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Experimental procedures

2.1 Introduction:

In hydrothermal process due to the change in the physical and chemical properties at high pressure, the temperatures needed to synthesize specific inorganic compounds are much lower than in a conventional solid state synthesis. Additionally, purer and defect free materials are often obtained. As extended, high temperature treatment is not required, thermodynamically metastable phases can be obtained, and since it is easy to change the chemical environment in the synthesis by altering e.g. the pH value or oxidation potential, it has been shown possible to synthesize complex inorganic materials [1]. The crystallite size and morphology can furthermore often be altered on the nanoscale by simply adjusting the synthesis parameters, i.e. temperature, precursor concentration, pH etc. Additionally, the process is easily scalable, especially when using continuous apparatuses. The precursors are often simple metal salts which are cheap and readily available. Compared to advanced soft chemical techniques, hydrothermal synthesis uses no toxic solvents, expensive and toxic additives such as organic surfactants or harsh reductants are not needed in the reaction [2-4]. The hydrothermal method thus shows great promise for several different applications and fields. In recent years, much attention has also been given to improvements of the method. The continuous flow approach is in fast progress, with new mixing technologies, setups for core-shell nanoparticle synthesis etc. being built. The microwave hydrothermal synthesis method was first reported in 1992 by Komarneni et al, [5] and has since then been used for several different systems [6]. Other combinations of technologies include ultrasonic-
hydrothermal synthesis, electrochemical-hydrothermal synthesis as well as mechanochemical-hydrothermal synthesis [7].

2.1.1 Temperature, pressure and boiling of liquids:

A liquid boils at the temperature at which its vapour pressure equals the surrounding pressure. The standard boiling point is defined as the temperature at which the liquid boils under a pressure of 1 bar [8]. Increasing the pressure of the system allows a liquid to contain more thermal energy whilst remaining in a saturated state, thereby increasing the boiling point. This temperature of saturation can increase with pressure to a critical point at which its gas and liquid properties become identical, and cannot increase further, as shown for water in Fig. 2.1. Likewise, the boiling point decreases with decreasing pressure until a triple

![Pressure–Temperature diagram showing the phase change boundaries of water](image)

**Fig. 2.1** Pressure–Temperature diagram showing the phase change boundaries of water [10].
point is reached at which it cannot be further reduced. Moreover, when a nonvolatile solute is added to a solvent the boiling point of the solution will be higher than the solvent [9]. This colligative property, i.e. dependent on the presence of dissolved particles and their number, irrespective of their identity, is called boiling point elevation. In thermodynamic terms, boiling point elevation is entropic and can be explained in terms of the chemical potential of the solvent, as shown in Fig.2.2. Chemical potential is the change in energy of a species in a system if an additional particle of that species is introduced, with the entropy and volume held fixed. At the boiling point, the liquid and vapor phase have the same potential, i.e. they are energetically equivalent. When a non-volatile solute is added, the chemical potential of the solvent in the liquid phase is decreased by dilution, whilst the chemical potential of the solvent in the vapor phase is not affected. Hence, the equilibrium established between a liquid and the vapor phase is at a higher temperature in a solution than a pure solvent.

Fig.2.2 Schematic of change in the chemical potential of a solution illustrating boiling point elevation [11].
2.2 Particle Nucleation and Growth Theory:

2.2.1 Nucleation of Particles in a Liquid:

Classic, text-book nucleation theory builds on theoretical considerations for solid particles in melts, but these are often extended to other solid/liquid systems e.g. hydrothermal synthesis. Although many approximations are done when considering a hydrothermal synthesis in this context, the approach is useful when trying to understand the basic processes. The theory uses simple thermodynamic functions to describe the formation of the nuclei that lead to particles. Two different mechanisms are often considered, namely homogenous or heterogeneous nucleation, and here, homogenous nucleation is introduced. Generally, atoms in a melt (or another liquid phase) will fluctuate in the liquid phase due to thermal motion. Sometimes, these fluctuations will lead to formation of atomic assemblies with local structures resembling that of a solid phase. If there is a thermodynamic gain related to this cluster formation, the assembly might stay stable, and act as nuclei for particle formation. However, when forming a new particle, an interface between the liquid and solid phase is created. This costs energy, and the total expression for the change in Gibbs free energy can be written as:

$$\Delta G_v = -V_s \Delta G_v + A_{SL} \gamma_{SL}$$  \hspace{1cm} (1)

