Chapter 2

Literature Review

2.1 Introduction

Method of synthesis of nano-particles plays a significant role in deciding their properties. Different approaches used for synthesizing nano-particles can be grouped under two broad groups as top-down approach and bottom-up approach. In the top-down approach several physic-chemical methods are used to convert bulk materials into nano-size particles having large specific surface area and high activity. But the top-down approaches are costly, require large labour, take a lot of time to manufacture and are not eco-friendly. High temperature conditions are required hence not suitable for large-scale production. In case of bottom-up approach molecules are aggregated to large size and the aggregates are stabilized. Compared to the top-down approach, the bottom-up approach is simple, need normal conditions of pressure and temperature and is less energy intensive and eco-friendly. Acid precipitation and green synthesis methods are typical examples of bottom-up approach. In green route plant extracts or micro-organisms are used to prepare nano-particles by the biological components present in the extract or microbial cells that act as reducing, capping and stabilizing agents in the synthesis process. Under suitable conditions (pH, light wavelength and plant extract/micro-organism) practically most compounds can be reduced and converted to nano-particles. A large variety of nanoparticles having applications in analytical to medical fields have been synthesized using this route and several excellent reviews are available in the literature (Goutam et al., 2018, Rajakumar et al., 2012). As the present work is focused on nano-particles of silica (SiO_2) and titania (TiO_2), in the following sections available information on the synthesis these nano-materials is summarized in the following pages. Available information on the green synthesis using plant extracts, characterization and application of synthesized nano-particles are included in this summary.

2.2 Synthesis of TiO_2 Nano-particles

There are several techniques used for the synthesis of TiO_2 particles and these are basically known as sol-gel (Sugimoto et al., 2002), deposition methods (Chen et al., 2007), sonochemical and microwave-assisted methods (Yu et al., 2001), hydro/solvothermal methods (Kim et al., 2003, Nian et al., 2006) and oxidation methods (Varghese et al., 2003). These methods include costly - toxic chemicals, high temperature and high pressure which make the process complex and less eco-friendly. So green synthesis of nanoparticles using leaves extract is an alternative way to synthesis TiO_2 NPs for various applications.

2.3 Green Synthesis of TiO_2 NPs

Herein, a brief and comprehensive study is carried out to understand the mechanism involved for the formation of TiO_2 nanoparticles using different parts of plant and to identify the functional groups present in them that are responsible for green synthesis of TiO_2 nanoparticles.

Green synthesis from plants involves usage of extracts from various plant parts like, root, stem, leaves, fruits, flowers, etc. The bio-molecules present in them helps to synthesize the nano-particles through reduction and stabilization mechanisms. Extracts from various parts of plants have been used. Their advantages and disadvantages are discussed in the following pages.

2.3.1 Leaf Extract

The leaf extract of *Jatropha curcas* (common name: physic nut) was used for the first time to carry out the synthesis of TiO_2 nanoparticles (Goutam et al., 2018), where titanium chloride was used as the precursor. The mixing of *Jatropha curcas* extract and $TiCl_4$ in 1:1 volume ratio exhibited a colour change from transparent to whitish-brown, due to the reduction of Ti^{4+} ions to Ti, which demonstrated the synthesis of TiO_2 nanoparticles. The reduction took place due to the presence of hydroxyl (OH^-) group (responsible for reduction /capping of Ti^{4+} ions) in *Jatropha curcas* leaf, which could be due to the presence of phenols. In the poly-phenolic tannins in *Jatropha curcas* leaf extract, which act as capping agent to cover the surface of TiO_2 nanoparticles to prevent agglomeration. The schematic representation of synthesis mechanism is shown in Figure (2.1**)**.

