Chapter III

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EXPERIMENTAL TECHNIQUES

3.1. Introduction

Nanotechnology is the combination of physical science, biology, computational science & engineering in nanoscale. It is meant for science & engineering targeted by forming the particles, matters and gadgets at atomic & molecular level [1]. Certain nanoparticles will manifest in nature as such. The preparation of nanoparticles & its structures are explained mainly with two methods.

The nanoparticles may synthesized by the use of various methods, commonly categorized as bottom-up and top-down methods. In bottom-up approach, the shape of nanomaterials is formed by atoms & molecules [2]. In top-down approach, a material is reduced to nanosize by cutting, grinding & etching methods. The nanoparticles were organized from large entities negligible at certain atomic-level [3].

The techniques for synthesizing nanoparticles are classified to three most important groups. Firstly, the group includes the liquid-phase methods that follow chemical reaction in solutions. It leads into colloids that may be neutralized towards coagulation through surfactants & ligands for nanoparticle formation [4]. The next group includes strategies on the basis of surface growth underneath vacuum conditions. The nanoparticles can be viewed as island that is formed by the diffusion of tiny clusters and atoms [5]. Gas-phase synthesis is the final group. Many strategies of nanoparticle synthesis were primarily based on homogeneous nucleation in the gas segment as subsequent condensation & coagulation [6]. The homogeneous nucleation works in gas phase & heterogeneous nucleation takes vicinity on substrate.

Numerous structural & chemical methods may be utilized for the preparation of huge quantities of metallic nanoparticles in a brief duration of time. In general, nanoparticles are formed & stabilized utilizing physical, chemical and biological techniques [7]. Metallic nanoparticles are organized through two simple techniques:

- metal aggregates through mechanical separation (physical methods)
- nucleation & boom of a “nucleus” (chemical methods)

Physical strategies involve mechanical pressure, active radiations, electrical power to motivate substance rubbing, melting, evapouration to create nanoparticles. Those strategies commonly function on top-down approach & are fantastic as free from solution impurity & form similar monodisperse nanoparticles. Simultaneously, the considerable waste formed while physical approaches are much less affordable. High electricity ball milling, laser ablation, electrospraying, etc. are mainly utilized to create nanoparticles [9].

Chemical synthesis is an important method for manufacturing of substances that typically includes many steps taking vicinity in liquid or gas phase [10]. The atoms are formed by utilizing chemical reactions underneath regulated however slight reaction strategies. Newly prepared atoms may endure basic nucleation succeeded by growth techniques lead to form described nanoparticles. The formation of nanoparticle through chemical techniques is precipitation reactions, oxidation- reduction, hydrolysis, thermolysis, polymerization & condensation. Sol-gel method, microemulsion technique, hydrothermal synthesis, polyol synthesis, chemical vapour synthesis and plasma enhanced chemical vapour deposition methods are the generally used chemical techniques for nanoparticles formation [11].

3.2. Materials and Methods

Materials & methods segment is the backbone of the research report that reveal the reliability & logic of the assignments. Materials are simply the raw materials, tools, subject and important chemicals used in experiments [12].

3.2.1. Hydrothermal method

Hydrothermal method is a generally utilized technique for nanoparticle synthesis. Herein, nanoparticles are formed from a broad range of room temperature to higher temperatures. It's basically a solution reaction-based approach. A specially covered reaction vessel containing aqueous solution as reaction system to create a high-temperature, pressure reaction surrounded by heating & pressurizing it [13].

It is a technique of forming various compounds through keeping the substance in a watery solution at 100°C & < 1 atmosphere inside a covered system. This technique is based on enhancement of the solubility of liquid & an aqueous solution underneath higher temperature & pressure then the materials that are insoluble beneath regular conditions, like certain oxides, silicates & sulfides, might have mixed into solutions to prepare nanoparticles [14].

