped ZnO nanomaterials.

By analyzing the XRD patterns of the Cu doped ZnO nanomaterials, the diffraction peak of doped copper in Cu (2%):ZnO nanomaterials was only found with the plane (311) that is shown clearly in figure 3.5 (b). The reason behind this is the increment of copper percentage up to 2% in ZnO nanomaterials i.e. the cooper plane is (311). The structure of ZnO is Wurtzite and the structure of copper doped ZnO is tripod type [4]

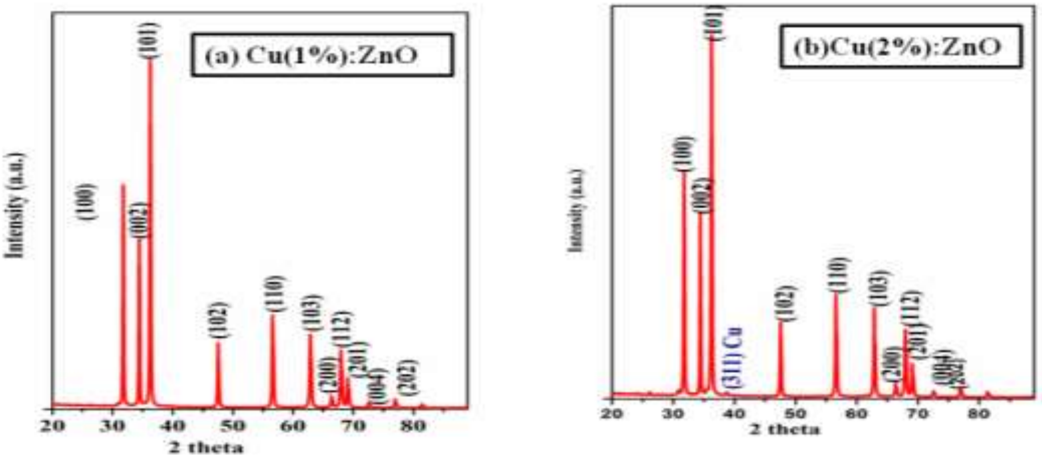


Figure 3.5: XRD patterns of (a) Cu(1%):ZnO nanomaterials and (b) Cu(2%):ZnO nanomaterials

3.2.2 Scanning Electron Microscopy/Field Effect- Scanning Electron Microscopy/ Energy Dispersive X-ray Analysis (FE-SEM/EDAX)

In this section, we have analyzed the surface morphology and the chemical composition of the ZnO nanomaterials as a pure ZnO nanomaterials and the ZnO nanomaterials at 600^{o}C and 800^{o}C annealing temperatures. Then, the pure ZnO nanomaterial is doped with the different weight percentage ratio of copper metal in the pure ZnO nanomaterials.

3.2.21 Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis of ZnO Nanomaterials

Figure 3.6 show the SEM images from SEM (*JEOL Ltd.*) was taken the image of the ZnO nanomaterials of surface morphology of the ZnO nanomaterials and the EDX analysis of the constituent percentage elements of ZnO nanomaterials on glass substrate, which was prepared a thin film of the synthesized ZnO powder by master blade method.

The SEM analysis shows that the morphology of ZnO nanomaterials is spherical and short-rod shape, and there are no more differences in the shape of pure ZnO nanomaterials and calcinated ZnO nanomaterials at different temperatures. The surfaces of the film are rough and micro-porous which helps to absorption the photons at the obtained energy band gap such ZnO nanomaterials may be used in solar as well as water purification applications. The EDX analyses were done at atomic scale, which are shown in the Table 3.1 [5].

Table 3.1: EDX analysis of ZnO nanomaterials at different calcinated temperatures [**1**].

Elements present in the pure ZnO	**Room temperature (A sample)**	**Calcination 600^{o}C Temp. (B sample)**	**Calcination 800^{o}C Temp. (C sample)**
Zinc (Zn)	26.30%	36.98%	30.01%
Oxygen (O)	73.70%	63.02%	69.99%
Total percentage of Zinc and Oxygen	100%	100%	100%

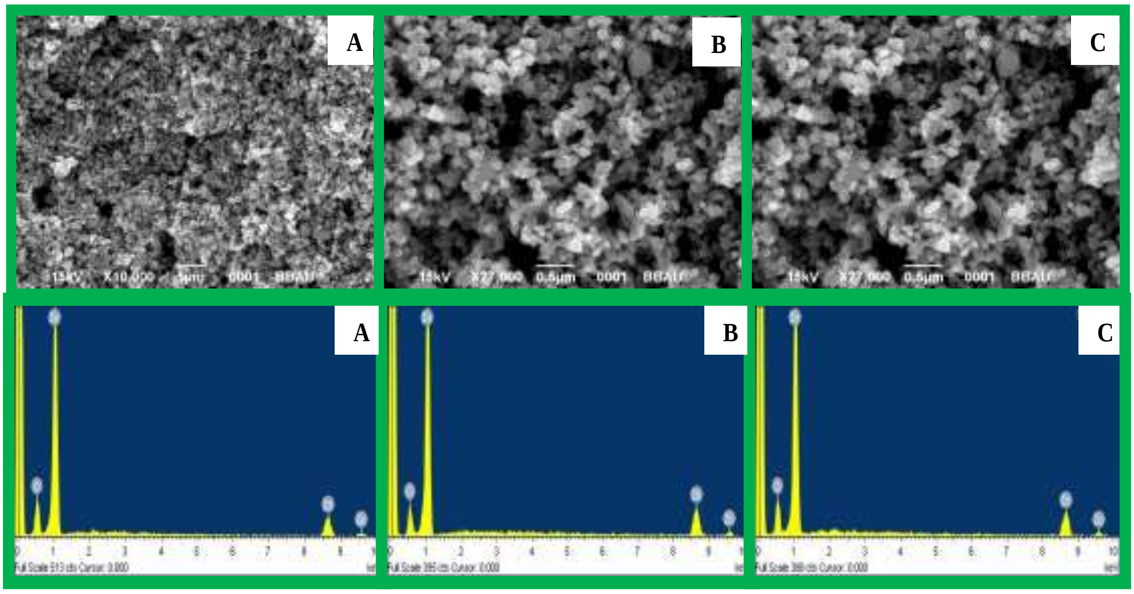


Figure 3.6: SEM and EDX images of A, B & C samples at room temperature, 600^{0}C and 800^{0}C calcinated temperatures respectively of pure ZnO nanomaterials [**1**].

