Synthesis of Nanomaterials

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3.1 INTRODUCTION

Nanomaterials, dimension size between 1 and 100 nanometers, are categorized in four sections [1]: (1) zero-dimensional (confined all dimensions in nanoscale such as clusters, quantum dots, and nanoparticles), (2) one-dimensional (confined two dimensions in nanoscale such as nanotubes, nanorods, and nanowires), (3) two-dimensional (confined one dimensions in nanoscale such as nanofilms, nanolayers, and nanocoatings), and (4) three-dimensional (confined no dimensions in nanoscale including nanocomposites, porous materials, powders, fibrous, multilayer, and polycrystalline materials) (see Figure 3.1).

In general, several methods that have been mostly used for preparation of nanomaterials are categorized into two main approaches: top-down and bottom-up [2,3]. Top-down approach refers to reducing the dimension of the original materials using physical techniques. Bottom-up or chemical approach is a popular method in which nanomaterials could be produced from the atomic or molecular scale [4]. Figure 3.2 shows physical and chemical approaches to obtain nanomaterials.

3.2 ZERO-DIMENSIONAL MATERIALS

3.2.1 SYNTHESIS OF METAL NANOCLUSTERS

Metal nanoclusters (NCs) containing a number of atoms are a new category of nanomaterials that cover the distance between metal atoms and nanoparticles (NPs). They have attracted a great deal of attention in recent years due to optical, electrical, chemical, and molecule-like features [5–8].

Wang’s group used a general approach for synthesis of nanocrystals such as noble metals [9]. This approach is using a general phase transfer and separation mechanism taking place at the interfaces of the liquid, solid, and solution phases existing through synthesis. In this technique, uniform

![FIGURE 3.1](See color insert.) Classification of nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, and (d) 3D nanomaterials.
noble metal quantum dots, or nanocrystals, were produced using the reduction of noble metal ions via ethanol at various temperatures of 20–200°C under hydrothermal or atmospheric situations.

Up to now, many researchers made considerable attempts at the synthesis of several noble metal nanoclusters such as Cu, Pd, Ag, Pt, and Au NCs [10–12], but between them, gold nanoclusters have received particular interest due to some good properties such as their facile synthesis, nontoxicity, outstanding photophysical features, and astonishing chemical stability. It is interesting to note that luminescent gold nanoclusters (AuNCs) are a new category of luminescent nanomaterials which have a particle size under 2 nm and contain about 100 gold atoms [13]. Various methods have been applied for preparation of uniform luminescent AuNCs with high quality.

It is well known that sodium borohydride (NaBH₄) is used normally for reduction of HAuCl₄ solution to Au nanoparticles (AuNPs) because the Au atoms have a great tendency to aggregation when a strong reducing agent such as NaBH₄ is utilized. Therefore, partially weak reducing agents could be applied to synthesize small luminescent AuNCs. Consequently, thiol-containing precursors are appropriate reducing agents and stabilizers for preparation of this kind of nanomaterial. Also the reaction conditions and synthesis processes could be controlled by different techniques [14].

### 3.2.1.1 Microwave-Assisted Synthesis

Microwave irradiation (MWI) is one of the most significant methods for the synthesis of nanomaterials because of several outstanding superiorities such as low energy consumption, uniform heating, environment-friendly features, and cost-effectiveness [15–17]. Furthermore, the main advantage of MWI in comparison to conventional heating is that this method is rapid and uniform.

Yue and coworkers prepared extremely fluorescent AuNCs containing 16 gold atoms using a one-step microwave-assisted technique with MWI for 6 h with power of 700 W. They utilized bovine serum albumin (BSA) as the reducing agent and the stabilizer which is reacted with HAuCl₄ as an Au precursor. In this method, the reaction was under particularly simple conditions (pH = 12) at 37°C via MWI as an alternative of direct heating to maintain the temperature [18].

Moreover, in this method the reaction time can be reduced from several hours to 1 h with modified processes using microwaves. For instance, Chen et al. applied eight cycles of consecutive microwave heating (5 min per cycle with the power of 90 W) to prepare the lysozyme-directed AuNCs [19].

A very rapid and strong microwave-assisted green synthesis of Ag nanoclusters with high fluorescent in the presence of a common polyelectrolyte, polymethacrylic acid sodium salt (PMAA-Na), was reported by Liu and coworkers [20]. In addition, we could reduce the reaction time to some minutes by controlling the irradiation power [21,22]. The microwave-assisted method provides fast and uniform heating; thus, it can speed up the synthesis of nanomaterials.
3.2.1.2 Sonochemical Synthesis

The sonochemical method is an additional important approach for synthesizing nanomaterials. This method has significant advantages such as fast reaction, harmless, easy to control the reaction conditions, and it produces monosize and uniform NPs with high purity [23].

In the following, we will explain the sonochemical method by an example of preparing highly water-soluble silver nanoparticles (AgNCs) by Liu et al. [23].

In this work, the BSA-stabilized AgNCs were synthesized by a facile, fast, green sonochemical synthesis method. In this method, briefly, 250 mg of BSA was dissolved in 9 mL water and mixed with aqueous AgNO₃ solution (1 mL, 100 mmol/L), reacting at ambient temperature for 5 min with vigorous stirring, then 0.50 mL, mol/L NaOH was added to the solution to adjust the pH to 12, where BSA acted as a stabilizing agent and reducing agent in this condition; finally, the mixture was exposed to ultrasonic irradiation (50 W/cm²) under low temperature (15°C) for 4 h. During this period, the color of the colloid solution changed from colorless to yellow, providing clear evidence for the formation of AgNCs [24]. The AgNCs solution is purified via dialysis using 7000 Da molecular-weight cutoffs (MWCO) dialysis bag.

Sonochemical reduction of Ag⁺ needs the use of a template or capping agent to avoid the aggregation of Ag nanoclusters to form large Ag nanoparticles. Xu et al. [25] used a simple polyelectrolyte, polymethylacrylic acid (PMAA), as a stabilizer agent. It should be noted that PMAA contains carboxylic acid groups, which have a great tendency to silver ions and silver surfaces; therefore, PMAA is a preferable capping agent for synthesis of Ag nanoclusters [26,27]. The charged carboxylate groups afford stability for Ag nanoclusters and avoid extra growth of nanoclusters to large nanoparticles.

To synthesize Ag nanoclusters, a fresh solution of AgNO₃ as Ag⁺ precursor was mixed with an aqueous PMAA solution. In this study, the molar ratio of carboxylate groups (from the methacrylic acid units) to Ag⁺ was 1:1. Then the pH was adjusted to 4.5 due to formation of compacted coil PMAA, which has been reported as the best reagent to produce Ag nanoclusters [25]. The solution was purged with Ar for 2 h and then sonicated for a different period of time. As shown in Figure 3.3a, under sonication, the first colorless solution slowly changes to pink (90 min) and then dark red (180 min). The producing Ag nanoclusters have a high fluorescence (Figure 3.3b). As it is illustrated in Figure 3.3c and e, the resulting Ag nanoclusters are less than 2 nm in diameter [25].

In addition to the methods of synthesis mentioned above, other techniques may also be used for preparing AuNCs, for example:

- **Photoreductive synthesis**: In this technique, ultraviolet light is employed as a reducing agent for preparation of AuNCs from Au(III) precursors.
- **Etching-based technique**: In this method, the AuNPs are etched with extra amounts of molecules, such as dendrimers, thiols, and Au₃⁺ ions to form the AuNCs [28].
- **Microemulsion method**: In this method, AuNCs is obtained by adding aqueous NaBH₄ solution to a microemulsion containing methanol, thiolates, and HAuCl₄ under vigorous stirring [29–32]. The microemulsion method will be explained in detail in the next section.

Figure 3.4 illustrates a schematic of different methods for preparation of AuNCs. As it is shown in this figure, Au³⁺ precursors and appropriate stabilizer agents are essential for synthesis of fluorescent AuNCs [14].

3.2.2 Synthesis of Quantum Dots

Semiconductor quantum dots (QDs) are nanoparticles with very high luminescence that have received great attention in bioanalysis, bioimaging, and optoelectronics. These colloidal nanocrystalline semiconductors are small and spherical particles or nanocrystals of a semiconducting material with diameters in the range of 1–12 nanometers (10–50 atoms). At such small sizes (smaller than
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The dimensions of the exciton Bohr radius, these nanocrystals act differently from bulk solids due to quantum confinement effects [33,34].

QDs have been prepared from a wide range of semiconductor materials. CdSe, CdTe, and their core/shell analogs, CdSe/ZnS and CdTe/ZnS, have received the most attention among QDs due to their well-established synthetic approaches [35].

![Figure 3.3](See color insert.) (a) UV–vis spectra and (b) fluorescence emission spectra of the solution containing PMAA and AgNO₃ in different length of sonication time; TEM images of as prepared Ag nanoclusters from different lengths of sonication: (c) 60 min, (d) 90 min, and (e) 180 min. (Reprinted with permission from Xu Hangxun, S. Kenneth Suslick, Sononochemical synthesis of highly fluorescent nanoclusters, American Chemical Society, 4, 3209–3214. Copyright 2010 American Chemical Society.)

![Figure 3.4](See color insert.) Synthesis of gold nanoclusters (AuNCs). (Adapted from M. Cui, Y. Zhao, Q. Song, Trends in Analytical Chemistry, 57, 2014, 73–82.)
However, there are frequent efforts and reports on preparation of QDs in aqueous media using suitable air-stable precursors, the actual breakthrough in preparation of highly fluorescent colloidal QDs happened when the Bawendi group reported [36] preparation of CdSe QDs with highly crystalline cores and size distributions of 8%–11% using a mixture of trioctyl phosphine/trioctyl phosphine oxide, TOP/TOPO with pyrolysis of organometallic precursors.

In the following, we will use this report as an example to exemplify the general method.

Dimethylcadmium (Me₂Cd) was utilized as the Cd precursor and bis(trimethylsilyl)sulfide ((TMS)₂S), trioctylphosphine selenide (TOPSe), and trioctylphosphine telluride (TOPTe) were used as S, Se, and Te sources, respectively. Mixed tri-n-octylphosphine (TOP) and tri-noctylphosphineoxide (TOPO) solutions were used as solvents and stabilizer agents known as coordinating solvents.

