Chapter 4

Synthesis of TiO$_2$ and Metal-Doped TiO$_2$ Nanoparticles

“An experiment is a question which science poses to Nature and a measurement is the recording of Nature's answer.”

— Max Planck
4.1 Introduction

The choice of synthesis technique can be a key factor in determining the effectiveness of the photocatalyst as studies have demonstrated that TiO$_2$ preparation and physical form are among the most important factors in determining the overall photocatalytic efficiency. According to the principle, the preparation of metal nanoparticles could be classified into two categories; physical and chemical methods. The prime importance of wet chemical technique is to control desired structural and morphological properties of materials on a nanometer scale from the earliest stages. The choice of the synthetic technique plays a key factor in determining the usefulness of the photocatalyst with the optimum properties. There are several chemical methods to produce titania nanoparticles such as sol–gel technique [1-3], hydrothermal method [4, 5], solvothermal [6, 7], electrochemical approaches [7], sonochemical reactions [8, 9], microemulsion technique [10], microwave [11], micelle and inverse micelle methods [12, 13], combustion flame–chemical vapor condensation process [14], and solution combustion [15]. The synthesis method used for undoped/doped TiO$_2$ nanoparticles has been introduced here. This research focuses on sol-gel processing techniques which will be discussed in great detail. However, an overview of other much used techniques is also provided.

4.2 Synthesis techniques

4.2.1 Hydrothermal synthesis

The hydrothermal method is widely used for the production of nanostructures. Hydrothermal synthesis is generally carried out in an autoclave
under pressure with the reaction in aqueous solution [16, 17]. The temperature
in the autoclave can be raised above the boiling point of water, reaching the
pressure of vapour saturation. Hydrothermal synthesis is extensively used for
the preparation of TiO$_2$ nanoparticles which can easily be obtained through
precipitating a titanium precursor with water [18-20]. The hydrothermal
method can be useful to control grain size, particle morphology, crystalline
phase and surface chemistry through regulation of the solution composition,
reaction temperature, pressure, solvent properties, additives and aging time
[21]. The drawbacks of this technique are the difficulty in controlling the
growth process and requirement of expensive autoclaves.

4.2.2 Solvothermal synthesis

The solvothermal method is identical to the hydrothermal method except
that a variety of solvents other than water can be used for this process. The
synthesis under hydrothermal conditions is usually performed below the
supercritical temperature of water (374 °C). In solvothermal synthesis, a
solvent under moderate to high pressure (typically between 1 atm and 10,000
atm) and temperature (typically between 100 °C and 1000 °C) that facilitates
the interaction of precursors during synthesis. The benefits of both the sol-gel
and hydrothermal techniques can be achieved by using solvothermal synthesis
method. A variety of geometries including thin films, bulk powders, single
crystals, and nanocrystals can be prepped by using this technique [22]. Also
this method can be used to prepare thermodynamically stable and metastable
states including novel materials. Solvothermal synthesis has been commonly
employed to prepare ultrafine, phase-pure, nanocrystalline TiO$_2$ nanoparticles
Solvothermal synthesis of nanoparticles is finding wide applications from nanocircuits and nano-optical circuits to nanomagnetics and biotech [24]. The solvothermal method normally has better control of the size and shape distributions and the crystallinity than the hydrothermal method, and has been used to prepare TiO$_2$ nanostructures with/without the aid of surfactants. However, the disadvantage of this method is also apparent that a relative long time is required to raise the temperature of solution in the autoclave to a target value [25].