The strong peaks are observed for Zinc (Zn) and Oxygen (O) element. The peaks of the Zn and O in the elemental constitution of the A sample i.e. pure ZnO nanomaterials are found atomic percentage 26.30% and 73.70% respectively. This study were confirmed the formation of pure ZnO nanomaterials in the co-precipitation method without any surfactants.

3.2.2.2 Field Effect Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis of ZnO Nanomaterials

The SEM images of the Cu:ZnO nanomaterials was taken by SEM (*JSM 7610F*) for investigation of surface morphology. The surface structure and growth of nanoparticles of pure ZnO was investigated by SEM characterization, and doped Cu(1%):ZnO and Cu(2%):ZnO nanoparticles were investigated by FE-SEM characterization.

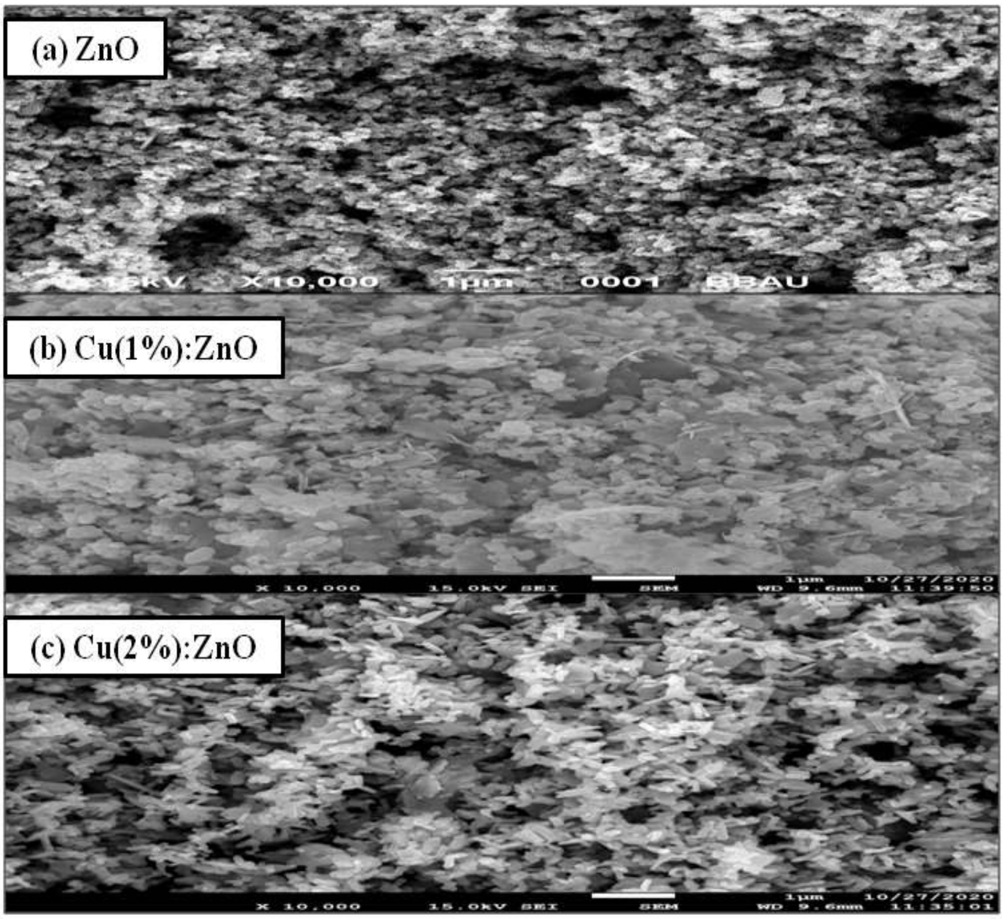
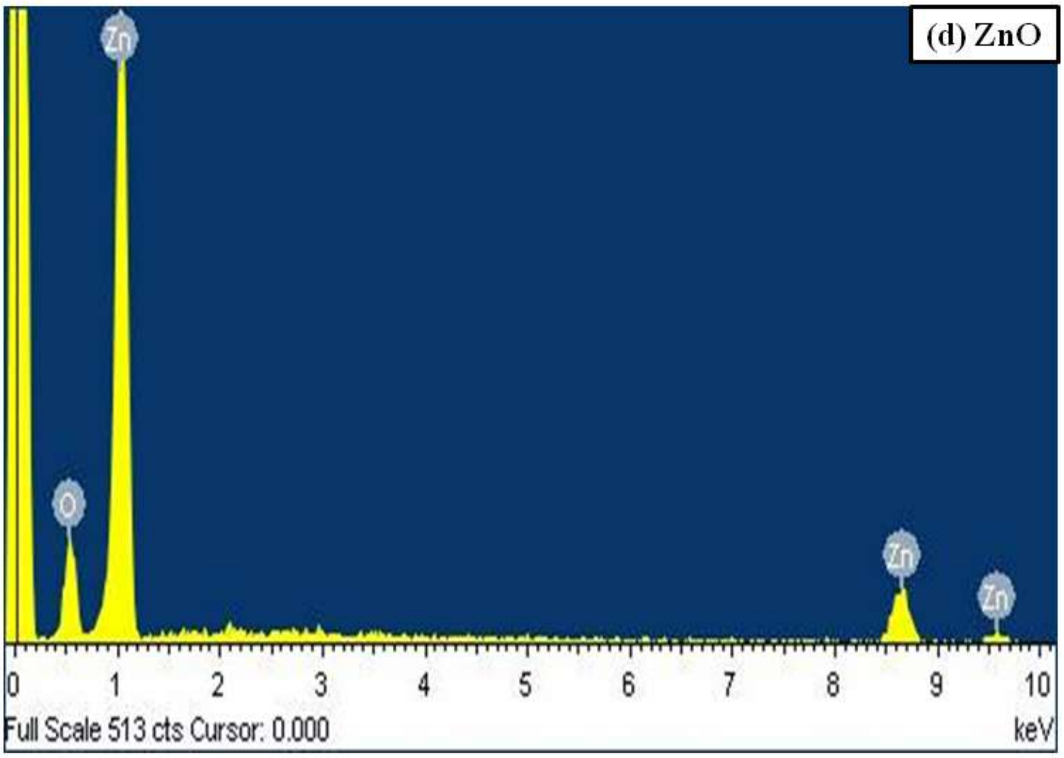