The process for synthesizing of TOP/TOPO capped CdSe nanocrystallites is briefly outlined below [36]. Fifty grams of TOPO is dried and purged in the reaction vessel via heating to 200°C at 1 torr for 20 min, and then it was purged with argon intermittently. The temperature of the reaction flask is then adjusted at 300°C under 1 atm of argon. One milliliter of Me₂Cd is added to 25.0 mL of TOP in the dry box, and 10.0 mL of 1.0 M TOPSe stock solution is added to 15.0 mL of TOP. Two solutions are then mixed and added to a syringe in the dry box. The heat is removed from the reaction vessel. The syringe holding the reagent mixture is rapidly removed from the dry box and its content is strongly stirred. The rapid introduction of these reagents results in an orange solution with an absorption feature at 440–460 nm. This is also accompanied by a sudden decrease in temperature to 180°C. Heating is restored to the reaction flask and the temperature is gradually raised to and aged at 230–260°C. Depending on the aging time, CdSe nanoparticles with a series of sizes ranging from 1.5 nm to 11.5 nm in diameter are prepared.

Produced colloidal dispersion is purified by cooling to 60°C, above the melting point of TOPO, and adding 20 mL of anhydrous methanol, which results in the reversible flocculation of the nanocrystallites. The flocculate and supernatant were then separated using centrifugation. Then flocculation was dispersed in 25 mL of anhydrous 1-butanol and a clear solution of nanocrystallites and a gray precipitate was obtained by additional centrifugation. In the next step, 25 mL of anhydrous methanol was added to the supernatant to flocculate the crystallites and remove excess TOP and TOPO. A final washing of the product with methanol followed by vacuum drying produces 300 mg of free flowing TOP/TOPO capped CdSe nanoparticles.

These CdSe nanocrystals are subsequently dispersed in anhydrous 1-butanol to form a transparent solution. Subsequently, methanol was added to the dispersion until opalescence persists. Finally, supernatant and flocculate were separated by centrifugation to produce a precipitate enriched of CdSe nanocrystallites. This dispersion and size-selective precipitation with methanol is repeated until no further narrowing of the size distribution as indicated by sharpening of the optical absorption spectrum.

A similar method joined with suitable organometallic reagents was used to coat the native CdSe core with different semiconducting, which has wider band gaps (e.g., ZnS and CdS) [37,38]. A summary of TOP/TOPO method is illustrated in Figure 3.5 [39].

It should be noted that QDs that are synthesized using this procedure are not aqueous soluble; therefore, phase transfer to aqueous solutions with surface modification using hydrophilic ligands or by encapsulating these nanocrystals in a thick hetero functional organic coating are required. These ligands facilitate both the colloid’s solubility and act as a point of chemical attachment for biomolecules [40].

The microemulsion method is another prevalent approach for preparation of QDs at room temperature. In this technique, reactions occur among the reagents inside the micelles. The formation of micelles is explained in the following.

When surfactants or block polymers, which generally contain two parts of hydrophilic head and hydrophobic chains, are dissolved into a solvent, they typically self-assemble at air/aqueous solution or organic/aqueous solution interfaces. The hydrophilic chains are turned to the aqueous
solution. When the concentration of the surfactants or block polymers is higher than a critical amount, they self-assemble to create micelles. Surfactants or block polymers remain at the interface of organic and aqueous solutions. Finally, a microemulsion is a distribution of fine liquid droplets of an organic solution in an aqueous solution which could be considered as normal microemulsions (oil-in-water emulsion) or inverse microemulsions (water-in-oil emulsion). In some conditions, other polar solvents such as alcohol could be applied instead of water. The microemulsion method could be employed for the preparation of nanoparticles. The reverse micelle process received the most attention for preparation of QDs, which two immiscible liquids such as water and long-chain alkane are mixed to create the emulsion. Nanoscale water droplets dispersed in different organic solutions might be achieved using added surfactant such as aerosol OT (AOT), cetyl trimethyl-ammonium bromide (CTAB), or sodium dodecyl sulfate (SDS) or triton-X.

These micelles are thermodynamically stable and could behave as “nanoreactors” [41]. The microemulsion technique needs the reaction of suitable initial resources, as an example, the reduction of metal ions or the decomposition of a single organometallic reagent could occur in the presence of a surfactant or polymer that avoids the particles growing and aggregating into bigger sizes. On the other hand, the nucleation and growth of the nanoparticles could happen in the presence of the surfactant. In this method, we could control size, shape, and feature of nanoparticles by adjusting the surfactant concentration and other factors such as reaction time, temperature, and concentrations of reagents [42].

3.2.3 SYNTHESIS OF NANOPARTICLES

The preparation procedures for nanoparticles (NPs) could be classified into three major collections. The first group includes the liquid-phase approaches, which employ chemical processes in solvents.
This results in colloids, in which the produced nanoparticles could be stabilized against agglomeration by surfactants or ligands.

The second group contains techniques based on surface growth under vacuum environments. In this method, diffusion of atoms or small clusters on appropriate substrates result in island creation, which can be consider nanoparticles. An important example of this method is Stranski-Krastanow, which is applied for growing III–V QDs. Finally, the last group is gas-phase preparation [43]. In the following, we will explain all these approaches by some example of metal, ceramic, and polymeric nanoparticles separately. First, we will emphasize the preparation of different sorts of nanoparticles using solution procedures. Synthesis of nanoparticles dispersed in a solvent is the most popular method, which has numerous advantages.

### 3.2.3.1 Synthesis of Metal Nanoparticle

Noble metal nanoparticles like gold, silver, and platinum have received great interest because of their size and shape and unique optoelectronic properties. These noble metal nanoparticles, especially gold nanoparticles, have obtained great attention for significant biomedical requests due to facile preparation, characterization, and surface modification. Preparation of noble metal nanoparticles such as Pt, Au, and Ag has attracted the most attention in recent decades. The most prevalent methods are chemical reduction, physical processes, and biological approaches.

#### 3.2.3.1.1 Chemical Reduction

The general procedure in the preparation of metal colloidal dispersions is reduction of metal complexes in dilute solutions, and different approaches have been advanced to start and adjust the reduction reactions [44]. Since this method is the most common method of synthesis for AuNP, we will exemplify it by the synthesis of AuNP in the following.

The formation of monosized AuNP is achieved by the reduction of gold salts in the presence of a reducing agent such as sodium citrate and a stabilizer [45]. Sodium citrate reduction of chlorauric acid (HAuCl₄) at 100°C was established more than 50 years ago [46] and remains the most frequently used technique. In this technique, HAuCl₄ dissolves into water to form a sufficiently dilute solution. Then sodium citrate is added into the boiling solution. The solution is kept at 100°C until color changes, while maintaining the overall volume of the solution by adding water. This synthesis of citrate stabilized AuNPs was based on a single-phase reduction of HAuCl₄ by sodium citrate in an aqueous medium and produced particles about 20 nm in size.

One of the most important reports on synthesis of AuNP was published in 1994 and is known currently as the Brust-Schiffrin method [47]. This method employed a two-phase synthesis that applied thiol ligands which could attach to gold intensely because of the soft properties of both S and Au. First, gold precursor is added to an organic solvent such as toluene with a phase transfer agent like tetraoctylammonium bromide, and then an organic thiol is added. Finally, an extra amount of an intense reducing precursor, such as sodium borohydride, is added to create AuNPs capped with thiol ligands [47]. The main benefits of this technique are the facile synthesis, uniform size distribution, thermally stable NPs, and ease of size adjustment [48].

Silver nanoparticles are an additional distinguished sample of chemical reduction technique. The easiest approach to produce silver nanoparticles is using reduction of silver nitrate (AgNO₃) as Ag⁺ precursor in ethanol in the presence of a surfactant [49]. Aggregation of Ag NPs could be prohibited by using some common stabilizers agents such as poly(vinylpyrrolidone) (PVP), bovine serum albumin (BSA), polyvinyl alcohol (PVA), and citrate and cellulose.

Dong’s group [50] reported work on controlling the size and morphology of silver nanoparticles via sodium citrate reagent in the pH range of 5.7–11.1. Reduction of the silver salt (Ag⁺) was increased by increasing the pH, due to the higher activity of the citrate reagent in high pH value. It is interesting that at higher pH, the morphology of nanoparticles was a mix of spherical and rod-like due to the rapid reduction rate of the precursor. However, in lower pH value, morphology of
nanoparticles was mostly triangle or polygon because of the slow reduction rate of the precursor.
Figure 3.6 illustrates the morphology of produced nanoparticles in different pH values.

3.2.3.1.2 Direct Laser Irradiation
Some other significant methods to prepare noble metal nanoparticles are UV irradiation, laser irradiation, and microwaves, which may not use reducing agents. For example, a new technique was reported [51] to prepare silver nanoparticles with a well-defined size and shape distribution using direct laser irradiation of an aqueous solution including a silver precursor and a surfactant without any reducing agents. The main purpose of this report was suggestion of a new technique for the synthesis of metallic nanoparticles using the laser irradiation of a metallic precursor solution without any reducing agent. In this work, about 3 mL of an aqueous solution of silver nitrate with concentrations of 0.833–4.166 mM was placed in a closed spectrophotometric cuvette and irradiated by laser beam in the presence of the surfactant sodium dodecyl sulfate (SDS) [51].

The mechanism of this synthesis method is explained by formation of radicals in the aqueous solution due to laser irradiation of the metal salt precursor in the absence of any reducing agent [52].

Photochemical reduction of gold precursor has also been applied to preparation of AuNPs [53]. This technique uses a continuous wave UV irradiation (250–400 nm), PVP as the stabilizer agent, and ethylene glycol as the reducing agent. The preparation rate of AuNPs with this technique is reliant on the glycol concentration as well as the viscosity of the solvent mixture [53].

3.2.3.1.3 Biological Methods
Another interesting method for nanoparticle fabrication is using biomolecules extracted from plants as a reducing agent of metal ions in a single-step green synthesis process. This method has a lot of significant advantages such as fast reaction, easy to perform in room temperature and pressure, and easily scaled up. It should be noted that preparation with plant extracts is an environmentally friendly approach. The extracted reducing agents comprise several water-soluble plants like alkaloids, phenolic compounds, terpenoids, and coenzymes. Silver (Ag) and gold (Au) nanoparticles have received the most important attention in the field of plant-based syntheses methods. Extracts

FIGURE 3.6 Transmission electron images for the silver nanoparticles synthesized under pH values of 11.1, 8.3, 6.1, and 5.7. (Adapted from X. Dong et al., The Journal of Physical Chemistry C, 113, 2009, 6573–6576.)
of a different plant species have been effectively applied in producing nanoparticles. In addition to plant extracts, live plants can be employed for the preparation of nanoparticles [54]. Up to now, different biomolecules such as microorganisms, plant tissue, their fruits, plant extracts, and marine algae [55] have been applied to preparation of nanoparticles. Biological synthesis methods are valuable not only due to their decreased environmental effect [56] contrary to many physicochemical synthesis approaches, but also because they could be applied to yield a lot of nanoparticles without any contamination with a suitable size and morphology [57].