Figure 3.1: Autoclave

Hydrothermal method is a technique of synthesizing unicrystal in hot water under high pressure which depend on the solubility of minerals. The formation of crystals is done by using metallic pressure container equipment known as autoclave shown in figure 3.1. The temperature gradient was regulated among both ends of the growth chamber. Hydrothermal method depends on the required dissolving reactants to form the oxide pottery. It can gain at reasonable temperatures (<200 °C) & excessive pressures through putting reagents in closed vessel. Commonly water was the solvent; sodium hydroxide was introduced as mineralizer whilst metallic alkoxides or salts distribute as the supply of metallic ions.

Hydrothermal technique works on implementing wet-chemical strategies to nanostructures by crystallizing substances. The procedure is done in an autoclave underneath temperature in between 100°C-250°C & higher vapor pressure [15, 16]. Hydrothermal synthesis is a highly effective method for creating functional nanoparticles from transition metallic compounds like oxide, hydroxide, & sulphide. For this work we use hydrothermal method for synthesizing Co_3O_4 nanoparticles.

3.3. Experimentation

The chemicals with high quality were used without anymore cleansing. Accordingly, in the traditional procedure, cobaltous nitrate of 1% wt [$Co(NO_3)2.H_2O$] were dissolved & well stirred in distilled water. The whole procedure was blended for 5 minutes by 1:8 mixtures of sodium nitrite ($NaNO_2$) & acetic acid (CH_3COOH). 5 M of aqueous NaOH solution was added dropwisely. The synthesized solution was regulated at a pH of 12. Different concentrations of dopants like 3%, 5% & 10% of dopants (ZnCl, FeCl, CuCl, NiCl) were added slowly at this stage and continuously stirred for 10 minutes. After transferring the solution to autoclave, for 17 h it was heated upto 200° C. Thereafter allowing autoclave to bring down at room temperature, it was centrifuged at 2000 rpm. Before drying the residue at 200° C for 3h in a muffle furnace, it was rinsed using distilled water & ethanol [17, 18]. The images of synthesized Co_3O_4 nanoparticles are shown in figure 3.2.

$$Co\,(NO_3)_2 + NaNO_2 + CH_3COOH = Na_3\,(Co(NO_2)_6) + NaNO_3 + CH_3COONa + H_2O$$

$$2Co(NO_3)_2 + 11NaNO_2 + 2CH_3COOH \rightarrow 2Na_3\,(Co(NO_2)_6) + 3NaNO_3 + 2CH_3COONa + H_2O$$