Figure 3.7: SEM/FESEM images (a) pure ZnO, (b) Cu(1%):ZnO, (c) Cu(2%):ZnO nanomaterials.


(d) ZnO
Zn
O
Zn
Zn
0
1
2
3
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5
6
7
8
9
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Full Scale 513 cts Cursor: 0.000
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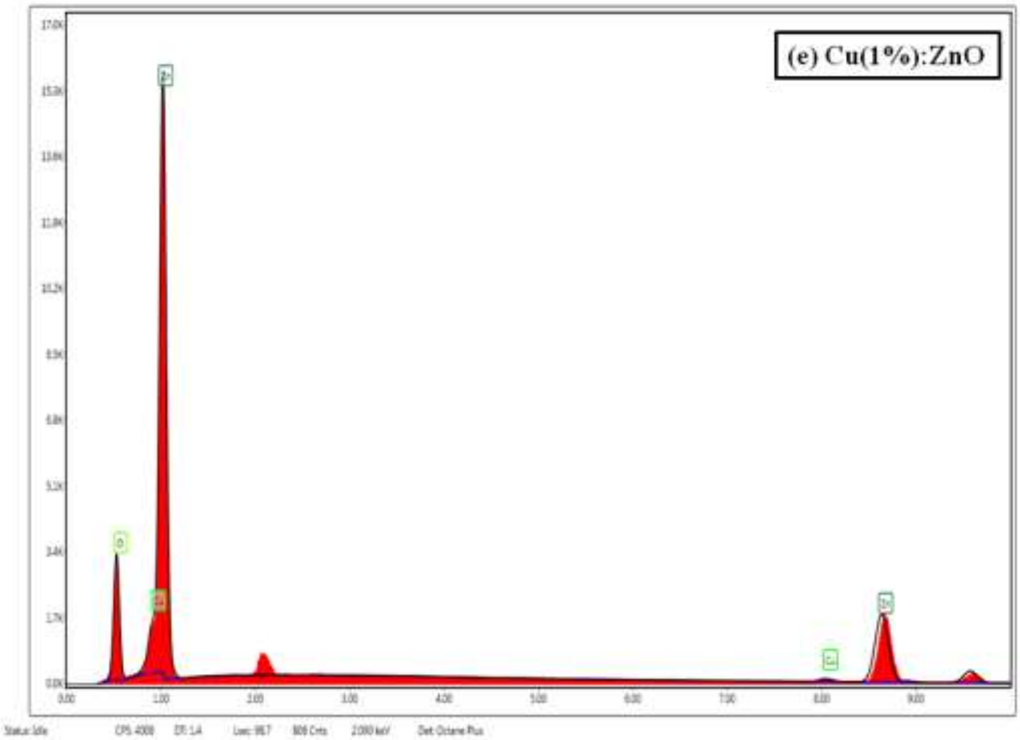
(e) Cu(1%):ZnO
17.0K
15.3K
13.6K
11.9K
10.2K
8.5K
6.8K
5.1K
3.4K
1.7K
0.0K
Zn
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Zn
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Status: Idle
CPS: 4008
DT: 1.4
Lsec: 98.7
808 Cnts
2.080 keV
Det: Octane Plus

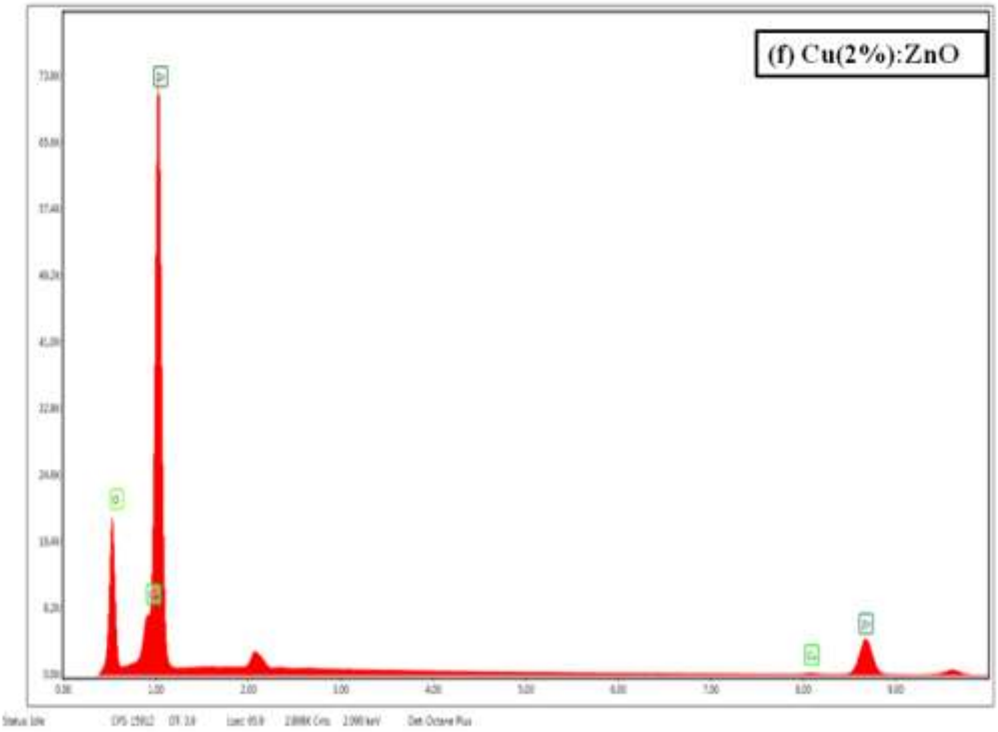

Figure 3.8: EDX images of (d) pure ZnO nanomaterials, (e) Cu(1%):ZnO nanomaterials, (f) Cu(2%):ZnO nanomaterials.