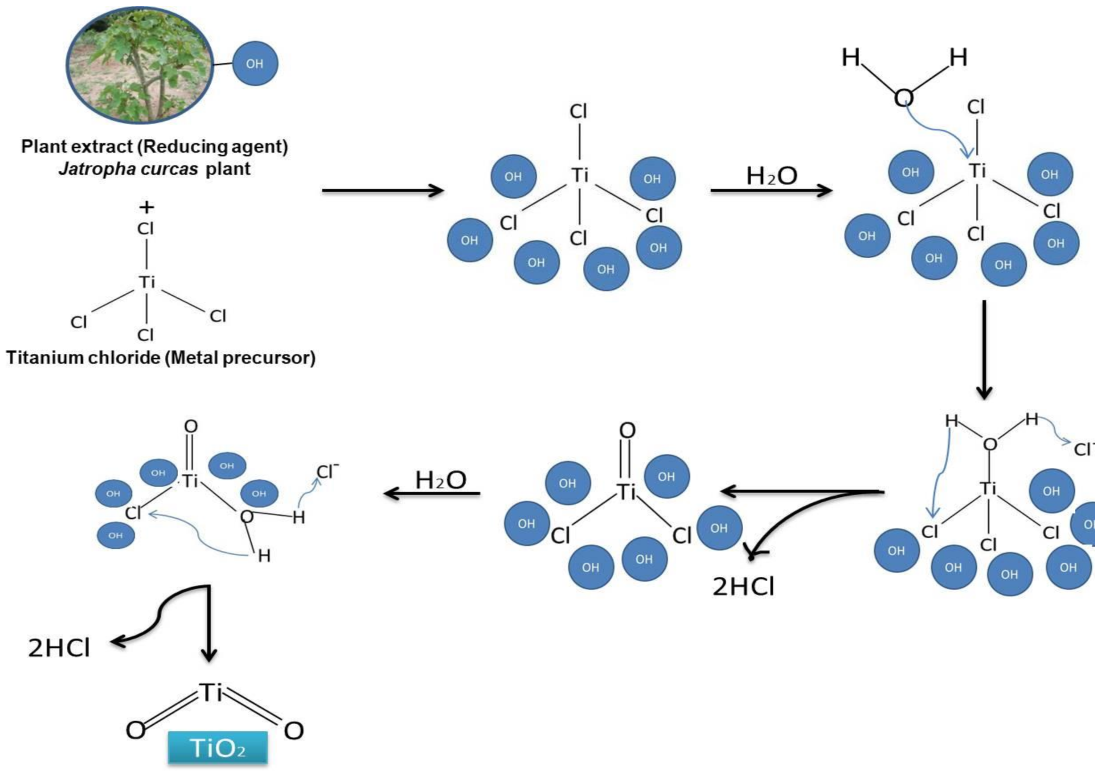

Figure 2.1 Mechanism of TiO_2 nano-particles synthesis from $TiCl_4$ and *Jatropha curcas* leaf extract

Rajakumar et al. (2012) used healthy leave of *Eclipta prostrata* (*E. prostrata*), commonly called as false daisy, species of sunflower family to obtainTiO_2 nanoparticles of an average size of 49.5 nm, by an aqueous reduction method. At room temperature, the aqueous leaf extract of *E. prostrata* was added to $TiO(OH)_2$ under stirring. As the reaction proceeded, the change in colour to light green indicated the synthesis of TiO_2 nanoparticles. It was concluded that the presence of alkanes, phenols, alcohols, primary amines and aliphatic amines in *E. Prostrate* may be assisting in the formation of nanoparticle. Also the existence of water soluble heterocyclic compounds like flavones might have helped in achieving the controlled size of particles by functioning as capping and reducing ligands of the nanoparticles.

Momordica charantia (*M. charantia*), most widely used herbal medicine belongs to Cucurbitaceae family was used by Gandhi et al., 2018 for the synthesis of TiO_2 nanoparticles. They carried out experiment using fresh aqueous extract of *M. charantia* and $TiCl_4$ solution at ambient temperature and the resulting solution became pink in colour. It was concluded that the involvement of the functional groups namely, hydroxyl groups, amide and amine groups, carboxylic acid group and aliphatic amines in the extract were responsible for the reduction and stabilization of TiO_2 nano-particles. A similar work using leaf-extract of another other medicinal plant was reported in literature (Subhapriya et al., 2018) where extract of healthy leave of *Trigonella foenum graecum* (local name: fenugreek) for the biosynthesis of TiO_2 nanoparticles. The leaf-extract was prepared and added to the solution of titanium oxy-sulphate and stirred. By adding NaOH drop-wise pH was adjusted at 8. The precipitate was washed and sintered at high temperature for the formation of well crystalline TiO_2. Here also, presence of functional groups like amine and hydroxyl group in the extract is responsible for the stabilization of TiO_2 nanoparticles.

2.3.2 Root Extract

The root extract of *Euphorbia heteradena Jaub*, from the family of *Euphorbiaceae*, which has phytochemicals such as terpenoids, phenolics, aromatic esters, saponins and steroids, was used for the synthesis of TiO_2 nanoparticles (Nasrollahzadehte al., 2015). $TiO(OH)_2$ was added to the aqueous solution of the root extract of *E. heteradena Jaub* with constant stirring and it was observed that the colour of solution changed to light gray which due to the excitation of surface plasmon resonance indicating the successful formation of nano-particles. The functional groups responsible for the reduction and capping of $TiO(OH)_2$ were identified as free OH in molecule and OH group forming hydrogen bonds, carbonyl group (C=O) and stretching C=C aromatic ring. The hydroxyl groups of phenolics in *E. heteradena Jaub* root extract play bifunctional role, they act as reducing agent thus are responsible for the reduction of titanyl hydroxide as well as capping ligands to avoid agglomeration of TiO_2 nanoparticles.

Glycyrrhiza glabra (G. glabra), commonly referred to as Licorice, extract was used by Bavanilatha et al., 2019 for the synthesis of TiO_2 nano-particles. An aqueous extract of *G. glabra* roots was prepared and added to titanium oxysulphate. The mixture was kept under stirring till the formation of milky white precipitate, and dried in a hot air oven for overnight to obtain the TiO_2 nano-particles. The analysis of these nano-particles indicated the presence of aromatic primary amine, NH stretch, hydroxyl stretch instigating the involvement of hydroxyl groups of carboxylic acids in synthesis. This could be due to the presence of various phenols and flavonoids in plant roots. Here also, the *G. glabra* root extract plays the role of reducing agent as well as stabilizing agent.

Extract of roots of *Desmodium gangeticum*, of Fabaceae family, the most important herb in Ayurveda was used to carry out the synthesis of TiO_2 nano-particles (Jamuna et al., 2014). The schematic representation of mechanism is shown in Figure (2.2**)**. Titanium tetraisopropoxide (TTIP) as metal precursor was added to the root extract and mixed thoroughly to obtain a sol-gel that was air dried and calcined to obtain nano-crystalline TiO_2. The interaction of *D. gangeticum* and TTIP led to O-H stretch of water and phenolic compounds, O-H stretch, normal polymeric aryl substituted C=C stretching and Ti-O stretching. The frequency bands which were observed confirmed the interaction between phyto-constituents and TiO_2.