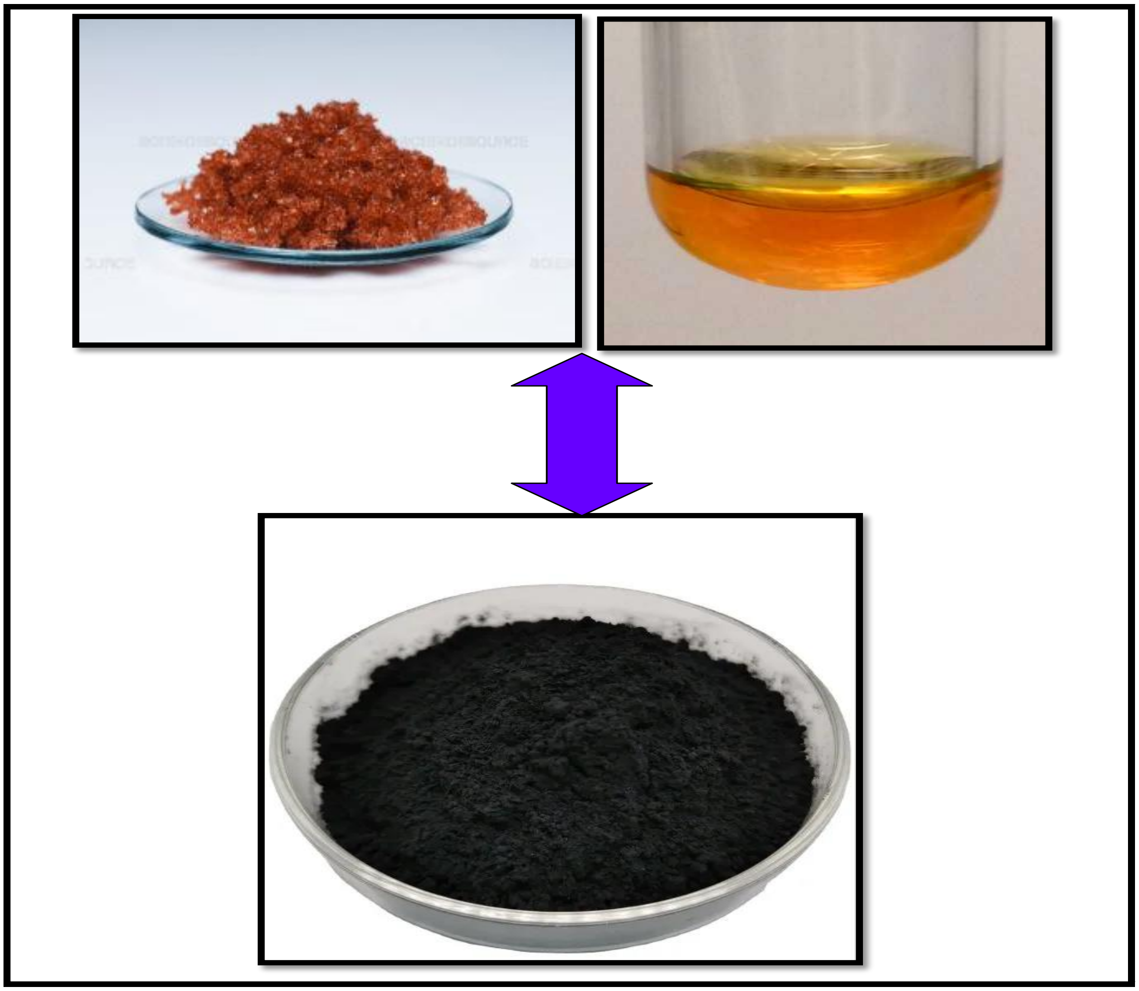

Figure 3.2: Synthesized Co_3O_4 nanoparticles

3.4. Factors effecting the experimentation

3.4.1. Molarity

Molarity is essential in chemistry. Molarity is defined as the amount of substances dissolved in the given quantity of solution. The solute can be measured in grams, moles, or based on the volume of the solute. Chemists use molarity is used by chemists to measure the volume of a solution, using chemicals during experimenting chemical reactions. An increased molarity causes remarkable changes in the physical, magnetic & thermal dissipation features of nanoparticles [19].

Molarity is the number of moles of solute dissolved in one liter of solution. Here, mass is considered as the mass of solute constitute in grams & volume is the total volume of solution considered in liters. Molarity is stated as:

Molarity = moles of solute / liters of solution.

Molarity is the method to analyze the presence of particular elements in some solution. Measuring the dilution of solution is one of the various purposes of molarity [20].

3.4.2. Effect of pH

pH means Hydrogen potentials used to indicate acidity or alkalinity of solution. pH represents the number of hydrogen ions within the solution. It is defined as the negative logarithm of H^+ ion concentration that meant for the power of hydrogen. pH is a reflection of solution's chemical condition that ranges between 0-14 scale using a litmus paper. The acidic solution indicates the pH value between 0-7 & basic solution ranges 7-14. Strong acidic solutions are recognized with a pH which reads 0 i.e, acidity of solution is inversely proportional to pH. Furthermore, strong basic solutions having a pH of 14 i.e, basicity is directly proportional to pH.

The potency of acids & bases relies upon amount of H^+ & OH^- ions created. In case of acids, if the number of H^+ ions is higher, then they belong to strong acids & vice versa [21].

pH may regulate the accessibility of nutrients, organic purposes, microbial functions & chemical's nature. At bascity pH, the steadiness of aggregate dispersal & colloid creation is elevated by reduced chance for cluster of substances because of entire charging of aggregates that maximize the electrosteric reactions. This is because at increased pH, the rate of reaction will be elevated by consecutive crystallization to tiny substances that included nucleation & growth methods [22]. The size and shape of nanoparticles are affected by various factors. With an increased pH, absorption elevates & provides narrow peak by uniform size distribution. However, we presume that fundamental circumstances are favourable for regulating the particle size [23].