The doping of copper strongly influences the morphology of ZnO nanoparticles. SEM & FESEM characterization has been observed wurtzite and tripod morphology in pure ZnO, Cu(1%):ZnO & Cu(2%):ZnO nanomaterials respectively. These outcomes are tally with XRD results. The existence of copper in pure ZnO, Cu(1%):ZnO and Cu(2%):ZnO is analysed by energy dispersive X-ray analysis spectroscopy (EDAX). The confirmation of Zinc, Oxygen and Copper in pure ZnO, Cu(1%):ZnO and Cu(2%):ZnO nanomaterials were investigated by EDAX characterization. EDX gives the information about the thriving doping of copper in ZnO lattice nanoparticles.

The XRD, SEM and EDX of the pre-synthesized ZnO nanomaterials at room temperature and different annealing temperatures reveal that the A sample of ZnO nano-material was found more crystallinity nature compared to the B and C samples at different annealing temperatures. Therefore, the pure ZnO nano-material is selected for the doped pure ZnO nanomaterials with the different weight percentage ratio of the copper metal. The pre-synthesized doped copper ZnO nanomaterials have been characterized to analysis the properties cooper doped ZnO nanomaterials by the XRD, SEM/FESEM, and EDX. The XRD, SEM/FESEM, and EDX data of the pure ZnO and cooper doped ZnO nanomaterials were compared. In comparison of XRD and SEM/FESEM, it conforms that the pure ZnO nanomaterials and cooper doped ZnO nanomaterials were found the porous morphology and the existence of the required chemical compositions.

On the basis of the above characterizations analysis of the pure ZnO nanomaterials and cooper doped ZnO nanomaterials, we conclude that the XRD characterizations give information about crystalline size, structure; SEM/FESEM images reveal the porous morphology of the nanomaterials, where investigation of EDX images reveal the elemental composition of nanomaterials.

Now the UV-Visible spectroscopy characterization has examined for copper doped ZnO nanomaterials in view of the enhancement of the conducting behavior. The absorption of the copper doped ZnO nanomaterials by UV-Visible spectroscopy characterization is used to calculate the band gap of the Cu doped ZnO nanomaterials. Next section, we have studied the UV-Visible spectroscopy characterization of the copper doped ZnO nanomaterials.

3.2.3 UV-Visible spectroscopy of Copper doped ZnO Nanomaterials

The optical absorption of copper doped ZnO nanoparticles with the different weight percentage ratio copper metal i.e. Cu(1%): ZnO nanomaterials and Cu(2%): ZnO nanomaterials was measured by using UV–Visible spectroscopy which are indicated in figure 3.9. In this figure 3.9 it can be observed that the strong band edge visible around 370 nm. It has been indicated that doping of Cu in ZnO lattice. The energy band gap Copper doped ZnO nanoparticles has been estimated by the Taue's plot method. The energy band gap character is played a vital role in the semiconductors to understand the optical behavior of the materials. The Taue's relation is given by [6]

$$\alpha h\nu = A\,(h\nu - E_g^{n}) \qquad (3.1)$$

where E_g = energy band gap, h = Planck's constant, α = absorption coefficient, ν = frequency of light radiation, A = band edge sharpness constant, and n = ½ for direct allowed transition.

The energy band gap (E_g) was calculated by plotting the graphs between $(\alpha h\nu)^{1/2}$ versus hν. Figure 3.10 shows the energy band gap of copper doped ZnO nanoparticles for both Cu(1%): ZnO nanomaterials and Cu(1%): ZnO nanomaterials. The energy band reveals that the changed in energy band gap (E_g) is easily found from the extrapolation of $(\alpha h\nu)^{1/2}$ versus hν curves. The band gap energies of the Cu(1%):ZnO and Cu(2%):ZnO nanoparticles are to be found 3.35eV and 2.98eV respectively. This is observed that energy band gap decline with increment of copper doped ZnO nanomaterials [**7**]. So that’s why it is useful in optoelectronic device applications like photocatalytic process.

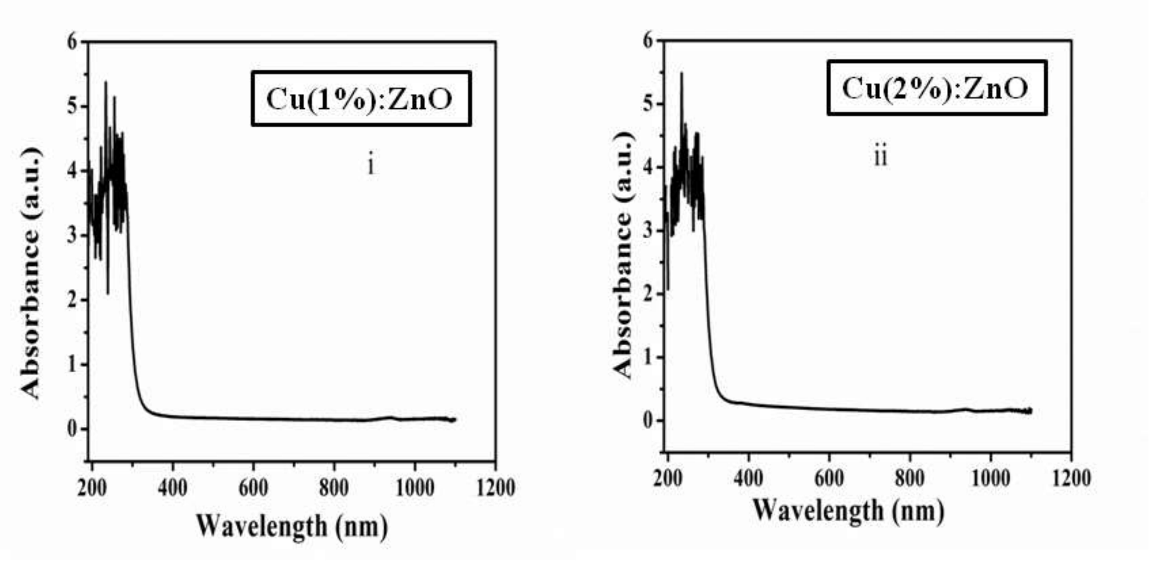

Figure 3.9: Optical absorption spectra of (i) Cu(1%):ZnO and (ii) Cu(2%):ZnO nanomaterials