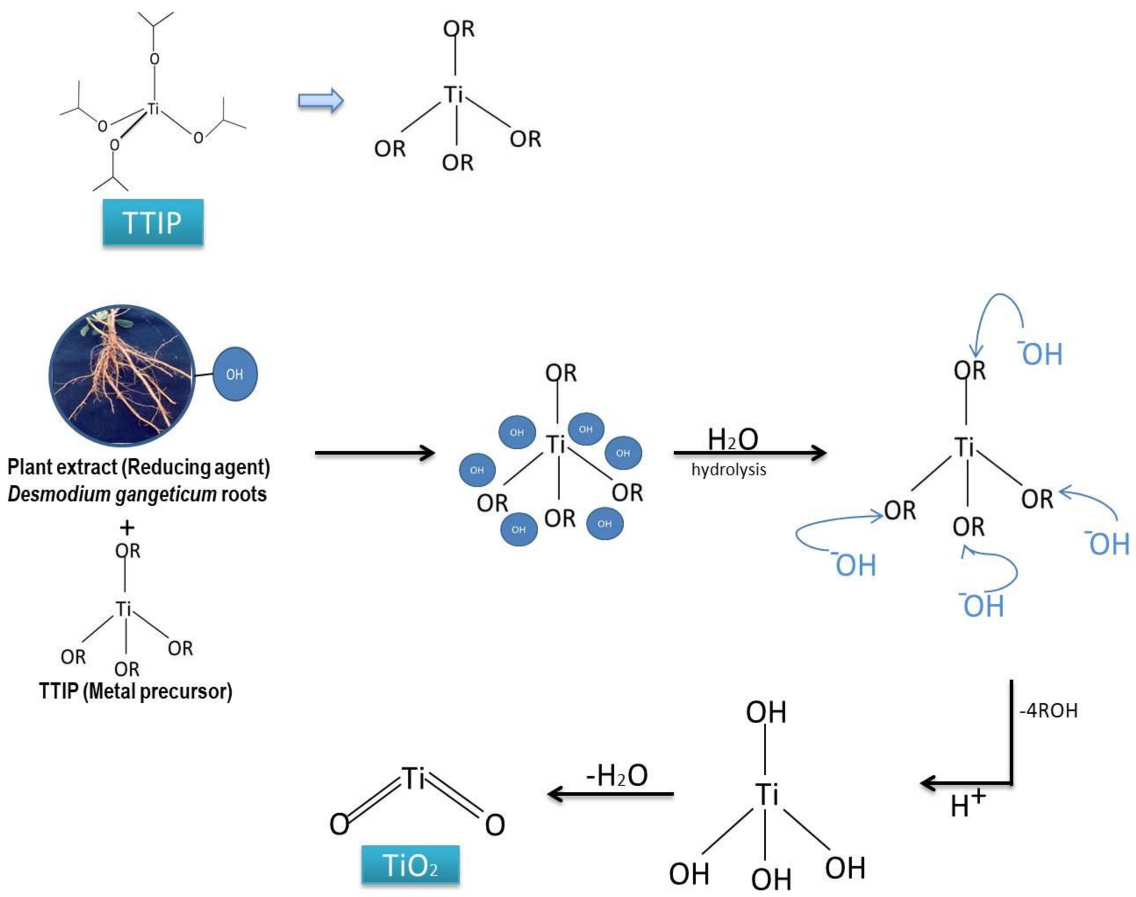

Figure 2.2 Mechanism of TiO_2 nanoparticles synthesis taking TTIP as metal precursor and *Desmodium gangeticum* root extract as reducing agent

2.3.3 Peel Extract

Annona squamosa (*A. squamosa*), commonly known as custard apple, is a source of variety of medicinal and industrial products. The fruit peel extract of *A. squamosa* was used for the synthesis of rutile TiO_2 nanoparticles (Roopan et al., 2012). Fresh peels of *A. squamosa* were powdered and extract was prepared and added to $TiO(OH)_2$ solution under constant stirring. Titanyl hydroxide was dehydrated to give TiO_2 nanoparticles on heating with an *A. squamosa* aqueous peel extract at about 60 ^{0}C. Hydroxyl groups present in *A. squamosa* extract served as the catalyst. The possible reaction pathway is illustrated in (Figure 2.3**)**. Hence, water soluble compounds containing hydroxyl functional groups are found to be responsible for the stabilization of TiO_2 nanoparticles.