3.4.3. Annealing Temperature

In metallurgy, annealing is the heat treatment which changes structural & chemical characteristics of substances to elevate their ductility & decrease hardness, makes them reliable [24]. In annealing, substances are heated above its recrystallization temperature, by controlling an appropriate temperature for a suitable time period and then cooling.

The variation in ductility & hardness is due to the transferring of atoms in crystal lattice & reduced misplacement. The heating /cooling rate establish the material characteristics such as crystal grain size and phase composition [25]. Annealing happens due to the spreading of atoms inside a stable substance by the substance develop closer to their equilibrium stage. The motion of atoms has impact of rearranging & eliminating the misplacements in metals. The changes due to current disarrays let in a metallic object to distort easily, elevating ductility [26].

The three degrees of the annealing method that proceed as the temperature of material is expanded are: recovery, recrystallization and grain growth. The first stage used to be recovery, and it outcomes in softening of the metallic via elimination of especially linear defects referred to as dislocations and the inside stresses they motive [27]. Recovery takes place at the decrease temperature stage of all annealing tactics and earlier than the look of new strain-free grains. The grain measurement and structure do no longer change. The 2nd stage is recrystallization, the place new strain-free grains nucleate and develop to substitute these deformed with the aid of interior stresses [28]. If annealing is allowed to proceed as soon as recrystallization has completed, then grain increase (the 1/3 stage) occurs. Thermal annealing is vital for attaining ultra small dimension ferromagnetic properties in next generation excessive overall performance nanocomposite magnetic substances [29]. Anyway, at some point of the annealing process, growth & agglomeration of nanoparticles typically happen that destroys the slender measurement distributions. Annealing is the procedures of protecting a substance at an increased temperature to acquire (positive) modifications in the micro-structure [30].

3.5. Materials Used for Synthesis

- Precursors: cobaltous nitrate [$Co(NO_3)2H_2O$], sodium nitrite ($NaNO_2$), acetic acid (CH_3COOH), ZnCl, FeCl, CuCl, NiCl
- Solvents: distilled water, aqueous NaOH, ethanol
- Glassware: beakers
- Instruments: Autoclave, muffle furnace, Mortar pestle, Digital weighing balance, Magnetic stirrer with pellet.

Chemicals are the fundamental substances which altered for experiments through the functions of chemical nanotechnology [31]. Precursor is a material which follows a reaction, formed as an intrinsic part of chemical output. Biochemistry defines "precursor" especially in a metabolic way to chemical compound preceding other like protein precursor. It's something that comes before another and may lead to it or influence its development. Precursors are the chemicals used to create another chemical through chemical reaction [32].

Cobaltous nitrate is an inorganic compound having $Co (NO_3)_2 \cdot xH_2O$ formula. It is a red-brown deliquescent salt which dissolves in water & polar solvents. Several hydrates of cobalt (II) nitrate exist as $Co (NO_3)_2 \cdot nH_2O$, where n = 0, 2, 4, 6. On reduction, metallic high purity cobalt is obtained. Cobalt nitrate is a supplier of high-purity cobalt due to greater solubility for various applications like electronics, metal-organic frameworks & polymers. Cobalt is a metallic element having an atomic number 27 [33].

Sodium nitrite ($NaNO_2$) is a hygroscopic inorganic compound & a significant nitrite salt. It's a crystalline powder with white to light yellow colour that dissolves in water. They act as an antimicrobial food preservative, antihypertensive agent, food antioxidant, poison & an antidote to cyanide poisoning. For industries, it is used for manufacturing organo nitrogen compounds. For converting amines to diazo compounds it is used as reagent like diazo dyes. Sodium nitrite is an affordable inorganic reagent which has applications in synthetic organic chemistry including a variety of metallurgical applications [34].

Acetic acid or ethanoic acid is an acidic, colorless liquid and organic compound having CH_3COOH formula. It is a significant chemical reagent & a simple carboxylic acid. It is an important chemical reagent and an industrial chemical utilized to produce dyes, perfumes, esters, etc. It is used as a laboratory agent [35].