Here, $V_s$ is the volume of the solid particle, $\Delta G_v$ the energy gain by forming the solid, $A_{SL}$ the area of the interface and $\gamma_{SL}$ the interfacial energy. Assuming that this energy is isotropic and that the particles are spherical with radii $r$, the following expression is obtained:

$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$  \hspace{1cm} (2)
This function is plotted in Fig. 2.3, where a maximum is seen at \( r = \frac{2\gamma_{SL}}{\Delta G_V} \). Thus, only above this limit, it is thermodynamically favorable to form particle nuclei. Below it, the clusters are unstable in equilibrium with the species still in solution. The local fluctuations and the amount of species in the liquid phase therefore have to be large enough for clusters above the critical size to form [12]. The critical cluster size may be considered in terms of supersaturation of dissolved species. The relative supersaturation is given as \( S_R = \frac{AP}{K} \), where AP is the activity product for dissolved species ready to precipitate, while K is the solubility product. The change in Gibbs free energy is related to the supersaturation as

\[
\Delta G_v = kT\ln(S_R)
\]

and higher relative supersaturation will thus decrease the critical nucleus radius required for stable cluster formation [13]. The equilibrium constant, K is heavily dependent on the dielectric constant, \( \varepsilon \), of the solvent, and a revised Helgeson-Kirkham-

![Fig. 2.3](image)

**Fig. 2.3** The size dependent change in Gibbs free energy for nucleation as function of the radius of the formed solid cluster.
Flowers (HKF) model can be used to calculate equilibrium constants for several inorganic compounds under hydrothermal conditions [14]:

\[
\ln K(T,\rho) = \ln K(T_0,\rho_0) + \left( \frac{\delta \ln K}{\delta (1/T)} \right) \left( \frac{1}{T} - \frac{1}{T_0} \right) - \frac{\omega}{T} \left( \frac{1}{\varepsilon(T,\rho)} - \frac{1}{\varepsilon_0(T_0,\rho_0)} \right)
\]

(3)

Here, \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constants at the actual temperature/pressure and standard ambient conditions, respectively. \( K_0 \) is the equilibrium constant at standard conditions and \( \omega \) is a constant parameter specific for the reaction system.

2.2.2. Growth of Particles in Solution:

When stable nuclei are formed in the liquid, the particles will start growing to minimize the energy loss related to the newly formed high surface area. This can happen through several different growth mechanisms, again depending on the chemistry and local environment. Classically, particle growth is described based on differences in surface energy of small and large particles.

For solid species present at the solid/liquid interface, the chemical potential increases with decreasing particle size, following the thermodynamic theory presented above. This leads to re-dissolution of the smallest, newly formed particles, creating a concentration gradient in the solution. Uniformity of the concentration is reestablished by material diffusion towards the larger particles, thus leading to particle growth. The process, illustrated in a simple diagram in Fig.2.4 was first described by Ostwald in 1897 [15] and the mechanism is therefore known as ‘Ostwald ripening’. Since the growth rate is dictated by material diffusion between particles, the process is often termed ‘diffusion limited growth’.
Fig.2.4 Particle growth by Ostwald ripening.