4.2.3 Electrochemical synthesis

Electrochemical synthesis may be used to prepare advanced thin films by varying electrolysis parameters like potential, current density, temperature, and pH which can easily control the characteristic states of the films [21]. Electrochemical synthesis involves the synthesis of chemical compounds in an electrochemical cell [26, 27]. Electrochemical synthesis is actively studied as a science and also has many industrial applications. The main advantage of electrochemical synthesis over an ordinary redox reaction is the ability to precisely tune the required potential. Various energy storages devices of TiO$_2$ nanoparticles have been synthesized by electrochemical method [28, 29]. Electrochemical synthesis represents a highly efficient method for the fabrication of nanostructured energy materials, and various nanostructures, such as nanorods, nanowires, nanotubes, nanosheets, and composite nanostructures. The advantages of this method are low cost, low synthetic temperature, high purity, simplicity, and environmental friendliness [30]. The limitations of this technique are electrolysis cells are unreliable and expensive,
consume large energy for large scale process and the performance of electrochemical process suffers from mass transport limitations and the size of the specific electrode area.

4.2.4 Combustion synthesis

It is one of the simplest ways to synthesize a wide variety of advanced materials including powders and near-net shaped products of ceramics, intermetallics, composites, and functionally graded materials [31]. Combustion synthesis can occur by two modes: self-propagating high-temperature synthesis and volume combustion synthesis. This process involves highly exothermic redox chemical reactions between metals and nonmetals, i.e. the metathetical (exchange) reaction between reactive components. In conventional SHS the initial reactants are in solid state (condensed phase combustion) while in solution-combustion synthesis initial reaction medium is an aqueous solution. However, synthesis of nanoparticles in flame is known as gas-phase combustion [32]. Solution combustion is synthesis carried out using salts, such as nitrates, metal sulfates and carbonates, as oxidants and, reducing reagents, fuels such as glycine, sucrose, urea, or other water soluble carbohydrates [33]. Nano TiO$_2$ photocatalytic powders have been synthesized by this technique [34, 35]. This process is used directly in the production of high purity, homogeneous ceramic oxide powders [33]. Solution combustion synthesis has the advantage of rapidly producing fine and homogeneous powders but a disadvantage is that this process consumes large amounts of energy.
4.2.5 Gas phase synthesis

There are a variety of methods to develop nanostructures by evaporating materials on different substrates. A properly designed vacuum system is required to avoid uncontrolled oxidation of materials during evaporation method. Gas phase methods are ideal for the deposition of different types of materials. Gas phase can be carried out chemically or physically. Chemical vapour deposition (CVD) is a hybrid method using chemicals in a vapour phase. CVD is a widely used industrial technique that can coat large areas in a short space of time, ease of processing, simple instrumentation, and economical viability. It is used to produce high-purity, high-performance solid materials. CVD is a process in which volatile precursors are transported via the vapour phase to the reaction chamber, where they decompose on a heated substrate [36]. Thin films of modified TiO₂ have been developed via a chemical reaction or decomposition of a precursor in the gas phase [37-40]. Film properties depend on the type of precursor, the activation process and on the working pressure [36]. The advantages of this method include the uniform coating of the nanoparticles or nanofilms. However, this process has limitations including the higher temperatures required, and its difficulty to scale up.

Physical vapour deposition (PVD) is another type of thin film deposition technique. Films are formed from the gas phase but without a chemical transition from precursor to final product. Gaseous stream follows a straight line from source to substrate. This leads to shadow effects, which are not present in CVD technique [36]. To evaporate the source material various heating methods are used, such as resistance heating, electron beam, pulsed excimer laser, or cathodic arc (where the source is the cathode). Source materials needs to be released under controlled pressure to minimize collisions.
of gas molecules and control the thickness of the deposited film. For TiO$_2$ thin films, a focused beam of electrons heats the titanium dioxide material. The electrons are produced from a tungsten wire heated by a current. This is known as electron beam evaporation. TiO$_2$ thin films deposited with electron beam evaporation have superior characteristics over CVD grown films such as, smoothness, conductivity, and crystallinity. However on the other hand, production is slower and more laborious [21]. Gaseous phase methods necessitate the use of complicated vacuum equipment whose disadvantages are the high costs involved and low productivity.