The pre-synthesized materials of ZnO and cooper doped ZnO nanomaterials were characterized to analysis the properties of the nanomaterials by the XRD, SEM/FESEM, EDX, UV-visible. The XRD study of ZnO nanomaterials and cooper doped ZnO nanomaterials reveal that the nanomaterials are crystalline size and wurtzite structure. The SEM/FESEM study of ZnO and cooper doped ZnO nanomaterials reveal the morphology of the nanomaterials. The EDX study of ZnO nanomaterials and copper doped ZnO nanomaterials investigates the required elemental composition of nanomaterials. The UV-visible spectroscopy study of ZnO and copper doped ZnO nanomaterials calculates the band gap energy for the photocatalytic process.

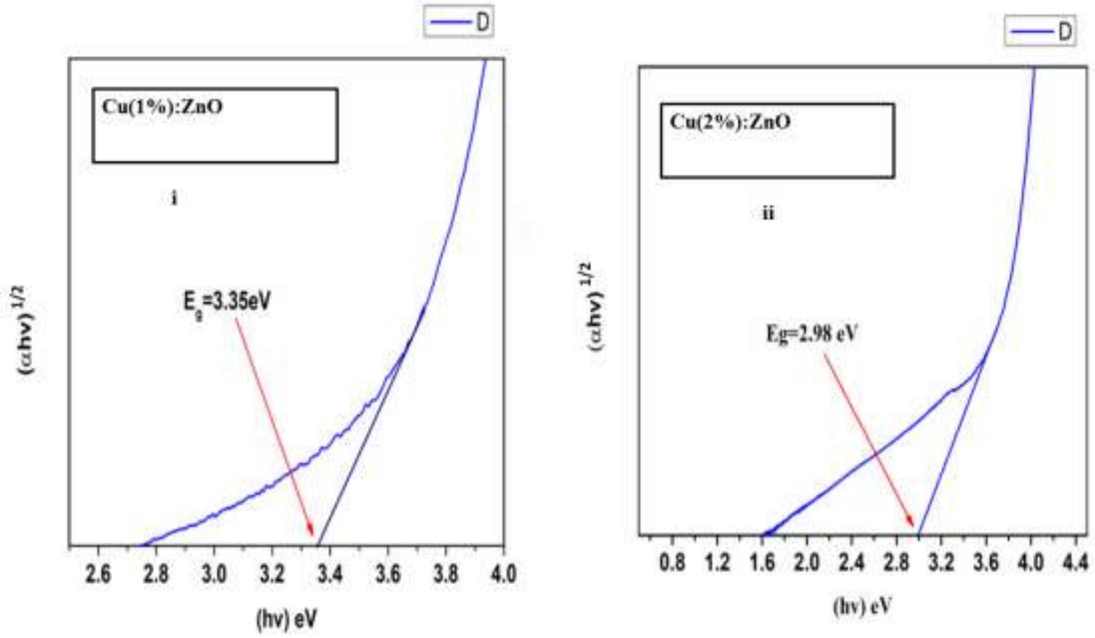

Figure 3.10: The $(\alpha h\nu)^{1/2}$ versus hν curves for the optical band gap determination of (i) Cu(1%):ZnO and (ii) Cu(2%):ZnO nanomaterials

Using the best, cheapest and feasible of the co-precipitation method, the ZnO nanomaterials and cooper doped ZnO nanomaterials were synthesized. The dopant of copper doping in the ZnO materials especially Cu(2%): ZnO nanomaterials is useful to enhance the efficiency of photocatalytic process and the photocatalytic process may be useful to remove pollutants from earth's water. As we know that the photocatalytic process is a beneficial technology to remove the impurities in water treatment especially Arsenic ingredient. Therefore, the XRD, UV-VIS, SEM and EDX characterizations were used to examine the ZnO nanomaterials and copper doped ZnO nanomaterials (Cu(1%): ZnO nanomaterials and Cu(2%): ZnO nanomaterials) properties. The analysis of XRD, UV-VIS, SEM and EDX characterizations for the Cu(2%): ZnO nanomaterials have found to support the photocatalytic process for removable the impurities especially Arsenic ingredient form earth's water.

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CHAPTER-4

Conclusion and Future scope

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Nano-catalysis system based on the photocatalytic may counterpart of the existing techniques for the removal of trace pollutants/impurities. Generally solar photo catalysis and artificial ultraviolet (UV) light photocatalytic activities are used for water treatment at room temperature and ambient pressure. These photocatalytic activity devices can be useful to destroy various chemical and microbiological contaminants in water. Due to this universal applicability of the Photocatalysis with nanoparticles, the nanocatalysts are used to reduce water pollutions or water purification. The encouraging method of nano-catalysts is used for the treatment of polluted water. Many semiconductors of SnO_2, TiO_2, ZnO nanomaterials have the photocatalytic activity and they are used for the treatment of polluted water or water purification.