The full mathematical treatment of the process was done in the 1960’s by Lifshitz and Slyozov [16] followed by work by Wagner [17] and is known as LSW-theory. It was shown that the diffusion limited growth process leads to time- growth dependence of the form:

$$r^3 - r_0^3 = Kt$$  \hspace{1cm} (4)

Here, $t$ is the time, $r$ the particle radius, $r_0$ the particle radius at time $t=0$ and $K$ a constant containing the interfacial energy, the diffusion constant of the system, the average concentration of the species and the temperature among other parameters. If the diffusion of material to the growing particles is faster than the actual reaction of the material with the particle surface, the growth is reaction-limited. In this case, it can be shown that the time dependency of the size is:

$$r^2 = K_R t$$  \hspace{1cm} (5)

Analysis of the growth curves can therefore give indications of which step in the particle growth determines the growth rate.

Although, in the present work, the growth of $\alpha$-Fe$_2$O$_3$ based nanoparticles have not been thoroughly explored via Ostwald ripening process, the details about the growth process, such as initial nucleation, influence of solution basicity/acidity and the particle interaction
depends on Ostwald ripening process during hydrothermal treatment [18]. In this context nanoparticle formation via Ostwald ripening is discussed particularly in section 2.4.1.1 using relevant literature.

2.3 Synthesis Techniques:

2.3.1 Hydrothermal synthesis:

Hydrothermal processing can be defined as any heterogeneous reaction in an aqueous solvent (or non-aqueous solvent for solvothermal processing) under high pressure and temperature conditions, which induces the dissolution and recrystallization of materials that are relatively insoluble under ordinary conditions. Fig.2.5 shows a pressure/temperature map of hydrothermal synthesis in relation to other material processing techniques [19]. In comparative terms, the hydrothermal processing of materials is considered environmentally benign. Further, the hydrothermal technique offers the highly controlled diffusivity of strong

Fig.2.5 Pressure/temperature map of material processing techniques [20].
solvent media in a closed system. In the context of nanotechnology, the hydrothermal technique provides an ideal method for producing ‘designer particulates’, i.e. mono-dispersed particles with high purity, high crystallinity and controlled physicochemical characteristics. Such particles are in great demand by industry. Fig.2.6 shows the major differences in particle products obtained by ball milling, sintering/firing and hydrothermal methods [21].

Fig.2.6 Particle processing by conventional and hydrothermal techniques, producing irregular shaped particles and ‘designer particulates’, respectively [21].

For example, ball milling involves breaking down bulk material into small irregular shaped particles, and hence is considered a crude fabrication method in comparison to the controlled growth provided by hydrothermal method. The hydrothermal product particle size can range from a few nanometres up to several microns, depending on temperature, nucleation seed
content, pH and solvent concentration. The behaviour of solvents under hydrothermal conditions allows the development of crystal structures under sub- and supercritical states (along with pH variations, viscosity, coefficient of expansion and density, etc.) to be understood in terms of varying pressure and temperature. Similarly, thermodynamic studies provide valuable information on the behavior of solutions with respect to varying pressure and temperature conditions. Some commonly studied aspects are solubility, stability, yield and dissolution/precipitation reactions, etc. However, fundamental understanding of the kinetics during hydrothermal crystallization is limited. This is due to an absence of data relating to the formation of intermediate phases and the inaccessibility of direct in situ investigation techniques under conditions of high pressure and temperature.

2.3.1.1 Instrumentation for hydrothermal processing:

Hydrothermal materials processing requires a vessel capable of containing a highly corrosive solvent, operating under extreme pressure and temperature conditions. The hydrothermal apparatus, commonly known as an autoclave, reactor, pressure vessel or high pressure bomb, must meet a variety of objectives, processing conditions and tolerances. A generic hydrothermal autoclave should be:

1) Leak-proof under high pressure/temperature conditions.
2) Easily assembled/disassembled.
3) Inert to acids, bases and oxidizing agents.
4) Resilient to high pressure and temperature experiments, so that no machining or treatment is needed after each experimental run.
In view of the above requirements, autoclaves are generally fabricated from thick glass or quartz cylinders and high strength alloys, such as austenitic stainless steel, iron, nickel, cobalt-based super alloys or titanium and its alloys [22]. The primary parameters to be considered in the selection of a suitable reactor are the experimental temperature and pressure conditions, including corrosion resistance in the pressure/temperature range for a given solvent. Materials processing from aqueous phosphoric acid media or other highly corrosive media, i.e. extreme pH conditions, require the use of an un-reactive Teflon lining, as shown in Fig.2.7 or inert tubes (platinum, gold or silver) to protect the autoclave body.