### 4.2.6 Microemulsion synthesis

Water in oil microemulsion has been successfully used for the synthesis of nanoparticles. Microemulsions are thermodynamically stable systems, optically isotopic solutions of two immiscible liquids composed of microdomains of one or both stabilized by an interfacial film of surfactant. The surfactant molecule generally has a polar (hydrophilic) head and a long-chained aliphatic (hydrophobic) tail [21]. The main idea behind the microemulsion technique is very simple: two reactants are introduced in two identical microemulsions. After mixing both microemulsions, droplets collide and interchange the reactants. Then the reaction can take place inside the nanoreactors [41]. Advantage of this method is the biocompatibility and biodegradability of synthesized materials. A large number of nanoparticles of metals and semiconductors have been synthesized using microemulsions method [42]. Recently, ultrafine TiO$_2$ particles have been generated in water-in-oil microemulsions developed by researchers [42–44]. Despite promising
early studies, there have been only limited reports of controlled TiO\textsubscript{2} synthesis from these microemulsions [10, 45].

4.2.7 Microwave synthesis

Several TiO\textsubscript{2} nanostructures have been synthesized using microwave radiation [46]. Microwave techniques eliminate the use of high temperature calcination for extended periods of time and allow fast, reproducible synthesis of crystalline TiO\textsubscript{2} nanomaterials. However, there are few drawbacks of microwave over the conventional heating. The monitoring of the reaction course or, in the case of inorganic species, the time dependent monitoring of the particles growth is not possible.

4.2.8 Precipitation method

Nanocrystals can be prepared from solutions that precipitate the bulk matter under conditions unfavorable for the growth of particulates in the precipitate [47]. By a chemical reaction or by diffusion in a liquid solution, the solid formed is called the precipitate. Precipitation normally occurs when the concentration of a compound exceeds its solubility. Nanocrystals of metal oxides have been prepared by arresting the growth of precipitates formed under hydrolytic conditions [47]. pH plays an important role in the precipitation reactions. To precipitate basic oxides by scavenging the large number of liberated protons high pH is needed while low pH is required for amphoteric oxides. The size of the particulates in the precipitate can be controlled by adjusting the pH [47]. Crystalline TiO\textsubscript{2} powders have been prepared by
precipitation method [48–50]. Precipitation method has several disadvantages, such as extensive agglomeration, poor morphology, and particle size distribution.

4.3 Sol–gel technique

Interest in the sol–gel processing of inorganic ceramic and glass materials began as early as the mid–1800s with Ebelmen’s [51, 52] and Graham’s [53] studies on silica gels. These early investigators observed that the hydrolysis of tetraethyl orthosilicate under acidic conditions yielded SiO₂ in the form of a “glass–like material”. However, due to the extremely long drying times required to obtain large monolithic pieces there was little technological interest found in this technique. Gels regained attention from the late 1800s through the 1920s because of the phenomenon of Liesegang rings [54] explored by Ostwald and Lord Rayleigh. Despite the huge volume of descriptive literature published about these studies, the physical–chemical properties of gels were only sparsely understood.

Later on, Roy and coworkers [55, 56] who recognized the potential for achieving very high levels of chemical homogeneity in colloidal gels. They recognized the place of the sol–gel method in the arsenal of the ceramic industry in the 1950s and 1960s by synthesizing a large number of novel ceramic oxide compositions (Al, Si, Ti, Zr, etc.) unavailable by traditional ceramic powder methods.

In the 1980s, the sol–gel method was intensively used by the micro–optical and heterogeneous catalytic industry [57].
Sol–gel process

Among wet–chemistry methods, sol–gel routes are by far the most extended approach for preparing TiO$_2$ nanoparticles. Originally a technique known to the ceramics industry, the sol–gel method was rediscovered by heterogeneous catalysis in the 1980s. The process witnessed an enormous increase in popularity in the 1990s and is considered to be one of the leading new synthesis methods of the discipline. Although it is not mandatory that only oxides are formed by sol–gel process, often oxides ceramics are best synthesized by a sol–gel approach. The advantage of this method relies on the ability to control the morphology, particle size and crystallinity, along with high homogeneity, low processing temperature, stability and versatility of processing [3]. As sol–gel process is usually a low temperature process; this means less energy consumption and less pollution. A number of potential advantages and disadvantages and relative economics of sol–gel method are reported by Mackenzie [58]. One of the key factor for the increased scientific understanding of the sol–gel method is the availability of new analytical approaches capable of investigating on a nanometer scale for the chemical process of materials [57]. This research focuses on sol–gel processing techniques for synthesis of undoped/doped titania nanoparticles which will be discussed in great detail.