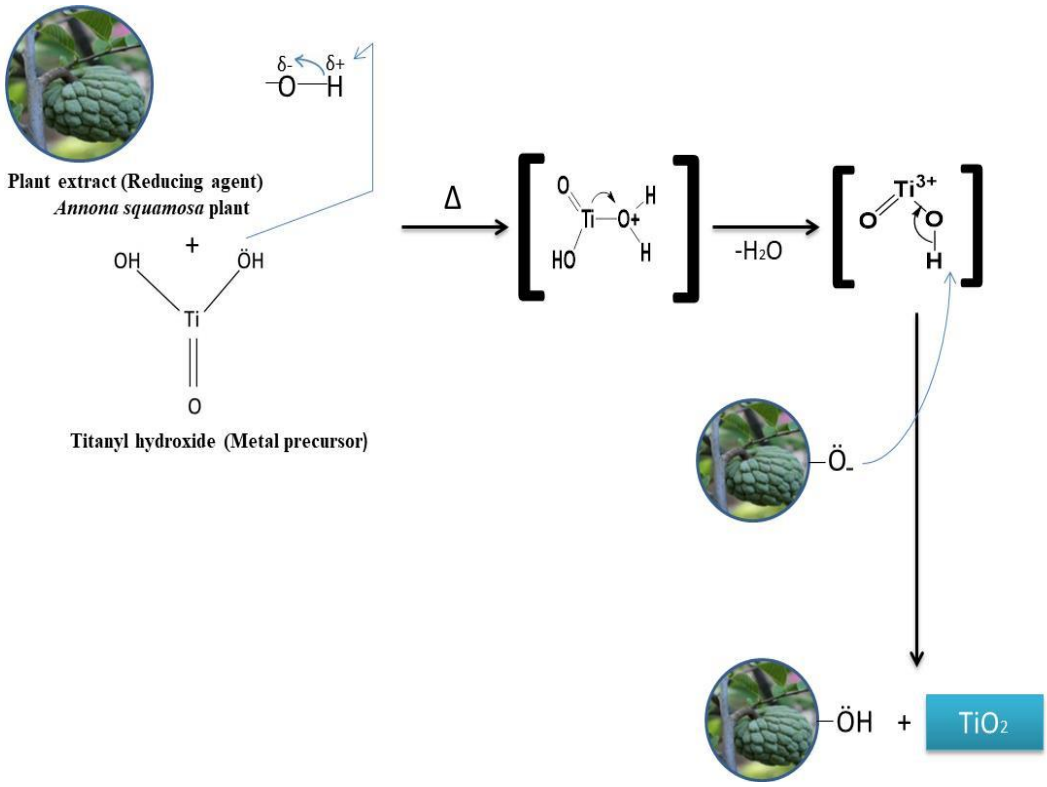

Figure 2.3 Mechanism of TiO_2 nanoparticles synthesis taking $TiO(OH)_2$ as metal precursor and *Annona squamosa* peel extract as reducing agent

In another study, the synthesis of TiO_2 nanoparticles was carried out using orange peel extract (Mobeen Amanulla,2019). The prepared extract was added slowly to titanium tetrachloride ($TiCl_4$) under magnetic stirring at pH 7. The prepared nanoparticles were washed with deionized water to remove the impurities, then dried and calcined. The presence of glucose, furfural and residual insoluble polysaccharides and carboxylic groups in the orange peel extract helped in the synthesis of TiO_2 nano-particles.

2.3.4 Flower Extract

The flower of *Calotropis gigantea (C. gigantea)*, commonly known as the crown flower, was used to carry out the synthesis of TiO_2 nanoparticles (Marimuthu et al., 2013). The fresh flower extract of *C. gigantea* was prepared and combined with $TiO(OH)_2$ under continuous stirring. The mixture was subjected to ultra-sonication to separate out the agglomerates formed and the powder was filtered to get the synthesized TiO_2 nanoparticles. It was confirmed that the functional groups alcohol, alkyl, aldehyde and primary amine present in the extract acted as capping/reducing agents for the synthesis of TiO_2 nanoparticles.

Kigelia africana (K. africana), a flower which constitutes anthocyanin as a predominant flavonoid pigment, was also used for the green synthesis of TiO_2 nanoparticles (Shalini at al., 2018), using HCl with titanium isopropoxide as metal precursor. Petals of *Kigelia afriana* flower were washed and dried and soaked in citric acid and finally washed several times with hexane to remove impurities. The flower contains terpenoids which generate OH free radicals and these radicals reduce TTIP to TiO_2 nanoparticles.

2.3.5 Seed Extract

The synthesis of TiO_2 nano-particles using *Vignaun guiculata* (cowpea) seeds extract was reported in a study by Chatterjee et al. (2017). The seed extract preparation involves washing, drying and boiling in distilled water. The extract was mixed with titanium oxide solution and then incubated at room temperature followed by filtration and calcinations. The existence of the primary amines and alkanes functional groups in the extract, helped to form TiO_2 nanoparticles.

Cucurbita pepo (pumpkin) seeds, a rich natural source of polyunsaturated fatty acids, phyto-sterols, proteins and various other elements were used to carry out the synthesis of TiO_2 nano-particles (Abisharani et al., 2019). The seed extract was prepared and added to titanium trichloride ($TiCl_3$) solution and the mixture was subjected to stirring. The biomolecules with alcoholic and C=O groups present in the extract reduced $TiCl_3$ to TiO_2 nanoparticles. Table 2.1 presents a summary of the available information on the functional groups present in the extract, proposed mechanism. and properties of TiO_2 nano-particles prepared through green route.

Table 2.1 Mechanism & properties of green synthesized TiO_2 nanoparticles using extracts from different parts of plants

Extract	Functional group present in extract	Mechanism	Properties of TiO_2 nanoparticles	Reference
Jatropha curcas leaf extract	Phenolic group, primary	Phenolic group- responsible for capping and reduction of Ti^{4+}	• Avg. crystallite size- 13nm • Surface area-	Goutam et al., 2018

	amine group	to Ti^0.	27.038m^2/g • Pore size diameter- 19.100nm • Total pore volume- 0.1291 cm^3/g	
Eclipta prostrate leaf extract	Alcohols, alkanes, phenols, flavones, primary amines and aliphatic amines	Flavones- responsible for capping and reduction of $Ti^{4+}$to Ti^0.	• Poly-disperse • Avg. size- 49.5nm	Rajakumar et al., 2012
Piper betle leaf extract	Biomolecules (Polyols, carbohydrates, proteins & flavonoids)	Biomolecules (Polyols, carbohydrates, proteins & flavonoids)- responsible for bioreduction ($Ti^{4+}$to Ti^0) and Stabilization of TiO_2 nanoparticles.	• Regular spherical like shape • Avg. particle size- 8nm	Hunagund et al., 2016
Vitex negundo Linn leaf extract and	Phenolic hydroxyl groups, polyols,	Polyols- responsible for bioreduction ($Ti^{4+}$to Ti^0) and Stabilization ofTiO_2	• Rod-shape morphology • Avg. size- 26nm	Ambika and Sundrarajan, 2016