**Fig.2.7 General purpose pressure autoclave and white Teflon lining used for hydrothermal process.**

corrosion. Further, the hydrothermal technique offers the highly controlled diffusivity of strong solvent media in a closed system. In the context of nanotechnology, the hydrothermal technique provides an ideal method for producing ‘designer particulates’, i.e. mono-dispersed particles with high purity, high crystallinity and controlled physicochemical characteristics. Such particles are in great demand by industry. In the present work and inorder to develop nanostructures of different architectures as a function of various hydrothermal synthesis processing conditions, a standard 50 ml capacity Teflon-lined stainless steel pressure
autoclave was employed. In this chapter different architectures like disc and horse shoe shaped $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles employing glycine and $\alpha$-$\text{Fe}_2\text{O}_3/\text{SnO}_2$ nanoheterostructures with different SnO$_2$ Wt. ratios have been fabricated by hydrothermal process. The experiments conducted are explained clearly in the forthcoming sections.

2.3.2 Solution mixing method:

To prepare mixed metal oxide nanocomposites, various synthesis methods including solid state reactions (i.e. thermal decomposition of mechanical mixtures of metal salts), mechanical mixing of metal oxides (i.e. ball milling), chemical co-precipitation and electrochemical anodic deposition from solutions containing metal salts and solution mixing method have been employed. Among these, solution mixing is a simple method to fabricate graphene/semiconductor nanocomposites. The oxygenated functional groups on graphene oxide (GO) facilitate the uniform distribution of metal oxide under vigorous stirring or ultrasonic agitation [23]. Graphene-based nanocomposites can be obtained after the reduction of GO in the nanocomposite. For example, Bell et al. [24] fabricated TiO$_2$/graphene nanocomposites by ultrasonically mixing TiO$_2$ nanoparticles and GO colloids together, followed by ultraviolet (UV)-assisted photocatalytic reduction of GO to graphene. Similarly, GO dispersion and N-doped Sr$_2$Ta$_2$O$_7$ have been mixed together, followed by reduction of GO to yield Sr$_2$Ta$_2$O$_{7-x}$N$_x$/graphene nanocomposites under xenon lamp irradiation [25]. Paek et al. [26] prepared the SnO$_2$ sol by hydrolysis of SnCl$_4$ with NaOH, and then the prepared graphene dispersion was mixed with the sol in ethylene glycol to form the SnO$_2$/graphene nanocomposite. Liao et al. [27] fabricated GO/g-$\text{C}_3\text{N}_4$ nanocomposites via sonochemical approach, which was realized by adding g-$\text{C}_3\text{N}_4$ powder into GO aqueous
solution followed by ultrasonication for 12 h and then drying at 353 K. Very recently, Perera et. al. [28] have prepared graphene/TiO$_2$ nanotube composite with different GO compositions through an alkaline hydrothermal treatment. In the present work α-Fe$_2$O$_3$/graphene nanocomposites with different graphene compositions were prepared by solution mixing method followed by annealing the samples in air.