There are many methods to synthesis of semiconductors SnO_2, TiO_2, ZnO nanomaterials by the Chemical Co-precipitation, Hydrothermal and Solvothermal methods. If we compare these methods for synthesis of the of semiconductors SnO_2, TiO_2, ZnO nanomaterials, then the co-precipitation synthesis method is one of the best, simplest and low cost method to synthesis the of semiconductors SnO_2, TiO_2, ZnO nanomaterials because this method is taken less time, economical, uncomplicated and easy process etc. So that in this dissertation work, we have selected co-precipitation method for synthesis zinc oxide (ZnO) nanomaterials and copper doped (Cu(x%):ZnO) nanomaterials where x=1 and 2. The results of this dissertation are given below:

- The synthesized nanomaterials by co-precipitation method are highly cheapest and feasible processes for the treatment of wastewater due to the incredibly large surface areas of the nanomaterials. The major advantages for water treatment using nanomaterials are: a) low operating cost b) low energy cost c) discharge/less waste water d) reduction of pollutant and e) more efficient.
- The ZnO nanomaterials and Cu:ZnO nanomaterials synthesized by co-precipitation method which is one of the best and cheapest method and it may

be productive nanomaterials for the nano-catalysis to remove hazardous impurity of arsenic from polluted water.

- The SEM, FE-SEM and EDAX characterizations showed that pre-synthesized ZnO, Cu (1%):ZnO and Cu (2%):ZnO nanomaterials are in nano-crystalline nature. SEM & FESEM characterization has been observed Wurtzite structure and tripod morphology. The Wurtzite structure was confirmed by XRD characterization. The existence of Copper, Oxygen and Zinc elements in the chemical compositions were detected by EDAX characterization.
- The synthesis of the ZnO and copper doped ZnO nanomaterials for treatment of water pollutants/purification was revealed. The copper doped zinc oxide nanomaterials by the co-precipitation method may be considered for the effective treatment of water contaminants and are always met four conditions (a) safety of environment, (b) recycle of treatment agents, (c) cheapest method, and (d) highly efficient treatment.
- XRD patterns of the Cu:ZnO nanomaterials were investigated these planes: (100) (002) (101) (311) (102), which explains that the synthesized material is in single-phase of the copper doped ZnO nanomaterials. Plane (311) showed copper is presented in the synthesized sample of Cu (2%): ZnO nanomaterials; and the crystallite sizes of the Cu (1%): ZnO and Cu (2%): ZnO nanomaterials are to be found 45nm and 43nm respectively. This result reveals that the ZnO nanomaterials were doped with the copper metal successful. No impurity peaks were found in XRD characterization. The optical band-gaps of Cu (1%): ZnO and Cu (2%):ZnO nanomaterials were found to be 3.35eV and 2.98eV respectively by UV-Visible Spectroscopy.
- On the basis of the characterization results, we reveal that Cu(2%):ZnO nanomaterials has found to be 43nm crystallite size, 2.98eV band gap and the tripod morphology. Therefore, the Cu(2%):ZnO nanomaterials has characteristic properties of the photocatalytic, strong adsorption towards pollutants and enhanced redox properties that lead to effective treatments of pollutants in water. The obtained characterization results for Cu(2%):ZnO nanomaterials is the best for removable hazardous impurity of arsenic from water. The Cu(2%):ZnO nanomaterials is more better than the Cu(1.08%):ZnO

nanomaterials in the reported paper [Vaino, *Applied Catalysis B: Environmental 18, (2018), 30634*] because the large amount of the copper in the ZnO semiconductor has the low energy bang gap. The low band gap may be more useful for solar photocatalysis and artificial ultraviolet (UV)-light photocatalytic activity.

The outcome results were also found to be fruitful for water treatment and water disinfection because of the ZnO nanomaterials and Cu:ZnO nanomaterials have the nano-catalytic system based on the photo catalyst process. Besides this, it may also be fruitful for nano-sunscreens, makeup products, climate remediation, dietary supplements, paints, disinfectant coatings, medications etc. The obtained results of Cu(2%):ZnO nanomaterials may be applied to fabricate Pyrex cylindrical batch reactor equipment for removing hazardous impurity of Arsenic in water for further research in the future, which may be fruitful in treatment or purification of water.

LIST OF PUBLICATION

Paper Published

Varsha Gautam, Krishan Pal, Narendra Kumar, Girijesh N. Pandey, B. Suther, Khem B. Thapa and S. P. Ojha, “Low cost synthesis of ZnO nano-particles, and characterization study for the device of water disinfection”, *AIP Conference Proceedings*, 2220, 020170 (1-4), 2020.

Conference Attended

International Conference on ‘3rd International Conference on Condensed Matter & Applied Physics (ICC 2019), organized by Department of Physics , Govt. Engineering College, Bikaner (Rajasthan)’ during 14-15 Oct, 2019.

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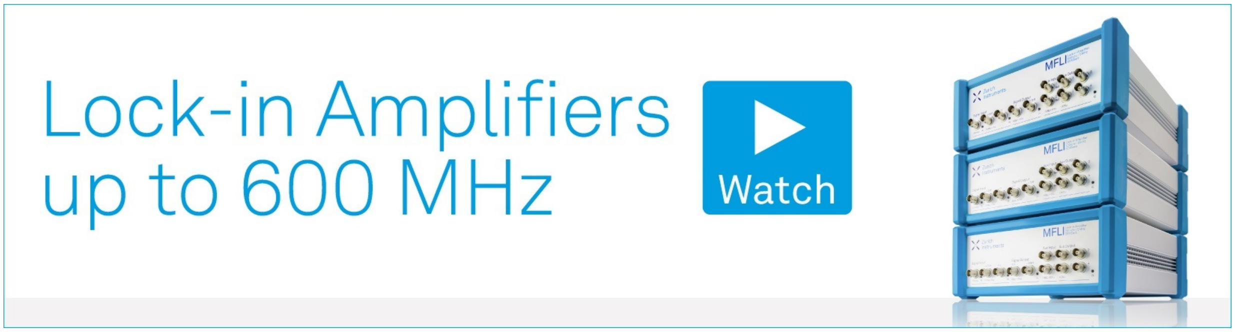

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Low cost synthesis of ZnO Nano-particles, and characterization study for the device of water disinfection

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Abstract: The most fascinating trouble in this world is the water because water is the most central asset of human society. Several research groups across the world are working on it to solve the water problems particularly water impurities like organic, inorganic, and biological. Wastewater treatment industrials with nanomaterials are vital and extensive devices using the field of nanoscience and nanotechnology. Presently offered technologies are very effective for water treatment, but their costs are too high and have time overwhelming process. Hence, the synthesis of zinc oxide (ZnO) nanoparticles is proposed with help of co-precipitation method with no surfactant due to low cost and fast process for water disinfection/treatment. The antibacterial mechanism of ZnO nanoparticles is due to the nanoparticles size effect. The photocatalytic production of H_2O_2 is accountable for antimicrobial action of ZnO, and antibacterial activity may be existed by both Zn^{+2} ion and ZnO nanoparticles. XRD, SEM and EDS of ZnO nanoparticles were used to evaluate shape-size, morphology of particles and element constituent. The ZnO nanoparticles at nanoscale may be useful for antibacterial behavior on a huge spectrum of bacteria that is found in water impurities.