In sol–gel method, the overall reaction is the conversion of precursor solution (metal salt or alkoxide) into an inorganic solid via inorganic polymerization reaction by solvent (water or organic) and drying. A sol is a stable dispersion of colloidal particles or polymers in a solvent. Colloids are solid particles with diameters of 1–1000 nm [57]; while nanoparticles are the special class of colloids with dimensions less than 100 nm usually. The
particles may be amorphous or crystalline. An aerosol is the dispersion of solid particles in a gas phase, while a sol is the dispersion of solid particles in a liquid medium. A gel is a interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer [57]. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles.

The first step in a sol–gel reaction is the formation of an inorganic polymer by hydrolysis and condensation reactions. A homogeneous solution is prepared by dissolving metal organic precursor in water or water miscible organic solvent, i.e. the transformation of the molecular precursor into a highly cross linked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles in a liquid, and further condensation results in a gel, an interconnected, rigid, and porous inorganic network enclosing a continuous liquid phase. This transformation is known as sol–gel transition. The gel can be dried in critical condition to form aerogel, without collapsing the network. The gel dried under ambient conditions produces a xerogel with shrinkage of the pores [59]. Sol–gel method involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes. The sol–gel process can be characterized by a series of distinct steps.

**Step 1:** Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

In hydrolysis step, the alkoxide groups (−OR), where R is CH₃, C₂H₅, C₃H₇ are replaced via the nucleophilic attack of the oxygen atom of a water molecule under release of alcohol and the formation of a metal hydroxide.
Step 2: Gelation resulting from the formation of an oxide– or alcohol–bridged network (the gel).

Condensation reactions between two hydroxylated metal species leads to formation of Ti–O–Ti bonds under release of water (oxolation), whereas the reaction between a hydroxide and an alkoxide leads to formation of Ti–O–Ti bonds under release of an alcohol (alkoxolation). Condensation reactions can proceed to form large chains of molecules through polymerisation. The electrophilicity of the metal, the strength of the entering nucleophile and the stability of the leaving group all have an influence over the thermodynamics of the hydrolysis and condensation reactions.
By polycondensation process, sols are nucleated and ultimately sol–gel is formed. Furthermore, polycondensation or esterification reaction results in a dramatic increase in the viscosity of the solution. Additional linkage of $\equiv$Ti–OH tetrahedral occurs as a result of polycondensation reaction and ultimately results in a TiO$_2$ network. The alcohol and water expelled from the reaction remains in the pores of the network. When sufficient interconnected network of Ti–O–Ti bonds are formed in a region, they respond cooperatively as colloidal particles in the scale of submicrometer. The size of the colloidal particles and the cross–linking within the particles mainly depend upon the pH and the amount water and alkoxide precursor.
Step 3: Aging of the gel (Syneresis), during which, polycondensation continues along with localized solution and reprecipitation of the gel network, which further increases the thickness of interparticle necks and decreases the porosity. Aging process also increases the strength of the gel.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. Further the liquid is removed from the interconnected pore network by drying the gel. The pH of solvent plays a important role in the kinetics of gelation. Gelation can be either acid or base catalyzed [60-63]. Heating the porous gel at high temperature causes densification to occur [57]. The pores are removed to get xerogel.

Step 5: Dehydration, during which surface–bound M–OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcinating the material at high temperatures.

Step 6: Densification and decomposition of the gels at high temperatures. The pores of the gel network are collapsed, and remaining organic species are
volatilized. The typical steps that are involved in sol–gel processing are shown in the Figure 3.1.