2.4 Sample preparation and formation mechanism:

2.4.1 Hydrothermal synthesis of α-Fe$_2$O$_3$ nanoparticles using glycine:

Iron (III) chloride (FeCl$_3$·5H$_2$O), pure was purchased from Merck, Mumbai and glycine (NH$_2$CH$_2$COOH), pure was purchased from NICE, Cochin. α-Fe$_2$O$_3$ nanoparticles were synthesized by hydrothermal approach using FeCl$_3$ as an iron source. In a typical synthesis, equimolar ratio (1:1) of glycine (0.3 M in 20 mL) and FeCl$_3$ (0.3 M in 20 mL) were separately dissolved in double distilled water under stirring, for 10 min. The above two solutions were mixed, magnetically stirred for 30 min and transferred into a 50 mL Teflon-lined stainless steel autoclave, followed by hydrothermal treatment of the mixture at 160 °C for 19 h. After hydrothermal reaction, the reddish brown precipitates were centrifuged with double distilled water several times. The washed precipitates were air dried in an oven (KEMI) at 80 °C overnight and labeled as G$_1$ for further characterizations. Similarly the molar ratios of FeCl$_3$ to glycine were varied to 1:3, 1:9, 1:12 and 1:15, labeled as G$_2$, G$_3$, G$_4$ and G$_5$ respectively.

2.4.1.1 Possible formation mechanism:

FeCl$_3$ undergoes hydrolysis in aqueous solution to form Fe(OH)$_3$ and also releases
proton. In presence of glycine amino acid, probably the protons are absorbed by NH₂ group and thereby NH₃⁺ with Cl⁻ counter ion is formed as given below.

\[
\text{FeCl}_3 + 3\text{H}_2\text{N-CH-COOH} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{Cl}^{-} + \text{N}^+\text{H}_3\text{-CH-COOH}
\] (6)

α-Fe₂O₃ nanocrystals are formed by a two step phase transformation [29].

\[
\text{Fe(OH)}_3 \rightarrow \text{β-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 \text{ (phase transformation)}
\] (7)

The positively charged protonated glycine interacts with Fe(OH)_3 via electrostatic and hydrogen bond, thereby controls the size of α-Fe₂O₃ nanoparticles. Greater the concentration of glycine, larger is its interaction and control over the particle size. The growth process, such as initial nucleation, influence of solution basicity/acidity and the particle interaction depends on Ostwald ripening process during hydrothermal treatment [21]. The detailed size determination using TEM is discussed in chapter IV.

### 2.4.2 Hydrothermal synthesis of α-Fe₂O₃ hexagonal disc/SnO₂ nanoparticle semiconductor nanoheterostructures (SNH’s):

#### 2.4.2.1 Synthesis of bare α-Fe₂O₃ hexagonal discs (HD’s):

Iron (III) nitrate (Fe(NO₃)₃), anhydrous and sodium hydroxide (NaOH) pellets were purchased from Merck, Mumbai. Sodium acetate (CH₃COONa) was purchased from Fisher inorganics & aromatics, Madras. Stannic chloride pentahydrate (SnCl₄·5H₂O) was purchased from High media, Mumbai. α-Fe₂O₃ HD’s were synthesized by hydrothermal method. In a typical method, 0.1 M Fe(NO₃)₃ and 0.3 M CH₃COONa were dissolved in 40 mL of double distilled water under magnetic stirring. The above solution was transferred into a Teflon-lined stainless steel autoclave and heated at 160 °C in an electric oven for 24 h. The suspensions were centrifuged with double distilled water several times to collect the reddish
brown precipitates. Then the precipitates were air dried in an electric oven (KEMI) at 80 °C overnight to obtain α-Fe$_2$O$_3$ HD’s and labeled as S$_1$.