It is claimed that biosynthetic approaches can really produce nanoparticles with even better size and morphology than some of the physicochemical techniques [58].

In preparation of nanoparticles by plant extracts, the extracted agent is easily mixed with a solution of the metal precursor at room temperature. The reaction is complete within minutes. Different nanoparticles of silver, gold, and many other metals have been prepared with this method [59].

Several plants such as tea (*Camellia sinensis*), aloe vera, neem (*Azadirachta indica*), and *Catharanthus roseus* have been applied for the biosynthesis of nanoparticles.

In this method, the production rate and properties of nanoparticles depend on some factors such as the nature of the plant extract, concentration of extract and metal precursor, the pH value, temperature, and reaction time [59].

### 3.2.3.2 Synthesis of Ceramic Nanoparticles

Recently, a new group of nanomaterials, ceramic materials, for biomedical application are developing rapidly. Nanoscale ceramics such as hydroxyapatite (HA), zirconia (ZrO$_2$), silica (SiO$_2$), titania (TiO$_2$), and alumina (Al$_2$O$_3$) have received great attention to produce new synthetic methods to increase their physical–chemical features toward decreasing their cytotoxicity in biological applications [60].

#### 3.2.3.2.1 Sol–Gel Method

The sol–gel process is the most widely used technique to prepare pure silica particles because of some significant advantages such as easy to control the particle size, size distribution, and morphology nanoparticles by systematic adjustment of reaction condition [61]. For a long time, the sol–gel approach was broadly used to prepare silica, glass, and ceramic materials because of its ability to form pure and homogenous products in moderate situations. The sol–gel method is a wet chemical procedure for the preparation of colloidal dispersions of inorganic and organic–inorganic hybrid materials, especially oxides and oxide-based hybrids.

This procedure includes hydrolysis and condensation of metal alkoxides (Si(OR)$_4$) like tetraethylorthosilicate (TEOS, Si(OC$_2$H$_5$)$_4$) or inorganic precursors such as sodium silicate (Na$_2$SiO$_3$) in the presence of mineral acid (e.g., HCl) or base (e.g., NH$_3$) as catalyst [62–64]. A general flowchart for the sol–gel procedure, which leads to the fabrication of silica using silicon alkoxides (Si(OR)$_4$), is illustrated in Figure 3.7.

The general reactions of TEOS make the formation of silica particles in the sol–gel procedure as the following reaction [61].

\[
\text{Si(OC}_2\text{H}_5)_4 + \text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{Si(OC}_2\text{H}_5)_3\text{OH} + \text{C}_2\text{H}_5\text{OH} \tag{3.1}
\]

\[
\equiv \text{Si} - \text{O} - \text{H} + \text{H} - \text{O} - \text{Si} \equiv
\]

\[
\xrightarrow{\text{Water condensation}} \equiv \text{Si} - \text{O} - \text{Si} \equiv +\text{H}_2\text{O} \tag{3.2}
\]

\[
\xrightarrow{\text{Alcohol condensation}} \equiv \text{Si} - \text{O} - \text{Si} \equiv +\text{C}_2\text{H}_5\text{OH} \tag{3.3}
\]
Alumina is one of the most important materials as inert biomaterials applied in implants that has been produced by the sol–gel technique.

It is therefore a biodegradable material, well endured by the biological environment. Different work on producing Al₂O₃ by the sol–gel technique using various precursors such as aluminum triisopropylate in a hydrolysis system consisting of octanol and acetonitrile [62], aluminum nitrate—in aqueous medium [63,64], aluminum secondary butoxide—in an alcoholic medium [65] have been reported thus far. To a general group of precursors include inorganics such as aluminum chloride (AlCl₃) and organics such as aluminum triisopropylate (C₃H₇O)₃Al [66] have been used for synthesis of Al₂O₃ by the sol–gel method.

We explain the synthesis of Al₂O₃ by the sol–gel technique with an example of using an inorganic precursor such as AlCl₃ in the following.

In this method, at first a solution of 0.1 M AlCl₃ in ethanol should be prepared. Then a 28% NH₃ solution was added to form a gel. This gel was kept at room temperature for 30 h and then dried at 100°C for 24 h.

Another example is using C₉H₂₁AlO₃ as a precursor, again first 0.1 M (C₃H₇O)₃Al solution in ethanol was prepared, then NH₃ solution (28%) was added in order to form a gel. It was put under slow stirring at 90°C for 10 h. This gel was kept at room temperature for 24 h and then dried at 100°C for 24 h. The produced gels were calcined in a furnace for 2 h (heating rate 20°C/min), at temperature values of 1000°C and 1200°C.

3.2.3.2.2 Coprecipitation Method

Coprecipitation (CPT) method is applied by a precipitate of materials, which is generally soluble under the conditions employed. Magnetite nanoparticles were prepared by the chemical coprecipitation technique by using ammonium hydroxide as the precipitating reagent.

We could adjust the particle size by changing the temperature of reaction and also by surface functionalization.

Nano- and micro-sized magnetic particles have received great attention in the field of biomedical applications and magnetic recording [67].

In the following, we will exemplify the coprecipitation method by synthesis of functionalized magnetic core–shell Fe₃O₄@SiO₂ nanoparticles [68]. Fe₃O₄ nanoparticles were produced by the coprecipitation of Fe²⁺ and Fe³⁺ precursor (molar ratio 1:2) in an alkali solution. A black precipitation
of Fe$_3$O$_4$ was obtained and then was constantly stirred for 1 h at room temperature and then heated to 80°C for 2 h. The produced Fe$_3$O$_4$ was collected by a permanent magnet after washing with deionized water and EtOH. Subsequently, it was dried at 100°C in a vacuum for 24 h. In the next step, silica coated magnetic nanoparticles was synthesized, in this way, 1 g of produced Fe$_3$O$_4$ under ultrasonic bath for 1 h at 40°C was dispersed in 80 mL of methanol. Then, concentrated ammonia solution was added to this dispersion and stirred at 40°C for 30 min. Then, tetraethylorthosilicate (TEOS, 1.0 mL) was added to the obtained mixture, and continuously stirred at 40°C for 24 h. Finally, the silica coated magnetic nanoparticles were collected by a permanent magnet, then washed with and dried at 60°C in vacuum for 24 h.

3.2.3.2.3 Aerosol Method

The aerosol-based method is one of the most attractive and simple methods for synthesis of nanoparticles. In contrast to the conventional solution methods, the aerosol process has many advantages, such as fast particle production, low fabrication cost, green method, simple and cheap particle collection, and produce material with high purity. Generally, this technique is based on homogeneous nucleation, condensation, and consequent coagulation in the continuous gas phase. Nanoparticles can also be produced by the ablation of a solid source with a pulsed laser [69].

Spray drying is another aerosol-based method that produces nanoparticles with a few process steps and high purity. In this method, liquid precursors were atomized directly into the furnace with high temperature to evaporate the solvent and resulting nanoparticles were collected on the filter. It should be noted that this gas phase method has the ability to produce dry powder with mesoporous structure and spherical shape [70].

In addition to the aforementioned methods, aerosol-polymerization is a simple and novel method to produce core–shell nanoparticles, consisting of an inorganic scaffold and polymeric shell, in a continuous gas-phase process. In this method, the polymerization was initiated in “flight” and avoids the need of surfactants and solvent. Furthermore, the resulting core–shell nanoparticles, leaving the aerosol set-up, were collected directly on the filter. Recently, Poostforooshan et al. have published an article about the in situ coating of inorganic nanoparticles with a polymer shell in a continuous aerosol-based synthesis [71].

In this method, silver and silica nanoparticles were initially produced in the gas-phase as inorganic cores by spark discharge and nebulization, respectively, and the particle-laden nitrogen gas flow was then passed through the saturator containing the glycidyl methacrylate (GMA) as organic monomer at 80°C. Behind the saturator, when the gas temperature dropped to room temperature, a super saturation was achieved resulting in the heterogeneous condensation of GMA vapor on the inorganic nanoparticle surface. Subsequently, the monomer coating was chemically polymerized to form a solid polymer shell by addition of ammonia vapor as initiator. The average aerosol residence time in the reactor is about 2 min. The continuous experimental setup consists of four main components: a core particle generator, a GMA monomer saturator, an ammonia addition, and a polymerization reactor, as illustrated in Figure 3.8.

3.2.3.3 Synthesis of Polymeric Nanoparticles

Recently, polymer nanoparticles have been considered in numerous applications. Two main procedures are used for their synthesis: (1) polymerization of monomers and (2) dispersion of synthesized polymers. There are various techniques to produce polymer nanoparticles including solvent evaporation, salting out, dialysis, supercritical fluid technology, microemulsion, miniemulsion, surfactant-free emulsion, and interfacial polymerization. A number of factors such as particle size, particle size distribution, and area of application as final product properties should be considered to affect choice of synthesis methods. In the next sections, methods for preparation of such particles will be discussed.
3.2.3.3.1 Emulsion Polymerization Method

The inverse emulsion polymerization of polymer nanoparticles is carried out in a 250 mL five-neck reactor equipped with a mechanical stirrer, heating system, reflux condenser, and submicron dropping injector for reaction ingredients and nitrogen gas as shown in Figure 3.9. A typical recipe for the inverse emulsion polymerization is presented in Table 3.1.

Tamsilian and Ramazani S.A. have synthesized polymeric core–shell nanostructure by in situ inverse miniemulsion to use in the enhanced oil recovery (EOR) process [72–78]. Their works are divided into four categories: (1) synthesis of polyacrylamide (PAM) nanoparticles [72,73], (2) synthesis of PAM-polystyrene (PS) core–shell nanostructure [74,75], (3) synthesis of PAM/PAM-c-PS [76,77], and (4) synthesis of thermoviscosifying polymer (TVP)/PAM-c-PS [78].