![Figure 3.1 Sol–gel processing options.](image)

To achieve a better control over the evolution of the microstructures, it is desirable to separate and temper the step of hydrolysis and condensation by means of coordinating agents, precipitation condition (acidic or basic), controlling the water content and reducing working temperature. Sol–gel derived TiO$_2$ nanoparticles with controlled size and morphology are of great interest for many applications in the proposed investigations.
4.4 Synthesis of TiO$_2$ and metal–doped TiO$_2$ nanoparticles

Figure 3.2 shows a flow diagram of the preparation metal–doped TiO$_2$ nanoparticles. Metal–doped TiO$_2$ nanoparticles in the optimum compositions (0.0 mole% – 3.0 mole%) were prepared by sol–gel method at room temperature. For this, 5 mL glacial acetic acid and 15 mL titanium (IV) isopropoxide were taken in a 250 mL round–bottom flask. The content was stirred at room temperature for 15 min followed by addition of aqueous solution of sodium dodecyl sulfate. The content was stirred at room temperature for 2 h. The required stoichiometric amount of dopant was dissolved in 10 ml distilled water. This dopant solution was added to the above titanium precursor and stirred at room temperature for 2 h. The pH of the resulting solution was adjusted to 10.00 using ammonia solution. The solution was stirred at 60 °C for 3 hrs and then cooled to room temperature and filtered. The residue was slurried in 80 mL distilled water at room temperature for one hour, followed by constant stirring at 60 °C for 3 h. The content was cooled to room temperature, filtered and washed with 50 mL of ethanol. Residue was dried at 110 °C and calcinated in air at 500 °C for 5 h, which resulted in colored metal doped titania nanoparticles depending on concentration and type of metal dopant.

Similar experimental route was adopted for undoped TiO$_2$ nanoparticles without addition of aqueous solution of metal precursor as a dopant source. In the doped TiO$_2$ nanoparticles, various metal precursors such as Fe(NO$_3$)$_3$·9H$_2$O, CuSO$_4$·5H$_2$O and NiSO$_4$(H$_2$O)$_6$ were used as the sources of iron, copper and nickel dopants, respectively.
4.4.1 Synthesis of iron-doped TiO\textsubscript{2} nanoparticles

The method described above was used to prepare iron-doped TiO\textsubscript{2} nanoparticles. The iron was introduced into the reaction mixture by dissolving Fe(NO\textsubscript{3})\textsubscript{3}\cdot9H\textsubscript{2}O into water after adding the surfactant. The Fe–doped TiO\textsubscript{2} nanoparticles were slightly yellowish in color. Different samples such as 1.0
mole% Fe–doped TiO₂, 2.0 mole% Fe–doped TiO₂, and 3.0 mole% Fe–doped TiO₂ are designated as Fe₁–TiO₂, Fe₂–TiO₂, and Fe₃–TiO₂, respectively.

### 4.4.2 Synthesis of copper-doped TiO₂ nanoparticles

Copper-doped TiO₂ nanoparticles were prepared by adding aqueous solution of CuSO₄·5H₂O into the reaction mixture. The resulting Cu–TiO₂ nanoparticles were faint bluish in color. Various samples such as 1.0 mole% Cu–doped TiO₂, 2.0 mole% Cu–doped TiO₂, and 3.0 mole% Cu–doped TiO₂ are designated as Cu₁–TiO₂, Cu₂–TiO₂ and Cu₃–TiO₂, respectively.

### 4.4.3 Synthesis of nickel-doped TiO₂ nanoparticles

Optimum composition of nickel-doped TiO₂ nanoparticles were prepared by similar rout as described above. For nickel doping in TiO₂ aqueous solution of NiSO₄(H₂O)₆ was used. The synthesized Ni–TiO₂ nanoparticles were yellowish in color. Various samples such as 1.0 mole% Ni–doped TiO₂, 2.0 mole% Ni–doped TiO₂, and 3.0 mole% Ni–doped TiO₂ are denoted as Ni₁–TiO₂, Ni₂–TiO₂ and Ni₃–TiO₂, respectively.
References


