Review on recent advance biosynthesis of TiO₂ nanoparticles from plant-mediated materials: characterization, mechanism and application

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Abstract. Titanium dioxide, TiO₂ nanoparticles are being utilized in various application of science and technology including membrane, medical, electrical and chemical field for their respective worth which generally attributed to the self-cleaning and photocatalytic ability, good band gap, an antibacterial as well as physical and chemical stability. As commonly known conventional TiO₂ nanoparticles synthesized using chemicals as reducing agents has become accountable for various biological risks due to their general toxicity, thus engendering the serious concern in developing environment friendly processes. Naturally derived products, such as extracts of plants that composed of biomolecules, have been used intensively recently as a reductant agent, that also sometimes can be acting as capping agents after synthesis process. These natural biomolecules mostly consisted of polyphenols have been identified to be actively play a role in this biosynthesis of nanoparticles from any plants extract that able to form different shapes and sizes of nanoparticles with better surface reactive area, characteristic and properties. Therefore, biosynthesis can be considered as a driving force for the greener, safe and environmentally friendly for many applications that have used TiO₂ particles either used as additive, purely or in composite form. The present review targets on the ‘greener’ routes of synthesis TiO₂ nanoparticles with an emphasis on experimental conditions based on sustainable methodologies and also explores the huge plant diversity to be utilized. The use of ‘greener’ not only reduces the cost of synthesis but also minimizes the need of using hazardous chemicals and stimulates green synthesis. This review also focuses on aspects characteristic and properties that generated from the output of this green process that make it strongly applicable to certain applications as for binding of biomolecules, to the biosynthesized is significantly benefit to biomedical fields. It is expected that these outstanding findings will encourage researchers and attract newcomers to continue and extend the exploration of possibilities offered by nature and
the design of innovative and safer methodologies towards the synthesis of nanomaterials, possessing desired features and exhibiting valuable properties that can be exploited in a profusion of fields.

Keywords: Titanium dioxide; TiO₂; Biosynthesis; Plant extract; Green synthesis

1. Introduction
Nanoparticles has been integrated in membrane for various application such as water treatment [1–4], gas separation [5], wound dressing [6,7] etc. The use of nanoparticles as an additive in nanoscale range is considered important as it can provide larger surface area resulting in good characteristics and membrane performance such as anti-fouling, photocatalytic and anti-bacterial activity. However, there is an issue that need to pay attention regarding to nanoparticles potential to human health and environmental risk of nanoparticles [4]. Recently, biosynthesized nanoparticles have drawn great attention resulting in exploration of green technology through biosynthesis method with added functions such as antibiotic resistance [8,9] and biocompatibility [10] compared to the chemical and physical method. Incorporation of these biosynthesized nanoparticles as an additive with well-defined nanostructure bring significant effect in their properties and characteristics also can produce a good membrane performance. Some reviews have already described the overview particular biosynthesized nanoparticles development with various application [11–14].

There is various synthesis approach have been used in nanoparticles production include chemical, physical and green synthesis methods. These methods are still experiences problems such as aggregation and stability, crystal growth control, size, morphology and distribution because they are still in the development stage. Besides, the separation of the nanoparticles produced become an important consideration for further applications [15]. The approach of green technology through biosynthesis using bacteria, actinomycetas, yeasts, fungi, algae and plant extract provides advancement over chemical and physical method. It also in fact able to eliminate the use of hazardous chemicals, cost effective, eco-friendly, easily scaled up for large scale synthesis [15] and more energy efficient without using high pressure and temperature [16]. Although chemical and physical methods are extensively used for nanoparticles production but they require the use of reactive and toxic reducing agents such as sodium borohydride (NaBH₄), N, N-dimethyl formamide (DMF), Tollen’s reagent and hydrazine hydrate [17]. This will cause undesired detrimental impacts on the environment, plant and animal life it supports [11].

The development of facile, reliable and effective green synthesis process is continuously in progress for the nanoparticles production. The efforts made by all researchers is vitally important to produce nanoparticles that is stable, more reliable and well-functionalyzed. In application such as biomedical, biosynthesis of nanoparticles is still under exploitation to avoid adverse effects [13]. Thus, there is a need to explore sustainable process for nanoparticles synthesis. The concern may include the viability of economy, sustainability of environment, adaptability of social and the local resource availability (see Fig. 1.) [11,18–20]. Generally, nanoparticles involved two main synthesis approaches which is either from “top to bottom” or “bottom to up” (see Fig. 2.). In top to bottom approach, lithographic technique such as milling, sputtering thermal and grinding are used to break down bulk material into fine particles by size reduction while in bottom to up approach, atoms are self-assemble to form new nuclei which grow into nanoscale particles as shown in Fig. 2. Certain limitation and drawback from these techniques mentioned before leads to the green synthesis technology via biosynthesis that does not required toxic chemicals thus develop environment friendly processes. Moreover, limitation to biomedical applications using the resulting nanoparticles could be reduced because biosynthesis routes mostly are free from contamination of toxic by-products produced by physicochemical route that normally will attached to the nanoparticles during synthesis [21].

Recent studies have point out the potential of biosynthesized TiO₂ nanoparticles for various application including remediation of environmental. The interest is increasing due to its self-cleaning and photocatalytic ability, good band gap, an antibacterial agent as well as physical and chemical
stability. Thus, the possibilities offered by nature and the design of innovative and safer methodologies towards the biosynthesis of TiO$_2$ nanoparticles is a great step forward in the development of nanomaterials, possessing desired features and exhibiting valuable properties that can be exploited in a profusion of fields. The current review intends to discuss on the important of biosynthesis of titanium dioxide nanoparticles as an additive by focusing on the characteristic and properties that applicable to certain applications with an emphasis on experimental conditions based on sustainable methodologies and also explores the huge plant diversity to be utilized.

![Sustainable green technology](image)

Fig. 1. Sustainable green technology.
2. Biosynthesis of TiO$_2$ nanoparticles by plant extracts – the important

Many researchers from literature mentioned that TiO$_2$ nanoparticles have potential oxidation strength, non-toxicity, high photocatalytic activity, interesting optical and chemical stability. They also possess antimicrobial property and antibacterial catalytic which leads to various industrial applications such as photocatalyst, catalyst supports and pigments [13,22]. Moreover, biosynthesized nanoparticles may have different properties prepared by other techniques and also can have enhanced biocompatibility and stability probably due to the active biomolecules or capping agent coated on the surface. Mainly, the stabilization of nanoparticles in biosynthesis perspective depend much on the choice of the reducing agent, solvent medium and non-toxic material. A green and facile biosynthesis using plant materials was achieved in continuation of the efforts of recent biosynthesis by bacteria, actinomycetes and fungi [23].

To date, TiO$_2$ nanoparticles have been synthesized mostly using different type of plant extracts. Extracts of plants commonly obtained by using leaves, flowers, roots and stems. Most of them are categorized as herbs in order to apply in biomedical application. Common herbs are not only used as fragrance or flavour in the food industry but most of them sometimes can exhibit antimicrobial properties [24]. The use of these extracts in the nanoparticle production assembly was shown more stable because their reaction rate as reducing agent (able to reduce metal or metal oxide ions) as well as stabilizing agent is much faster than fungi, bacteria or other organisms. Furthermore, plant extract provides advanced advantage as the organism mostly required stringent control on cell culture. The green method is also easy and safe for industrial production scale-up of well-dispersed nanoparticles as it does not require harmful and toxic chemicals [15] (see Fig. 3.). Commonly, water or organic solvents are used to extract phytochemicals based on the group or type and the process is done with less temperature which is not greater than 100°C (see Table 1.). Moreover, there is a significance effect

Fig. 2. Important approaches of nanoparticles synthesis.
of plant extract concentration on the size, shape as well as distribution of the nanoparticles revealed by previous studies [25].

The combination of functionalized surface that contains biological molecules compounds in plant extracts such as polysaccharides, alkaloids, tannins, phenolics, saponins, carbonyl and hydroxyl are responsible for reduction and stabilization of TiO$_2$ ions and already established in several reported journals [26,27]. The plant extracts are employed for focusing on the principles of green chemistry such as aloe vera, neem, lemon grass, Indian gooseberry, tulsi and corriandrum [13,28]. They also have medicinal values, environmental benign with substantial health benefits yet having a complex chemical structure which are not present in physical and chemical synthesized nanoparticles [12,19]. Moreover, in order to optimize the extraction of these biological molecules compounds, various studies have been carried out including extraction temperature, type of solvent as well as plant drying technique [19,29,30].

Several experimental parameters were screened, namely extraction temperature, solvents used, precursor type, plant extract volume, drying temperature, reaction time and calcination step as shown in Table 1 with pictures of the extract plants illustrated in Fig. 4. Generally, different experimental sets generate similar nanoparticles mostly spherical in shape. To summarized the screened parameters, the biosynthesized TiO$_2$ nanoparticles composed as result from the mixing of plant extract from 5 to 80 ml with titanium dioxide precursor. Then, they were dried at either room temperature or using temperature not higher than 100°C with reaction time from two hours or until overnight. Some experiment involved calcination step ranging from 450°C to 600°C with a maximum 4 h reaction time to remove organic groups. Most experiment that using TiO$_2$ as precursor specifically TiO$_2$ bulk particles may not require calcination step as in experiment conducted by Abdul Jalill et al. [31] and others shown in Table 1. A study by Kharisssova et al. [18] added some common assumptions about green chemistry that at least one role in biomolecules supposedly present in plant either the hydrolysis of the Ti(IV) antecedent, polymerization of the different intermediates, solubilizing or most importantly the reduction of the metal salts roles.

The first step of preparation of plant extract normally involved collection of the plant of interest from local garden or at common available place. The plants were cleaned and washed thoroughly with either distilled water or tap water to remove dust. Some were shade dried for about 2 weeks at room temperature under dust free condition and cut before further sieved, grinded or blended to obtain the finest powder such as experiment conducted by Sundrarajan and Gowri [28]. Then the dried powder was boiled at certain temperatures with a known gram of the dried powder. This extraction technique namely infusion filtered the resulted infusion extract containing all the biochemical that will be used as a reducing and stabilizing agent in the biosynthesis. Usually, after biosynthesis, the obtained precipitate of nanoparticles was filtrated to separate them from the solution then the ionic impurities were removed by ethyl alcohol through washing. Lastly, they were dried or calcined depends on the parameter used. The leaf extract of *Nyctanthes arbortristis* as reported by Sundrarajan and Gowri [28] promotes the production of higher crystallinity and purity of TiO$_2$ nanoparticles with spherical in shape and 100 nm in size where the experimental conditions were as follows: 0.4M of titanium tetraisoproxide (TTIP) in ethanolic leaf extract (50ml of ethanol mixed with 1g dried leaves) stirred at 50°C and calcined at 500°C at 3 hours. Patidar et al. [32] also used shade dried leaves of Moringa Oleifera by mixing 0.5M of TTIP in ethanolic leaf extract (10g dried leaves was mixed with 100 ml ethanol), stirred at 50°C and calcined at 500°C for 5 hours producing tetragonal body-centred titanium dioxide with average size of 12 nm. The color change during stirring or autoclave might indicate the proof of nanoparticles formation due to surface plasmon resonance excitation which is dependent on the size distribution and shape of the nanoparticles [33]. But technically, some reaction didn't show any color change and there was no proof for the formation of nanoparticles such as experiment conducted by Rajakumar et al. [34] and Santhoskumar et al. [35] where the pure TiO(OH)$_2$ and aqueous leaf extract of P. guajava. Usually, those pure TiO$_2$ and leaves extract didn’t show any color change unless if they were mixed under certain conditions.
The biomolecules extraction from plant is an important step in the biosynthesis. Here, researcher need to choose which extraction method to be used as type of plant, temperature control, stirring rate, plant volume/concentration and types of solvents used such as water or organic solvent (hexane, ethanol, methanol, ethyl alcohol etc.) that have difference in polarity can bring impact in term of accuracy of type of bioactive molecules present and the total amount of the bioactive compounds obtained [36]. Generally, most researchers used conventional extraction methods due to its simplicity to facilitate the extraction of biomolecules with high concentration with systems that consume safe solvents such as pure ethanol [37] as illustrated in Fig. 5. In selection of solvents, it is important to consider solubility, cost and safety as it is crucial part for solvent extraction [30]. Besides, solvent used are chosen based on the solute (plant extract) polarity and usually researcher eliminate the water interference by employed a dry powder of plant material. The solute will properly dissolve if the solvent has a similar polarity. Common solvents, from high polarity to less polarity is listed as follows: Water > Methanol > Acetone > Ethy lacetate > Chloroform > Hexane. There are many research study suggested that high polarity solvents can extract antioxidant effectively [29]. In addition, Koffi et al. [38] reported that higher concentrations of phenolics compound was extracted from ethanolic extracts of Ivorian plants compared to methanol, water and acetone.

On the other hand, the size of nanoparticles can be affected by the pH value of the medium under formation [21]. In this review, it was suggested that alkaline pH values (pH 7) using various extracts of plants can change the charge of natural biochemical that further affects their capability to bind and reduce TiO$_2$ ions efficiently thus producing variety of yield and morphology includes shape and size of nanoparticles. For example, in the case of biosynthesis of TiO$_2$, the extracts peels of Citrus sinensis (L.) was added dropwise until pH 7 producing a rutile phase, tetragonal in shape with size of 19nm. A spherical TiO$_2$ nanoparticles with distinct edges without aggregation and size 7 nm was obtained using extract of Hibiscus rosa sinensis. Rajkumari et al. [39] obtained a spherical, polydispersed biosynthesized TiO$_2$ nanoparticles with size ranging from 20 to 50 nm using the leaf extracts of Aloe barbadensis mill. Another example of size and shape controlled biosynthesized nanoparticles by pH 7 is Rao et al. [40] which reported that by using Aloe vera leaf extract, an irregular shape with 20 (tetragonal), 32 and 60-80 nm in size was obtained using XRD, PSA and SEM analysis technique. In addition, a finding by Pratap et al. [41] has reported that the low pH of biosynthesized TiO$_2$ nanoparticles solution using leaf extracts of Jatropha curcas. L might promote agglomeration of the nanoparticles however biochemical present perhaps can enhance the dispersion of the nanoparticles thus reduce the agglomeration.

Most experimental procedure that involved calcination process obtained TiO$_2$ biosynthesized nanoparticles with tetragonal structure as reported by Patidar et al. [32], Rao et al. [42], Rao et al. [40], Pratap et al. [41] and Sundrarajan et al. [43] except for Sundrarajan and Gowri [28] who obtained cubic structure. Specifically, the biosynthesized TiO$_2$ nanoparticles are produced when calcined by 400°C to 600°C from 3 to 5 hours producing those two structure. Thus, it is possible to obtain biosynthesized TiO$_2$ nanoparticles with significant output (type of biochemical content, extract volume, yield etc) depending by experimental conditions/parameter such as listed in Table 1. In addition, a study by Singh et al. [23] has reported that biosynthesized nanoparticles require time shorter than physiochemical approaches by utilizing various sources of plant.
Fig. 3. Procedure of biosynthesis of TiO₂. Adapted from Nabi et al. [44] with some modification.

Fig. 4. Plant-mediated materials used for biosynthesis of TiO₂ nanoparticles (sort according to name)

MACERATION
Powdered crude sample mixed with solvent

INFUSION
Powdered crude sample mixed with cold/boil water

DIGESTION
Powdered crude sample mixed with water and macerated with gentle heat

DECOCTION
Powdered crude sample mixed with solvent heated inside the apparatus for a specific period of time

PERCOLATION
Powdered crude sample mixed with solvent and boiled

SOXHLET
Soxhlet apparatus
| No | Name and part of plant | Extract method | Titanium precursor | Extract volume, ml | Stirring temp, °C / Time, h | Drying temp, °C / Time, h | Calcined temp, °C / Time, h | Ref |
|----|------------------------|----------------|-------------------|-------------------|-----------------------------|---------------------------|-----------------------------|-----|
| 1  | *Nyctanthes arboritris*, leaf | Ethanol, 50°C | TTIP | 1 g dried leaves + 50 ml ethanol | 50 / 4 | - / 4 | 500 / 3 | [28] |
| 2  | *Cynodon dactylon*, leaf | Water, Boil | TTIP | 100 | 50 / 1 | 80 / 2 | 500 / 5 | [45] |
| 3  | *Moringa oleifera* leaf | Ethanol, 50°C | TTIP | 10 g extract + 100 ml ethanol | 50 / 4 | Room temperature / | 500 / 5 | [32] |
| 4  | *Citrus sinensis* (L.) (orange waste), peel | Water, 90°C | TTIP | Dropwise (until pH 7) | Room temperature / 3 | 80 / overnight | 600 / 3 | [42] |
| 5  | *Azadirachta indica*, leaf | Water, 60°C | TTIP | 10 | 50 / 5 (dark brown color) | - | - | [46] |
| 6  | *Hibiscus rosa sinensis* (shoe black plant), petals | Water, 70°C | TiOSO₄ | 5 (dropwise until pH 7) | - / 3 | 100 / 3 | - | [47] |
| 7  | *Catharanthus roseus*, leaf | Water, Boil | TiO₂ (powder) | 20 | 50 / 4 (light green) | - | - | [48] |
| 8  | *Curcuma longa* (turmeric), leaf | Water, 40°C | TiO₂ (bulk particles) | 50 | Room temperature / | - | - | [31] |
| 9  | *Echinacea purpurea*, leaf | Water, 90°C | TiO₂ (aqueous solution) | 10 | - | - | - | [49] |
| 10 | *Vigna radiate*, seed | Water, Boil | TiO₂ (aqueous solution) | 20 | - | - | - | [45] |
| 11 | *Cassia fistula*, leaf | Water, Boil | TiO₂ | 20 | - / 24 (milky color) | - | - | [50] |
| 12 | *Citrus limon*, leaf | Water, Boil | TiO₂ | 20 | - | - | - | [51] |
| 13 | *Aloe barbadensis*, mill, leaf | Water, 70°C | TiCl₄ | Dropwise (until pH 7) | - / 3 (brown) | 100 / 7 | - | [39] |
| 14 | *Aloe vera*, leaf | Water, 90°C | TiCl₄ | Dropwise (until pH 7) | - / 4 | 100 / overnight | 500 / 4 | [40] |
| 15 | *Jatropha curcas*, leaf | Water, 80°C | TiCl₄ | 80 | Room temperature / | Air dried / - | 450 / 3 | [41] |
| No. | Plant Name                       | Part                | Extraction Method | Concentrate | Temperature | Reactant | Yield | Notes                          |
|-----|----------------------------------|---------------------|-------------------|-------------|-------------|----------|-------|--------------------------------|
| 16  | *Tinospora cordifolia*            | stem                | Organic solvent, water | TiCl₄      | 500 mg of extract + 20 ml ethanol | 70 / - | -    | [52]                           |
| 17  | *Morinda citrifolia* (M. citrifolia) | leaf                | Ethanol, 50°C | TiCl₄      | 50          | 100 / 5 | 400 / 4 | [43]                           |
| 18  | *Ageratina altissima*             | leaf                | Water, 60°C   | TiO(OH)₄  | 25          | -       | -    | [53]                           |
| 19  | *Calotropis gigantea* (Crown flower) | leaf                | Water, 60°C   | TiO(OH)₂  | 50 mg       | 90 / 2  | -    | [54]                           |
| 20  | *Solanum trilobatum* (purple fruited pea eggplant) | flower      | Water, 60°C   | TiO(OH)₂  | 20          | -       | -    | [55]                           |
| 21  | *Euphorbia heteradenae Jaub*      | root                | Water, 70°C   | TiO(OH)₂  | 15          | Room temperature / 2 | - | [56]                           |
| 22  | *Eclipta prostrate L.* (False daisy), leaf | leaf | Water, 60°C / 10 | TiO(OH)₂  | 15          | -       | - | [34]                           |
| 23  | *Euphorbia prostrata*             | leaf                | Water, 60°C   | TiO(OH)₂  | 20          | -       | -    | [57]                           |
| 24  | *Jatropha curcas,* latex          | 0.3% latex          | TiO(OH)₂      | 1 ml crude latex | Room temperature / 2 | - | [58]                           |
| 25  | *Mangifera indica L.* (leaf)      | leaf                | Water, 60°C   | TiO(OH)₂  | 15          | -       | -    | [59]                           |
| 26  | *Psidium guajava,* leaf           | leaf                | Water, 60°C   | TiO(OH)₂  | 20          | -       | -    | [35]                           |
| 27  | *Glycosmis cochinichensis,* leaf  | leaf                | Water, 85°C   | TiO(OH)₂  | 25          | -       | -    | [60]                           |
| 28  | *Annona squamosa* (sugar-apple), peel | leaf | Water, 25°C | TiO(OH)₂  | 20          | -       | -    | [33]                           |
| 29  | *Aloe vera* gel                   | Water, boil         | TiO(OH)₂      | 20 / 24 (light green) | 120 / 1 | - | [61]                           |
Fig. 5. Conventional methods used for plant extraction.
3. Characterization of biosynthesized TiO$_2$ nanoparticles – control of size and shape

There are many techniques have been applied to characterize biosynthesized nanoparticles and the characterization field is still in trend. Many discussions regarding which suitable techniques should be performed to provide information data and researchers currently try to find standard regulatory methodologies or protocols for the biosynthesized characterization in various field includes environmental and biomedical field [44]. Understanding of these techniques will really help readers to get appropriate techniques for their research needs. Given here is some important techniques and relevant references for details.

The biosynthesized TiO$_2$ nanoparticles are characterized by certain attributes such as surface area [62], morphology [28], size [63], thermal stability [64], optical activity [60] etc. These characteristic parameters can bring direct effects on the nanoparticles behaviour especially in downstream application. The significant characterization techniques for TiO$_2$ nanoparticles that often used are Fourier transform infrared spectroscopy (FTIR) [34], X-ray diffraction (XRD) [32], field emission scanning electron microscopy (FE-SEM) [51], scanning electron microscopy (SEM) [28], energy dispersive analysis of X-rays (EDX)/(EDAX) spectroscopy [35], ultraviolet visible (UV–Vis) spectroscopy [31], [49], atomic force microscopy (AFM) [65], particle size analyzer (PSA) [40], dynamic light scattering (DLS) [66], transmission electron microscopy (TEM) [60] and zeta potential [67].

The most necessary parameters sought for characterization of biosynthesized nanoparticles are size and surface functional group. Regarding this need, XRD, DLS, TEM, PSA and AFM can provide information of the size. XRD can clarify a crystal structure, crystalline phase as well as diffraction pattern of the nanoparticles. The structural information and the rendered pattern obtained then will be compare with the standards. Here, Debye-Scherer’s formula is used to calculate the average crystallite size. In PSA technique, ultrasonicator is used to dispersed the nanoparticles in the distilled water in order to obtain a mean value from histogram of the dispersed nanoparticles. DLS is also a simple technique for average size determination in the liquid solution phase. Besides size, AFM is preferable technique to characterize topography, roughness, morphology, surface texture and granularity volume of the biosynthesized nanoparticles.

Meanwhile FTIR is used to identify all the functional groups of the compounds for chemical bond analysis. The stability of the colloidal suspensions is the main challenge in the biosynthesis. Usually, biosynthesized nanoparticles tend to aggregate in order to reduce surface tension because the surface are coated with other compounds present [68,69]. To stabilize it, capping agents are commonly needed to keep the nanoparticles from aggregating during the procedure. That is why those compounds (capping agent) as well as compounds present in the biosynthesis solution need to be identified by FTIR. In fact, if difference bonds (C–C, C=C, C≡C, C–O, C=O, O–H, and N–H) are present, they can be identified because they have diverse vibrational frequencies [35]. Thus, the surface of nanoparticles can be well characterize using this technique through the determination of organic functional groups, surface chemical residues and surface chemistry by detecting their frequency absorption band characteristics in the infrared spectrum.

Morphology information such as shape of the nanoparticles can be obtained by using SEM, FESEM, TEM and AFM. In fact, FESEM is used in order to get a more accurate data of surface properties. In comparison, TEM provide better resolution and internal structure information of the nanoparticles. All these techniques also can be used to estimate the average size of the biosynthesized nanoparticles. EDX and EDS basically has same function as they are used to proves and estimate the chemical and elemental composition, type as well as concentration of the nanoparticles.

Other techniques may be needed depending on the applications. For example, the light absorption properties of nanoparticles and their interaction information are needed for environmental remediation. Common TiO$_2$ only have absorbance not more than 380 nm [65] but can extend into visible range if they have ligands attached on their surfaces or by doping [70]. Regarding this need, UV-VIS technique is used for qualitative and quantitative analysis to obtain the reflectance and absorbance spectra in order to identify
their optical properties and certain classes of compounds (pure and biological mixtures) in the ultraviolet and the visible light region. UV-Vis spectroscopy can detect natural compounds such as phenolic including polymer dyes, tannins and phenols that formed complexes with iron in the UV range [71]. This technique was found to reduce cost, less selective, can give information of the total content of phenolic extract (280 nm), phenolic acids (360 nm), flavones (320 nm), and also less time consuming compared to other techniques [72]. In fact, various nanoparticles ranging size from 2 to 10 nm can be characterized using light wavelength within the 300-800 nm [73]. Moreover, photocatalytic activity could be enhanced with the help of stronger UV absorption intensity where higher separate electrons or holes produced and higher electrons could be promoted from the valence band into the conduction band [52].

Besides, other techniques that useful in the characterization is the TG/DTA and zeta potential. The thermal and thermal stability of the nanoparticles can be expressed by using TG/DTA technique. Zeta potential is also important because most nanoparticles have a surface charge. Some studies mentioned that zeta potentials either positive or negative that have an absolute value of more than 30 mV can maintain colloidal stability by electrostatic repulsion [74,75]. Generally, nanoparticles suspension contains ions that affect the measurement of zeta potential through its strength and valency of ions. Increased ionic strength and valency can reduce the zeta potential by compressing the electric double layer [76]. Besides, the concentration of hydrogen ions in medium and the pH can also influence the zeta potential because the nanoparticles acquire more positive charge when the suspension is acidic. So, it is important to give information of the nanoparticles suspension with indication of solution pH including the composition of the medium and ionic strength [74]. For example, Sanker et al. [46] obtained biosynthesized TiO2 nanoparticles with interconnected spherical in shape having a zeta potential of -24 mV in 124 nm of nanoparticle size. 5 mM titanium isopropoxide solution was reduced at 50 °C with pH 1.5 indicating that the biosynthesized TiO2 nanoparticles using Azadirachta indica leaf extract were synthesized successfully. It is said that the electrical charge on the nanoparticles surfaces is high resulted from the high zeta potential’s absolute value.

Taking advantage of plant resources in Table 2, the biosynthesis of TiO2 produce nanoparticles with size ranging from 7 to 150 nm. Mostly they are spherical in shape. Some of them are oval, aggregated, poorly dispersed, agglomerated and even have irregular shape. This might due to the biomolecules compounds coated at the surface that responsible as capping agent during the biosynthesis. Sahaya et al. [47] has compared their biosynthesized TiO2 nanoparticles using dried petals identified as Hibiscus-rosa-sinensis L. with chemically synthesized nanoparticles. They found that their functionalized biosynthesized TiO2 nanoparticles are spherical with distinct edges without aggregation and stable with good dispersibility compare to chemically synthesized TiO2. Besides, in chemically synthesized TiO2, there was a sharp diffraction peak observed whereas there is slight broadening and less intensity observed in biosynthesized TiO2 nanoparticles with calculated crystallite size were 24 nm and 7nm, respectively. The broadening of the peak of biosynthesized TiO2 nanoparticles confirms the size reduction which indicates that their size is smaller than the chemically synthesized TiO2 nanoparticles supported by green synthesis protocol [77]. In addition, Sahaya et al. [47] has suggested that the surface of biosynthesized TiO2 nanoparticles was coated by the phytochemicals present in the petals extract thus reducing the XRD peak intensity probably due to an internal strain in the particles that make signal:noise ratio to decrease. This result also may enhance the dispersibility, stability as well as their bioavailability. On the other hand, the chemically synthesized TiO2 nanoparticles are bare and uncapped indicated by its high intense peaks. Moreover, the effect of toxic related on size is expected none due to the reduced capability of nanoparticles to penetrate the cellular structure caused by the agglomeration of nanoparticles [52].

Another comparative study was reported by Hariharan et al. [45]. They have compared powder between biosynthesized TiO2 and leaf extract powder of Cynodon dactylon, namely powder A and powder B, respectively. Both were calcinated at 500 for 5 hours. No peaks were observed for the powder B whereas there was broad XRD diffraction peaks were obtained for powder A indicating anatase TiO2 and powder A
has small crystalline size. There were no clear peaks observed for the powder B might be due to the organic compounds present in the *Cynodon dactylon* leaf powder. In this part, it could conclude that by altering the bioactive functional group and environmental growth can control of the shape and size of biosynthesized TiO2 nanoparticles including by improving the reaction conditions/parameters as supported by Singh et al. [78]. An interesting finding by Hudlikar et al. [58] mentioned that the integrity and stability of their nanoparticles contributed from the surface bound capping proteins can be check by treating them with 1% sodium dodecyl sulfate (SDS) detergent and heated at 85 °C for 30 min. This treatment lead to an aggregation/clumping of nanoparticles at a short period of time due to protein denature supported by FTIR spectroscopy analysis where most of the bands disappear including C-H stretch, N-H stretch and carbonyl stretch (C=O-C or C=O). From this finding we can note that the surface coating (peptide/protein) can be removed rather than utilized as capping agent depend on applications where surface coating is not needed such as in thin film formation and particle annealing.
Table 2. Characterization technique, size, morphology and application of biosynthesized TiO$_2$.

| No | Name and part of plant          | Characterization                                      | Size (nm)                  | Morphology                     | Application                        | Ref  |
|----|---------------------------------|-------------------------------------------------------|----------------------------|--------------------------------|------------------------------------|------|
| 1  | *Nyctanthes arbortristis*, leaf  | XRD, SEM, PSA                                         | 100 (XRD)                  | Spherical                      | Biomedical systems                | [28] |
|    |                                 |                                                       | 100-150 (SEM)              |                                |                                    |      |
| 2  | *Cynodon dactylon*, leaf         | XRD, FTIR, Laser Raman spectroscopy, SEM, FTIR        | -                          | Irregular shape                | Antibacterial and anticancer activity | [45] |
| 3  | *Moringa oleifera* leaf          | XRD, UV-VIS                                           | 12                         | -                              | -                                  | [32] |
| 4  | *Citrus sinensis* (L) (orange waste), peel extract | XRD, PSA, FTIR, TG/DTA                                  | 19 (XRD – rutile phase, tetragonal) 24 (PSA) | -                              | Antibacterial and anticancer activity | [42] |
| 5  | *Azadirachta indica* (Neem), leaves | FESEM, EDAX, XRD, UV-Vis, FTIR, Zeta potential             | 124 (DLS)                  | Spherical, interconnected      | Photocatalytic degradation activity | [46] |
| 6  | *Hibiscus rosa sinensis* (shoe black plant), flower | XRD, SEM, FTIR                                         | 7 (XRD)                    | Spherical, dispersed, aggregated | Antibacterial activity             | [47] |
| 7  | *Catharanthus roseus*, leaf      | XRD, FTIR, SEM, AFM                                    | 100 (XRD - cubic)          | Irregular, uneven and clustered | Antiparasitic activity             | [48] |
|    |                                 |                                                       | 25-110 (SEM)               |                                |                                    |      |
| 8  | *Curcuma longa* (turmeric), leaf | AFM, UV-VIS, XRD, SEM                                  | 43.08-92.6                 | Spherical                      | Reduced fungal growth, pathogenicity and spores | [31] |
| 9  | *Echinacea purpurea*, leaf       | UV-VIS, SEM, TXRF, FTIR                                | 120                        | Spherical, agglomerated, poorly dispersed | -                                  | [49] |
| 10 | *Vigna radiate*, seed            | FTIR, SEM                                             | -                          | Oval                           | Antibacterial activity             | [45] |
| 11 | *Cassia fistula*, leaf           | UV-Vis, XRD, FTIR, AFM                                 | crystalline, cubic         | Nearly spherical, agglomerated | Antibacterial activity             | [50] |
| 12 | *Citrus limon*, leaf             | FTIR, FESEM-EDS                                        | -                          | Irregular shape                | Antibacterial activity             | [51] |
| 13 | *Aloe barbadensis mill*, leaf    | UV-Vis, SEM, HRTEM, FESEM, EDS, FTIR, XRD, Raman spectra | 20-50 (SEM)                | Spherical, polydispersed       | Biofilm                            | [39] |
| 14 | *Aloe vera*, leaf                | TEM, XRD, SEM, PSA, TG/DTA                             | 20 (XRD – tetragonal)      | Irregular shape                | -                                  | [40] |
|    |                                 |                                                       | 32 (PSA)                   |                                |                                    |      |
|    |                                 |                                                       | 60-80 (SEM)                |                                |                                    |      |
| No. | Plant Species | Leaf | Characterization | Activity |
|-----|---------------|------|------------------|----------|
| 15. | *Jatropha curcas* L | Leaf | UV-Vis, FESEM, EDS, FTIR, XRD, DLS, BET, BJH | Spherical | Wastewater treatment, Photocatalytic activity |
| 16. | *Tinospora cordifolia* | Stem | XRD, SEM, UV-Vis | Irregular shape | Photocatalytic activity |
| 17. | *Morinda citrifolia* (M. citrifolia) | Leaf | XRD, FTIR, UV-Vis, DRS, UV-Vis, Raman spectroscopy, SEM, EDX | Spherical (SEM) | Antibacterial activity, Antimicrobial activity |
| 18. | *Ageratina altissima* | Leaf | UV-vis, FTIR, XRD, FESEM, EDX | Spherical | Photocatalytic activity |
| 19. | *Calotropis gigantea* (Crown flower), flower | XRD, FTIR, SEM, EDX | 60-100 (polycrystalline) | Spherical, oval, aggregated | Acaricidal activity |
| 20. | *Solanum trilobatum* (purple fruited pea eggplant), leaf | XRD, FTIR, SEM, EDX, AFM | 8-10 (XRD), 160-220 (SEM) | Spherical, oval, aggregated, uneven | Antiparasitic efficacies, Larvacidal and pediculocidal activities |
| 21. | *Euphorbia heteradena* Jaub, root | UV-Vis, XRD, TEM | 20 ± 3 | Spherical, rutile | - |
| 22. | *Eclipta prostrata* L (False daisy), leaf | FESEM, FTIR, XRD, AFM | 36-68 (XRD) | Spherical, quite polydispersed | - |
| 23. | *Euphorbia prostrata*, leaf | TEM, XRD, FTIR, GC-MS | 83.22 (XRD) | Spherical, quite polydisperse | Antileishmanial activity |
| 24. | *Jatropha curcas*, latex | TEM, SAED, XRD, FTIR, EDAX | 25-50 (TEM), >50 (irregular shape) | Spherical and uneven | Biotechnology, environmental, biomedical and electronic systems |
| 25. | *Mangifera indica* L, leaf | Leaf | UV-Vis, FTIR, XRD, AFM, SEM, TEM | Spherical, oval | Larvicidal activity |
| 26. | *Psidium guajava*, leaf | XRD, FTIR FESEM, EDX | 32.58 (XRD) | Spherical, cluster (FESEM) | Antibacterial and antioxidative activity |
| 27. | *Glycosmis cochinicensis*, leaf | XRD, UV-Vis, FTIR, SEM–EDS, TEM | 40 ± 5 | Spherical | Antibacterial activity |
| 28. | *Annona squamosa* peel | EDS, UV-Vis, TEM, SEM, XRD | Polydisperse and spherical clusters | Bio therapeutic, bioengineering and electronics |
| 29. | *Aloe vera* gel | XRD, FTIR, UV-Vis, DRS, AFM | Spherical | Photocatalytic activity | 23 ± 2 (XRD – tetragonal) | 80-90 (PSA) |

References: [33], [61]
4. Mechanism of biosynthesized TiO$_2$ nanoparticles

Researchers have given attention on the detection, characterization of biomolecules as well as biomolecules mechanisms involved in the biosynthesis. But yet at the present time, the actual mechanism of biosynthesized nanoparticles by plant extract is still not clear however many studies proved that biomolecules compounds such as alkaloids, polysaccharides, alcoholic and phenolic compounds in plant materials could be involved in formation, stabilization and bioreduction of the nanoparticles [11], [20]. Many research study also suggests that in synthesizing nanoparticles, different plant species exhibit different mechanisms [21]. Reducing capacity of plants and reduction potential of ions can affect the production of nanoparticles which depend on the biomolecules presence in plants. For example, Nasrollahzadeh and Sajadi [56] have determined a possible mechanism of bioreduction of titanyl hydroxide illustrated in Figure 5. At first, they carried out FTIR analysis to identify the biomolecules present. As a result, they found, it was confirmed that the hydroxyl groups of phenolics in _E_. _heteradena_ Jaub root extract is responsible for TiO(OH)$_2$ reduction and also as capping ligands to the surfaces of the nanoparticles. Furthermore, the FT-IR data shows demonstrative differences in the location and shape of signals indicate that there is interaction with involved sites of phytochemicals in the biosynthesis process thus revealed that polyphenolics might be adsorbed on the surface of the nanoparticles.

It has been reported that biomolecules components such as flavonoids, alkaloids, polyphenols, terpenoids, heterocyclic compounds, and polysaccharides have significant roles in reduction, stabilization as well as capping agent of highly monodisperse nanoparticles as well as preventing their aggregation [47]. It has been reported that these biomolecules could coat and cap the nanoparticles thus lead to a synergistic effect in biomedical applications [79]. For instance, Rajkumari et al. [39] showed that carboxylic acids of the major phytocompound of Aloe vera leaf extract represented by the broad OH stretch in FTIR analysis which also indicate the presence of terpenoids, flavonoids and proteins could assist in forming and fabrication of the biosynthesized TiO$_2$ nanoparticles thus acts as capping and reducing agent in the biosynthesis process. The same result was obtained by Sankar et al. [46] using _Azadirachta indica_. A study research by Pratap et al. [41] showed the presence of hydroxyl group in _Jatropha curcas L._ indicating that the surface of the biosynthesized TiO$_2$ nanoparticles was capped by the presence of phenols or polyphenolic tannins. They also proved the evidence of biosynthesized process by revealed a significant absorption peak at 336 nm in the range 200 to 800 nm. The proposed reaction mechanism can be seen in Figure 6. Moreover, Nithya et al. [61] have reported that stretching vibration of hydroxyl group and amino groups present in alcohols, phenols and amines was observed in FTIR spectrum thereby confirming the existence of TiO$_2$ in biosynthesis by biomolecule attachment using aloe vera extract.

Roopan et al. [33] has showed possible mechanism of TiO$_2$ nanoparticles formation where hydroxyl group from the _A. squamosa_ aqueous peel extract serves as catalyst in the reaction. Here, titanyl hydroxide, TiO(OH)$_2$ was hydrated to produce TiO$_2$ nanoparticles by heating it with the extract at 60 °C. They also reported that hydroxyl functional group from water soluble compounds are responsible for the TiO$_2$ nanoparticles stabilization as shown in the pathway. Future investigations might focus on the optimization of reaction conditions for high amounts of biomolecules involved in the production process as well as the stabilization of biosynthesized nanoparticles. Although there is no specific information/ explanation (biochemically elucidated) on the biochemically mechanism, there is no doubt that those biochemical molecules significantly involved in the reduction, stabilization process reaction as well as great capping agent. Thus, by understanding the processes will help improvement of the nanoparticles productivity and accumulation capacity.
Fig. 6. (A) General mechanism for biosynthesis of TiO₂ nanoparticles; (B) Chemical structures of some compounds of plant extracts.

Fig. 7. Possible reaction mechanism of bioreduction of titanyl hydroxide to TiO₂ nanoparticles. Adapted from Nasrollahzadeh and Sajadi [56].
5. Applications of biosynthesized TiO$_2$ nanoparticles using plant extract

The use of materials in biosynthesis of TiO$_2$ nanoparticles such as plant extract (flower, seed, leaf, peel etc.) provide compatibility and eco-friendliness benefits for pharmaceutical, biomedical, as well as other applications as they can minimize the use of toxic and harmful chemicals. They also have superior photocatalytic oxidation properties that attracted great interest for water and waste water treatment. Some stabilized biosynthesized TiO$_2$ nanoparticles discussed before also can be useful for remediation of pollutant [11]. The reactive superoxide and hydroxyl radicals generated by TiO$_2$ under UV light help
to degrade toxic as well as organic pollutants present in the water such as bacteria, viruses and other inactive microorganisms [80]. In this review, we try to discuss some potential applications that use biosynthesized TiO$_2$ nanoparticles using plant-mediated materials based on the applications listed in Table 2.

5.1. Biomedical application

There are several published reports on antibacterial activity effects of biosynthesized TiO$_2$ nanoparticles using various plant extract such as leaf, seed, stem and flower part. For example, biosynthesized TiO$_2$ using *Cynodon dactylon* leaf extract exhibited a good antibacterial activity against gram–negative bacteria as reported by Hariharan et al. [45], using agar well diffusion method. They found a trend where activity of bacteria increased when TiO$_2$ concentration increased. Nonetheless, only when the inhibition concentration was 10μm, the effect of antibacterial activity was minimum. Stabilized TiO$_2$ nanoparticles by using Hibiscus flower extract prepared by Sahaya et al. [47] is considered to have antimicrobial property against pathogenic bacteria. In comparable with standard antibiotic they also claim that their nanoparticles are efficient for antibacterial activity thus have potential in biomedical applications due to its enhanced stability, surface coatings and dispersibility compare to chemically synthesized TiO$_2$ nanoparticles. The antibacterial activity tested by Swati et al. [50] against pathogenic strains of *Escherichia coli* and *Staphylococcus aureus* shows effective effect through biosynthesized TiO$_2$ using *Cassia fistula*. Besides, an eco-friendly biosynthesis of Titanium nanoparticles using leaf extract of Citrus limon investigated by Farook et al. [51] show interesting finding where they reveal the irregular shape nanoparticles can inhibit the growth of *Escherichia coli* even in low concentration while the growth - inhibitory effects of *Pseudomonas aeruginosa* were mild with Ampicillin as positive control. The obtained result was considered to be effective against clinical pathogen due to the presence of hydroxyl bonds and can be further used in antibiotic drugs.

Biosynthesized TiO$_2$ nanoparticles using plant mediated namely *Cynodon dactylon* are demonstrated not only can show the inhibitory effect on *E. coli* growth, they also can enhance anticancer activity against lung cancer (A549). Cancer has universal properties as tumor cells where they cannot control their own cell proliferation with changes of enzymatic and biochemical parameters Akhtar et al. [81]. So by using controlling agents such as bio-based nanoparticles perhaps the growth of cancerous cell can be regulated with systematic mechanism of cell cycle. Another study by Suman et al. [82] reported that the biosynthesized silver nanoparticles exhibited a strong cytotoxic effect in HeLa cell lines compared to other conventional synthetic drugs. In continuation, recent studies using other biosynthesized nanoparticles shows that nanoparticles derived from plant can potentially control cell growth tumor as free radical formation can be control relatively from the cell. These common free radicals usually damage the function of a normal cell and induce cell proliferation.

Antiparasitic activity of biosynthesized TiO$_2$ nanoparticles has been reported by Velayutham et al. [48] and Rajakumar et al. [55] by using *Catharanthus roseus* and *Solanum trilotubatum* (purple fruiting pea eggplant) leaf, respectively. Velayutham et al. [48] has utilized *Catharanthus roseus* against the adults of hematophagous fly, Hippobosca maculata Leach (Diptera: Hippoboscidae), and sheep-biting louse, Bovicola ovis Schrank (Phthiraptera: Trichodectidae). They prepared concentration ranging from 6.12 to 100 mg/L and 5.0 to 25 mg/L for aqueous plant extracts (TiO$_2$) and synthesized TiO$_2$ NPs, respectively. Within 24h exposure, the dead parasites numbers were counted and mortality percentage from five replicates in average were calculated. As reported by Rajakumar et al. [55] the adulticidal activity of biosynthesized TiO$_2$ NPs using *Solanum* trilotubatum showed maximum activity against P. h. capitii and H. a. anatolicum and larvae of A. subpictus. Base on the result it was conclude that bio synthesized can controls the adult head louse P. h. capitii, larvae of cattle tick H. a. anatolicum,and fourth instar larvae of malaria vector A. subpictus effectively. Other acaricidal and larvicidal activity is reported by Rajakumar et al. [59] using extract leaf of *Mangifera indica L.* against the larvae of Rhipicephalus (Boophilus) microplus, Hyaolves anatolicum anatolicum and Haemaphysalis bispinosa (Acari: Ixodidae), fourth instar larvae of Anopheles subpictus,and Culex quinquefasciatus (Diptera:
Culicidae). All the published report can provide a great excellent by helping in parasite control and widen the biosynthesized nanoparticle based technologies. Lastly, Sundrarajan et al. [43] also demonstrated that their green synthesized TiO2 nanoparticles has superior antimicrobial activity against pathogen namely Staphylococcus aureus, Escherichia coli, Bacillus subtilis, Pseudomonas aeruginosa, Candida albicans, and Aspergillus niger (gram-positive bacteria) by testing their inhibitory activity using agar well-diffusion method.