To produce PAM NPs based on inverse emulsion polymerization procedure, first, organic solvent and dispersion stabilizer with a modified hydrophilic–lipophilic balance (HLB range: 4–6) are introduced into the five-neck flask. The flask is then placed in a water bath at a constant temperature of 30°C with a stirring rate of 2000 rpm. After complete dissolution of the dispersion stabilizer in
the solvent for 1 h under nitrogen gas bubbling, hydrophilic monomer such as polyacrylamide dissolved in deionized water is dripped into the reactor by submicron dropping injector within a specified time to form inverse water in oil (W/O) emulsion. Then, temperature and stirrer speed are set at 60°C and 400 rpm, respectively, and azobisisobutyronitrile (AIBN) initiator solution in hexane is then charged into the reaction mixture. The polymerization reaction is performed for 150 min at 60°C and stirrer speed of 400 rpm [72,73].

To synthesize PAM-PS core–shell nanostructure, 60 mL of hexane solvent and 0.0035 mL of span80 surfactant are mixed in a reactor with three necks, and after mixing those by using a mechanical mixer with speed around 2000 rpm, the water phase, including 5 g hydrophilic monomer of acrylamide and 20 mL of deionized water, is dispersed to the previous solution. Then, the water phase is injected to the mixed organic phase in the reactor via a microinjection. After the mixing water and organic phases, the initiator system (redox), including ferrous sulfate and potassium persulfate, is injected (5:2 ratio) in temperature condition −15°C by entering this material into the reactor. The first time period of polymerization is selected that the reactor remains under mentioned conditions for 30 min and after that immediately is moved to the very low temperature condition for 3 or 4 days without mechanical mixing. After this time, nanoparticles of polyacrylamide with high molecular weight are produced and are the time to inject the second initiator and monomer of nanolayer with hydrophobic properties. Therefore, in the second steps of the process, the redox initiator and styrene monomer are injected for making a nanolayer in low temperature conditions. It is interesting to point out that the initiator of the second steps and the organic monomer must be injected simultaneously, and the initiator on the surface of the polymer nanoparticle causes a chain of polystyrene to form, and this chain is propagated continuously. The transfer of the chain must be done in a special time and extra propagation of a polymer nanolayer chain is prevented. In this way, by considering the short time for a second polymerization process (about 30 min), the thin layer of polystyrene is made on nanoparticles of polyacrylamide and after this time, the reaction process is terminated. Further purification must be considered to prevent core–shell nanostructure agglomeration. Finally, the synthesized powders have core–shell nanostructure that its nanocore of polyacrylamide with 10 million Dalton (molecular weight) and its size is 80 nanometers, and its shell is a nanolayer of polystyrene with 40,000 Dalton (molecular weight) and its size is 10 nanometers.

As mentioned before, a third category is due to synthesize core–shell nanostructure with binary properties. This type of core–shell nanoparticle is the future work of Ramazani S.A. and coworkers. The object of this section is design and preparation of a smart system, including a core made up of a hydrophilic polymer nanoparticle such as PAM, HPAM, TVP, and a hydrophilic–hydrophobic coating nanolayer (surfactant properties) such as PAM-b-PS copolymer made up of long hydrophilic and short hydrophobic blocks that are grafted chemically or inverse polymerized surfactant (surfmeter). Two procedures to prepare the smart system are described. The first one involves inverse emulsion polymerization of polymeric cores using the surfmert as the emulsifier, whereas the shell is obtained via polymerization using the surfmert as the hydrophobic monomer of the shell. Consequently, the

---

**TABLE 3.1**

**Typical Recipe for the Inverse Emulsion Polymerization of Polyacrylamide**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamide monomer</td>
<td>15</td>
</tr>
<tr>
<td>Water</td>
<td>35</td>
</tr>
<tr>
<td>Hexane solvent</td>
<td>45</td>
</tr>
<tr>
<td>Span80 surfactant</td>
<td>5</td>
</tr>
<tr>
<td>AIBN initiator</td>
<td>0.0068</td>
</tr>
</tbody>
</table>
term nanostructure of hydrophilic core–surfmer shell is proposed to demonstrate the application of the double function surfactant-monomer (Figure 3.10).

The second one relates to a nanostructure of the hydrophilic core-block copolymer shell. The polymer cores are obtained via inverse emulsion polymerization using some hydrophilic monomers that are polymerized and terminated, whereas the shell is obtained via polymerization using other live radical chains which are propagated without any termination agents. Hydrophobic monomers are grafted with the hydrophilic open end chains to produce the monolayer of block copolymers (Figure 3.11).

This core–shell system consists of hydrophilic polymer-surfmer or hydrophilic polymer-block copolymer nanocomposites and not only acts as a protective layer for water soluble polymer from

**FIGURE 3.10** (See color insert.) The schematic diagram for inverse emulsion polymerization of hydrophilic polymer–surfmer core–shell nanostructure. (Adapted from Y. Tamsilian, A. Ramazani S.A., The International Conference on Nanotechnology: Fundamentals and Applications (ICNFA 2013), Canada, 2013.)

**FIGURE 3.11** (See color insert.) The schematic diagram for inverse emulsion polymerization of hydrophilic polymer-block copolymer core–shell nanostructure. (Adapted from Y. Tamsilian, A. Ramazani S.A., The International Conference on Nanotechnology: Fundamentals and Applications (ICNFA 2013), Canada, 2013.)
degradations but also targeting delivery is another approach in some applications such as the enhanced oil recovery process. The investigation and characterization of the core–shell nanoparticle properties are done by DSC, IR, SEM, EDX, NMR, UV, XPS, and AES. It can be seen that the nanoscale coating of hydrophilic polymer nanoparticles is successfully done and there is no effect of virgin monomers in the reaction environment. In addition, the behavior of polyacrylamide release from its nanolayer coating and effects on rheological properties of the water phase in underground reservoirs with wettability variable is investigated via dilute viscometer. The obtained results show that the dissolution of pure polyacrylamide with 6 million Dalton (molecular weight) under the temperature 90–100°C takes 6 days (Figure 3.12a), but the total release of nanoparticles of polyacrylamide from a nanolayer of polystyrene to dissolve in the water phase under similar condition takes 21 days (Figure 3.12b).

Due to the initial experiments by Tamsilian and Ramazani S.A., the obtained results show that the core–shell nanostructure idea can considerably optimize the EOR process and remove the existing pitfalls. However, viscosity of aqueous polymer solution including PAM nanoparticles as core nanomaterial in the previous works decrease by temperature elevation due to PAM chain degradation. So, the best selection for the core material could be thermoviscosifying polymers (TVPs) whose viscosity increases on increasing temperature and salinity to optimize mobility ratio in the oil reservoir, may overcome the deficiencies of most water soluble polymers during EOR. In last study by the mentioned group, a novel core–shell nanostructure of TVP as an active thermosensitive polymer and an organic material as a nanolayer for the core material protection is designed and prepared to intelligently control mobility ratio in oil reservoirs and overcome weakness and limitations of classical polymer flooding such as mechanical, bacterial, or thermal degradations. This intelligent nanostructure releases TVP in oil–water interface after dissolution of organic nanolayer in oil phase, which could result in dramatically increasing water viscosity in the interface layer. This study is divided into three phases, including (1) synthesis of TVP nanocore–organic nanoshell, (2) characterization and rheology studies to investigate the structure of the synthesized nanomaterials and thermo-thickening properties, respectively, and finally (3) smart EOR study by the prepared materials [78].

Another example of polymer NP synthesis by emulsion mechanism is starch nanoparticles. A starch solution is prepared by dissolution of 0.5 g native sago starch powder in 50 mL of NaOH solution with concentration of 0.5 M. The mixture is heated to 80°C for 1 h under magnetic stirring.
to obtain a homogeneous starch solution. One milliliter of starch solution after cooled to room temperature is added drop-wise to an organic phase (e.g., 15 mL of cyclohexane, 5 mL of ethanol, and a certain amount of surfactant) under mixing at 900 rpm for 1 h. The same procedure is repeated by varying the surfactant’s concentrations, oil-co-surfactant ratios, oil phases (hexane, olein palm oil, sunflower oil, and oleic acid), cosurfactants (methanol, propanol, butanol, and acetone), and water/oil ratios [79].

Based on Figure 3.13a, native sago starch particles are mostly of large, oval granular shape with smooth surface in the range of a diameter size around 20–40 μm. The microsizes of starch granules have converted into nanoparticles by dissolution of the prepared native starch into aqueous solution and also reprecipitation of the starch solution into ethanol. Thus, the nanoprecipitation technique is suitable for nanoparticle formation. The mixing rate can affect the morphology of starch nanoparticles to aggregate and have wider particle size distribution (Figure 3.13b) as compared to using mixing during the synthesis (Figure 3.13c). At low mixing rates, the nucleation species are not dispersed uniformly through the solution; leading to agglomerate particles and higher stirring rates, enhanced mobility of nucleated species causes to be uniform, homogeneous dispersion and smaller nanoparticles [80].

### 3.2.3.3.2 Microfluidic Method

This section shows a fantastic tubing technique to irreversibly interconnect polydimethylsiloxane (PDMS) microfluidic devices with external equipment. This structure can keep a pressure of up to 4.5 MPa by experimental and theoretical investigations [81].

During leakage tests, the microfluidic chip has a straight channel with dimensions $50 \times 50 \times 50$ μm³ (Figure 3.14a). To prepare the nanoparticles, the semicircular channel is 300 and 50 μm for wide and deep dimensions, respectively, and also 5 cm for the total length. Degassed PDMS is injected into the mold and heated to 80°C for 2 h. The PDMS slab is removed from the silicon substrate by a blade, and then a flat-tipped needle is used to make a hole with diameter 0.5 mm in the channel inlet. The PDMS chip is pressed down in a Petri dish and contact between the embedded microchannel and the dish surface is made. An adhesive sealant is smearing the end of the tube before inserting a plastic tube into the hole (Figure 3.14b). Another PDMS layer on top of the PDMS chip is placed to protect this tubing interconnection and then the device placed in the Petri dish is baked at 80°C for 2 h.

Poly(lactic-co-glycolic acid) (PLGA) nanoparticles is synthesized with varying flow rate rations (FRs) based on the fabricated microfluidic device. Small size of PLGA nanoparticles, approximately 55 nm, is synthesized at a high flow rate. The sizes of the nanoparticles show a variation by adjusting the FR (Figure 3.15) and a good dispersion of PLGA nanoparticles are presented by TEM and DLS results. Table 3.2 shows FR effects on particle size and polydispersity (PDI). This size difference is because of diffusion mixing against convective mixing. The convective mixing
Nanocomposite Materials

can provide a rapid interfacial deposition of small size PLGA nanoparticles. Moreover, choice of the flow rate can directly influence the particle size distribution to prepare a narrow size distribution by high flow rate and vice versa.

