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Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications

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Abstract

This chapter covers different routes of preparation of hierarchical nanostructures (HNS) of titanium dioxide. Keeping the interest in developing modern and sustainable methods of materials chemistry, this chapter focuses on synthesis routes for TiO_2 HNSs reported by researchers from all over the world. The chapter includes the details of chemical reactions taking place during the synthesis and the effects of various process parameters like: type of surfactants, organic/inorganic titanium salts, temperature and pressure on products. The obtained TiO_2 HNSs from different synthesis routes are subsequently compared in terms of their morphology, crystallite size, surface area, particle size and phase. The merits and demerits of all synthesis techniques are also added for comprehensive information. At the end, various applications of HNSs are discussed and their performance is analyzed with respect to the morphologies obtained from different synthesis techniques.

Keywords: hierarchical nanostructures (HNSs), nanoflowers, TiO_2 , Titania, microwave synthesis

1. Introduction

Depletion of fossil fuels and environmental pollution has reached an alarming situation. New techniques are being searched now to overcome this situation by switching toward sustainable and renewable energy resources [1–4]. Severe pollution threats like global warming demand such materials and devices that are environment-friendly and green. The main idea is to fabricate materials that are not only cost-effective [5] but are also more capable to deal with energy crisis in the world.

Recently, different renewable energy resources like wind, solar, bioenergy and geothermal energy have been deployed for energy production [6]. New materials are being explored and synthesized to harness energy from these alternate energy sources. The goal is to improve the competence of these devices by synthesizing materials that provide maximum energy harvesting and power control. For solar energy harvesting by photovoltaic devices, i.e., direct conversion of sunlight to electricity, different generations have been evolved depending upon materials and technologies used in device fabrication.

Various material types are employed for their use in renewable energy resources like organic, organometallic, metallic, semiconductors, etc. Wide band gap semiconductors have been exploited due to their substantial applications so far in cosmetics [7], drugs, electronics [8], photovoltaic devices [9], energy storage materials [10–12] and catalysis [13, 14] like photo-degradation (**Figure 1**). The third-generation photovoltaics utilize nanomaterials that have attracted much attention recently due to their novel electric, photochemical, piezoelectric, mechanical and catalytic properties [15].

In PV devices [17], semiconductor materials are mostly chosen on the basis of many properties like band gap, electronic mobility, mesoporosity [18, 19], toxicity levels, robustness [20, 21] and high surface area. So far, many semiconductor oxides have been prepared and tested. Nanomaterials of transition metal oxides like TiO_2 , SnO_2 , and ZnO are being further explored now because of their properties and applications. Titania [22] is the best material among all having distinguished optoelectronic and photochemical properties.

Titania is a promising material [12, 23] as it has high refractive index, biocompatibility and high dielectric constant. It exhibits redox reactions and has excellent optical transmittance in the visible and near IR regions. It is preferred because of its high performance as a photocatalyst for water splitting, oxidation capability [7] and degradation of organics [24]. **Table 1** highlights some of the properties of Titania.

Titanium dioxide also known as Titania exists in many crystalline forms among which rutile, anatase and brookite are of particular importance in nanomaterials. These forms can exist

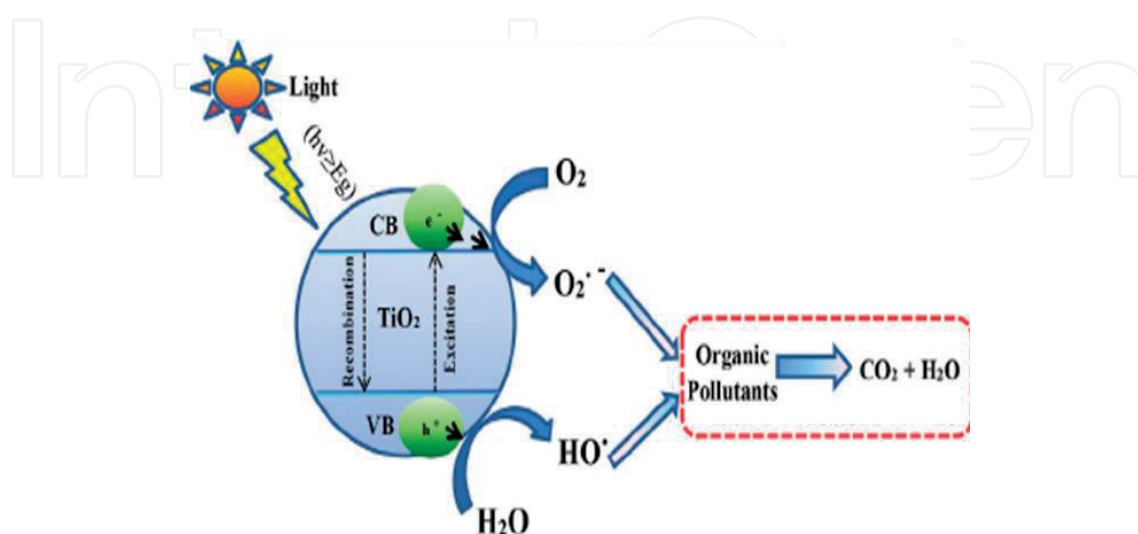


Figure 1. Application of TiO_2 for photodegradation of organic pollutants [16].

Properties of Titanium dioxide	
Natural forms	Anatase, rutile and brookite
Crystal structure	
Anatase	Tetragonal
Rutile	Tetragonal
Brookite	Orthorhombic
Melting point	1941 K
Boiling point	3546 K
Thermal conductivity	22Wm ⁻¹ K ⁻¹
Band gap	3.0 eV (rutile) 3.3 eV (anatase)
Solubility in water	Insoluble
Color	White-yellow
Molar mass	79.8 g/mol
Density	4.23 g/cm ³ (rutile), 3.78 g/cm ³ (anatase)
Flash point	Non-flammable

Table 1. Physical properties of Titania.

individually as minerals but only rutile and anatase have been synthesized in their pure form yet [13, 25]. Both anatase and rutile phases have tetragonal, while brookite has orthorhombic crystal system [9] (**Figure 2**).

The properties of Titania depend on particle morphology, crystallinity, particle size and surface area. Titania has a band gap from 3.0 to 3.23 eV, which makes it photocatalytic only in ultraviolet radiation region [26]. It is desirable to shift its band gap [27] so that it may absorb radiations of the visible light spectrum to enhance its photocatalytic properties. Titania nanostructures offer a larger surface area for light absorption in solar cells and catalytic properties for dye and pollutant degradation [28].

Titania nanostructures can be synthesized using various techniques. Some of them are hydrothermal [26, 29–34], solvothermal methods [10, 11, 35], sol-gel synthesis [1, 15, 36], microwave irradiation [8, 24, 37, 38], physical and chemical vapor deposition [4, 32, 39], electrochemical methods [40, 41] and anodization [42–44].

Generally, anatase Titania shows superior properties to rutile Titania because of slow recombination of electron-hole pairs and higher potential energy of photogenerated electrons [45]. Nano-Titania exists in many forms like nanoparticles [15, 40–42], nanorods [10, 24, 46], nanowires [3, 31, 32, 47], nanotubes [43, 48], nanospheres [49], nanoflowers [8, 32, 46, 50], nanoforests [44, 50], etc. as shown in **Figure 3**. Nanotubes show enhanced charge percolation and direct electronic transport than nanoparticles because of their 1D structures [51].

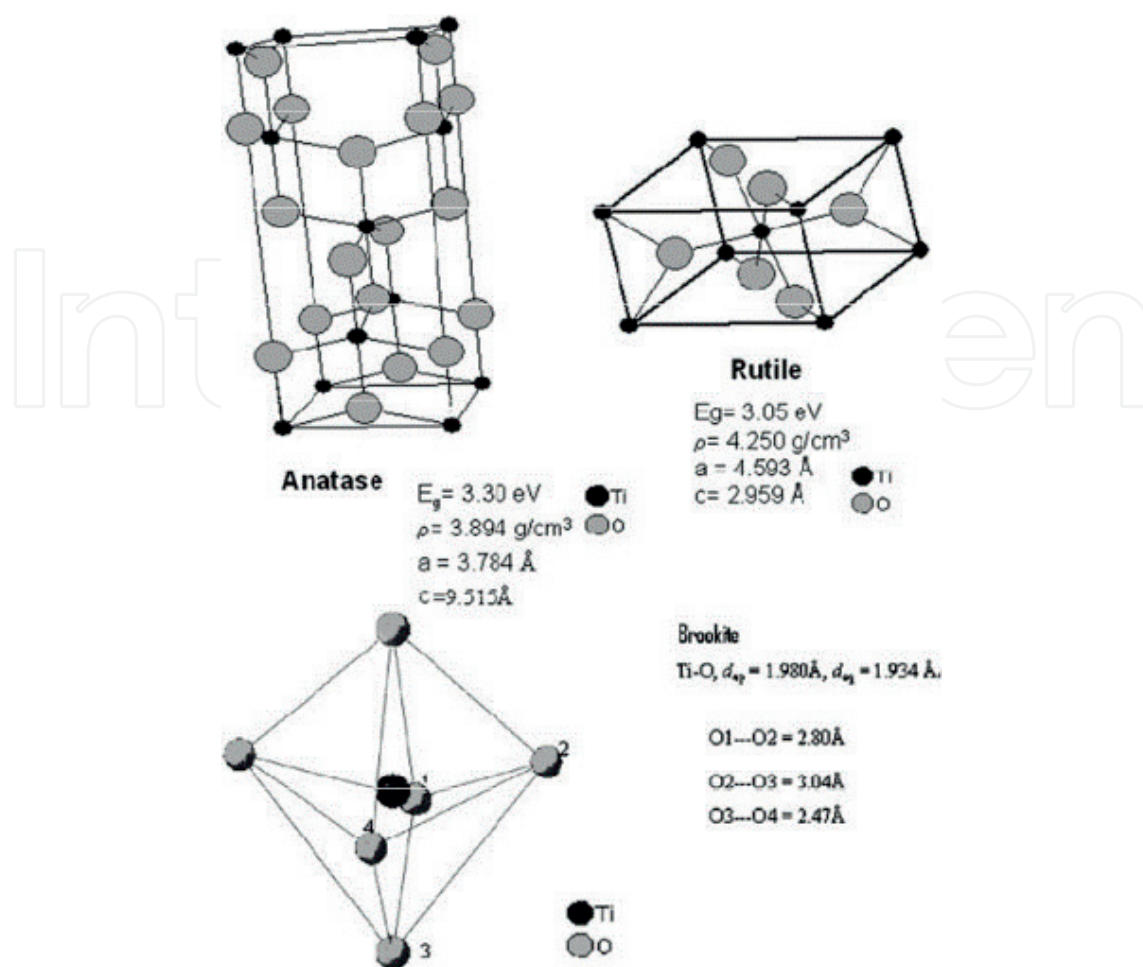


Figure 2. Different crystalline forms of TiO_2 [9].

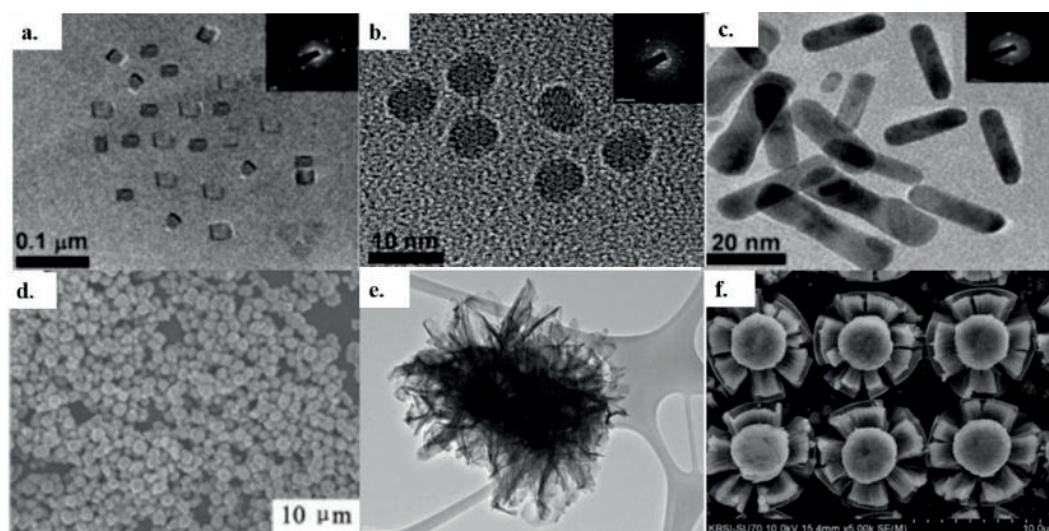


Figure 3. Different forms of TiO_2 : (a) nanocubes [24], (b) nanospheres [24], (c) nanorods [24], (d) nanoparticles [52], (e) nanoflowers [8], (f) nanoforest [48].

1.1. Hierarchical nanostructures

Hierarchical nanostructures are composed of 3D self-assembly of primary structure (nanoparticle, nanorod, nanotube or nanosheets) in nanoscale. Recently, materials with hierarchical morphology have attracted great attention as compared to spherical nanoparticles. Many experiments have been done in order to perk up the efficiency of nanomaterials by synthesizing hierarchical structures and enhancing the specific surface area and porosity of these structures [8, 38, 40, 53]. These types of structures show utmost light harvesting due to maximum and efficient scattering (hence absorption) of incident light within [40]. Hierarchical TiO_2 nanostructures provide a significant improvement in properties due to enhanced porosity [54, 55] and many devices can be optimized using HNSs [43]. Hierarchical morphology can enhance the photon absorption capability [8] as compared to spherical nanoparticle as there is increased absorption of light due to scattering. The mesoporosity acts as distribution channels increasing adsorption of visible light sensitizers. It also creates an ideal environment for mass transportation [39] of electrons.

This chapter presents a compilation of different synthesis routes and control measures employed for the synthesis of “hierarchical nanostructures of TiO_2 .” A brief overview of each synthesis route is provided. Investigation on the synthesis parameters and the correlation with the characteristic properties of the products are also discussed.

2. Synthesis of hierarchical nanostructures of TiO_2

Various types of surfactants, organic/inorganic titanium salts, high temperatures and pressures may be used for the preparation of hierarchical nanostructures of Titania. Following are the reported methods for the synthesis of TiO_2 HNSs.

- Hydrothermal method
- Solvothermal method
- Microwave treatment
- Pulsed laser deposition
- Anodization
- Photolithography
- Vapor deposition method
 - Chemical vapor deposition
 - Physical vapor deposition

2.1. Hydrothermal synthesis

As the name indicates, the method involves heating in aqueous medium. Generally, in this method, sealed Teflon-lined steel autoclaves are used under controlled temperature

and pressure conditions. Sometimes, surfactants are also added to control the growth and morphology of target materials.

Internal pressure is set up by the amount of temperature and solution used. This process is mainly used for the preparation of small-sized particles for achieving enhanced surface area. Basically, this synthesis is used for preparation of crystalline TiO_2 from amorphous one. The morphology of the particles can be varied by changing crystallization temperature, time and concentration of etching chemicals. **Table 2** shows the various routes by which hierarchical TiO_2 structures have been prepared by hydrothermal route.

Reference	Phase	Surface area ($\text{m}^2 \text{g}^{-1}$)	Particle size (diameter)	Precursor materials	Morphology	Used in application
Lin et al. [56]	Rutile	67	1–1.5 μm	Tetrabutyl titanate (TT)	Flower-like structures	DSSCs
Wang et al. [50]	Rutile	75.53	(4.4 μm length) 150 nm diameter	Titanium tetrabutoxide	1D/3D nanorods	DSSCs
Qiang et al. [3]	Anatase	—	NW trunk 95 nm, NR 5 nm	$\text{K}_2\text{TiO}_2(\text{C}_2\text{O}_4)_2$ and diethylene glycol (DEG)	Nanowire trunk on which nanorods are grown	DSSCs
Xiang et al. [57]	Anatase	—	300–600 nm	Dodecylamine and titanium isopropoxide	Nanoparticle-based HNs	DSSCs
Zheng et al. [60]	Anatase	27.4	4–6 μm	Primary Titania microspheres	Hierarchical microspheres	Photocatalysis
Shao et al. [58]	Anatase	36.93	15–25 μm	Ti foil	Flower-like structure formed from nanobelts	DSSCs
Zhu et al. [29]	Anatase	170	350 nm	Titanocene dichloride	Flower-like shapes formed from nanosheets	Photocatalysis
Wang et al. [32]	Anatase	64.8	1–1.5 μm	Titanium powder	Radial nanoflakes	Gas sensing
Gao et al. [2]	Anatase	116.6	3–4 μm	Tetrabutyl titanate (TBT) and acetic acid	Overlapped subunits of nanoflakes	Lithium sulfur battery
Yang et al. [59]	Anatase	—	20–50 nm	Titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) and urea ($\text{CO}(\text{NH}_2)_2$)	Nanothorn-like hierarchical structures	Gas sensing
Min et al. [59]	Anatase	168.3	2–4 μm	Titanium powder	Nanospheres composed of nanosheets	Photocatalysis

Table 2. Hierarchical TiO_2 nanostructures produced by various hydrothermal routes.

2.1.1. Examples

Lin et al. have reported rutile TiO_2 hierarchical flower-like structures via hydrothermal synthesis without using any surfactant. Precursor tetrabutyltitanate (TT) is first mixed with HCl for acidification and is subsequently hydrolyzed using distilled water. To ensure complete hydrolysis, the reaction mixture is stirred for about one and a half hour. Next, the mixture is transferred to a Teflon-based autoclave and is placed in an electric oven for 5 h at 150°C for crystallization. Hierarchical nanoflower-like structures are obtained as an end product. By increasing the HCl concentration, the etching rate of TiO_2 structures is enhanced and symmetric flower-like structures are produced [56] (**Figure 4**). These structures are employed for DSSCs and 8.6% of conversion efficiency is achieved.

Wang et al. have prepared rutile Titania 1D/3D structures via hydrothermal treatment. The precursor Titanium tetrabutoxide (0.9 m) is acidified using HCl (16 ml) and then hydrolyzed using DI water (16 ml). The reaction mixture is subsequently heated to 150°C and kept at this temperature for 10 h for crystallization. The position of FTO substrates is varied to obtain different HNSs. 1D/3D HNSs are produced while the FTO substrate lied flat on the bottom of the reactor with the conductive side facing up. 3D nanorods are produced when the conductive side of substrate is placed downwards.

Rutile Titania 3D flower-like nanorods are grown on 1D nanorods with length in microns [50] (**Figure 5**). These structures are employed as a photo anode material in DSSCs and significant improvement in device performance is seen. 1D structure provides directed pathway for electron percolation and 3D morphology provides large surface area for light scattering and dye-loading. Also, the structures exhibit long life time due to less electron-hole recombination.

Qiang et al. have obtained hierarchical anatase TiO_2 nanowire trunks with short nanorod branch HNSs by facile one-way hydrothermal synthesis on FTO glass without using any surfactant/stabilizing agent. The solution is prepared using precursor $\text{K}_2\text{TiO}_2(\text{C}_2\text{O}_4)_2$ (0.002 mol)

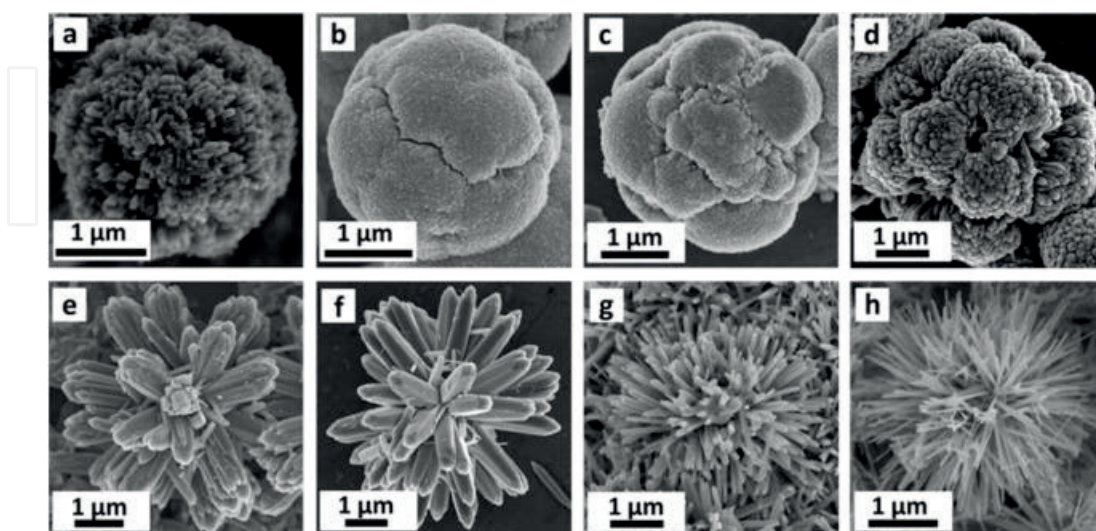


Figure 4. FESEM images of TiO_2 structures. Change in morphology is produced from changing HCl conc. at (a) 1M (b) 2M (c) 3M (d) 4M (e) 5M (f) 6M (g) 7M (h) 8M [56].

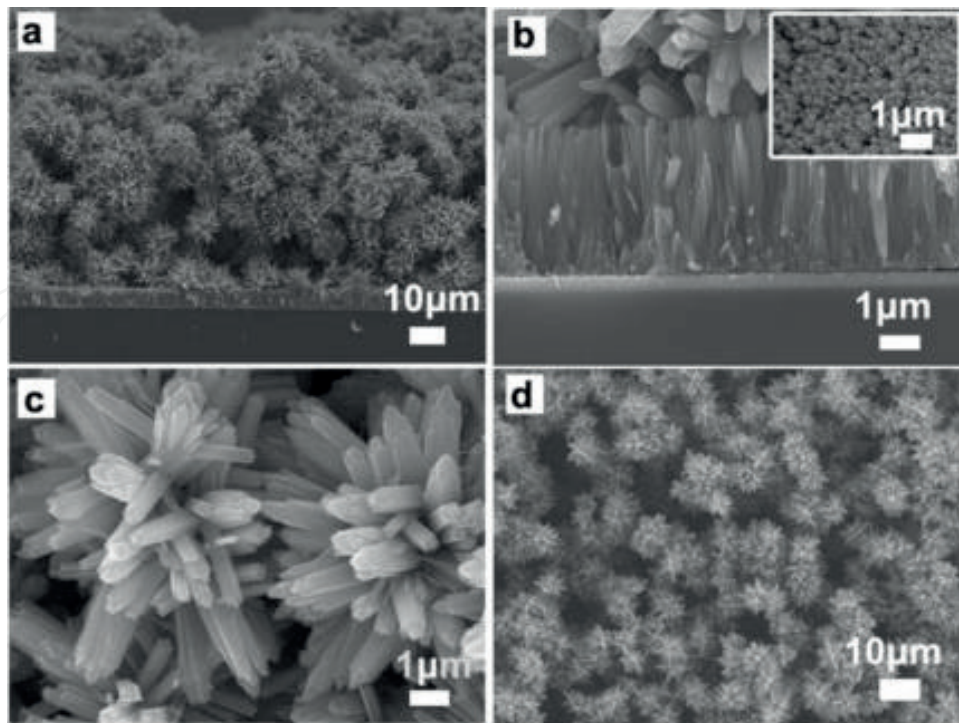


Figure 5. (a,d) SEM images of 1D/3D nanorod structures (b) 1D nanorods (c) 3D nanoflower-like structures [50].

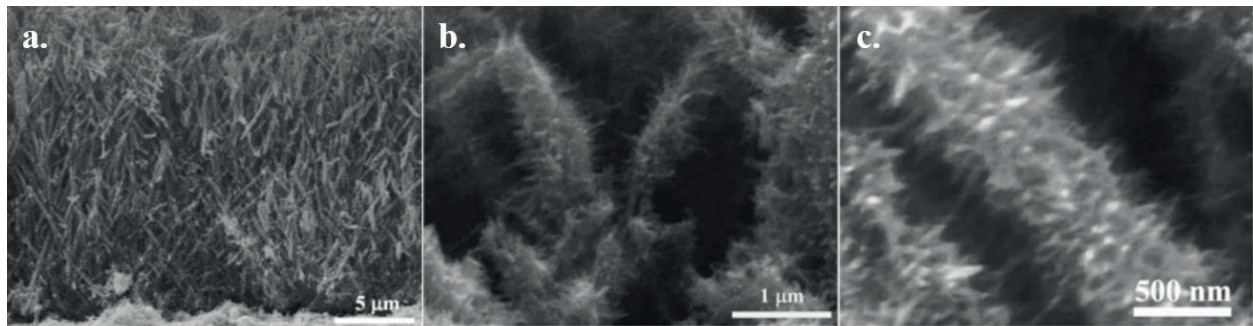


Figure 6. SEM images of hierarchical anatase nanowire trunk covered by short nanorod branches (a) Nanorods covering the nanotrunk (b) Enlarged image of nanorods (c) Nanotrunk covered by nanorods [3].

and diethylene glycol (DEG) (30 ml) as Titania precursor. About 10 ml H_2O is used for hydrolysis. The solution is then spin coated on FTO substrate for seeding of TiO_2 structures. The spin-coated substrate is immersed in Teflon-based autoclave, which is kept at 180°C for 1–12 h for crystallization of Titania structures. **Figure 6** shows nanotrunk produced having nanowire-like structures grown on them [3].

These structures are employed as a photo anode material in DSSCs and impressive power conversion efficiency of 7.34% is achieved. Hierarchical morphology aids in efficient electron transfer but these structures provide additional recombination sites so results are inferior to bare TiO_2 nanowires.

Xiang et al. have reported Ta-doped and -undoped hierarchical TiO_2 nanostructures. Dodecylamine (8 g) and titanium isopropoxide (TIP, 8 g) are used as precursor materials and are

mixed with ethanol (360 ml) and DI water (120 ml) for hydrolysis under vigorous stirring at ambient room temperature. HNO_3 formed during reaction is removed from the reaction mixture and white powder of anatase Titania is obtained, which is then washed with water and ethanol to maintain the pH of particles at 7. After that, TaCl_5 is added in reaction mixture in different ratios. The solution is transferred to Teflon-lined autoclave, kept at 250°C for 12 h to dope Ta particles with TiO_2 .

HNSs made up of symmetrically arranged interconnected spherical nanoparticles are obtained as a result of these syntheses [57]. These structures are employed as a photoanode material in this article. The large spheres can provide maximum scattering of sunlight for light-driven reactions like photocatalysis (**Figure 7**).

Shao et al. have prepared hierarchical TiO_2 flower-like structures on Ti foil by placing it in Teflon-lined autoclave at an inclined angle in 5 M NaOH solution for its reduction. Sodium titanate is formed as a result of this reaction. The temperature is maintained at 220°C for 24 h for complete reaction of converting Ti foil to TiO_2 nanostructures. The sample is then washed with water and ethanol to remove all the acidic content and to maintain its pH at neutral. The sample is then immersed in HCl solution so that all Na^+ ions of sodium titanate would get replaced by H^+ ion. After calcination, nanobelts (**Figure 8**) forming nanoflower-like structures are formed [58].

Reaction of TiO_2 nanoparticles with NaOH results in the formation of Na_2TiO_3 , which is a nanoporous structure. The reaction that takes place is as follows.



These Na^+ ions can be replaced with H^+ ions by washing them with deionized water or acid. It can be shown as:

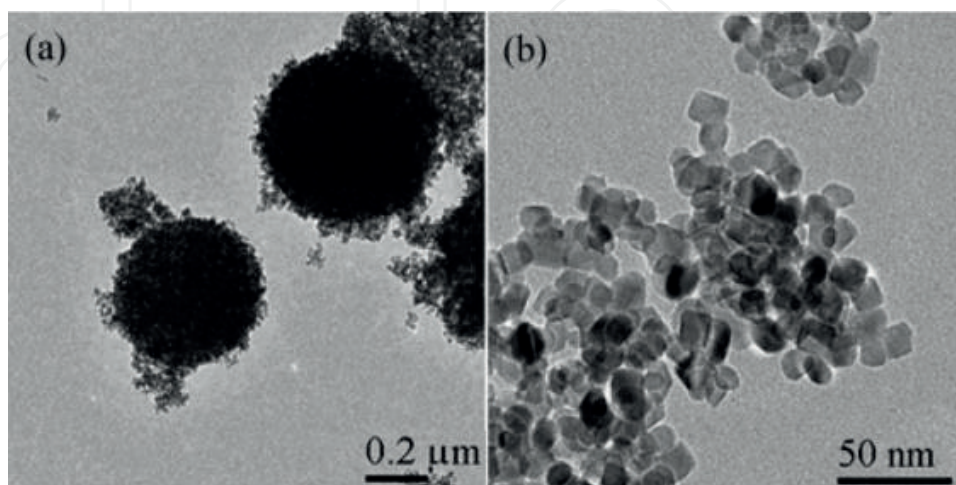
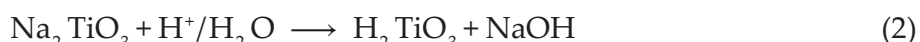


Figure 7. TEM images of hierarchical TiO_2 spherical structures composed of nanoparticles (a) Agglomerated TiO_2 nanoparticles (b) Dispersed TiO_2 nanoparticles [57].

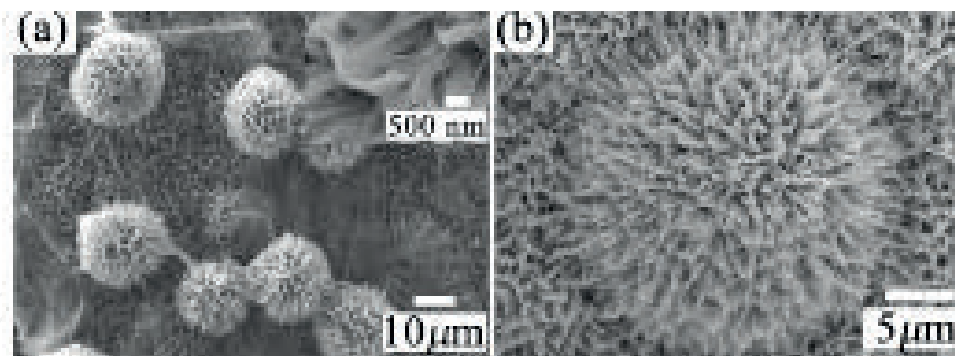


Figure 8. SEM images of nanoflower-like hierarchical TiO_2 structures produced after annealing at 500°C [58].

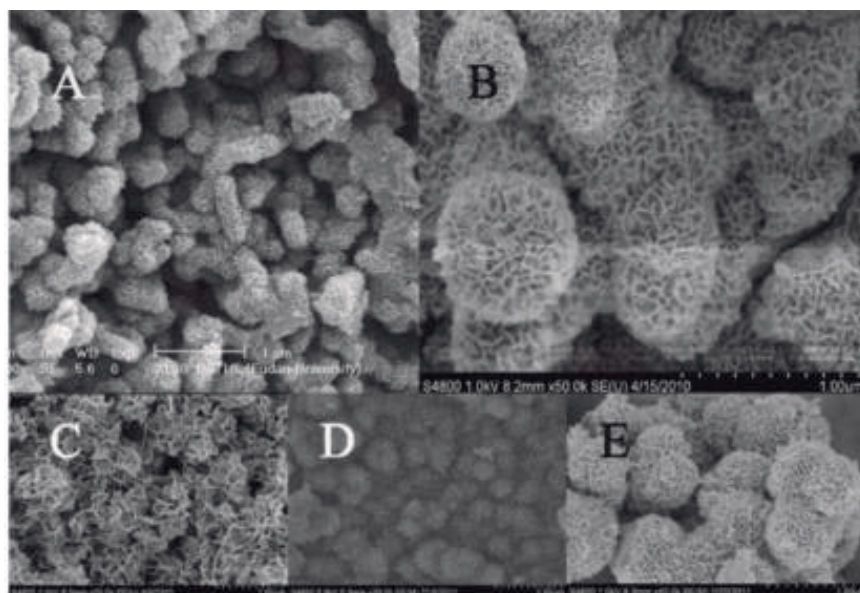


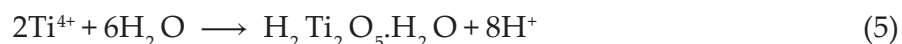
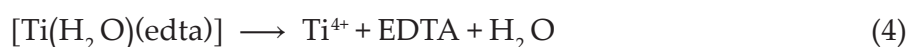
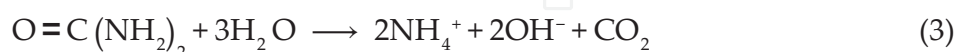
Figure 9. SEM images of hierarchical TiO_2 prepared by hydrothermal heating: (A) after 1 h, (B) after 2 h and (C) after 12 h. (D, E) Annealed powder of sample B [29].

By reduction of nanoparticles and increasing time duration of crystallization, nanoflower-like structures can be grown.

Zhu et al. have prepared HNSs of TiO_2 using titanocene dichloride ($\text{Ti}(\text{Cp})_2\text{Cl}_2$) (20 mg) as precursor. DI water (10 ml) is added for hydrolysis, and ethylene diamine (EDA) (2 drops) acts as chelating agent. This results in the production of TiO_2 nanocrystals. The mixture then after sonication is placed in an autoclave at 120°C for 1–12 h. The powder obtained is then washed with water and ethanol and is annealed at 400°C for 2 h. Flower-like HNSs (**Figure 9**) are formed in this process [29].

By increasing the duration of hydrothermal synthesis, the nanoparticles have attained more flower-like mesoporous morphology due to increased time provided for etching. These structures have proved to be better photocatalytic agents as compared to nanocrystals of TiO_2 as they can provide maximum enhanced surface area, and due to their mesoporosity, maximum dye can be loaded on them. Hence, these structures can be used with perspective of various solar cells and photocatalysis for efficient light-driven reactions.

Yang et al. prepared hierarchical Titania structures by hydrothermal synthesis. Titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) and urea ($\text{CO}(\text{NH}_2)_2$) were used as precursor materials. Ethylene diaminetetra acetic acid (EDTA) disodium salt was added in them as the chelating agent for TiO_2 formation. $\text{Ti}(\text{SO}_4)_2$ (3 mmol), urea (24 mmol) and EDTA (3 mmol) were mixed and NH_4F (9 mmol) was added in the mixture for attaching $[\text{Ti}(\text{H}_2\text{O})(\text{edta})]$ with F^{-1} ions. The reaction mixture was dissolved into 60 ml of deionized water for formation of H_2TiO_3 . After stirring for 3 h, the reaction was complete and white powder was obtained, which was then moved in Teflon-lined autoclave at 180°C for 10 h for its complete crystallization. The powder formed was washed with DI water and ethanol to maintain pH at neutral and annealed to recrystallize. Reactions that took place were:



Mesoporous nanothorn-like structures are produced as a result of this process [59] shown in **Figure 10**. These structures are employed for gas sensing application of acetone. This hierarchical morphology provides much higher sensitivity and fast response time with minimum recovery speed.

Min et al. prepared hierarchical Titania structures by hydrothermal synthesis. About 1 g of Titanium powder was being dissolved in (0.5 M) 30 ml HF for its oxidation as it is a powerful oxidizing agent. The solution was then mixed with 3 ml NH_3 . This solution was moved to Teflon-lined autoclave at 150°C for crystallization for 5 h. The powder obtained was washed via centrifugation and was then dried at 80°C . Nanosheets (**Figure 11**) are being produced as a result of this process [52].

These structures are employed as a photocatalyst material for photodegradation of organic dye. Methylene blue is used as a model dye in this article. Complete photodegradation of organic compound is observed in just 60 min.

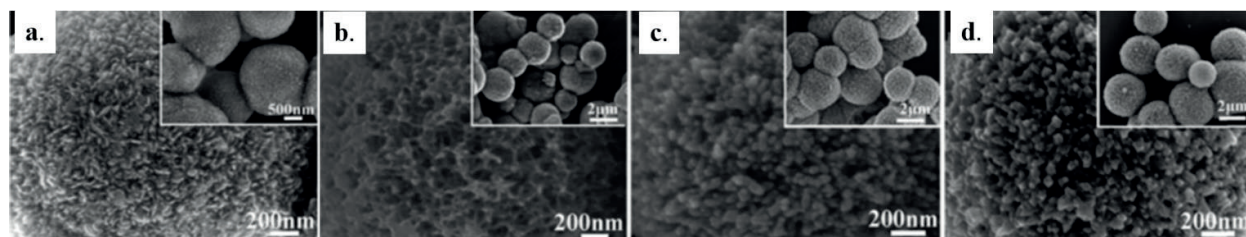


Figure 10. FESEM images of hydrothermal synthesis at (a) 5 min, (b) 1 h, (c) 3 h and (d) 5 h [59].

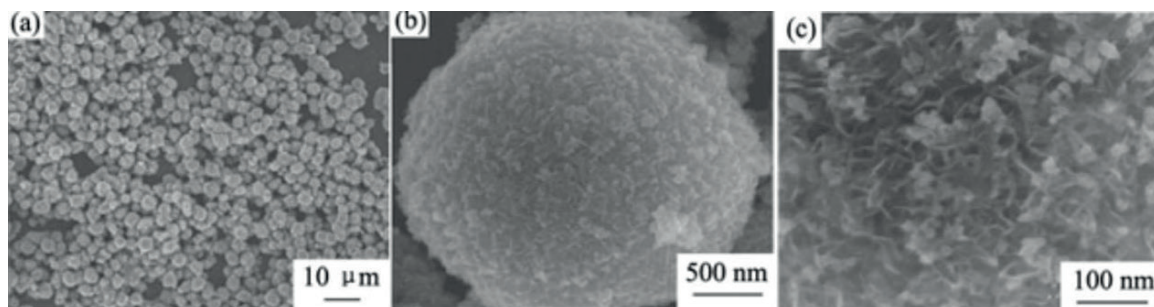


Figure 11. FESEM images of Titania hierarchical nanospheres composed of nanosheet-like structures [52].

2.1.2. Merits

The hydrothermal method has got the following advantages:

- This method is comparatively easy.
- Titania formed via this process can range from nanoparticle- to nanoflower-like structures depending on temperature.
- By increasing the duration and time in hydrothermal reactor, the crystallization of particles can be improved.
- The structures produced are diverse so they can be used in various applications.
- If NaOH or other reducing or oxidizing agents are used, they can be removed easily by washing with deionized water.
- By controlling temperature, one can grow anatase or rutile Titania phase depending on application.
- Hierarchical morphology can be attained.
- A variety of precursors is used for the production of TiO_2 HNSs.

2.1.3. Demerits

The demerits of this method are listed below:

- Water is used as solvent in this synthesis, so the temperature for crystallization cannot be increased from 100 to 150° C. Otherwise, water will dry out and crystallization may hinder.
- Proper time should be given to materials during synthesis as complete etching should be done for desired morphology.
- Sometimes crystallization times are very prolonged as compared to microwave technique. So it can be termed as a slow process than microwave.

2.1.4. Summary of hydrothermal synthesis

To summarize, hydrothermal treatment of various precursors under control parameters of temperature, pressure and duration gives a variety of morphologies in HNSs of Titania. The

morphology ranges from hierarchical arrangement of nanoparticles to nanorods producing flower-like structures. Increasing temperature increases crystallization of TiO_2 particles, and by increasing duration of hydrothermal synthesis, better etched morphology was obtained. **Table 2** summarizes reported examples of hydrothermal synthesis of HNSs with respect to precursor used for the synthesis and various properties of obtained HNSs together with the application studied. The HNSs obtained from this method varies in size from 20 nm to 4.5 μm . The surface area of the resultant HNSs ranges from 27 to 170 m^2g^{-1} . These structures are exploited in various applications including solar cells, photocatalysis and sensors, etc. and have improved respective performance owing to their unique structural properties.

2.2. Solvothermal synthesis

In this synthesis, the conditions are the same as for a hydrothermal method but non-aqueous solvent is used instead of water. The process takes place in an autoclave and temperature can be increased because of high boiling of certain organic solvents as compared to water. This method results in uniform particle size distribution and high purity products. Also by changing the temperature, morphology of the grown crystals can be varied. In addition to that, different morphologies result due to differences in steric hindrance offered by different functional groups in various organic solvents. **Table 3** shows various routes adopted to synthesize TiO_2 HNSs via solvothermal route.

2.2.1. Examples

Ochanda et al. have presented TiO_2 HNSs by solvothermal synthesis technique. Their method involves mixing of 15 ml of 4 M NaOH solution with 0.5 g TiO_2 fibers. Then, 15 ml ethanol solvent is added to this solution followed by heating in a 50 ml Teflon-lined autoclave at 150°C for 0.5, 1, 6 and 12 h. The resultant white precipitates are then dried in air. Nanoflower-like structures are grown over the nanorod structures with average crystallite size of 4 nm (**Figure 12**) [10].

These structures are then employed for photocatalytic degradation of methylene blue dye. Complete degradation of organic dye has been achieved in 120 min by these structures. Hence, these HNSs can be used for determining photocatalytic behavior and applications like solar cells.

Reference	Phase	Surface area (m^2g^{-1})	Particle size (diameter)	Precursor materials	Morphology	Application
Ochanda et al. [10]	Anatase	94.01	50–70 nm	TiO_2 fibers	3D nanoflowers grown on nanofibers	Photocatalysis
Xiang et al. [35]	Anatase	37	2.5–3.0 μm (microspheres), 20–40 nm (nanorods)	TiCl_4	3D urchin-like structure composed of nanoneedles	Photocatalysis

Table 3. Hierarchical TiO_2 nanostructures produced via solvothermal method.

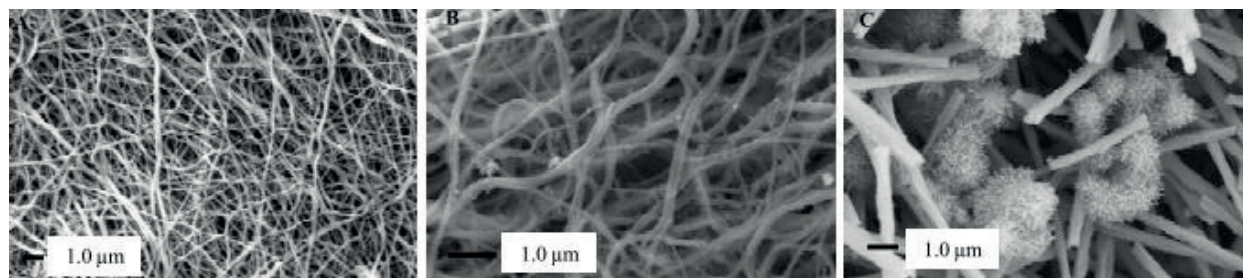


Figure 12. (a) 1 h solvothermal treatment, showing TiO_2 particle nucleation on nanofiber surface. (b) Hierarchical TiO_2 formed after 6 h showing the inception of flower-like structures. (c) After 12 h showing nanoscale flower-like nanostructures, completely covering the nanofiber surface [10].

Xiang et al. have prepared HNSs of Titania by solvothermal synthesis method using toluene. First, TiCl_4 is mixed with distilled water in ice water bath. In another assembly, toluene (30 ml) is mixed with tetrabutyltitanate (TBT). Both solutions are then stirred together for 1 h. The solution is placed in Teflon-lined autoclave for 24 h at 150°C . Micron ranged hierarchical Titania needles are obtained [35] as shown in **Figure 13**. Temperature plays an important role in defining the morphology of the products as HNSs are produced only above 120°C . Sea urchin-like HNSs are formed via ‘nucleation–self-assembly–dissolution–recrystallization’ growth mechanism without adding any surfactant or template. These structures are then tested for photocatalytic degradation of methylene blue and complete degradation study is completed in 240 min.

2.2.2. Merits

Following are some of the advantages of this technique:

- Better controlled morphologies due to control on temperature and treatment duration.
- Reliable method because of better reproducibility.
- High boiling organic solvents can be used.

2.2.3. Demerits

The method has the following demerits:

- Sometimes solvents are difficult to separate from the materials produced due to high boiling points of the solvents.
- Different solvents will have different effect on growth of target materials.

2.2.4. Summary of solvothermal synthesis

The solvothermal method in addition to the advantages offered by hydrothermal method allows the use of higher temperatures. This is sometimes advantageous in producing better

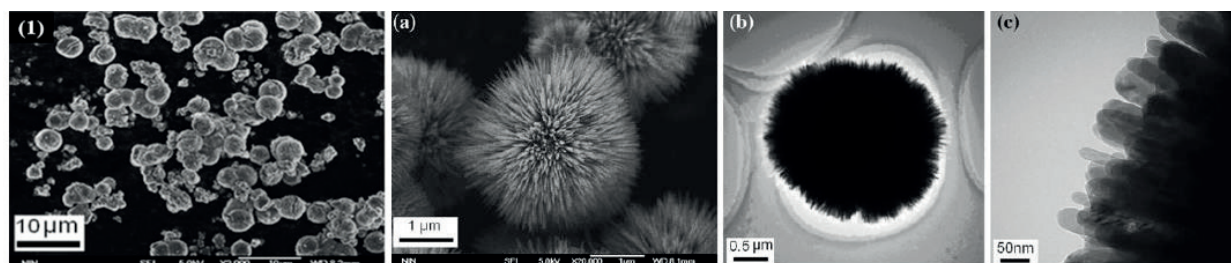


Figure 13. SEM images (1) nonhierarchical TiO_2 structures grown at 90°C . (a–c) TEM images of 3D hierarchical urchin-like structures having 1D nanoneedles [35].

crystallinity in the products. **Table 3** gives a summary of the reported work on solvothermal synthesis. The prepared HNSs obtained using this method range in size, from a few micrometers to several nanometers. They possess large surface area up to $94 \text{ m}^2\text{g}^{-1}$. The products have good crystallinity due to high crystallization temperatures offered by possible use of high boiling solvents. Different solvents can provide different chelating effects and hindrance to control morphology of structures. In addition to the type of solvent used, temperature and time control the growth and crystallization of particles during synthesis. These types of HNSs can be used for various photocatalytic applications like solar cells and organic pollutant degradation.

2.3. Microwave synthesis

This is relatively a new technique with many advantages. The key feature of this method is to heat the reaction mixture in less time via electromagnetic radiations. The frequency is kept from 800 to 2450 MHz range. Although it is not much explored for the HNS synthesis, much literature is available on microwave synthesis of nanoparticles [61], nanospheres [62], nanorods [63], nanowires [64] and nanotubes [65] of TiO_2 . Dipole molecules rotate in the presence of these radiations and localized “superheating” occurs at ambient pressure. This heat energy provided is used for crystallization of amorphous materials. By this method, reactions can be completed in just a couple of minutes as compared to conventional heating.

Although dedicated microwave lab reactor is the best equipment, modified/non-modified domestic microwave ovens can also be used for the preparation of HNSs. From a few reports found on HNS synthesis, it appears to be an efficient, quick and cost-effective method of HNS synthesis. The key characteristics of prepared samples are given in **Table 4**.

2.3.1. Examples

Javed et al. have prepared 3D-HNSs by microwave irradiation of anatase nanopowder in 10 M NaOH solution at 1 atm without any surfactant. Submicron-sized flower-like HNSs are produced as shown in **Figure 14** [8]. The crystalline phase is anatase with a decrease in surface area as microwave treatment duration increases from 5 to 20 min. The product is applied as photoanode in DSSCs, whereby the use of HNSs has two-fold improved the device efficiency. One reason being the larger light scattering due to morphology of the HNSs.

Reference	Phase	Surface area (m ² g ⁻¹)	Particle size (diameter)	Crystallite size (nm)	Morphology	Application
Javed et al. [8]	Anatase	18	500 nm	5.6	Nanoflower-like structures	DSSCs
Calatayud et al. [38]	Anatase	113	1–2 μm	—	Nanoparticle agglomerates	Photocatalysis
Wang et al. [37]	Anatase	86.90	500 nm	10	TiO ₂ nanoagglomerates	DSSCs
Rahal et al. [66]	Anatase	47	200–300 nm	—	Flower-shaped nanoparticle agglomerates	Photocatalysis
Martínez et al. [67]	Anatase	73	500 nm	56	Cauliflower-like hierarchical structures	—

Table 4. Hierarchical TiO₂ nanostructures produced via microwave treatment.

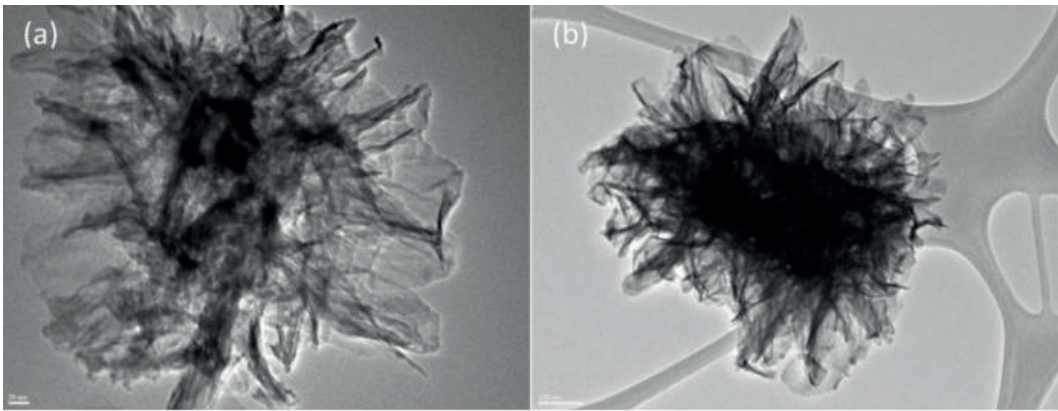


Figure 14. TEM images of hierarchical structures produced via microwave irradiation (a) after 5 min and (b) after 20 min [8].

Calatayud et al. prepared hierarchical crystalline TiO₂ via microwaves from amorphous powder using titanium (IV) tetrabutoxide (Ti(OBut)₄) and anhydrous ethanol as precursor materials. The solution is stirred for 6.5 h for complete hydrolysis and replacement of -butoxide group from -hydroxyl groups. Then, the powder is dried under atmospheric conditions. The powder obtained is washed with water and ethanol and irradiated in microwaves for different time durations. This microwave treatment provides the crystallization temperature and time for conversion of amorphous Titania to crystalline one. Anatase TiO₂ spherical HNSs (**Figure 15**) are produced having size from 1 to 2 μm [38].

These HNSs are employed for photodegradation of methyl orange (MO), which is completed in 6 h. By increasing microwave irradiation up to 10 min, clear agglomerated structures are produced, but as crystallization time is increased under microwaves, surface area decreases as particle size increases.

Wang et al. have synthesized HNSs by microwave irradiation using TiCl₄ (0.5 ml) in ethanol (14 ml) shown in **Figure 16**. After stirring for an hour, the reaction mixture is subjected to microwave irradiation for 10 min at 150°C under pressure of 300 Pa. TiCl₄ is hydrolyzed and

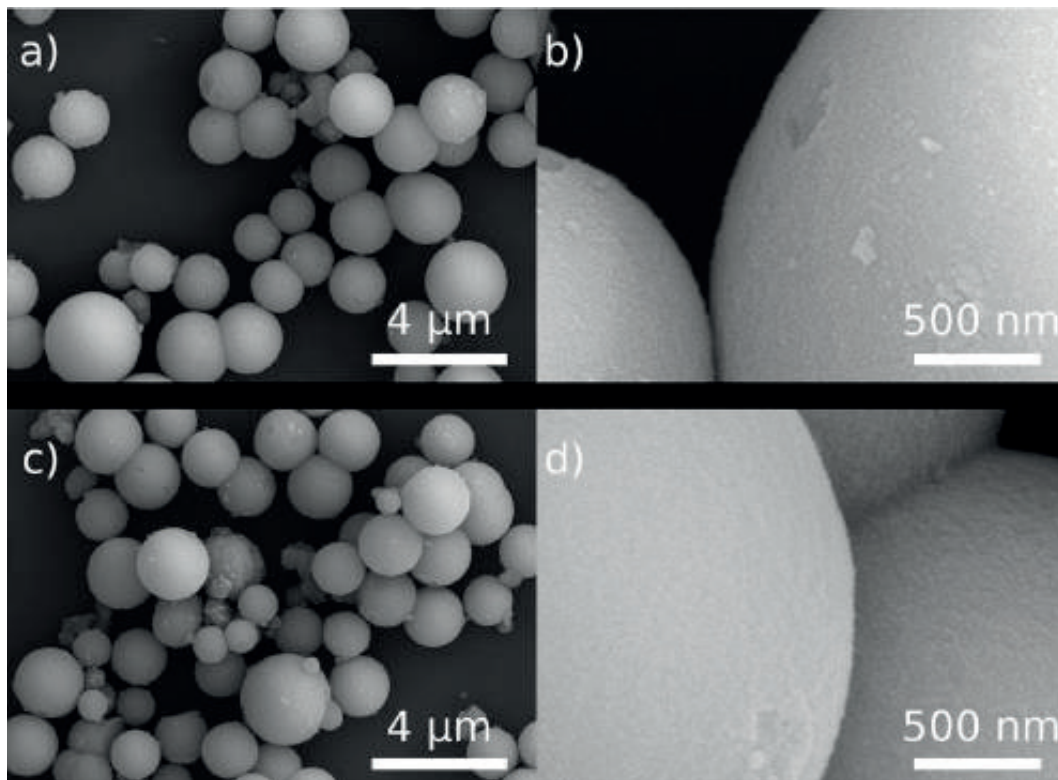


Figure 15. SEM images of TiO_2 spherical structures after microwave treatment: (a and b) after 7 min, (c and d) after 15 min [38].

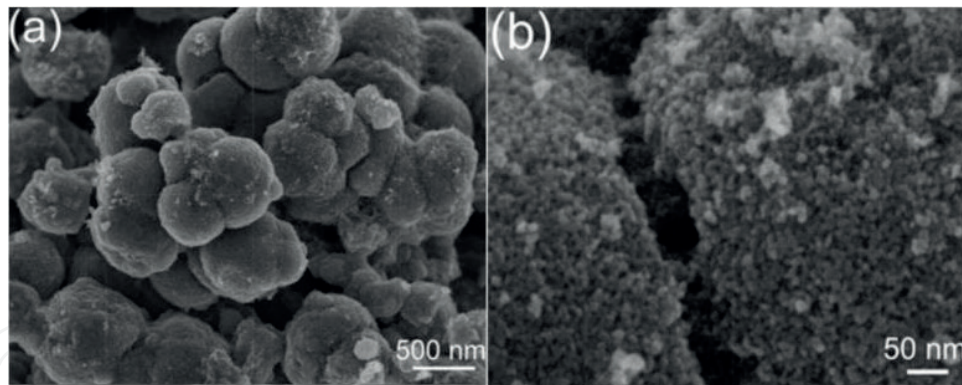


Figure 16. SEM images of 3D TiO_2 agglomerates [37].

crystallized in microwaves and TiO_2 nanoagglomerates with particle size up to 10 nm are prepared in spherical geometry [37]. The crystallite size is measured to be as small as 10 nm. In the presence of microwave, TiO_2 nanoparticles begin to nucleate and then their growth and aggregation occur during crystallization.

So, microwave heating provides quick crystallization of particles as particles begin to cluster within 3–5 min. Mesoporous structures are produced as a result of this synthesis and they are employed as a photoanode material in DSSCs. A maximum conversion efficiency of 7.64% is reported.

Rahal et al. have prepared TiO_2 hierarchical structures by mixing cetyltrimethyl ammonium bromide (CTAB, 11 mmol) and urea (2.4 g, 40 mmol) in 200 ml H_2O for hydrolysis (**Figure 18**). CTAB is used as a surfactant to control morphology and $(\text{NH}_2)_2\text{C}=\text{O}$ provides steric hindrance. To this reaction mixture, cyclohexane and 1-pentanol are added after stirring of 30 min. Then, TiF_4 (5.94 g, 48 mmol) is added to the solution and whole liquid media is transferred to Teflon-lined microwave reactor at 800 W. The mixture is irradiated under microwaves for 5 min at 120°C . The product is then washed thoroughly to remove impurities and other compounds and centrifugation is done to take out less dense particles.

Flower-shaped HNSs made of nanoparticle agglomerates (**Figure 17**) are produced with anatase phase [66]. Microwave treatment even for 5 min provides enough time for crystallization of TiO_2 nanoparticles. The prepared structures are utilized in photodegradation of Rhodamine B dye and complete degradation is observed within 1 h.

Martínez et al. [67] have recently reported TiO_2 HNSs prepared by stirring 3 ml of titanium tetra isopropoxide in 50 ml of H_2SO_4 and subsequent microwave treatment in a Teflon vessel at 120°C for 2 h. Anatase Titania is formed as a result of this scheme. Concentration of H_2SO_4 is changed to study the effect on particle size. Cauliflower-shaped HNSs are obtained. The increase in H_2SO_4 concentration increases the particle size.

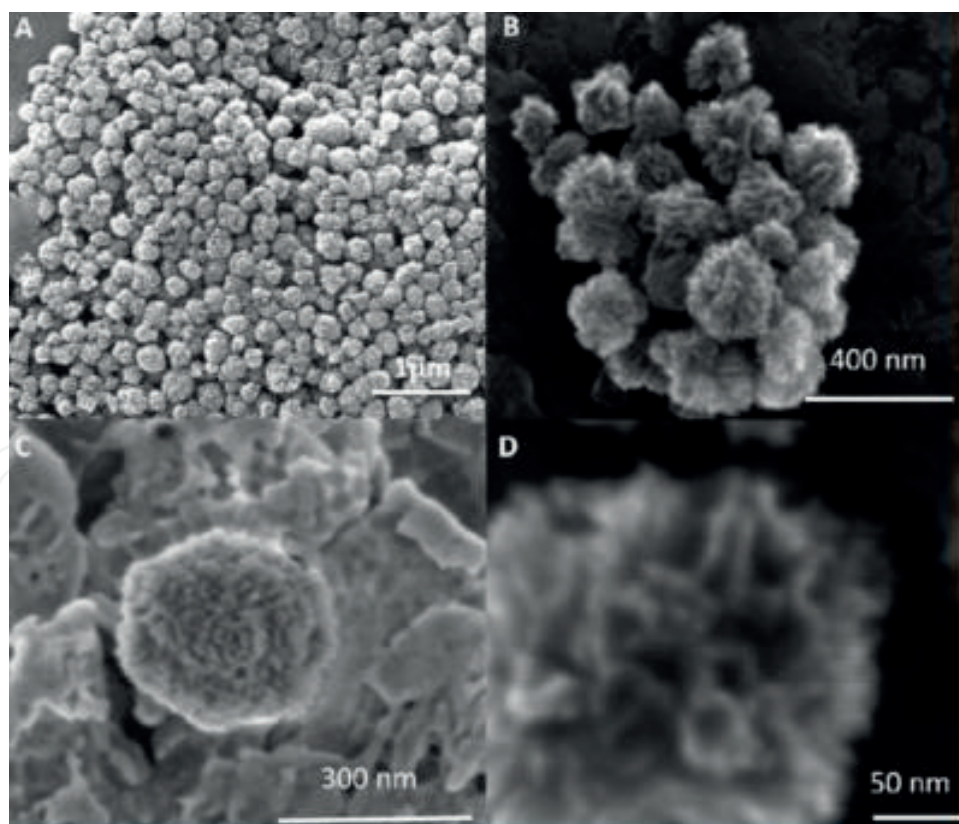


Figure 17. SEM images (a–d) of TiO_2 hierarchical structures having flower-like shapes after microwave irradiations for 5 min [66].

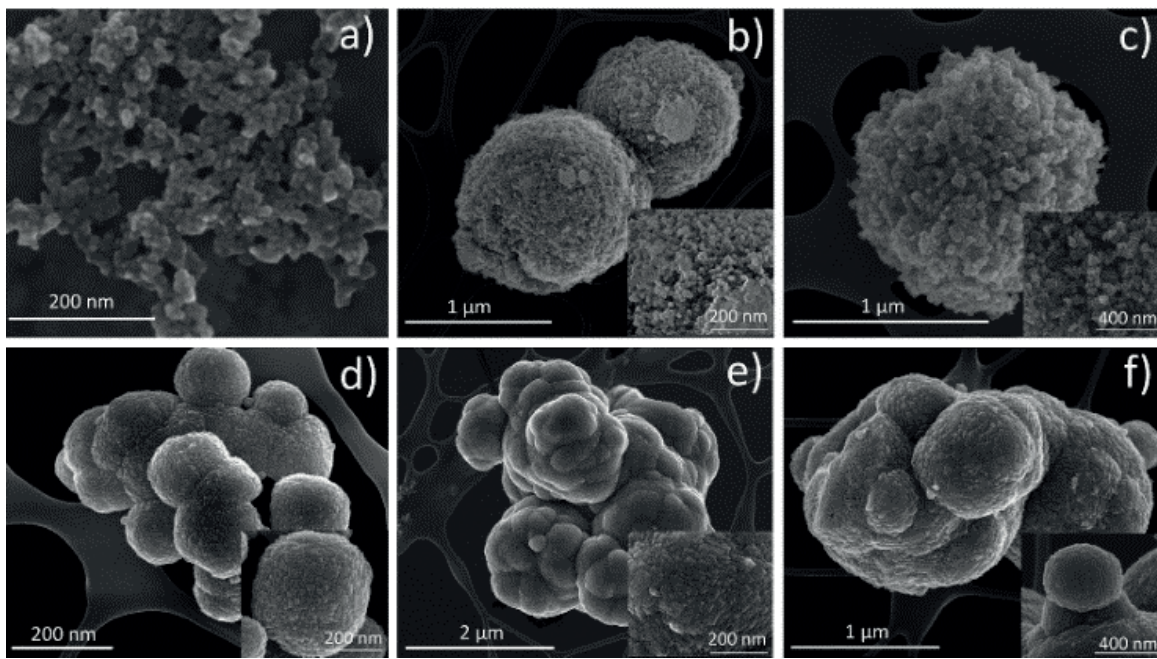


Figure 18. Hierarchical structures of TiO_2 (a) H_2SO_4 free- TiO_2 , (b) 0.5M- TiO_2 , (c) 1M- TiO_2 , (d) 1.5M- TiO_2 , (e) 2M- TiO_2 , (f) 3M- TiO_2 [67].

2.3.2. Merits

- Shorter crystallization time is required.
- Electromagnetic radiations provide much temperature for nucleation and growth during crystallization within less time.
- It is a time-saving process.
- Large material can be synthesized in less time, so a better yield is expected.

2.3.3. Demerits

- The duration of microwaves should be carefully controlled so that optimum crystallization of Titania is done.
- Microwave treatment for longer times and high temperature transform anatase TiO_2 to rutile.

2.3.4. Summary of microwave synthesis

In short, microwave treatment is a quick technique to attain hierarchical morphology in TiO_2 nanostructures. By controlling temperature and exposure duration, HNSs ranging in sizes from micron to nanometers are produced. Localized heating caused by microwaves make this method an energy-efficient one with the possibility of acquiring environment-friendly conditions. The use of NaOH has resulted in submicron-sized HNSs made of radially arranged

nanosheets, whereas by using other precursor materials, simple microwave treatment produces HNSs made of nanoparticle agglomerates. Hence, flower-like hierarchical morphologies are obtained as a result.

2.4. Pulsed laser deposition (PLD)

This technique is well known for its flexibility to grow variety of materials. Nanotree-like structures can be grown via this synthesis route without using any surfactant and prior treatment. Pressure treatment and laser ablation are used for preparation of hierarchical structures by this technique.

It is a top-down approach in which pulsed laser is used to decompose the precursor material and then these materials are deposited on substrates. By controlling the parameters like laser power, temperature, chamber geometry and pressure, one can grow structures of different morphologies from columnar structures to dense forest-like [39] structures. The porosity of structures is increased when grown at high pressure because of fast process. Also the surface area can be controlled by controlling inter columnar spacing and thickness. **Table 5** shows features of structures prepared via dot patterning technique.

2.4.1. Examples

Fonzo et al. have prepared hierarchically organized nanostructured TiO₂ by ablating Titanium foil with KrF excimer laser pulses (h 248 nm, duration 10–15 ns, energy density 4 J/cm²) in dry air (O₂) background with pressure. Thin films of Titania are grown both on silicon and pure titanium substrates. Annealing is done at 400°C for 1 h for crystallization of samples prepared. By changing the pressure of chamber, thickness of the sample is varied from dense columnar structures to tree-like structure [39] (**Figure 19**). This technique can be employed for preparation of HNSs as it provides a stimulating outlook both for photocatalytic and for advanced photovoltaic application, and it also substitutes the time-consuming deposition of different layers and longlasting annealing steps.

Sauvage et al. have prepared hierarchical TiO₂ structures by PLD. Nanoparticles of TiO₂ are grown directly on FTO substrate by ablating Titanium target in the presence of O₂ background. TiO₂ nanostructure attained the symmetry of tree-like structures. Height and thickness of trees increase with respect to deposition time [44]. By increasing pressure from 10 to 40 Pa, the particles formed nanoforest-like structures. The structures formed are shown in **Figure 20**.

Reference	Phase	Surface area (m ² g ⁻¹)	Particle size (diameter) (nm)	Crystallite size (nm)	Morphology	Application
Fonzo et al. [39]	Rutile	300	260	—	Nanoforest composed of nanotrees	Photocatalysis
Sauvage et al. [44]	Anatase	86	20	25	Nanoforest composed of nanotree-like structures	DSSCs

Table 5. Hierarchical TiO₂ nanostructures produced via PLD.

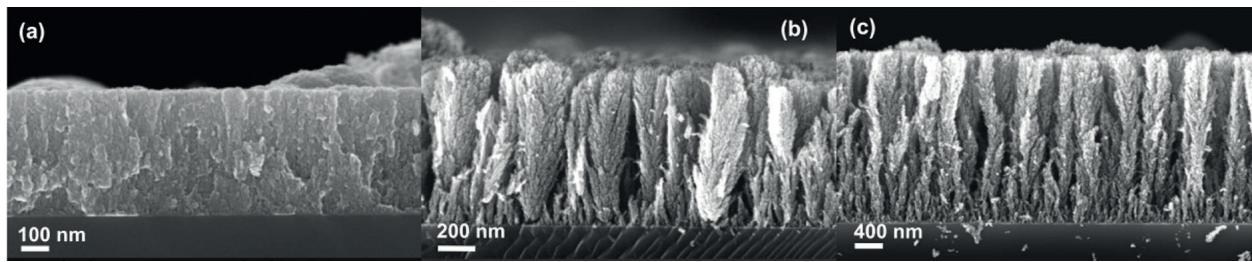


Figure 19. SEM images of different morphologies of TiO_2 at (a) 10 Pa, (b) 20 Pa, (c) 40 Pa [39].

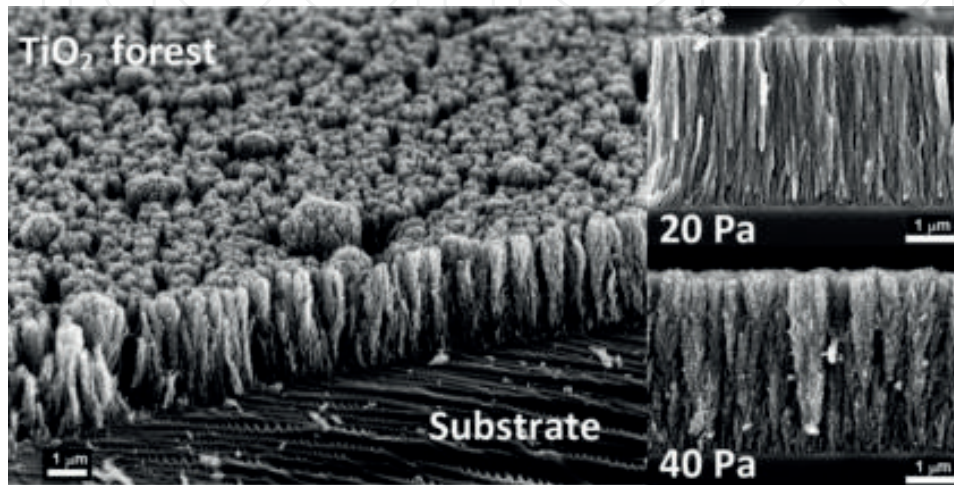


Figure 20. SEM images of nanoforest-like structures prepared at (a) 20 Pa and (b) 40 Pa [44].

This type of assembly hampers electron-hole pair recombination and it facilitates the efficiency if employed in solar cells. This assembly also promotes mass transport of electrons in mesoporous structures. This morphology provided efficient light trapping and high surface area for dye adsorption and efficiency of 5% is obtained. The porosity and surface area can also be optimized for making these structures highly competent for photovoltaic devices.

2.4.2. Merits

- This technique produces better results than anodization.
- The surface area of materials synthesized can be controlled.
- Nanotree-like structures can be formed.
- Large surface area structures can be achieved.
- It is a flexible technique and parameters can be controlled.
- Porosity can be controlled by using high pressure.
- Synthesis can be done without surfactants and chelating agents.
- The photocatalysis is better than anatase powder and TiO_2 produced via anodization [68].

2.4.3. Demerits

- This technique is difficult.
- High pressure is required.
- It is an expensive process to synthesize materials.
- Temperature and pressure relation on particle growth should be clearly known to attain desired morphology.

2.4.4. Summary of PLD

So, by controlling parameters like pressure, temperature and time, nanoforest-type structures were grown via pulsed laser technique. By using intermediate pressure, columnar structures were grown and density of structures decreases by increasing pressure [69]. The particle size was in nanometer ranges. Pulsed laser was used to ablate Titania target on which structures were grown. This technique can be used to synthesize different materials by using different target materials. Hence, the prepared structures can be employed in different applications like dye sensitized solar cells, perovskite solar cells and photodegradation of pollutants.

2.5. Anodization

It is an electrochemical process in which metal sheets are decorated and electrolytic passivation¹ takes place. The thickness of oxide layer is increased in this process. The surface is decorated and finished with more durable and corrosion-resistant surface. The reactions that occur during anodization for oxidation of metals are [70]:



And for titanium,



TiO₂ is formed on titanium surface. The fluoride ion (F⁻) present in solution causes dissolution of oxide layers and etching in nanopits starts to prepare nanotubes. Water is the main source of oxidation in anodization. Hydroxyl ions from electrolyte are injected into the body of anodic oxide layer [71]. These anions impede ion transport, which is necessary for movement of metal-ion interface into metal. The anodization also depends on solution diffusion rate and local electric field supplied to a specific area [72]. **Table 6** shows features of structures prepared via dot patterning technique.

¹It is a process of coating of protective coating on substance.

Reference	Phase	Surface area (m ² g ⁻¹)	Particle size (diameter) (nm)	Crystallite size (nm)	Morphology	Application
Ali et al. [43]	Anatase	—	100	40	Nanotubes	—
Ali et al. [73]	Anatase	—	75–90	—	Nanotube arrays	Water splitting
Zhang et al. [42]	Anatase	—	200	—	Nanotubes	Photoelectrocatalytic decomposition
Tang et al. [40]	Anatase	33.4	65	33.3	Microspheres	Photocatalysis
Smith et al. [72]	Anatase	—	120–170	—	Nanotubes	Photoelectrocatalytic decomposition

Table 6. Hierarchical TiO₂ nanostructures produced via anodization.

2.5.1. Examples

Ali et al. have prepared hierarchical Titania structures (**Figure 21**) by using Ti foil, ammonium fluoride and ethylene glycol as precursor. DI water has been used in electrolyte preparation. Ti foils are being anodized in ethylene glycol electrolyte containing 0.5 wt% NH₄F and 0.2 wt% DI H₂O for oxidation of titanium. In this process, Ti foil is taken as a working electrode and platinum foil is used as counter electrode. Both electrodes are placed 10 mm apart. Voltage is maintained at 60 V for 24 h using DC power source and Titania nanotubes are prepared. The sample is being annealed at 450°C for 2 h [43]. These structures can provide highly mesoporous structures for various photocatalytic applications.

Ali et al. have prepared hierarchical structures of Titania by anodization technique. Ti foil is used as precursor and glycerol with ammonium fluoride is used as electrolyte. Anodization of Ti foils has been done in glycerol containing 10 wt% H₂O and 0.25 M NH₄F electrolyte solution. The voltage has been set at 30 V against the Pt counter electrode for 4 h. The nanotubes are

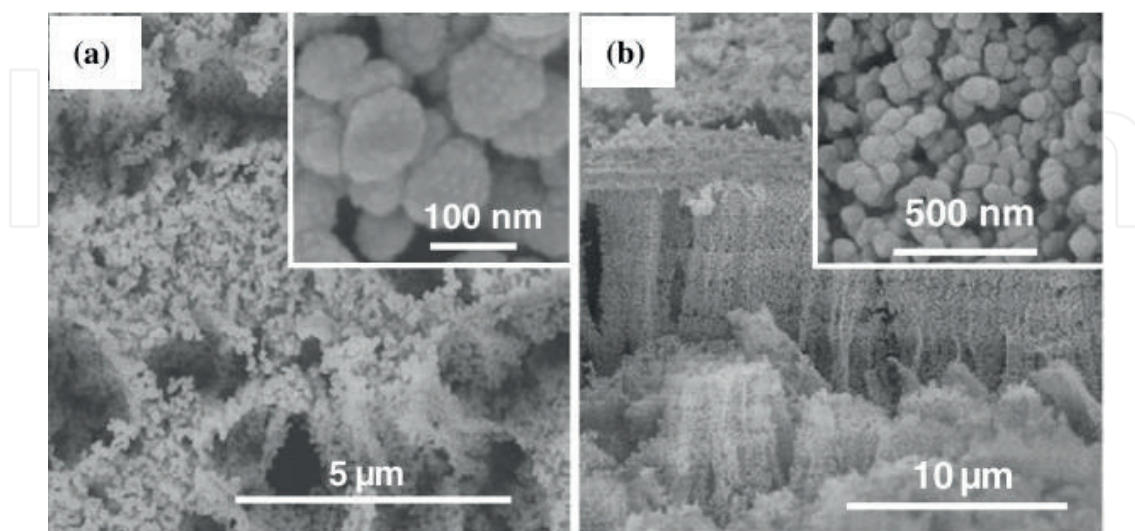


Figure 21. (a) SEM images of hierarchical TiO₂ prepared via anodization of TNT in F- residue and (b) cross-sectional view [43].

then dried under a stream of N_2 gas. The sample is annealed at 400°C for 2 h for crystallization of Titania nanotube arrays (TNTAs). The sample obtained is then immersed in 80 mM TiCl_4 for different time intervals and then sintered at 400°C to produce photoelectrodes. Nanorods (**Figure 22**) having flower-like structures are produced after treatment at 120°C with TiCl_4 [73]. These structures are then utilized for water-splitting application. H_2 can also be produced from these structures and can be stored for energy applications.

Zhang et al. prepared hierarchical nanotube-like structures via anodization [42]. The titanium foil is sonicated in ethanol and cold distilled water to remove impurities. After that, N_2 stream is used to dry the foil. Anodization is done using Ti as anode and Pt as cathode material. NH_4F is added in ethylene glycol (EG), which is present in 2 vol% distilled water as electrolyte solution. This electrolyte is used for oxidation of Titanium sheet. Anodization is performed at room temperature in two steps. In step 1, Ti sheet is anodized for 10 min at 50 V and grown nanotubes are removed ultrasonically in DI water. In step 2, the same sheet is anodized under the same condition for 30 min. The powder obtained is cleaned with distilled water under N_2 atmosphere.

Anodized TiO_2 nanotubes are annealed in air at 450°C for 1 h with a heating rate of $5^\circ\text{C}/\text{min}$ for crystallization of pure anatase phase as shown in **Figure 23**. These structures are used for photodegradation of organic pollutants. These types of structures show improved photocatalytic activity in degradation of organic dye. The enhanced surface area facilitated the reaction rate.

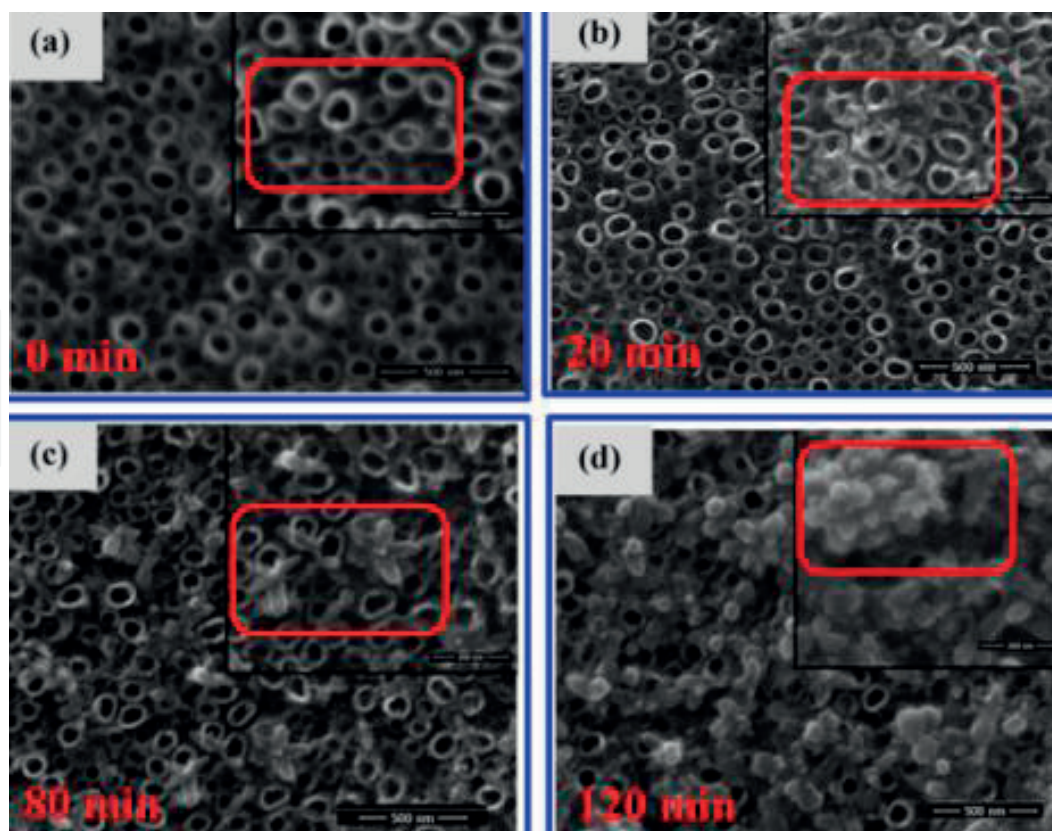


Figure 22. FESEM images of (a) TNTA, (b) TNTA/ TiCl_4 20 min, (c) TNTA/ TiCl_4 80 min, (d) TNTA/ TiCl_4 120 min [73].

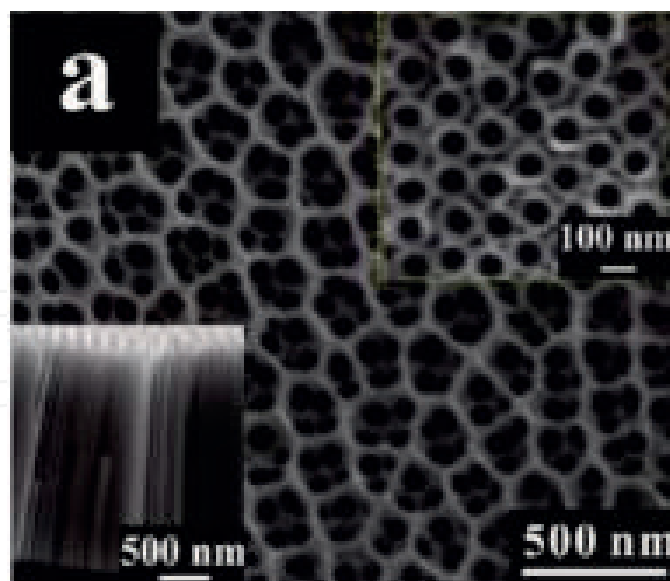


Figure 23. (a) SEM image of top view of porous TiO_2 nanotubes; Top enlarged image shows the diameter and bottom enlarged image shows the side walls [42].

Tang et al. [40] have prepared nanoflakes/nanoparticles hierarchical structures via anodization technique. In this synthesis, electrochemical spark discharge spallation (ESDS) method is applied in an electrolyte of 10 M NaOH in aqueous solution while using as platinum counter electrode. Titanate hierarchical microspherulite structures are produced as a result of this synthesis. The Na^+ ions are replaced by H^+ ions by soaking the prepared sample in HCl. The sample is then washed to remove the acidic content and to make pH neutral. The samples obtained are annealed at different temperatures to crystallize them [40].

Dislocations in the sample decrease as the sample is heated above its crystallization temperature. **Table 6** shows some properties of anatase TiO_2 obtained via this synthesis route. The difference in morphology can be seen in SEM image in **Figure 24**. By increasing the time for heat treatment, nanosheets were converted into nanoflakes and nanoparticles due to crystal re-growth with larger energy and with minimal stresses. These structures are employed for photodegradation of organic pollutants.

Smith et al. have prepared hierarchical nanotubular structures via anodization technique [72]. The synthesis follows basic principle of anodization. Titanium foil is etched in the presence of HF, HNO_3 and DI water in volumes of 1:3:50 ml for different time intervals. The etched powder is washed with DI water immediately and is anodized at 60 V for 1 h in presence of NH_4F and ethylene glycol electrolyte. The powder obtained is annealed at 500°C for 2 h. The etching treatment before anodization removed small layers of titanium and provided ripple-like surface. Due to surface roughness, the electric field becomes localized at grains. An initial oxide layer formed during etching is then oxidized during anodization.

The smooth etched layers on foil cause a uniform electric current and porous nanotubes grow in those areas. The prepared hierarchical structures as shown in **Figure 25** showed better results for photoelectrochemical applications. Hierarchical structures provided large surface area for photocatalytic reactions.

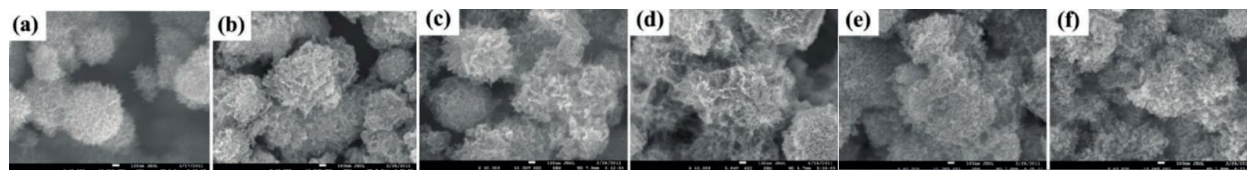


Figure 24. (a) H-TMS calcinated at different temperatures: (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, and (f) 700°C [40].

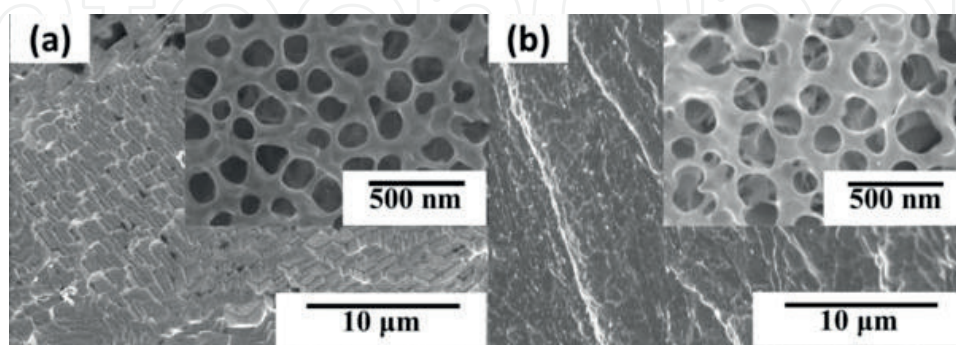


Figure 25. SEM image of foil's surface: (a) After 30 s etching (inset shows anodization after 1 h at 60 V) and (b) after 90 s etching [72].

2.5.2. Merits

- The thickness and lengths of the nanotubes produced can be varied by changing voltage time and voltage itself [74].
- High aspect ratio tubes are formed.
- Ease of fabrication.
- The change in anodization conditions does not affect the chemical composition of TiO_2 nanotubes.
- Increasing the electrolyte concentration can cause etching to increase and nanotubes can be formed of long lengths and diameters.
- Structures are highly recommended for DSSCs as high aspect ratio tubes are formed.

2.5.3. Demerits

- Extended warranties of products are not offered in this process.
- Average growth rate can be decreased with increase in anodization time [74].

2.5.4. Summary of anodization

So, hierarchical Titania nanostructures were prepared from anodization technique and nano-tube-like structures were prepared. The particle diameter was in nanometer ranges. The diameter and length of nanotubes increase by increasing voltage and voltage time up to optimum

level [75]. The prepared powder was used in water-splitting application, which can be used for nuclear thermal and solar thermal plants.

2.6. Photolithography

This is a technique that is used in microfabrication to pattern thin films and bulk materials. Light is being used to transfer pattern onto the light-sensitive photoresist. Photoresist basically is a light-sensitive material, which is used to form pattern coating on the surface. Photoresist is of two types, which are as follows:

- Positive photoresist: The resist is applied over the area on which the underlying material is to be removed.
- Negative photoresist: The resist is applied over the area on which the area other than resist is to be removed.

Then, etching is done to form patterned hierarchical 3D structures. When photopositive resist coating is done over the substrate, then the growth of structure takes place on the same area where we seed/coat the material. The mask contains the exact copy of resist, which we deposit on the substrate and vice versa. **Table 7** shows features of structures prepared via photolithography technique.

2.6.1. Examples

Kim et al. have reported HNSs of Titania by photolithography. A negative PR is prepared on 5 mm Ti foil by baking at 120°C. Upon exposure to UV light, PR gets developed. The foil is etched via reactive ion etching. Titanium foil's area that is not covered with the PR is etched out in this process. TiO₂ nanoflowers composed of nanotubes (**Figure 26**) are prepared in this procedure [48].

So, flower-like HNSs are produced via dot patterning technique. The particles are in the micron ranges (diameter). The prepared product is employed in dye-sensitized solar cells and exhibits maximum surface area for dye adsorption. Hence, these show better result for photocatalytic processes.

2.6.2. Merits

- If viscosity of photoresist is controlled, we can achieve well-formed structures.
- Cost-effective process.
- No need of specialized equipment.

Reference	Phase	Surface area (m ² g ⁻¹)	Particle size (diameter)	Precursor materials	Morphology	Application
Kim et al. [48]	Anatase	—	1.5–2 μm	Ti foil	Flower-like structures on nanotubes	DSSCs

Table 7. Hierarchical TiO₂ nanostructures produced via dot patterning/photolithography.

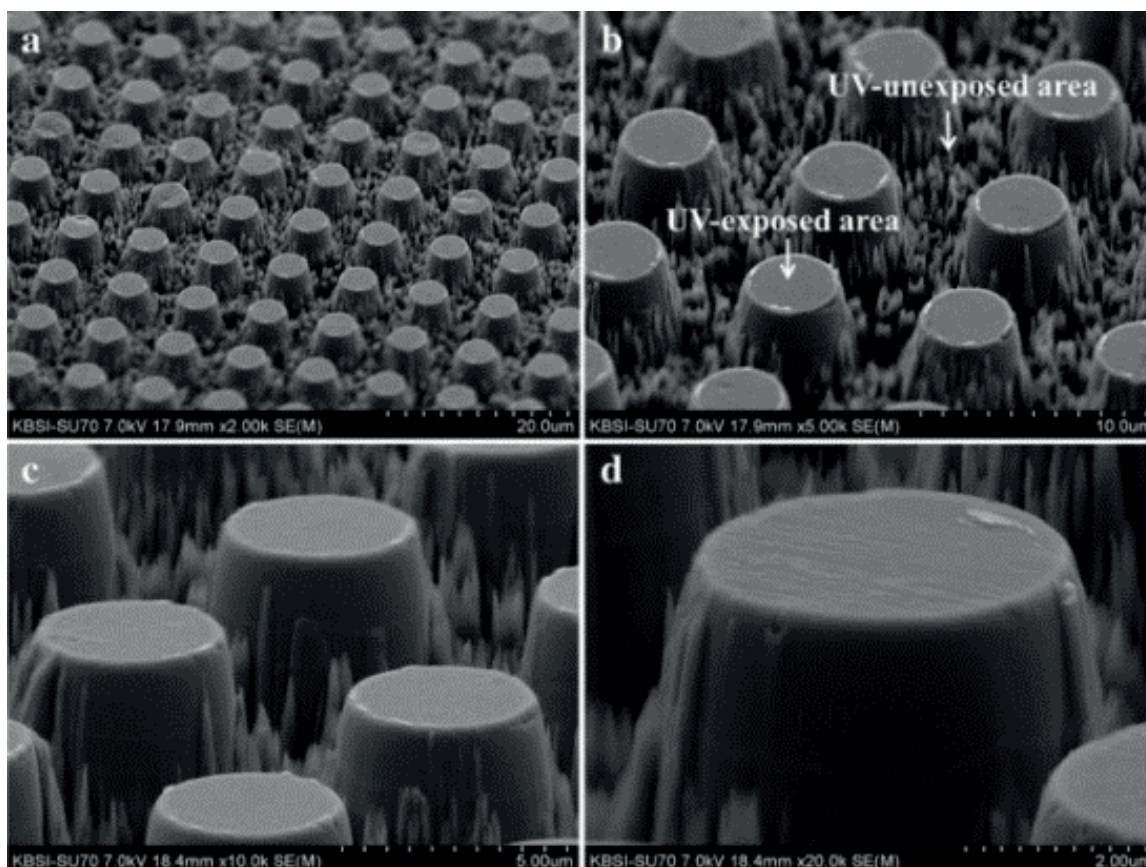


Figure 26. Hierarchical flower-like structures produced by dot patterning [48].

2.6.3. Demerits

- The nature of solvents, sensitizers and additives should be well studied.
- Sometimes, the step coverage can be poor, i.e., the ability of photoresist to cover the side-edge of the surface steps.

2.6.4. Summary of photolithography

HNSs of Titania are formed via various techniques and different types of structures are formed by these processes. **Table 7** shows the different characteristics of materials obtained by dot patterning. By changing the reaction conditions like time, temperature and pressure and precursor material, different morphological structures are formed, which have different surface area and porosity for applications like dye-sensitized solar cells, photocatalysis, gas sensing and lithium ion batteries.

2.7. Vapor deposition method

As the name suggests, this method involves deposition of vapors of the required material. The material is vaporized from the source and condenses on the substrate. It may or may not involve chemical reactions. Vapors can be deposited on the substrates by two main processes:

- Chemical vapor deposition (CVD)
- Physical vapor deposition (PVD)

Very little work has been done by these techniques to grow TiO_2 HNSs. By these techniques, we can grow hierarchical structures. The film cost, thickness, source material and compositions can be controlled by these processes.

In CVD process, precursors are introduced in the reaction chamber and flow of molecules is regulated by control values. The precursor molecules get deposited over the surface of substrates after chemical reactions take place. Heat energy is provided for chemical reactions to take place. While in PVD, deposition occurs by various routes like evaporation, sputtering and molecular beam epitaxy (MBE). **Table 8** shows different characteristics of HNSs prepared via these processes.

2.7.1. Examples

Flipin et al. [76] grew hierarchical TiO_2 nanotubes by plasma-enhanced chemical vapor deposition technique. Porphyrins and phthalocyanines were used as cost-effective precursor molecules. First of all, seed layer was grown by polycrystalline anatase films for highly dense and homogenous organic nanowires. Physical vacuum deposition was done to grow organic nanowires (ONWs) of phthalocyanine molecules with sublimation temperature of 250°C . As a result, tunable ONWs in the range between 1 and $30\ \mu\text{m}$ and diameters between 50 and 120 nm were produced. Then, PECVD was done to cap ONWs with TiO_2 shells.

Multistacked nanotrees composed of TiO_2 nanowires were grown as a result of this synthesis as shown in **Figure 27**. These nanotubes were grown as 1D structures provide maximum electron percolation as compared to 0D nanoparticles due to less grain boundaries. These structures were then employed for DSSCs to evaluate their efficiency for current production.

Yoshitake et al. [77] prepared hierarchical TiO_2 structures by CVD method. Titanium tetraisopropoxide (TTIP) was used as a precursor material. About 40 g of water was added to 8 g of TTIP with 2.6 g of dodecyl amine at 273 K. The mixture was stirred with 0.1 M HCl and was kept overnight for aging. The reaction mixture was transferred to autoclave at 373 K for 4 days. The powder obtained was washed with methanol and dry ethyl ether.

Reference	Phase	Surface area ($\text{m}^2\ \text{g}^{-1}$)	Particle size (diameter) (nm)	Crystallite size (nm)	Morphology	Application
Flipin et al. [76]	Anatase	—	50–120	Below 100 (for all structures)	Nanoforest composed of nanowires	DSSCs
Yoshitake et al. [77]	Anatase	518	3.03	3.30	Worm-like spherical agglomerated structures	—

Table 8. Hierarchical TiO_2 nanostructures produced via vapor deposition processes.

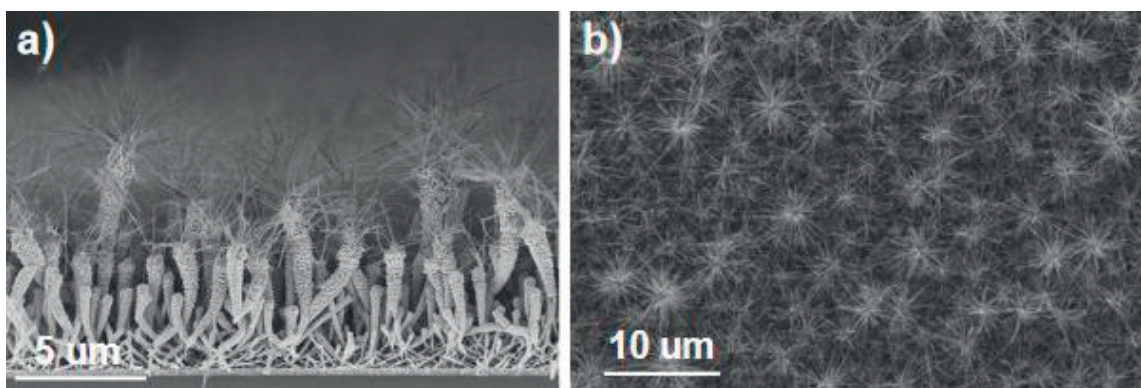


Figure 27. (a and b) SEM images of multistacked nanoforest [76].

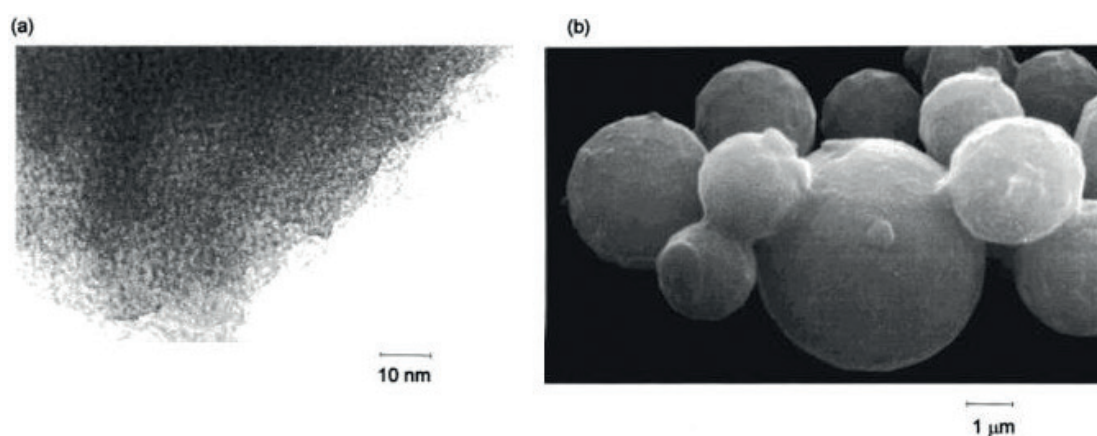


Figure 28. (a) TEM images of structures formed by CVD and (b) worm-like agglomerated 3D TiO_2 structures grown by CVD [77].

CVD of TTIP was done in Pyrex reactor. Pure argon was passed through liquid TTIP at 293 K into the tube where the powder formed by former process was already deposited. After deposition for 24 h, the gas was switched to N_2 , which passed through water at 293 K. TTIP was decomposed completely for 12 h and finally the powder was treated in dry air at 393 K for 2 h. Spherical agglomerated structures were produced as a result of this synthesis (**Figure 28**).

2.7.2. Merits and demerits of CVD

- There is less wastage of chemicals and substrate.
- If laser is used to heat the precursor material, the deposition becomes selective to the path of laser.
- High temperature is required in case of CVD to initiate chemical reactions. CVD runs at much higher temperature.
- Substances that cannot tolerate high temperatures, which decompose or sublime, cannot be deposited by CVD.

2.7.3. Merits and demerits of PVD

- Processes like sputtering can initiate and undergo PVD, so less use of energy in terms of less usage of heat is required for deposition.
- By process like MBE, we can achieve atomic level growth control.
- Sputtering does not require the use of specific precursor materials as in CVD.
- Cost of the process is very high.
- Vacuum conditions may be required in some depositions.

2.7.4. Summary of vapor deposition processes

These processes can form well-defined structures. Nanocoatings can also be formed as a result of these processes. Temperature, time and target materials need to be well optimized for distinct structure growth. Pressure in the chamber should be controlled in case of physical vapor deposition processes for growth of hierarchical structures.

3. Conclusions and future prospects

In conclusion, this chapter gives an overview of synthesis of HNSs of Titania via different routes. The chemistry and different parameters affecting the properties of HNSs are also briefly discussed. It can be seen that the employed techniques are very powerful in synthesizing TiO_2 HNSs in the form of agglomerated nanoparticles, nanospheres, nanoflakes or 1D/3D heterostructures. In hydrothermal synthesis, by changing parameters of temperature, concentration of precursors, etching reagents and time, the morphology of TiO_2 particles can be changed to 3D HNSs. By providing prolonged time for crystallization, the morphology of particles changes. However, in case of solvothermal synthesis, different solvents provide different structures. By using solvents that provide maximum steric hindrance, the morphology of structures can be controlled. Also, solvents with high boiling points can be used. In microwave synthesis, irradiation time, temperature and solvents are key factors in controlling morphology. This method provides short time for crystallization in the presence of radiations and more nucleation sites are formed. In pulsed laser deposition process, nanotree- and nanoforest-like structures are grown from agglomeration of nanoparticles. Pressure plays an important role in controlling the morphology. By increasing voltage in anodization technique, when the energy provided to target material is increased, the diameter and length of structures formed are increased leading to formation of 3D hierarchical-like structures as end products. In photolithography, the structures engraving are much easier and microfabrication can be done by these structures. Vapor deposition processes are new and very little work has been done for TiO_2 HNSs preparation. These processes can be used to grow very thin films of materials and morphologies can be opted by varying parameters like pressure, temperature, precursors (in case of CVD) and mean free path.

Hence, TiO_2 HNSs with different morphologies can be obtained via different synthetic pathways. These structures can help to achieve maximum scattering with high specific surface area for sunlight entrapment. Hierarchical morphology further helps in better absorption of light and efficient electron-hole pair generation can be achieved. Also, reduced recombination rates are being observed by these structures. These mesoporous structures can help in maximum adsorption of dye molecules. So, these properties shown by TiO_2 hierarchical structures increase the efficiency of phenomena taking place at the interfaces and hence efficient results are seen. These facts make HNSs promising candidates for photovoltaic and photocatalytic applications as can be seen in much of the reported work. These structures can be also employed and exploited in future, for increasing efficiency of various devices like:

- Photoelectrochemical cells (PECs)
- Photovoltaic devices (PVs)
- Organic pollutants degradation
- Water splitting
- Supercapacitors
- Li/Na ion batteries

Hierarchical nanostructures can be mixed with nanoparticles to enhance surface area for photocatalytic reactions. These structures can also be doped, codoped or their hybrid structures can be made to increase efficiency of prepared products.

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