2.4.2.2 Fabrication of SNH’s:

Initially SnO$_2$ was prepared using 40 mL of 0.015 M SnCl$_4$ and 0.045 M NaOH by hydrothermal method at 160 °C for 3 h and the yield was 0.0912 g of SnO$_2$. SNH’s were also prepared by the simple hydrothermal strategy. Typically, 0.1824 g of α-Fe$_2$O$_3$ HD’s were dispersed in 40 mL of double distilled water containing 0.015 M SnCl$_4$ and 0.045 M NaOH to set 1:0.5 ratio of α-Fe$_2$O$_3$:SnO$_2$. The solutions were mixed thoroughly under magnetic stirring and hydrothermally treated in an autoclave at 160 °C for 3 h. The precipitates were centrifuged with double distilled water several times and dried in an electric oven (KEMI) at 80 °C overnight to obtain SNH’s and labeled as S$_2$. Similarly the weight ratio of α-Fe$_2$O$_3$ to SnO$_2$ was varied in the ratio 1:1 and 1:2, by mixing 0.0912 and 0.0456 g of α-Fe$_2$O$_3$ in the solution, labeled as S$_3$ and S$_4$ respectively.

2.4.2.3 Possible formation mechanism:

The possible reaction mechanism for the formation of bare α-Fe$_2$O$_3$ HD’s (S1) in the CH$_3$COONa system may be illustrated as follows [30].

\[
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COOH} + \text{OH}^- \quad (8)
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3/\text{FeOOH} \quad \xrightarrow{\text{Hydrothermal160}^\circ\text{C}} \quad \alpha\text{-Fe}_2\text{O}_3 \quad (9)
\]

\[
\alpha\text{-Fe}_2\text{O}_3 + 6\text{CH}_3\text{COOH} \leftrightarrow 2\text{Fe}^{3+} + 6\text{CH}_3\text{COO}^- + 3\text{H}_2\text{O} \quad (10)
\]

As shown above, Fe$^{3+}$ reacted with OH$^-$ produced by hydrolysis and formed Fe(OH)$_3$/FeOOH suspension. During hydrothermal process, Fe(OH)$_3$/FeOOH powders are
easily dehydrated to form $\alpha$-Fe$_2$O$_3$ HD’s. CH$_3$COONa is used as a structure directing agent [31] and leads to the formation of HD’s due to the different adsorption ability of CH$_3$COO$^-$ on different planes of $\alpha$-Fe$_2$O$_3$. The CH$_3$COO$^-$ stemming from the added CH$_3$COONa can charge the surfaces of as obtained nanoparticles negatively. As a result, well dispersed $\alpha$-Fe$_2$O$_3$ HD’s are obtained with the addition of CH$_3$COONa. Also the hydrothermal route and formation mechanism for fabricating SNH’s is shown in scheme 2.1. Growth of NP’s occurs by a solution-solid process due to the dissolution of precipitate and homogeneous nucleation [32]. The chemical mechanism for the formation of SnO$_2$ NP’s during hydrothermal process is given below [33].

$$\text{SnCl}_4 + 4\text{NaOH} \rightarrow \text{Sn(OH)}_4 \downarrow + 4\text{NaCl} \quad (11)$$

$$\text{Sn(OH)}_4 \xrightarrow{\Delta} \text{SnO}_2 + 2\text{H}_2\text{O} \quad (12)$$

**Scheme 2.1 Hydrothermal route and formation mechanism for fabricating SNH’s.**

In seed-mediated growth method, the shell formation involves two steps [34]. First, SnCl$_4$ reacts with NaOH and forms Sn(OH)$_4$, according to reaction (11). When the HD seeds are dispersed into the solution containing Sn(OH)$_4$, it is adsorbed on the surface of $\alpha$-Fe$_2$O$_3$ via electrostatic effects [35]. When the surface energy decreases, SnO$_2$ NP’s are randomly heteronucleated on the surface of HD’s through dehydration of Sn(OH)$_6^{2-}$ [36]. Second during hydrothermal process, with slow heating rate, the adsorbed Sn(OH)$_4$ decompose and
form SnO$_2$ NP shell layer (reaction (12)) on the surface of $\alpha$-Fe$_2$O$_3$ HD seeds, and finally forming core–shell SNH’s. The detailed heterostructure architecture is analyzed using TEM in chapter IV.