### 3.2.3.3 Grafting Method

Grafting of N-isopropylacrylamide and acrylic acid to produce poly(NIPAM-co-AA) nanoparticles as thermosensitive polymer is synthesized by grafting onto route [82] (Figure 3.16). In this way, NIPAM monomer is grafted onto AA and is subsequently conjugated with potassium persulfate (KPS) initiator at 80°C to synthesize poly(NIPAM-co-AA) nanoparticles.

The solution of poly(NIPAM-co-AA) nanoparticles is significantly affected by temperatures. The obtained results represent that the solution of poly(NIPAM-co-AA) nanoparticles at 37.2°C is opaque, whereas it changes to become transparent at room temperature. Ultraviolet (UV)-visible results in Figure 3.17 demonstrate that absorbance of poly(NIPAM-co-AA) nanoparticles is abruptly increased over 37.2°C, whereas the absorbance below 37.2°C is steadily constant, showing low critical solution temperature (LCST) in 37.2°C.

**FIGURE 3.14** (See color insert.) (a) Schematics of fabricating a tubing interconnection for PDMS microfluidic devices. (b) A cross-sectional view of the tubing interconnection fabrication. (Adapted from J. Wang et al., *Lab on Chip*, 14, 2014, 1673–1677.)

**FIGURE 3.15** (See color insert.) TEM images of PLGA nanoparticles with (a) FR: 40, (b) FR: 30, (c) FR: 20, (d) FR: 10, and (e) size distribution of PLGA nanoparticles versus FR. (Adapted from J. Wang et al., *Lab on Chip*, 14, 2014, 1673–1677.)
3.2.3.3.4 In-Situ Polymerization Method

Most researchers have good attention to polymer/clay nanocomposites in research and industrial applications due to the effective optimization of different properties of polymer nanoparticles. These nanocomposites show improvements to mechanical and barrier properties, flammability and solvent resistance, and environmental stability [83–86]. Ramazani S.A. and coworkers have synthesized polyethylene/clay nanocomposites from mineral clay by Ziegler-Natta catalyst system with exfoliated structure of clay. To achieve this goal, they have used an acid treatment method to improve clay structure for production of highly active catalyst to produce polyethylene clay nanocomposites [87–89].

### TABLE 3.2
Comparison of Precipitated PLGA Nanoparticles Using Microfluidic (High and Low Flow Rates)

<table>
<thead>
<tr>
<th>Total Flow Rate (mL/h)</th>
<th>Minimum Size (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfluidics 41–44</td>
<td>110</td>
<td>0.2</td>
</tr>
<tr>
<td>Microfluidics 410</td>
<td>55</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Source: Adapted from J. Wang et al., *Lab on Chip*, 14, 2014, 1673–1677.*

![Synthesis of poly(NIPAM-co-AA) nanoparticles using KPS initiator at 80°C.](NIPAM.png)

**FIGURE 3.16** Synthesis of poly(NIPAM-co-AA) nanoparticles using KPS initiator at 80°C.

![Absorbance vs. Wavelength](Absorbance.png)

To remove the OH groups on the silicate layers, clay is dehumidified for 6 h at 400°C. Then Mg(OEt)$_2$ and toluene are added to the clay at continuous argon flow. The slurry is heated to 80°C under mixing conditions. In the next step, TiCl$_4$ and electron donor are added to the slurry and heated to 115°C. The product is washed several times with fresh toluene and treated with TiCl$_4$ for 4 h at 115°C.

To prepare polyethylene/clay nanocomposites by \textit{in situ} polymerization method, propylene in hexane is synthesized by slurry polymerization procedure in the Buchi (1 L) type reactor at a pressure of 4 bars and boiling point of hexane. To inject into the reactor, triisobutylaluminum (TIBA), DMCHS, and hydrogen are used as cocatalyst, external donor, and chain transfer agent, respectively. In the final step, the polymer is washed with ethanol several times, filtered, and dried in a vacuum oven at 70°C for 24 h.

The final properties of produced nanocomposite such as mechanics, morphology, and dispersion are investigated by a wide range of characteristic techniques. The obtained results show that the thermomechanical properties of the nanocomposites are considerably improved by introducing a small amount of clay. However, the clay must be significantly intercalated and/or exfoliated during the preparation process of the nanocomposites.

3.2.3.3.5 \textbf{Synthesis of Conductive Polymer Nanoparticles}

To synthesize conducting polymers, there are a number of methods including electrochemical oxidation of the monomers, chemical synthesis, and some less common ones such as enzyme-catalyzed and photochemically initiated polymerization [90]. Chemical or electrochemical polymerization is widely used to synthesize polyaniline (PANI) in the aqueous acid media. The synthesized polymer is called an emeraldine salt. For bulk production, the chemical oxidation of aniline is the more feasible method. The limitation of this method is the poor processibility of the obtained polymer due to its insolubility in common solvents, although it can be improved by using different dopants [91,92].

In electrochemical oxidation synthesis, PANI is synthesized in acidic media by constant potential and current and on an inert metallic electrode, for example, Pt or conducting indium tin oxide (ITO) glass.

In chemical synthesis, monomer (aniline) is synthesized in aqueous solution containing oxidant, for example, ammonium peroxydisulfate and acid, for example, hydrochloric. In this type of synthesis, the monomer is converted directly to conjugated polymer by a condensation process. However, an excess of the oxidant leads to materials that are essentially intractable, which is one of its disadvantages. By progressing the oxidative condensation of aniline, the color of solution turns to black which probably is due to the soluble oligomers. The type of the medium and the concentration of the oxidant are the effective parameters on the intensity of coloration. The major effective parameters on the course of the reaction and on the nature of the final product are as follows: type and temperature of medium, concentration of the oxidant, and time. To obtain desirable results, some factors such as low ionic strength, volatility, and noncorrosive properties should be controlled although no medium satisfies all of these requirements [93].

In the polymerization mechanism, there is a close similarity in the electrochemical or chemical polymerization mechanism of aniline. The following mechanism proceeds in both cases: the first step is the formation of the aniline radical cation, which has several resonant forms and is formed by transferring the electron from the 2 s energy level of the nitrogen atom.

Among the different resonance forms shown in Figure 3.18, form (c) is the more reactive one due to its important substituent inductive effect and its absence of steric hindrance. The next step is the dimer formation between the radical cation and its resonant form.

Then, as shown in Figure 3.19, a new radical cation dimer is formed by oxidizing the dimer with having two possible reactions including the reaction with the radical cation monomer and with the radical cation dimer to form a trimer or a tetramer, respectively. PANI polymer is formed with following steps (Figure 3.20).
FIGURE 3.18 The formation of the aniline radical cation and its different resonant structures. (Adapted from I. Harada, Y. Furukawa, F. Ueda, *Synthetic Metals*, 29, 1989, 303–312.)


FIGURE 3.20 One possible way of PANI polymer formation. (Adapted from I. Harada, Y. Furukawa, F. Ueda, *Synthetic Metals*, 29, 1989, 303–312.)
It is known that only the emeraldine state of PANI can be used for nonredox doping process to produce conductive polymer. Charge transfer is a kind of doping process with the number of electrons of the polymer unchanged. Angelopoulos et al. for the first time converted emeraldine base form of PANI to highly conducting metallic regime by this doping method [93]. They did this doping process by treating emeraldine base with aqueous protonic acids as shown in Figure 3.21. It is known that the conductivity of PANI when doped with this method is about 9–10 times greater than that of nondoped ones.

Earlier studies show the formation of a stable polysemiquinone radical cation as shown in Figure 3.22 [85].

Here PANI (emeraldine salt, ES) is synthesized by two chemical oxidation methods: (1) conventional emulsion polymerization to produce binary doped PANI and (2) homogeneous solution polymerization to produce single-doped PANI.

In a conventional emulsion system 5.768 g of SDS was dispersed in 40 mL HCl (1 M) in a two-necked round bottom flask, then 0.745 g aniline in 10 mL HCl (1 M) was introduced to the mixture with vigorous stirring at room temperature under nitrogen atmosphere for 30 min. Then, 10 mL HCl (1 M) aqueous solution with 0.923 mL ammonium persulfate (APS) as an oxidant were added drop-wise into 100 mL of reaction mixtures during 20–30 min. After the purging period of about 20–40 min, the homogeneous recipes were turned into a bluish tint and the coloration was pronounced as polymerization proceeded without agitation for 24 h at room temperature. Finally, dark green colored PANI dispersions were obtained without any precipitation. In the experiments, the molar ratios of APS to aniline and SDS to aniline were kept 0.5 and 2.5, respectively. Excess amounts of methanol were added into the SDS–HCl binary doped PANI dispersion to precipitate PANI powder by disrupting the hydrophilic–lipophilic balance of the system and stopping the reaction. After that, the solution was centrifuged for 20 min at 8000 rpm. The precipitation was washed with methanol, acetone, and water to remove unreacted materials, aniline oligomers, and initiators. The obtained binary-doped emeraldine salt PANI cakes were dried in a vacuum oven at 50°C for

![Figure 3.21](image1.png)

**FIGURE 3.21** Protonic acid doping of PANIs. (Adapted from I. Harada, Y. Furukawa, F. Ueda, *Synthetic Metals*, 29, 1989, 303–312.)

![Figure 3.22](image2.png)

**FIGURE 3.22** A stable polysemiquinone radical cation. (Adapted from I. Harada, Y. Furukawa, F. Ueda, *Synthetic Metals*, 29, 1989, 303–312.)
The solution polymerization prepared with the same molar ratio of oxidant to monomer was stirred for 24 h at room temperature under N2 purging, to obtain PANI by the same procedure. The obtained product (single-doped emeraldine salt PANI) was dried in a vacuum oven at 50°C for 48 h. Emeraldine base (EB) PANI also was prepared as a control by suspending prepared PANI-ES with 100 mL of NH₄OH (24%) solution to convert the PANI hydrochloride (emeraldine salt) to PANI (emeraldine base), shown in Figure 3.24.