EMIMBF 4 ionic liquid	amines	nanoparticles.		
Glycyrrhiza glabra root extract	Aromatic primary amine, hydroxyl groups (phenols & flavonoids), aldehydes	Flavonoids, phytosterols act as green reducing agent & stabilizing agent.	• Spherical shaped particles • Avg. size- 69nm • Anatase phase	Bavanilatha et al., 2019
Annonas quamosa peel extract	Hydroxyl group	Hydroxyl functional group- responsible for the stabilization of TiO_2nanoparticles.	• Spherical shape • Polydisperse • Avg. size- 23nm	Roopan et al., 2012
Hibiscus rosa-sinensis flower extract	Carboxylate group, carbonyl groups and secondary amines, phenolic group	Phenolic groups & amines- act as capping agent prevent them from aggregation.	• Dispersed & disaggregated TiO_2 nanoparticles • Spherical with distinct edges • Size- 7 to 24 nm	Sahaya et al., 2014
Echinacea purpurea	Alcohols, carboxylic	Flavonoids, in the free form and glycosidically	• Avg. size- 120nm.	Dobrucka, 2017

plant extract	acids, esters and ethers, flavonoids	bound kaempferol, quercetin, and luteolin, rutoside,isorhamnetin,apigenin,)- act as bioreductant.	• Agglomerated spherical shape clusters	
Starch	Soluble starch	By the leaching process, amylose is obtained from starch which is responsible for reducing TTIP to TiO_2. This complete process takes place in boiling water.	• Anatase crystalline nanoparticles • Avg. particle size- 64.19nm • Specific area- 87.2m^2/g	Muniandy et al., 2017

2.4 Leave extract ratios used for the green synthesis of nanoparticles

The important parameter affecting the size of particle and thus its efficiency is molar ratio or weight ratio of precursor to reducing agent. A detailed study based on the quantity of extract and precursor is discussed in detail in Table 2.2.

Table 2.2 Ratio of leaves extract to metal precursors in the synthesis process

Extract	Quantity	Reference
Euphorbia heterophylla leaf extract	20 mL extract: 40 mL $AgNO_3$-0.003 M and 1.0 g of TiO_2.	Atarod et al., 2016
Jatropha curcas leaf extract	0.50M $TiCl_4$in the ratio of 1:1 (v/v).	Goutam et al., 2018
Moringa oleifera	5 mM titanium dioxide solution of 90 ml :	Sivaranjani and

leaves	10ml of filtered aqueous leaf extract solution.	Philominathan, 2016
Annona squamosa peel extract	20ml of the aqueous extract : 80ml of 5mM TiO_2	Roopan et al., 2012
Starch	Soluble starch was dissolved in 150ml of boiling distilled water to which 0.01 mol of TTIP was added.	Muniandy et al., 2017
Vitex negundo Linn leaves	25ml of leaves extract :0.4M titanium isopropoxide:1ml EMIM BF_4 ionic liquid	Ambika and Sundrarajan, 2016

2.5 Characterization and applications of TiO_2 nanoparticles synthesized from different parts of plant

Few characterization techniques are applied to confirm the synthesized particles and other parameter which plays a key role for a particular application. Crystal structure and phase is analyzed by powder X-ray Diffraction (XRD). Morphology and size of TiO_2 NPs are determined by High Resolution Scanning Electron Microscopy (HRSEM). The composition of TiO_2 NPs is determined by X-ray Energy-Dispersive Spectrometer (EDS). Dynamic Light Scattering (DLS) determines the average particle size distribution. The target functional groups involved in the green synthesis of TiO_2 NPs are confirmed by Fourier Transform-Infrared spectrometer (FTIR). Surface area, pore size and volume of the green synthesized TiO_2 NPs before used for any application are analyzed by the techniques i.e. Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH). Optical properties of TiO_2 NPs are analyzed by UV–Visible spectrophotometer. **Table 2.3** summarizes the different types of extract and precursor used for the synthesis of TiO_2 nanoparticles of different shape, size and its applications.

Table 2.3 TiO_2 nanoparticles synthesized from different plants species

Plant	**Precursor**	**Shape**	**Size (nm)**	**Characteri za-tion**	**Applica-tion**	**Referenc e**
Leaves						
Ageratinaaltis sima	$TiO(OH)_2$	Spherical	60-100	FTIR,FSEM, XRD	Photo-catalytic activity	Ganesan et al., 2016
Aloevera	$TiCl_4$	Irregular	60	SEM,XRD, TEM, TGA, PSA, UV-Vis	-	Ganapath iRao et al., 2016
Anisomeles malabarica	TTIP	-	18	XRD	Materials used for electronic devices	Saravana n et al.,2016
Catharanthus roseus	TiO_2 solution	Cluster	25	FTIR, XRD,SEM	Significant parasitic activity	Velayuth am et al., 2012
Eclipta prostrata	$TiO(OH)_2$	Spherical	36-68	XRD,FTIR,A FM,FESEM	Food additives, coating, cosmetics, etc.	Rajakum ar et al., 2012
Euphorbia prostrate Aiton	$TiO(OH)_2$	Poly disperse	83.22	SAED,TEM, AFM	Anti-leishmanial agents	Zahir et al., 2015
Jatropha	$TiCl_4$	Spherical	13	UV-Vis,	Photo-	Goutam