Keywords: ZnO, ZnO nano-particle, Disinfection water, low cost co-precipitation method, XRD, SEM, EDS

INTRODUCTION

Throughout the world, water pollution is the major problem due to climate change, increasing water scarcity, population growth, and urbanization. According to WHO report 2019 the half of the world's population will be living in water problems by 2025. India will become a water worried nation by 2022; and about 67 million Indians in 20 states at danger due to water disinfection [1]. Therefore, the scientists are working towards such major problem that can be solved scientifically. The most new technologies used in water disinfection are synthesized/fabricated nanoparticels through nanoscience & nanotechnology. This technology mainly emphasize on the greater application of small and tiny particles having strong environment friendly. The size of nanoparticles is 1nm to 100 nm with at least one dimension in nanometer. Nanomaterials have strong adsorption capacities and relatively high compare to others due to their small and tiny size of the particles. Nanoparticles have tendency to remove heavy metals, organic pollutants, inorganic anions, and bacteria from the water [2].

Zeolite, Graphene, fullerenes, TiO_2, Ag NPs and carbon nanotubes and other nanoparticles (NPs) such a akaganeite, $A_{l2}O_3$, anatase, CdS, cobalt ferrite, Cu_2O, gold, maghemite, iron, Fe_2O_3, iron hydroxide, Ni_2O_3, silica, SnO, ZnO, ZnS, zirconia, and some alloys are also engaged for water treatment [3]. Zinc oxide (ZnO) nanomaterial

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has tendency to remove bacteria from water, and works as antibacterial agent. Zinc oxide is being wide band-gap semiconductors about 3.36eV and has unique properties of optical, electrical, and chemical [4].

As we know that Zinc oxide (ZnO) is harmless, good thermal permanence and low cost material. So that it is a very capable material for water treatment applications. The structure of ZnO is a steady wurtzite structure with sides a=0.325nm and b=0.521nm. In addition to this, the availability of a wide range of nanostructure makes ZnO is an ideal material for nanoscale optoelectronics and piezoelectric nano-generators. Furthermore, zinc oxide appears powerfully refuse to accept microorganisms [5]. Even the small amount of zinc oxide shows the strong activity and uses in the water disinfection activity. Zinc oxide is regarded as a good antiseptic agent because it is steady under harsh processing circumstances, and is well thought-out as a safe material for human beings and nature [4]. Besides this, ZnO is usually added in sunscreens, coatings and paints to soak up ultra violet light and is played a vital role in a range of industries material such as rubber, pharmaceuticals and food.

Thermal decomposition, co-precipitation, CVD, sol-gel and spray pyrolysis methods are used to fabricate zinc oxide with uniform morphology and nano size particles [1]. Among all the methods, the co-precipitation method is the best method for low cost and has the controlling shape, size, and morphology of ZnO NPs [5].

In this paper, we have synthesized ZnO NPs with the help of co-precipitation method without surfactant and it may be the best method for low cost and may be use for water treatment application. The XRD, SEM and EDS characterization are done for estimated particle size, surface morphology and contain of the element of the composition.

MATERIAL AND SYNTHESIS METHOD

$Zn(CH_3COO)_2.H_2O$ and NaOH were used without any further purification which was purchased from Thermo fisher, China. Laboratory grade distilled water was used for polarized solvent. The low cost co-precipitation method was used to synthesize ZnO nanoparticles using without any surfactants. 0.2M of $n(CH3COO)2\cdot 2H_2O$ and de-ionized water were mixed forcefully 3 hours at 60^0. Then 150ml solution of distilled H_2O and 1M of NaOH were added drop-wise with rate of 1.5ml/minute. The white color precipitate (ppt) was obtained when pH of the solution is equal to 9 and then ppt was filtered. The byproducts was removed by filtrating precipitate with washing several times with the de-ionized water and ethanol, and dried overnight at 80^0 in a simple oven. We prepared three samples A, B and C of ZnO material without and with calcinations. The A sample is taken without calcinations, however B and C samples are taken with calcinations at 600^0C and 800^0C respectively.

CHARACTERIZATION

XRD characterization of the synthesized ZnO powder was done by using the XRD (X-pert Powder) in the angle of diffraction $20^o \leq 2\theta \leq 80^0$ with monochromatic CuK_α emission ($\lambda = 1.5418A^0$) source. SEM and EDS of the synthesized ZnO were done by JEOL system from USIC, BBAU, Lucknow. The images and the composition element constituent were studied for the water treatment applications.

RESULT AND DISCUSSION

X-ray diffraction patterns of ZnO without calcination (Green), calcinated at 600^0C (Red) and 800^0C (Blue) in the open atmosphere is shown in the Fig.1. The diffracted X-ray peaks of ZnO nano particles were found at the planes (100), (101), (102), (110), (103), (112), (002) and (201) planes [6]. The XRD patterns of calcinated ZnO nanoparticles (NPs) at different temperatures were confirmed that all peaks are in Wurtzite arrangement as shown in Joint Committee on Powder Diffraction Standards [7]. The angle 31.7518^0, 34.4014^0 and 36.2366° are located at for strong peak of the crystallographic planes (100), (101) and (002) lines shown in the Figs. 1(a), 1(b), and 1(c) respectively. The other impurity peaks in crystalline material of the ZnO was not identified. However, the diffraction peaks were become sharper with increases the calcination temperature and improved the crystallinity property of the material. The obtained result is justified with the results in Ref [8].

Using the XRD data and Debye Scherer formula, we were calculated the usual crystallite size of pure ZnO was found about 28.16nm, and the usual crystallite size of calcinated ZnO NPs at 600^0C and 800^0C was found about 22.54nm. After study the all ZnO NPs structures at temperature variation, lattice parameters are found a=0.3248nm and c=0.5205nm and good accord with previously reported paper [9].

The SEM image shows the surface morphology of the ZnO NPs, and the EDS analysis shows the constituent percentage elements of ZnO NPs as shown in the Fig. 2. For the SEM, the film of synthesized ZnO powder NPs was prepared on glass substrate by master blade method. The spherical and short-rod shape morphology was shown in the SEM images of ZnO NPs, and no more different shapes of pure ZnO NPs was shown at the calcinated temperatures. The surfaces of the film are rough with micro-porous may work as the adsorptions of the microbes' bacteria at the energy band gap of ZnO NPs. The EDS study at atomic level of each sample is also shown in the Fig. 2.

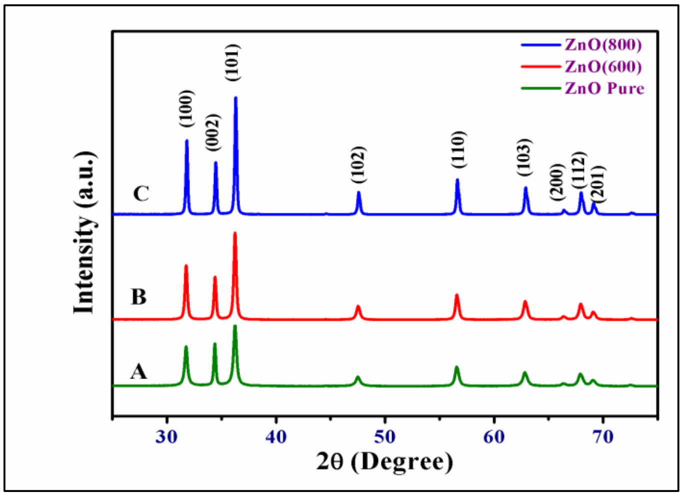
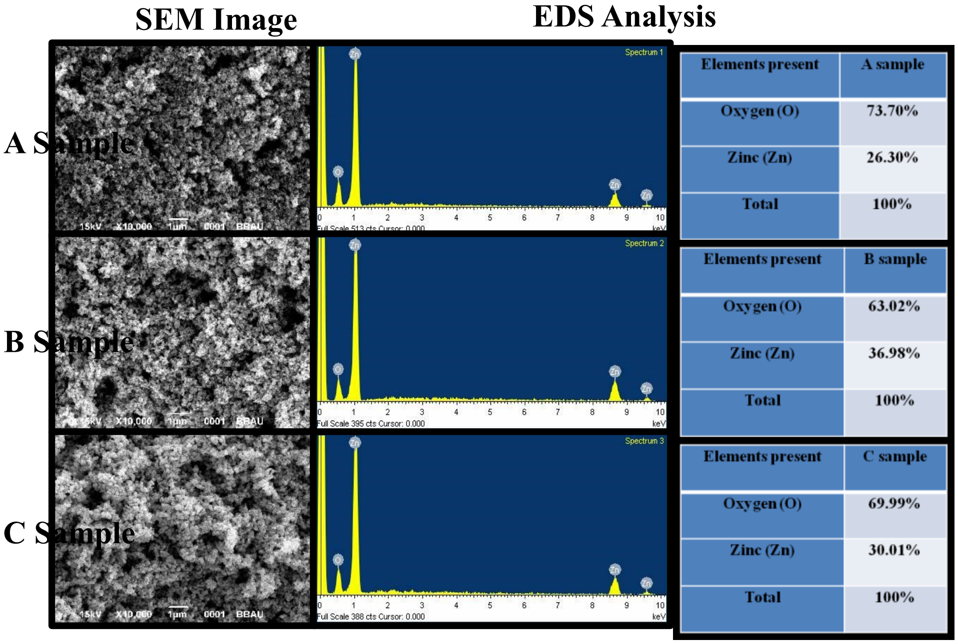


FIGURE 1: XRD patterns of ZnO NPs (a) A-ZnO pure (b) B-ZnO (600^0C) and (b) C-ZnO (800^0C).



Elements present	A sample
Oxygen (O)	73.70%
Zinc (Zn)	26.30%
Total	100%

Elements present	B sample
Oxygen (O)	63.02%
Zinc (Zn)	36.98%
Total	100%

Elements present	C sample
Oxygen (O)	69.99%
Zinc (Zn)	30.01%
Total	100%

FIGURE 2: Scanning Electron Microscope and Energy Dispersive Spectroscopy images of sample: A without calcinations, B with calcinations at 600^0C and C with calcinations at 800^0C.

Zinc (Zn) and Oxygen (O) elements were observed strong peaks with high percentage of the element constituents. The EDS peaks study for A sample have found atomic 26.30% and 73.70% for Zn and O respectively. The same study was obtained for ZnO NPs at different calcinations temperatures that confirmed the formation of ZnO NPs.

CONCLUSION

The low cost efficient co-precipitation method exclusive of any surfactant was used to synthesize the ZnO NPs. The XRD of synthesized ZnO sample was in pure hexagonal Wurtzite arrangement, and the lattice parameter of polycrystalline structure of the ZnO was found with a=0.3248nm and c=0.5205nm. The nanoparticles of ZnO with size ≤28.16nm may be highly useful for antibacterial behavior on a wide range of bacteria. The size of ZnO was also able to tune by the calcinations temperature. The current study reviled that the obtained size of ZnO nanoparticles may also be used for water disinfection as given in the Ref. [2] which was synthesized by low cost method with hardly a surfactant [5]. Our study may be beneficial to fabricate the low cost and commercially cheap device for water disinfection.

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