To increase electrical conductivity of polyaniline nanoparticles, one can add highly conductive nanoparticles such as graphene. The PANI/graphene nanoparticles were prepared with a similar method described for aniline with the difference that prescribed amounts of graphene were dispersed in 1 M HCl solution of aniline monomer with sonication and the monomer-graphene dispersion was used for both emulsion and solution polymerization. Figure 3.25 shows schematically the preparation of PANI/graphene nanocomposite. The graphene amounts were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, and 1 wt% according to the monomer net weight [95].
3.3 ONE-DIMENSIONAL NANOMATERIALS

3.3.1 SYNTHESIS OF NANOTUBES

CNTs have the simplest chemical composition and atomic bonding configuration, representing the extreme versatility and enrichment in structures and structure–property relations [96]. There are several main methods to produce CNTs including CVD, electric field nanotube growth, arc-discharge, and laser ablation. Tangled nanotubes could be produced by the last two methods and using CVD and electric field methods on catalytic patterned substrates grow nanotube arrays at controllable locations that are site selective.

3.3.1.1 Chemical Vapor Deposition

CNT synthesis by CVD involves heating a catalyst material (metal nanoparticles typically supported on high surface area materials such as alumina materials) and flowing a hydrocarbon gas through the tube reactor for a period [97]. The catalyst particles are considered as seeds to nucleate the growth of nanotubes. Today, patterned growth approaches have developed to obtain organized nanotube structures, positioning catalyst in arrayed locations for the growth of nanotubes from specific catalytic sites [98].

The earlier work has presented the ordered arrays of CNT consisting of multiwalled nanotubes (MWNTs) by CVD growth on porous silicon and silicon substrates patterned with iron particles in square regions (700°C; carbon source, C2H4; alumina-supported iron catalyst) [99]. The nanotubes are well aligned along the direction perpendicular to the substrate surface, resulting from nanotubes grown by closely spaced catalyst particles due to strong intratube van der Waals binding interactions. The arrayed nanotubes exhibit excellent characteristics in electron field emission to create the spatially defined massive field emitter arrays derived by simple chemical routes to apply in flat panel displays.

Dai at Stanford University [99] with his colleagues have carried out arrayed patterned growth for both multiwalled and single-walled nanotubes, including self-assembly and active electric field control to manipulate the orientation of nanotubes. The ordered nanotube arrays and networks were formed at the synthesis stage of nanotubes as results of these works.

Contact printing technique is used to transfer catalyst materials onto the tops of pillars, and SWNTs with ordered networks with the desired nanotube orientations are formed by the CVD method on the substrates (900°C; carbon source, CH4; supported iron catalyst) [100,101]. In this case, the arrayed nanotubes are self-orientated by van der Waals forces between nanotubes and the silicon posts.

3.3.1.2 Electric Field-Directed Nanotube Growth

Zhang’s group has controlled the growth directions of SWNTs by electric fields [102], produced a large alignment torque to direct the nanotube parallel to the electric field. One of the advantages of

![Figure 3.25](See color insert.) Schematic process of preparing PANI/graphene nanocomposites. (Adapted from I. Harada, Y. Furukawa, F. Ueda, Synthetic Metals, 29, 1989, 303–312.)
using electric field against thermal and gas flow fluctuations is stability of the alignment during the growth procedure. However, further studies of both suspended molecular wires and complex nanotube fabric structures on flat substrates can be interested by applied fields varying during nanotube synthesis.

### 3.3.1.3 Molecular Seeds Self Assembly

The CNTs self-assembled by organic precursor molecules on a platinum surface is represented by the researchers in the *Nature* journal [103]. In this research, starting molecule into a three-dimensional object is transferred, named as germling, on a hot platinum surface using a catalytic reaction to split off hydrogen atoms and form new carbon–carbon bonds. The germ, the defined parameter for the nanotube’s atomic structure, is folded out of the flat molecule. The lid of the growing SWCNT is formed by this end cap. More carbon atoms attach and originate from the catalytic decomposition of ethylene on the platinum surface (Figure 3.26). Scanning helium ion microscope (SHIM) shows that the produced SWCNTs have lengths greater than 300 nm.

![Diagram](image_url)

**FIGURE 3.26** (See color insert.) Two step bottom-up synthesis of SWCNTs: (1) singly capped ultrashort (6,6) SWCNT seed formation via cyclodehydrogenation (CDH) as polycyclic hydrocarbon precursor \( \text{C}_{96}\text{H}_{54} \) (P1) and (2) nanotube growth via epitaxial elongation (EE). Orange and blue: short CNT segment of the seed S1; red dashed lines: new C–C bonds; green: epitaxial elongation. (Adapted from J.R. Sanchez-Valencia et al., *Nature*, 512, 2014, 61–64.)
3.3.1.4 Microwave Heating Method

MWCNTs are synthesized using a microwave oven to calcinate polystyrene with nickel nanoparticles under N\textsubscript{2} purging at 700 or 800°C for 15 or 10 min [104]. The synthesized MWCNTs are characterized by TEM (Figure 3.27), a Raman spectrophotometer, and a wide-angle x-ray diffractometer. The obtained results show that a relationship between the outer diameter of the carbon nanotubes and the diameter of catalytic nickel nanoparticles is correlated by a linear function, \( D_{\text{CNT}} = 1.01D_{\text{Ni}} + 14.79 \) nm and \( D_{\text{CNT}} = 1.12D_{\text{Ni}} + 7.80 \) nm for the calcination condition of 800°C, 10 min and 700°C, 15 min, respectively.

3.3.1.5 Laser Ablation Method

In the laser ablation method, a high power laser is used to vaporize carbon from a graphite target at high temperature to produce both MWNTs and SWNTs using metal particles as catalysts to generate SWNTs process [105,106]. The laser is focused onto carbon targets, placed in a 1200°C quartz tube furnace under the argon atmosphere (~500 torr) [107]. Argon gas carries the vapors from the high temperature chamber into a cooled downstream. The nanotubes will self-assemble from carbon vapors and condense on the walls of the flow tube to produce SWNTs with a varied diameter distribution between 1.0 and 1.6 nm. The quantity and quality of these carbon nanotubes depend on several synthesis parameters such as amount and type of catalysts, laser power and wavelength, inert gas type, temperature, pressure, and the fluid dynamics near the carbon target.

3.3.1.6 Arc Discharge Method

The carbon arc discharge is the most common and easiest method to produce CNTs or complex mixtures of components through arc-vaporization of two carbon rods placed end to end with

![FIGURE 3.27](image-url) TEM images of CNTs for calcination at 700°C for 15 min using different nano Ni diameters (D\textsubscript{Ni}), (a) 10, (b) 20, (c) 50, and (d) 90 nm. (Adapted from K. Ohta et al., *Journal of Materials Chemistry A*, 2, 2014, 2, 2773–2780.)
approximately a 1 mm gap, in a chamber filled with inert gas at low pressure. It requires further purification to remove catalytic metals from the produced CNTs. A potential difference of 20 V is applied to drive a direct current of 50–100 A, following a high temperature discharge between the two electrodes to vaporize the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. To obtain high yield CNTs, the uniformity of the plasma arc and the temperature of the deposit are two of the most important parameters [107,108].

### 3.3.1.7 Bottom-Up Chemical Synthesis

Two basic areas of research are considered for the bottom-up synthesis of CNTs: (1) using aromatic macrocyclic templates and (2) development of these templates to obtain longer CNTs by polymerization reactions. This template approach is an attractive method to produce both zigzag and armchair CNTs with different diameters, as well as to chiral CNTs with different helical pitches. There are several advantages for the organic synthesis approach to control CNT chirality compared with the current methods as follows:

- First, the process is easier to troubleshoot and optimize because of its mechanistically well-understood reactions.
- Second, the synthesis condition for organics is typically at temperatures below 200°C compared with temperatures closer to 1000°C for the current techniques.
- Last, it is possible to produce CNTs with incorporation of nitrogen, boron, or sulfur by the organic synthesis approach.

Omachi et al. initiated well-defined carbon nanorings to grow carbon nanotubes [109]. In this study, a solution of cycloparaphenylenes (0.5 mM in toluene) was spin-coated at 4000 rpm on a C-plane sapphire substrate plate (5 mm × 5 mm). The reaction plate was placed in the chamber, followed by heating at 500°C for 15 min under ethanol gas purging. The CNTs formed were analyzed by TEM and Raman spectroscopy.

After extensive investigations, it was found that CNTs could be grown from CPPs by simply heating these seed molecules with ethanol (Figure 3.28a). Figure 3.28b and c are TEM images of CNTs synthesized under the previously mentioned conditions. Regarding the Raman spectroscopy result in Figure 3.28d and e, residual cycloparaphenylenes was not found on the reaction plate. Figure 3.28d shows the radial breathing mode regions and a relationship between diameter (d) and frequency of radial breathing mode. Raman spectroscopy results indicate that the CNTs were distributed in the diameter range 1.3–1.7 nm, very close to that of CPP (1.7 nm). Also, the diameter distribution histogram in Figure 3.28f was derived from the number of nanotubes with different diameters observed by TEM. It is also consistent with this size regime to conclude that the high percentage of the CNTs was between 1.7 and 1.3 nm in diameter.

In addition, Mogilevsky and his coworkers succeeded to prepare a hybrid nanostructure including graphene and TiO₂ by a bottom-up synthetic approach of alizarin and titanium isopropoxide [110]. It would be amenable to synthesize photocatalytically active materials with maximized graphene–TiO₂ interface (see Figure 3.29).

Special advantage of a photoactive material (e.g., TiO₂) is the charge transfer degree after photoexcitation at the interface with graphene. Figure 3.30 shows the movement of electrons away from, or toward the graphene at the interface. It was found that contacting the graphene patch with the TiO₂ surface causes to transfer electrons from graphene to the oxygen molecules in the top layer of TiO₂ which were also confirmed for the TiO₂-sandwiched graphene and graphene ribbons. Positive and negative of the charge difference density (CDD), charge density in the interaction of the two substrates, denote the addition of electrons and the removal of electrons, respectively. The CDD measurement in this case shows clearly charge transfer from graphene to the top oxygen layer of TiO₂, to produce positive graphene and negative TiO₂, which the total charge transfer is approximately 0.017 e⁻ per carbon atom.
3.3.2 Synthesis of Nanorods

3.3.2.1 Simple Hydrothermal Method

Using hydro/solvothermal treatment of salen ligand with nickel nitrate is of particular interest to synthesis solid Ni (salen) complexes at different temperatures (120–180°C), times (6–24 h), and solvents (water, ethanol, and H₂O, C₂H₅OH, and acetonitrile) [111]. In a typical synthesis, 0.75 mmol of Ni(NO₃)₂ · 6H₂O dissolved in 30 mL of H₂O is added to 0.75 mmol of N,N′-bis(salicylidene)ethylene diamine-70 mL of H₂O as aqueous solution, followed by mixing for 15 min and transferred into a stainless steel autoclave. The autoclave is cooled down to room temperature after hydrothermal treatment. The red-orange color precipitated material is collected and washed several times with distilled water and ethanol. The product obtained after 6 h consisted of separated nanorods (Figure 3.31a and b). It is interesting to point out that synthesis after reaction time to 13, 18, and

![Diagram](image-url)
24 h produced some agglomeration with nanoparticles (Figure 3.31c and d), a mixture of nanorods and nanoparticles (Figure 3.31e and f), and the more agglomerated nanorods with shorter length (Figure 3.31g and h), respectively.