curcas				FESEM, EDS,FTIR,XRD,DLS, BET,BJH	catalytic degradation of tannery wastewater	et al., 2018
Momordica charantia	$TiCl_4$	Spherical	47.6	UV-Vis, XRD, FTIR, HRTEM,EDX,DLS	Antimalarial activity	Gandhi et al., 2018
Morinda citrifolia	$TiCl_4$	Spherical	15-19	EDAX,FTIR, SEM,XRD	Anti-microbial activity against pathogenic diseases	Sundrarajan et al., 2017
Moringa oleifera	TiO_2 solution	Spherical	100	UV-Vis, SEM	Wound healing activity	Sivaranjani and Philominathan, 2016
Nyctanthes arbor –tristis	TTIP	Spherical	100	XRD,SEM,PSA	Bio-medical and nanotechnology	Sundrarajan and Gowri, 2011
Piper betle	Titanium n-butoxide(T	Spherical	7	FTIR,UV-Vis,XRD,	Anti-bacterial	Hunagund et al.,

	NB)			SEM	activity against multi-drug resistant microorganisms	2016
Psidium guajava	$TiO(OH)_2$	Spherical	32.58	FESEM, XRD,SEM	Anti-bacterial & antioxidant properties	Santhosh kumar et al., 2014
Solanum trilobatum	$TiO(OH)_2$	Spherical, oval	70	XRD, FTIR, SEM, EDX, AFM	Pediculocidal, acaricidal, and larvicidal activity	Rajakumar et al., 2014
Trigonella foenum-graecum	Titanium oxysulphate	Spherical	20-90	UV-Vis, HR-TEM, FTIR,HR-SEM, XRD	Anti-microbial activity	Subhapriya and Gomathipriya, 2018
Vitex negundo Linn **(+ $[EMIM]^+BF_4^-$)**	Titanium isopropoxide	Rod – shape	26	XRD, SEM, TEM, FTIR	Anti-bacterial activity	Ambika and Sundrarajan, 2016

***Vitex negundo Linn* (without $[EMIM]^+BF_4^-$)**	Titanium isopropoxide	Spherical	15	XRD, SEM, TEM, FTIR	Anti-bacterial activity	Ambika and Sundrarajan, 2016
Roots						
Acanthophylum laxiusculum	TTIP	Spherical	20-25	XRD, TEM, SEM, EDAX, FTIR	-	Madadi and Lotfabad, 2016
Desmodium gangeticum	TTIP	Spherical	31	UV-Vis, XRD, FTIR	Anti-microbial & antioxidant activity	Jamuna et al., 2014
Euphorbia heteradena Jaub	$TiO(OH)_2$	Spherical	20	XRD, FTIR, TEM	-	Nasrollahzadeh and Sajadi, 2015
Glycyrrhiza glabra	Titanium oxy-sulphate	Spherical	36	UV-Vis, FTIR, XRD, FESEM	Anticancer &potential bioactivity	Bavani latha et al., 2019
Peel						

Annona squamosa	$TiO(OH)_2$	Poly disperse	23	UV-Vis, XRD, SEM, TEM, EDS	Efficient phyto-synthesis	Roopan et al., 2012
Citrus sinensis	TTIP	Tetragonal	19	TEM, XRD,TGA, PSA	-	Kandregula et al., 2015
Orange	$TiCl_4$	Triangular	20-50	XRD, FESEM, FTIR, UV-Vis, EDX	Anti-bacterial, cyto-toxicity & humidity sensor applications	Mobeen Amanulla and Sundaram, 2019
Flower						
Calotropis gigantea	$TiO(OH)_2$	Spherical	10.52	XRD, FTIR, SEM, EDX	Acaricidal activity	Marimuthu et al., 2013
Hibiscus rosa-sinensis	Titanium oxy-sulphate	Spherical	7-24	XRD,SEM, FTIR	Bio-medical applications	Sahaya et al., 2014
Kigelia Africana	TTIP	Rod-shaped	10	FESEM,UV-Vis,FTIR	Enhanced photocurrent density	Shalini et al., 2018
Seed						

Cajanus cajan	TTIP	Spherical	10.5	XRD,AFM	Controlling the fouling of ultrafiltration PVDF membranes	Arif et al., 2019
Cicer arietinum	$TiCl_4$	Spherical	14	TEM,XRD, UV-Vis,TGA	Renewable resource for green synthesis	Kashale et al., 2016
Cucurbita pepo	$TiCl_3$	Tetragonal	Nano range	XRD, UV-Vis, FTIR	-	Abisharani et al., 2019
Vigna unguiculata	TiO_2 solution	Oval shaped	11.5	SEM,FTIR	Ant-imicrobial & anticancer treatments	Chatterjee et al., 2017
Whole plant						
Aloe vera	Titanium iso-propoxide	Irregular	60-80	XRD,PSA,SEM,FTIR	Electro/ photo-electrochemical applications	Khadar et al., 2015
Curcuma longa	TiO_2 bulk particles	-	50	AFM,SEM,XRD,UV-Vis	Reduce the fungal growth,spores and	Abdul Jalill et al., 2016