Sodium hydroxide or caustic soda is an adaptable material & also a byproduct of chlorine manufacturing. Sodium hydroxide is produced as a co-product in the production of chlorine [36]. In its pure form, it is crystalline solid, and colourless in nature. It is a common ingredient in cleaners and soaps. The concentration of NaOH was varied for synthesizing cobalt oxide nanoparticles because the size, shape, agglomeration & phase of the cobalt oxide nanoparticles are affected by the NaOH concentration.

Ethanol (CH_3CH_2OH) is an aliphatic alcohol belongs to a cluster of chemical compounds which consist of a hydroxyl group (OH) bonded to a carbon atom [37]. Ethanol is a volatile, flammable, colorless liquid having smell of wine & pungent taste. The significance of ethanol in chemical industries are as a solvent, for preparing organic chemicals & as an additive to automotive gasoline (gasohol).

Zinc chloride ($ZnCl_2$) named as butter of Zinc, is an inorganic chemical compounds is a colorless/white crystal dissolves in water [38]. The 9 crystalline forms $ZnCl_2$ are known. ZnO was formed due to the rapid reaction of zinc vapour by O_2 from air. $ZnCl_2$ utilized like Lewis acid catalyst for various biological preparation. $ZnCl_2$ is simple, cheap, less toxicity & wide spectrum for catalyst.

Iron (III) chloride or ferric chloride ($FeCl_3$ $(H_2O)_x$) is an inorganic compounds obtain as anhydrous & hydrated ways that have well-defined characteristics. It is an oxidizing agent. Usually, it is the source of iron in $^+3$ oxidation state [39]. Iron (III) chloride is a mild oxidizing agent. Basically, ferric chloride is utilized for wastewater treatment as a remover of smell & impurities from water. When iron (III) chloride is dissolved in pure denionized water, assuming it is from a fresh bottle, it will take hours to form a precipitate of iron hydroxides. Therefore, in order to perform this qualitative test, iron (III) chloride should be freshly made in water.

Copper Chloride is a brownish-yellow powder. Copper (II) chloride is a mild oxidant and is obtained by chlorination of copper [40]. At 1000^0C it disintegrates to copper (I) chloride & chlorine gas. $CuCl_2$ oxidizes within other metals to form CuCl & can synthesize metal copper by reacting by various metals. $CuCl_2$ is paramagnetic. Copper oxide (CuO) is an oxidizing agent. It can be utilized in petroleum, textiles, metallurgy, photography, agricultural products, feed additive & wood preservative.

Nickel (II) chloride ($NiCl_2$) is a significant chemical used for synthesizing nickel. Nickel Chloride is denser than water & a mild Lewis acid [41]. Anhydrous salt & hydrate of nickel (II) chloride, is yellow & green in colour respectively. It is utilized for nickel plating, electrolytic refining of nickel, nickel catalysts & complex nickel salts. Nickel chloride absorbs moisture to form solution. Nickel chloride creates nickel (II) ions into inorganic crystalline minerals. It may complex or adsorb on to organic & inorganic surfaces, might took part in cation exchange & could form as free-ion.

A muffle furnace is a laboratory device utilized to heat materials to extremely higher temperatures whilst isolating them from fuel and the byproducts of combustion from the heat source is shown in figure 3.3 [42]. Muffle furnaces allow for the isolation of a material to reduce the risks of cross-contamination and identify specific properties.

Figure 3.3: Muffle Furnace

The mechanism of muffle furnace is to attain the function of heat treatment, smelting & casting by igniting fuel inside the chamber to heat work piece using high temperature. Here, the material is detached from fuel, outcomes of ignition like gases & flying ash. Recent muffle furnaces rapidly changed into electric designs due to the enhancement of heating elements at higher temperature & worldwide electrification. Muffle furnace named from chemical industry is mentioned to the insulation & separation of heating elements from the contents of retort. The muffle furnace is used for burning down the sample to assess the impurities in it [43].

3.6. Conclusion

‘Materials’ is meant for the chemicals and devices used to synthesize pure & doped cobalt oxide nanoparticles. ‘Methods’ is the way to process the nanoparticles. This chapter explains the framework of study, experiment done by whom, when, where, utilized techniques & analysis of output.

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