Figure 3.32 shows the formation mechanism of a nanorod Ni(salen) complex as a sequential two-step growth mechanism, heterogeneous complex nucleation, and directional growth route due to the morphology observation.

Under hydrothermal conditions, the soluble Ni²⁺ cation reacted with salen ligand to form an insoluble Ni(salen) nucleus wherein it can be led to the precipitation transformation process in H₂O to form more insoluble Ni(salen). In the first stage, Ni(salen) nucleates heterogeneously due to a lower energy barrier than that of the nucleation in solution. Based on all reported crystal structures, the <100> and/or <010> directions are the favored directions for crystal growth. Under hydrothermal conditions, nanorod formation starts by the nucleation and spontaneous aggregation on the formed nuclei to decrease their surface area during the oriented attachment process. By domination of Ostwald ripening process during the reaction time, nanorods with smooth surfaces were produced.

3.3.2.2 Seed-Mediated and Seedless Methods

In the seed mediated route [112], 9.91 mL of 0.2 M CTAB is mixed with H AuCl₄. Then, 0.006 M NaBH₄ is added under magnetic mixing for 2 min. The growth solution of the gold nanorods is prepared by mixing 0.1 M of CTAB, 25.4 mM of H AuCl₄, 0.5 M of H₂SO₄, 10 mM of AgNO₃, and 0.1 M of ascorbic acid. Then, the mixture of 4 mL raw seed solution and 6 mL deionized water is centrifuged with 10,000 rpm for 7 min to remove aggregated seeds. Finally, the growth of the gold nanorods starts by addition of 30 μL seed solution to the recipe. The resulting mixture is stirred for
After 12 h, the reaction is stopped by centrifugation with 10,000 rpm for 10 min. The precipitate is redispersed in water.

In the seedless route [113], gold nanorods are prepared by mixing 0.15 M of CTAB, 25.4 mM of HAuCl₄, 100 mM of AgNO₃, 0.05 M of paradioxybenzene, and 1.19 M of HCl. The reaction is started by adding 0.01 M of NaBH₄ solution. Finally, the solution is stirred for 30 s to make it homogeneous. After 36 h, the reaction is stopped by centrifugation with 10,000 rpm for 10 min and the precipitate is redispersed in water.

The gold ions concentration also was tried to downregulate the width (Figure 3.33). The product yield began to decrease by reduction of the gold ions concentration to 0.3 mM (Figure 3.33e) whereas the width of rods still was 13.4 nm. High concentrations of Ag⁺ (0.12 – 0.5 mM) and CTAB (0.1–0.15 M) would be favored to form rods with higher aspect ratio using ascorbic acid, tartaric acid, paradioxybenzene, gallic acid, and a mixture of ascorbic acid and paradioxybenzene as the reducing agents.

The seeded or secondary growth method is manageable to scale up larger amounts of gold nanorods by the primary uniform gold nanorods solution [114]. This is possible to increase the reaction volume from 100 mL to 1 L. It should be noted that the primary uniform gold nanorods solution for all of the experiments was prepared by an identical procedure, except for the KBr removing in the primary growth solution through utilizing benzylidimethylhexadecylammonium chloride hydrate (BDAC). BDAC helps direct the shape into nanorods with higher aspect ratios to complete the primary growth phase (Figure 3.34).

### 3.3.2.3 Metal–Organic Chemical Vapor Deposition Method

Metal–organic chemical vapor deposition (MOCVD) has also been used for ZnO nanorods, thin film, and QD growth without any catalyst. High purity product and easy fabrications of nanorod
FIGURE 3.31  SEM images of Ni(salen) nanocomplexes prepared in H$_2$O at 140°C and various times: (a and b) 6 h, (c and d) 13 h, (e and f) 18 h, and (g and h) 24 h. (Adapted from M. Mohammadikish, CrystEngComm, 16, 2014, 8020–8026.)
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**FIGURE 3.32** Schematic illustration of a proposed mechanism for the formation of the Ni(salen) nanorods.

**FIGURE 3.33** TEM images of gold nanorods synthesized with different Au$^{3+}$ concentration (a) 0.6 mM, (b) 0.5 mM, (c) 0.4 mM, and (d) 0.3 mM. (e) Corresponding UV–vis–NIR spectra. (Adapted from X. Xu et al., *Journal of Materials Chemistry A*, 2, 2013, 3528–3535.)

**FIGURE 3.34** Secondary growth of the primary and final gold nanorods with BDAC in addition to the standard amount of CTAB: (a) optical absorbance spectra and TEM images of (b) the primary and final gold nanorods using (c) 0.25×, (d) 0.5×, (e) 1.0×, and (f) 1.5× BDAC. (Adapted from K.A. Kozek et al., *Chemistry of Materials*, 25, 2013, 4537–4544.)
quantum structures and heterostructures are the major advantages for this case (see Figure 3.35). Although the catalyst-free growth mechanism of ZnO nanorods has not been thoroughly investigated, it can be pointed out that anisotropic surface energy of wurtzite ZnO is the main reason for anisotropic growth. In addition, adsorption of fresh reactant gases just on nanorod tips is obtained by high-speed laminar gas flow, inducing turbulent flow between the nanostructures.

### 3.3.2.4 Vapor Phase Synthesis

The most extensively explored approach to the formation of 1D nanostructure including whiskers, nanorods, and nanowires is probably vapor phase synthesis where vapor species are generated by several methods (including evaporation, chemical reduction, and gaseous reaction), subsequently
transported and condensed onto a solid substrate surface with a temperature lower than that of the source material. With proper control over the super-saturation factor, 1D nanostructure can be obtained in large quantities. For example, Yi et al. [116] have written a review paper on ZnO nanorods works, focusing on current research activities, and investigated the physical and chemical methods of ZnO nanorods and nanowires.

### 3.3.3 Synthesis of Nanowires

Generally, semiconductor NWs can be synthesized by metal nanoclusters as catalysts via vapor–solid–solid (VSS) and vapor–liquid–solid (VLS) growth mechanisms. In a VLS growth, vapor-phase precursors are introduced at temperatures that should be higher than the eutectic point of the metal–semiconductor system, resulting in liquid droplets of the metal–semiconductor alloy. Continuous feeding of the precursors leads to the super saturation of catalytic droplets, on which the semiconductor material starts to congregate and grow into crystalline NWs. Unlike the VLS mechanism, in VSS, the metal nanoclusters exist as solid particles. The particles can provide low-energy interface for trapping the precursor materials and also yield high epitaxial growth rates. Specifically, various techniques have been applied to produce vapor-phase precursors for the NWs growth, including chemical vapor deposition (CVD), pulsed laser ablation, and molecular beam epitaxy (MBE). Among all, a CVD growth method utilizing the conventional tube furnace and solid powder source (solid-source CVD) has been widely explored in recent years for the growth of various III–V NWs because of its relatively low cost, simple growth procedures, and, importantly, no entanglement of toxic gas precursors, compared to other feigned growth systems such as MBE and metal–organic CVD. Source powder is put at the upstream of a two-zone tube furnace, while hydrogen is used as a carrier gas to forwarding the evaporated source material into the downstream, and a substrate precoated with catalysts is positioned at the downstream for the NW growth.

#### 3.3.3.1 Subdiffraction Laser Synthesis

Using the interposition of incident laser radiation and surface scattered radiation is an alternative method to produce nanowires with diameters of 60 nm. This condition causes spatially confined nanowires, which periodical heating is needed for the high resolution chemical vapor deposition [117]. Also, multiple parallel nanowires are produced on a dielectric substrate with controlled properties (i.e., diameter, length, and orientation), which can be controlled by the intensity and polarization direction of the incident radiation for the device fabrication.

Figure 3.32 illustrates the radiation interference for silicon nanowire diameter control, which the high numerical aperture of the zone plates is a critical point to forming a single nanowire. This is because the intensity peak of the focal spot must be narrow enough to produce sufficient intensity for heating the substrate.

SEM images of nanowires grown from horizontally polarized laser radiation in Figure 3.36 show single (a), double (b), and triple nanowires (c) with width of 60 nm. Also, these images show the polarization dependence of nanowire patterns for linear polarization 45° from the scanning direction (d), at linear polarization 90° from the scanning direction (e), and for circular polarization (f).

#### 3.3.3.2 Electrophoresis-Assisted Electroless Deposition

Another attractive structure is synthesis of core–shell nanowire (NW) arrays of ZnO/CuO with high aspect ratios by electrophoresis-assisted electroless deposition of CuO onto ZnO NWs [118]. During this procedure, CuO seeds are successfully manufactured on long ZnO NWs by the electrostatic attachment of colloidal Cu$_2$O NPs under thermal oxidation. The core–shell ZnO/CuO nanowires are fabricated by kinetic-limited deposition in the solution to prevail the inherent diffusion limitations in conventional electroless deposition method. The experimental observations and thermodynamic modeling results are presented to validate the supposed dielectrophoresis-assisted electroless deposition mechanism.
3.3.3.3 Microwave Heating Growth Method

ZnO nanowires for electrical and optical devices are extensively synthesized by the hydrothermal method. The main challenge in this method is to obtain a rapid procedure for the synthesis of long vertically aligned ZnO nanowire arrays on a transparent conductive oxide substrate. Recently, Liu et al. [119] proposed a microwave heating method to control growth of long ZnO nanowire arrays, which can avoid the growth timeout and retain the reactants concentration in dynamic equilibrium.

In nanoseed-mediated microwave heating growth method, initially, a ZnO thin layer is deposited on fluorine doped tin oxide glass substrate by pulsed-laser deposition technique (PLD). Then, the ZnO deposited substrate is dipped into a beaker including zinc nitrate hexahydrate and hexamethylenetetramine aqueous solution and heated with a microwave oven with frequency 2.45 GHz, followed by injection into the two Teflon tubes. The third Teflon tube is used for pumping the extra solution on the surface of the solution to keep the solution volume during the experimental process. The heating process is performed for 0.5–5.0 h with a power setting at 640 W. After finishing the reaction, the substrate is brought out from the growth solution, followed by washing several times with DI water, and dried in an air environment. The obtained results show that the length of the nanowires increases linearly with growth time. Also, it was found that ZnO nanowires were produced with a length 10 μm after growing for 2–3 h and the growth rate is 58–78 nm/min.