					Pathogenicity.	
Echinacea purpurea	TiO_2 solution	Poly disperse	120	UV-Vis, SEM, TXRF, FTIR	-	Dobrucka, 2017
Others						
Starch	TTIP	Tetragonal	9	XRD, SEM, NAA	Photo-degradation	Muniandy et al., 2017
Wheat starch	TiO_2	Spherical	-	UV-Vis,SEM	Starch/TiO_2 bio-nanocomposite for UV-protective food packaging material	Goudarzi et al., 2017

2.6 Synthesis of SiO_2 NPs

Earlier workers have mainly used tetraethoxysilane (TEOS) (Kim et al., 2002) and tetramethoxysilane (TMOS) (Niki et al., 2009) as precursors to produce silica nanoparticles. However, these chemicals are relatively expensive and toxic to environment (Hiroshi., 1994, Niki et al., 2009), hence attention has been focussed towards other silica bearing biological sources. Agricultural biomass like rice husk ash and bamboo leave have sufficient amount of silica (Ahmed et al., 2009). Silica obtained from biomass exists in the amorphous state with high surface area (Chandrasekhar et al., 2006, Shelke et al., 2010). Silica is used as adsorbent (Jang et al., 2009, Lakshmi et al., 2009, Wongjunda et al., 2010), support material, medical additive and filler in composite materials, etc. (Liu et al., 2005, Shin et al., 2008). The conventional chemical routes of obtaining silica are costly, time consuming and polluting. Hence there is a need to look for alternative less polluting feedstocks and route. Several workers have tried to obtain silica from rice husk and bamboo leave using different techniques such as thermal processing (combustion/pyrolysis), alkaline extraction, sol-gel method, laser ablation and microwave heating. A summary of the available information on synthesis, characterization and applications of SiO_2 obtained from biomass is presented below.

Nguyen et al. (2019) successfully synthesized SiO_2 nanoparticles from rice husk ash by the sol-gel method. Synthesized SiO_2 nano-particles were morphologically and chemically characterized. The Fe^{2+} ion adsorption capacity of the SiO_2 nano-particle was studied under different conditions. In addition, the synthesized SiO_2 with the size of around 50nm can be used for biomedical applications such as in drug delivery.

Almeida et al. (2019) synthesized the black SiO_2 nanoparticles from the rice husk ash by pyrolysis method. Synthesized particles were characterized by thermogravimetric analysis and loss of carbon mass was identified. The X-ray diffraction (XRD) denoted the presence of amorphous SiO_2 .The transmission electron microscopy (TEM) results showed the formation of nanoparticles having a particle size of about 10–20 nm. Through the scanning electron microscopic (SEM) images, the cellular porous structure was noted, and BET surface area was calculated near about $114m^2/g$. In this work, the physico-chemical and toxicological characteristics of rice husk (RH) and rice husk ash (RHA) by pyrolysis were investigated.

Mesoporous SiO_2 was successfully prepared from rice husk by thermal combustion and alkaline extraction process **(**Vu et al., 2019). It was used to synthesize the mesoporous composite by a facile impregnation method. The SiO_2 was used as support due to mesoporous structure with a high surface area (109.5m^2/g). The reaction rate and degradation efficiency of the organic dye (tartrazine) by the synthesized composite was evaluated.

Wee et al. (2019) extract silica from rice husk by acid/alkaline precipitation process. Particles were characterized by various characterization techniques like Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FE-SEM).

Enrique et al. (2018) used the microwave heating technique to obtain silica from rice husk. to improve the material characteristics and investigated its potential to remove methylene blue dye from aqueous solutions. The characterization techniques like XRD, FTIR, N_2 adsorption isotherms (BET and BJH), Gas picnometry, DSC and SEM revealed that the microwave modified nanosilica presented more interesting characteristics than the standard nanosilica. The purity of nanosilica was 98.8% and the particle size was around 93nm.

Song et al. (2018) extracted the high surface area SiO_2 nanoparticle from rice husk by sol–gel method with changing the parameters. A design optimization of the Taguchi approach was adopted to optimize the parameters. Synthesized particles were characterized by using the methods like, TEM, FT-IR, XRD and the nitrogen adsorption–desorption analysis. So biogenic SiO_2 nano-particle prepared from rice husk by employing Taguchi approach propose an efficient time saving and quality control strategy to optimize the synthetic process; resulting silica nano-particles with high surface area that can be extended to biomedical and catalytic application.

Bose et al. (2018) used rice husk, for the synthesis of silica nanoparticles by rapid microwave heating. The synthesized nano-particles having 4.9nm diameter exhibited excellent mono-dispersity and water dispersibility, high photo- and pH-stability and high quantum yield, and hold promise for a wide range of optoelectronic and bio-imaging applications.

Rangaraj et al. (2017) used bamboo leaf ash as the source of silica for the synthesis of SiO_2 nanoparticles through thermal combustion and alkaline extraction process. The synthesized particles were amorphous having spherical morphology with high surface area i.e. 428 m^2 g^{-1}. The authors suggested that synthesized particle can be used for drug delivery and other medical applications.

Bio-generated mesoporous SiO_2 nano-particles were successfully synthesized by Sankar et al. (2016) from rice husk ash through a simple acid pre-treatment method. Synthesized particles were amorphous spherical particles. The particle size was 3-10nm with the highest surface area of 247.18 m^2 g^{-1}. It was claimed that these materials could be considered for energy storage and drug delivery applications.