5.2. Water and wastewater treatment application

Recent eco-friendly nanoproducts available in commercial market with high demand is water purifier, water filter and other home-made products [83]. The material selection using titanium dioxide nanoparticles is preferable in photocatalytic reactions due to their abundance, photostability property as well as affordable in price. They also have excellent photocatalytic ability because of their strong oxidizing power, long-term stability and non-toxic [84]. However, the enriched photocatalytic degradation activity might be influenced by the charge, morphology and size of the synthesized nanoparticles. Organic compounds have been reduced effectively using biosynthesized TiO2 nanoparticles. For example, a study reported by Sankar et al. [46] shows that the colloidal biosynthesized TiO2 nanoparticles using Azadirachta indica (Neem) leaves extract with a mean particle size of 124 nm and a zeta potential of -24 mV have been used to degrade industrially harmful methyl red dye from aqueous solutions under bright sunlight catalytically. Their result also shows that the dye degradation regulated efficiently when the incubation time of titanium dioxide nanoparticles with methyl red solution increased.

Pratap et al. [41] demonstrated a remarkable potential for wastewater treatment where biosynthesized TiO2 nanoparticles using leaf extract of Jatropha curcas was applied in removal of chemical oxygen demand (COD) and chromium (Cr) simultaneous from secondary treated tannery wastewater (TWW). It was shown that the treatment can remove 82.26% and 76.48% of COD and Cr, respectively in a self-designed and fabricated Parabolic Trough Reactor (PTR) during the photocatalytic treatment of wastewater. The adsorption that related to the surface area increased of the biosynthesized TiO2 nanoparticles might be the main reason for Cr removal from TWW. This achievement can provide an alternative to a clean-green treatment solution. Moreover, this study revealed that nanoparticles with pure crystalline anatase phase, high surface area, size in nano and large amount surface hydroxyl groups might increase solar photocatalytic activity. Normally, Jatropha curcas L. leaves is considered as waste material in many Asian countries but they can be find easily, and environmental friendly. Thus, the utilization of the nanoparticles is a very promising approach in wastewater to overcome environmental threats. Maurya et al. [52] used Tinospora cordifolia extract to biosynthesize TiO2 nanoparticles to enhance photocatalytic activity of plant extract/TiO2 composites. The authors also revealed an enhanced absorption capability by using UV-vis measurements.

Ageratina altissima leaf extract that been used in biosynthesis of TiO2 nanoparticles shows enhanced percentage of decoloring of methylene blue, alizarin red, crystal violet, and methyl orange dyes with 86.79%, 76.32 %, 77.59 % and 69.06 % in percentage, respectively. The results present by Ganesan et al. [53] has indicated clearly that the biosynthesized nanoparticles can be used as an alternative to degrade and remove pollutants released from dyeing and textile industries as well as act as photocatalytic agent for water remediation in future. Nithya et al. [61] reported photocatalytic activity for Rhodamine B dye and the % of decolourization was effective for biosynthesized TiO2 nanoparticles as compared to TiO2 under visible light irradiation. The authors has been used Aloe vera gel extracts in the biosynthesis of TiO2 nanoparticles.

5.3. Other applications

There has been a great interest towards plant latex based strategies for nanoparticles fabrication in emphasizes to develop an economical and simple synthesis routes. Candidate such as Jatropha curcas can be considered as alternative facile approach for biosynthesis of TiO2 nanoparticles in the electronic production of photo electrochemical energy as reported by Hudlikar et al. [58]. A research study by
Abdul Jalill et al. [31] discussed that their biosynthesized TiO2 nanoparticles can give agronomical impact where they found out that fungal and spores were reduced more effectively by biosynthetic TiO2 nanoparticles using *Curcuma longa* aquatic extract (turmeric) compare with industrial synthetic nanoparticles. Their purpose is to investigated the effect of biosynthesized TiO2 nanoparticles using *Curcuma longa* aquatic extract on the growth, sporulation, pathogenicity of *Fusarium graminearum* and some wheat plants parameters and compare them with standards industrials nanoparticles. Their study is in agreement with the results of Abdul Jalil and Yousef [85] who agreed that the use of industrial TiO2 nanoparticles (50 nm of anatase shape) can increase the number of total chemical compounds in leaves plant thus give negative effect on the percentage of germination, rate of germination and the length of root and shoot. In addition, wheatgrass seeds that exposed to high concentration of TiO2 nanoparticles (80 ppm) can lead to diminished germination rate [86]. It is well mentioned that the effects of nanoparticles on plant growth strongly depends on the synthesis methods of nanoparticles where concentration, shape, size, chemical and physical properties of the nanoparticles can be altered. [87,88].

6. Concluding remarks
This review highlights the characterization and mechanism of TiO2 nanoparticles via biosynthesis method and their potential in biomedical, water and wastewater treatment as well as in other application. This review also discusses the characteristic such as size, morphology of the nanoparticles that related to the procedures and properties of the materials. Plant related materials has been proved to be a good reducing, stabilizing as well as capping agent for facile biosynthesis of TiO2 nanoparticles. In fact, they contain active compound that can enhanced properties of the nanoparticles with controlled shapes and sizes. By comparing to conventional methods, several studies confirm that nanoparticles produced via biosynthesis route using natural resources has great advantages such as are less toxic contaminants, less of subsequent complex chemical synthesis, environmental friendly, cost effective and stable nanoparticles production with controlled shapes and sizes. Therefore, much effort is being made to implement biological synthesis methods with these proven advantages.

To achieve the sustainability of nanoparticles biosynthesis and improvement of nanoparticles stability, focus is needed and more research need to be done to explore potential local and common natural resources available even though they are still at early stages, and considerable research is needed in this direction. Utilization of local resources will reduce their development cost that can lead to economically competitive with conventional methods as an alternative to the large-scale of nanoparticles production. As prerequisite to the success of this new technology, understanding the biomolecule binding mechanisms involved is a must as it brings significantly benefit to biomedical field. However, there is no clearly described on the mechanism of the biosynthesis therefore there is a need to explore the phytochemistry behind the biosynthesis. The lack of knowledge of the underlying mechanisms, the chemical components responsible for the synthesis and the nanoparticles stabilization remain as open challenge in taking benefits of natural resources such as plants for the nanoparticles synthesis. The mostly challenge faced in biosynthesis of nanoparticles is the separation of the nanoparticles from the biological material and contamination from biological cells that could lead to adverse effect in biomedical application. Therefore, it is important to understand which active groups are involved and how functional groups from the natural resources attach to the nanoparticle surface, that can produce nanoparticles with higher efficacy especially in terms of biocompatibility and bioavailability of nanoparticles. In conclusion, green technology through biosynthesis as described in this paper, provide outstanding findings that perhaps encourage researchers and newcomers to continue and extend the exploration of possibilities offered by nature and the design of innovative and safer methodologies towards the synthesis of nanomaterials, possessing desired features and exhibiting valuable properties that can be exploited in a profusion of fields.

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