3.4 TWO-DIMENSIONAL NANOMATERIALS

3.4.1 SYNTHESIS OF NANOFILMS

3.4.1.1 Chemical Precipitation with Subsequent Thermal Treatment

The synthesis of nanostructured oxide films is conducted via chemical precipitation with subsequent thermal treatment of the obtained product. This method is the most general because of mixing the initial reagents at the ionic-molecular level; this subsequently gives an opportunity to obtain oxide nanocrystalline powders of the given compositions with a high dispersion (from 1 to 100 nm) at sufficiently low temperatures (≤600°C) [120,121].

The solutions of cerium and zirconium nitrates and aqueous ammonia solution are used as the initial reagents and precipitator, respectively, to synthesize the CeO₂–ZrO₂ powders. After precipitation, the gel precipitates, including Ce(OH)₃ and ZrO(OH)₂, are filtered and then exposed...
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To fast freezing at –25°C for 24 h. Thermolysis of the synthesized powders based on CeO₂ are studied by DTA (Figure 3.37). In Figure 3.37a of the precipitated gels without freezing, two endothermic effects are recorded in 165°C (the removal of adsorption and crystallization water) and 360°C (the removal of hydroxyl groups). Figure 3.37b shows reduction of the water content by the freezing of the coprecipitated gels in the crystallohydrates of the amorphous hydroxides [122] (Figure 3.38).

3.4.1.2 Chemical Bath Technique
Deposition of CdS nanofilms have been deposited on well cleaned glass substrates. For deposition of nanofilms of CdS, an aqueous solution of 0.02 M cadmium chloride anhydrous has been taken in a glass beaker to add drop-wise ammonia solution (25%). Thereafter, a solution of TX-100 and double distilled water is added to the previous solution. The solution has been stirred for 15 min to obtain a clear homogeneous solution. After all, an aqueous solution of 0.01 M thiourea is added under mixing condition and constant bath temperature of 343 K and pH of the solution at 11.60. The resulted films with pale yellow, uniform and good adherence to the substrate have been found. Many gas bubbles have been formed in the bath through the chemical reaction. Nonionic surfactant TX-100 has been used to remove the gas bubble formation during the reaction. The chemical reactions leading to the layer formation may be represented as follows:

\[
[Cd(NH₃)n]^{2+} \rightleftharpoons Cd^{2+} + nNH₃, \; n = 1, 2, 3, \ldots 6
\]  \hspace{1cm} (3.4)

\[
CS(NH₂)₂ + 2OH⁻ \rightarrow CH₂N₂ + 2H₂O + S^{2⁻}
\]  \hspace{1cm} (3.5)

\[
[Cd(NH₃)n]^{2+} + CS(NH₂)₂ + 2OH⁻ \rightarrow Cds_{film} + CN₂H₂ + nNH₃ + 2H₂O
\]  \hspace{1cm} (3.6)

3.4.1.3 Molecular Layer Deposition
Continuous and uniform carbon nanofilms are synthesized by the pyrolysis of molecular layer deposition (MLD) formed-polyimide films [123]. The cycle numbers are a good parameter to easily control the film thickness at the nanometer scale.
In this method, the deposition of polyimide was done in a closed type, hot-wall ALD reactor. Ethylenediamine (EDA) and 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) precursors with N₂ carrying gas was followed by transferring into a quartz tube furnace and annealing at 600°C for 2 h under protecting H₂/Ar gas flow at normal pressure to produce continuous and uniform carbon nanofilms.

At first, spherical gold nanoparticles solution is dropped on a Cu grid supported with Al₂O₃ layer to deposit with polyimide films, after air-drying. Au nanoparticles coated with continuous and uniform carbon nanofilms are finally produced by annealing the above-mentioned procedure. After the deposition of polyimide on anodic aluminum oxide template with a 200 nm pore diameter, the sample is annealed at 600°C for 2 h under protecting H₂/Ar gas flow at normal pressure to produce continuous and uniform carbon nanofilms.

3.4.2 Nanocoatings

3.4.2.1 Hydrothermal Method Combined with a Mild Ultrasonic

A straightforward hydrothermal method based on a mild ultrasonic sonication is used to fabricate a magnetically recyclable thin-layer MnO₂ nanosheet-coated Fe₃O₄ nanocomposite [124]. This method provides MnO₂/Fe₃O₄ nanocomposite with good stability and photocatalytic efficiency to degrade methylene blue under UV–vis light irradiation and also acid resistance and stable recyclability. The ferromagnetic properties of the produced MnO₂/Fe₃O₄ nanocomposite have been verified by magnetic measurements. This property can be useful to separate by simply applying an external magnetic field after the photocatalytic reaction. The obtained nanocoating can be used in water treatment, dye pollutants degradation, and environmental cleaning.

3.4.2.2 Graphene-Based Nanocoatings

Several methods of graphene synthesis have been discussed by starting with micromechanical exfoliation (scotch tape method), a very easy method for isolating graphene from graphite. However, there are some limitations in this procedure. It uses adhesive tape to exfoliate patterned to generated highly oriented pyrolytic graphite (HOPG) [125].

The tape is then folded to obtain a few layered graphene sheets. At the end, the thin flakes are attached to the film that can be transferred to a suitable substrate such as silicon oxide [126]. Mechanical exfoliation is the simplest way to prepare micro-size graphene flakes for fundamental research purposes [127]. The advantage of this method is production of large size and unmodified
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graphene sheets. Its disadvantage is due to the very small scale of production. Geim and Novoselov used this method to isolate graphene for the very first time in 2004 [125].

The second method is the epitaxial growth from silicon carbide (SiC). In this method, SiC is heated at high temperatures under vacuum to produce graphene. In this time, silicon atoms sublimate from the substrate to rearrange themselves into graphene layers. The epitaxial graphene grown on the Si substrate shows the excellent crystal quality and large coverage.

The third method is chemical vapor depositions (CVD) in which substrates like copper or nickel are used as catalysts. In this method, the substrates are placed into a furnace and heated at low vacuum to 1100°C. One of the advantages of this method is mass production of high quality graphene.

The last method is a chemical method (Hummer’s method), which is the main method for the synthesis of graphene oxide and reduced graphene oxide. In this method, graphite flakes are oxidized into graphene oxide in the presence of sulfuric acid, hydrochloric acid, and potassium permanganate, and then graphene oxide is later reduced by a strong reducing agent known as hydrazine hydrate.

### 3.5 THREE-DIMENSIONAL MATERIALS

Three-dimensional or bulk nanomaterials are materials that are not limited to the nanoscale in any dimension. These materials have three dimensions beyond 100 nm, but may comprise one or more types of any kind of nanomaterials that are in close contact with the matrix. The most important examples of three-dimensional nanomaterials contain nanoporous, nanocomposites, and extremely intercalated multilayered materials such as clay and graphene oxide.

Synthesis of nanocomposite and multilayered particles are discussed in detail in other parts of this book; thus, in the following, we will briefly explain some facts about the preparation of nanoporous materials.

Nanoporous materials are classified into three groups by IUPAC:

- Microporous materials: 0.2–2 nm
- Mesoporous materials: 2–50 nm
- Macroporous materials: 50–1000 nm

Microporous and mesoporous materials, such as zeolites and mesoporous silica, have obtained great interest in the field of drug delivery and imaging. Zeolites are microporous, crystalline aluminosilicates or silicates with pore sizes typically ranging from 5 to 10 Å [128]. This material could be produced by various templates that lead to forming zeolites with distinguished pore sizes and connectivity. It should be noted that synthetic zeolites have some advantages in comparison to natural zeolites; for example, they can be produced with higher purity and also their morphology can be adjusted with controlling synthesis conditions [129].

The most significant method for preparation of zeolites is the hydrothermal technique [130]. In this technique, silicoaluminate as an appropriate precursor is put in a sealed reaction container, typically a Teflon-lined autoclave. In the following, a usual procedure for hydrothermal preparation of zeolite is described [131].

1. Amorphous precursors of silica and alumina are dissolved in a basic medium. Usually, alkali ion hydroxides, which are well known as mineralizing agents, are applied to obtain essential high pH values.
2. The aqueous solution is heated in a sealed reactor or in a preheated oven.
3. The reactants remain amorphous for a long time, and after passing the onset temperature producing the first zeolites crystals is observed.
4. Finally, all amorphous precursors dissolved in the solution convert to a nearly identical amount of zeolite crystals and could be obtained by purification, washing, and drying.
In a common example of synthesis of zeolite by the hydrothermal method, sodium metasilicate—well known as water glass—and sodium aluminate are used as precursors. By adding aluminate to silicate, a precursor make gel would be obtained in which both aluminate and silicate oligomer chains exist. This is known as the precrystalline phase, which features depend on various factors such as silicon/aluminum ratio, solution pH value, nature of reactants, and purity of the precursors. Heating the mixture causes depolymerization of chains to form smaller units.

Finally, in the presence of the above-mentioned mineralizing agent the crystalline zeolites, which comprise Si–O–Al bonds, could be produced. In this method, no considerable enthalpy change is observed due to a similar bond type in precursor oxides (Si–O and Al–O bonds) and produced zeolite (Si–O–Al bonds). For this reason, the total enthalpy change for thermal preparation of zeolite is generally negligible. Therefore, preparation of zeolite is mainly controlled by the kinetics of the total procedure [132–134].

An outstanding review by Cundy and Cox [135] on the synthesis of zeolites and its crystallization mechanism is very useful.

3.6 CONCLUSION

Nanotechnology is an interdisciplinary research area that has gained wide attention worldwide in the past few years. The nanomaterials have been categorized into four groups, including zero-, one-, two-, and three-dimensional. General and specific synthesis methods for preparation of different nanomaterials have been considered; however, emphasis was mostly on chemical methods such as microwave-assisted synthesis, sonochemical synthesis, sol–gel method, aerosol method, emulsion method, microfluidic method, laser ablation method, arc discharge method, chemical bath technique, and so on. It can be concluded that zero- and one-dimensional nanomaterials are priority groups, respectively. Nevertheless, it could be anticipated that two- and three-dimensional nanomaterials will find more attention in the near future.

REFERENCES

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