Athinarayanan et al. (2015) used rice husk as a natural bio- precursor for biogenic silica synthesis using the procedure used by Sankar et al. (2016)**.** Spherical particles with 10-30nm diameter were obtained. The authors claimed that the particles could be used for biomedical applications like bone tissue engineering.

San et al. (2014) reported successful preparation of silica nanoparticles using a laser ablation technique. Synthesized particles were confirmed by SEM, TEM, and DLS techniques. Results showed that the nano-particles obtained by laser ablation were significantly smaller (38–190 nm) than those prepared using chemical treatment.

Wang et al. (2011) used controlled pyrolysis method to obtain silica nano-particle from rice husk. High purity silica particle with 20-30nm diameter was prepared by this method. Various characterization techniques were followed to particle morphology and thermal stability. The authors claimed that the synthesized particle may replace silica gel and fumed silica for various applications.

Table 2.4 gives a summary of the available information on the synthesis of silica from biomass, characterization of particles and their application.

Table 2.4 Synthesis, characterization and application of SiO_2 nanoparticles obtained from biomass

Silica source	**Synthesis process**	**Shape**	**Size (nm)**	**Characterization**	**Application**	**Reference**
Rice husk Ash	Sol-gel	Spherical	50	FTIR, UV-Vis , TEM-EDAX and BET	Adsorptive removal of iron	Nguyen et al.,2019
Rice husk	Pyrolysis	-	10-20	FTIR, XRD,BET, SEM-EDAX and TEM	Not Studied	Almeida et al., 2019
Rice husk	Sol-gel	Spherical	24-87	FTIR, XRD,BET, SEM-EDAX and TEM	Biomedical and catalytic application	Song et al., 2018
Rice husk	Microwave synthesis	Spherical	4.9	UV-Vis, HR-TEM,EDAX	Fluorophores for white light emission	Bose et al., 2018
Bamboo leaf	Thermal combustion and alkaline extraction	Spherical	25	FTIR, XRD, SEM, TEM	Not Studied	Rangaraj et al.,2017
Rice husk Ash	Chemical method	Spherical	10-50	FTIR, XRD,BET, SEM-EDAX and TEM	Energy storage and biomedical application	Sankar et al., 2016
TEOS	Sol-gel	-	79.6	Particle Size	-	Azlina et al.,

			8-87.35	Analyzer, FESEM		2016
Rice husk	Acid treatment	Spherical	10-30	FTIR, XRD,BET, SEM-EDAX and TEM	Biomedical application	Athinarayanan et al., 2015
TEOS	Sol-gel	-	25	XRD, HR-TEM, FTIR	Not Studied	Dubey et al., 2015
Sugarbeet bagasse	Laser ablation	-	38-190	SEM, EDAX, DLS, TEM, FTIR, XPS	Not Studied	San et al., 2014
Tri-methoxy vinyl silane	Micelles entrapment approach		28-168	Particle size analysizer, TEM	Not Studied	Zainala et al., 2013
Rice husk	Sol–gel		3	FTIR, XRD, TEM	Not Studied	Le et al., 2013
Rice hulls	Pyrolysis		6-100	FTIR, XRD,SEM, TEM	Not Studied	Palanivelu et al., 2013
Agricultural biomass	Sol–gel	Spherical	50.9	FTIR, XRD, BET and TEM	Not Studied	Adam et al., 2011

From the above literature, it is clear that utilization of bio-waste for nano-particle synthesis is quite encouraging and the particles synthesized by the green route have the same potential, morphology and size as those synthesized by chemical route. The biological extracts used for the green synthesis of nano-particles are easily available at low cost, compared to the expensive chemicals required for chemical synthesis. It is also clear that plants or plant parts have chemicals having potential to act as a reducing, capping and stabilizing agent for the synthesis of titanium oxide nanoparticle.

Green TiO_2 particles using few plants and their parts are successfully synthesized by the researchers for many applications with effective results. Still there is scope for usage of new green sources synthesis of TiO_2 NPs.

Similarly, different techniques used to extract bio nano-silica from the biomass are reported. Different types of chemicals and surfactants have been used to synthesize the SiO_2 nano-particle, which increases the cost of the chemical route to obtain a nano-size particle. However, in the acid precipitation method, only easily available chemicals like hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) are used for the synthesis

of the SiO_2 nanoparticle. It was found that SiO_2 particle synthesized from the biomass have all properties to act as an adsorbent and support materials for different applications.

2.7 Justification for Present Work and Objectives

From the assessment of the available published literature on the synthesis of TiO_2 nano-particles it is seen that in spite of the use of plant extract from several plant species and their parts, still there are species specific to India and available throughout no reported information is available. Further, the use of the TiO_2 prepared through green route as a photo-catalytic material embedded in polymeric matrix has been explored only by a couple of workers. Similarly, though sufficient work is available in open literature on the extraction of silica from rice husk but little/no effort has been made to use it as the filler in membranes to improve their performance. Further there is a need to look for another biogenic source for recovering amorphous silica. In view of these the present work has been planned with following specific objectives:

1. Synthesis of nano-particles of TiO_2 using extract of Jamun (*Syzygium cumini*) leaves as capping/ stabilizing agent.
2. Characterization and use of the synthesized TiO_2 particles for photo-catalytic degradation of waste water.
3. Evaluation of the performance of photocatalytic degradation and separation of pollutants form an industrial wastewater
4. Extraction of amorphous SiO_2 from bamboo leaves, its characterization and act as support material with TiO_2 particles to enhance the photocatalytic degradation.
5. Use of extracted silica particles as filler in membrane for improving membrane performance.