2.4.3 Synthesis of $\alpha$-Fe$_2$O$_3$/graphene nanocomposites by solution mixing method:

2.4.3.1 Preparation of graphene nanosheets (GN’s) by Hummer’s method:

Graphite powder, < 20 μm, synthetic was purchased from Sigma Aldrich, Switzerland. Sulfuric acid (A.R.) was purchased from High media, Mumbai. KMnO$_4$ was purchased from HANS CHEM, India. Sodium acetate (CH$_3$COONa), hydrogen peroxide (H$_2$O$_2$) and iron (III) nitrate (Fe(NO$_3$)$_3$), anhydrous were purchased from Merck, Mumbai. GN’s were synthesized using a modified Hummer’s method [37]. 0.5 g of graphite powder and 0.5 g of NaNO$_3$ were added in 23 mL of 12.1 M H$_2$SO$_4$ and stirred in an ice bath for 15 min. Then 4.0 g of KMnO$_4$ was slowly added to the above mixture placed in the same ice bath to yield a purple-green mixture. This suspension was transferred to a 40 °C water bath and magnetically stirred for another 90 min. The dark brown colored paste was diluted with the slow addition of 50 mL of double distilled water (DD) and allowed to stir for a further 10 min. A 6 mL portion of H$_2$O$_2$ was slowly added to quench the solution and thus a golden-brown sol was obtained. The resultant product was centrifuged and washed with 50 mL of DD water repeatedly. Finally the product was dried at 80 °C for 24 h in an electric oven to collect the black precipitates.

2.4.3.2 Synthesis of $\alpha$-Fe$_2$O$_3$ nanodiscs (ND’s)/GN’s:

$\alpha$-Fe$_2$O$_3$ ND’s were prepared as mentioned in section 2.4.2.1. $\alpha$-Fe$_2$O$_3$/graphene
nanocomposites with different GN’s compositions were prepared through a simple solution mixing method. First, 5% of GN’s were sonicated in 30 mL of DD water for 1 h to achieve uniform dispersions of GN’s. Next, α-Fe₂O₃ ND’s were added slowly to the GN’s dispersions while stirring. The α-Fe₂O₃/GO mixture was further stirred for 1 h to ensure complete mixing. Then 10.5 g of NaOH was added to the above solution and stirred for another 10 min. The pH was noted as 14. Again 60 mL of DD water was added and this washing process was repeated several times until the pH reaches to 7. Finally the nonocomposites were filtered using a filter paper. The precipitates were dried in an electric oven overnight at 80 °C to collect the powders. In order to achieve a good anchoring of α-Fe₂O₃ ND’s on the surface of GN’s annealing was carried out at 400 °C for 3 h and the resulting nanocomposite was labeled as N₁. Similarly, the compositions of GN’s were varied as 10%, 15% and 25% and they were labeled as N₂, N₃ and N₄ respectively. The schematic representation of nanocomposite formation during solution mixing process and annealing is shown in scheme 2.2. The detailed nanocomposite architecture fabricated is analyzed using TEM in chapter IV.

![Scheme 2.2 Nanocomposite formation during solution mixing process and annealing.](image-url)
2.5 Conclusions:

α-Fe₂O₃ nanoparticles were synthesized by hydrothermal approach with the assistance of glycine. The formation α-Fe₂O₃ nanoparticles and the mechanism for size reduction are explained with the help of reaction equations during hydrothermal process. α-Fe₂O₃/SnO₂ SNH’s were also prepared by the simple hydrothermal strategy with the assistance of NaOH. In this case CH₃COONa served as a structure directing agent for preparing α-Fe₂O₃ HD’s. Also, the chemical mechanism for the formation of SNH’s during hydrothermal process is interpreted using reaction equations. α-Fe₂O₃/graphene nanocomposites with different compositions are synthesized by solution mixing method followed by annealing the samples in air. The formation mechanism of the nanocomposites is explained using scheme.
References:


