Green Synthesis and Characterization of TiO_2 Nanoparticles Using *Aloe Vera* Extract at Different pH Value

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ABSTRACT
The use of plant extracts for metal oxide nanoparticles synthesis has been extensively studied as a safer alternative to ordinary methods. The present work focused on the synthesis and characterization of Titanium dioxide nanoparticles (TiO_2NPs) by eco-friendly green synthesis method. The green synthesis was conducted at room temperature at different pH values (acidic, neutral, and basic) using Titanium tetrachloride ($TiCl_4$) as a precursor and *Aloe Vera* leaves extract as a reducing agent to avoid the use of hazardous chemicals. The characterization of TiO_2NPs was carried out by UV-visible spectrophotometry, Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD) and high-resolution transmission electron microscope (HRTEM). The influence of pH on the crystalline phase and size of the TiO_2NPs was also studied. The results revealed that, the maximum absorption of acidic, neutral, and basic TiO_2NPs were in the UV region at 318, 326 and 320 nm respectively. The synthesized nanoparticles were spherical in shape and highly pure. Formation of TiO_2NPs was further confirmed by FTIR spectrum showed characteristic peaks of Ti-O and Ti-O-Ti vibrations at 555 cm^{-1} and 1383 cm^{-1}, respectively. The average particle size of the acidic, neutral and basic TiO_2NPs was 22.86±0.85, 15.83±0.902 and 13.3±0.68 nm, respectively. Basic TiO_2NPs were composed of only one crystalline phase (anatase), neutral TiO_2NPs composed of a mixture of anatase and rutile phases while acidic TiO_2NPs composed of a mixture of anatase, rutile, and brookite phases. Basic TiO_2NPs exhibited the smallest particle size with the purest crystalline phase, therefore, they are favored for further biomedical applications.

Key Words: *Aloe Vera* leaves extract, green method, metal oxide nanoparticles, x-ray diffraction

INTRODUCTION
Nanotechnology is a rapidly growing field that deals with nano-sized particles and their wide applications in almost all the fields of sciences especially biology and pharmacology (Wang *et al*., 2010; Subhapriya and Gomathipriya, 2018). Recently, there is a great interest in developing novel techniques for synthesis inorganic metal oxide nanoparticles as they were proved to have beneficial applications in physical, chemical, biological, medical, optical, mechanical and engineering sciences (Kumar *et al*., 2015). Titanium dioxide (TiO_2), also known as titania, is a white color, poorly soluble, non-flammable and thermally stable metal oxide. It is not classified as hazardous according to the United Nations (UN) Globally Harmonized System (GHS) of Classification and Labeling of Chemicals (Mishra, 2014). Moreover, it is known to be excellent photocatalyst, disinfector and antiseptic (Ju *et al*., 2013; Kotta *et al*., 2018). Titanium dioxide nanoparticles (TiO_2NPs) have attracted great attention owing to their unique optical properties, low toxicity, high chemical stability, low cost and excellent biocompatibility (McNamara and Tofail, 2017). They are one of the most important materials for cosmetics, paints, plastics, papers, inks, food coloring, toothpaste and pharmaceuticals (Santhoshkumar *et al*., 2014). TiO_2 exists in three different phases in the nano range at different temperatures, such as anatase, rutile, and brookite. Both anatase and rutile have a tetragonal crystal structure, while brookite has orthorhombic structure (Mohan *et al*., 2013).
Several methods have been employed

to synthesis TiO_2NPs including physical methods such as low-pressure gas evaporation method, a sputtering method, plasma method, high energy ball milling, and chemical methods such as oxidation-reduction method, laser synthesis, hydrothermal and sol-gel method. However, these methods are potentially hazardous, costly and require high pressure and high energy (Alavi and Karimi, 2017). The green synthesis approach, a technique which involves the use of plant extracts, has been developed as an eco-friendly, economical, safer, non-toxic and simpler route of synthesis that is suitable for large scale production. Furthermore, this technique doesn't require high pressure, high temperatures, costly equipment or hazards chemicals, consequently, it could overcome the drawbacks of physical and chemical methods (Sundrarajan *et al*., 2017). Various plant extracts have been proved to be potential reducing agents, therefore, they could be successfully involved in the green synthesis of TiO_2NPs (Sivaranjani and Philominathan, 2016).

Aloe Vera, a plant belongs to succulent species, was used since the earlier centuries as a medicinal plant. It is a short stemless plant growing to 60-100 cm tall with very characteristic fleshy, thick leaves (Yuvasree *et al*., 2013). *Aloe Vera* contains a variety of vitamins (such as vitamin A, vitamin C, vitamin B12 and vitamin E), folic acid, various amino acids, enzymes, minerals, and sugars. Moreover, *Aloe Vera* leaves extract contains many water-soluble substances like Aloe emodin and many active constituents as lignin, hemicellulose, pectin which enable it to act as reducing agents (Surjushe *et al*., 2008). It has been used before as a reducing agent to produce gold and silver nanoparticles (Chandran *et al*., 2006; Tippayawat *et al*., 2016). Accordingly, *Aloe Vera* leaves extract was selected in this study as a reducing agent for green synthesis of TiO_2NPs from the precursor. The effect of pH of the media on the nanoparticle formation has been evaluated.

MATERIALS AND METHODS

Materials

Titanium tetrachloride ($TiCL_4$), purity≥99%, Hydrochloric acid (HCL) and Ammonium hydroxide (NH_4OH) were purchased from Merck. All chemical reagents were of analytic purity and used directly without further purification.

Methods

Preparation of *Aloe Vera* leaves extract

Healthy Leaves of *Aloe Vera* were collected from the botany department, Faculty of Science, Zagazig University, Egypt, and washed twice with tap water followed by distilled water to remove dust particles and other contaminants. Twenty-five g of the leaves were added to 100 ml distilled water and boiled for 2h at 90°C. The extract was purified by filtration using Whatman No.1 filter paper. The filtrate was stored for the synthesis of nanoparticles.

Green synthesis of TiO_2NPs

TiO_2NPs were prepared using $TiCL_4$ as a precursor. Briefly, 100 ml leaves extract was added dropwise to a 100 ml 1.0 N $TiCL_4$ solution in deionized water. The mixture was kept under constant stirring for 4h at room temperature, then divided into three different beakers with three different pH values: acidic ($pH<1$), neutral ($pH=7$) and basic ($pH=9$), respectively. The desired pH values were adjusted by adding NH_4OH and HCL. The obtained white suspension was filtered using Whatman No.1 filter paper to separate the formed nanoparticles which then washed with double distilled water repeatedly to remove the by-products and finally dried at 100°C overnight. The obtained dry powder was further calcined at 500°C for 4 hours to decompose all biomolecules at such high temperature were only the stable metal oxide nanoparticles are retained (Sundrarajan *et al*., 2017). The steps of green synthesis are illustrated in Fig. 1.

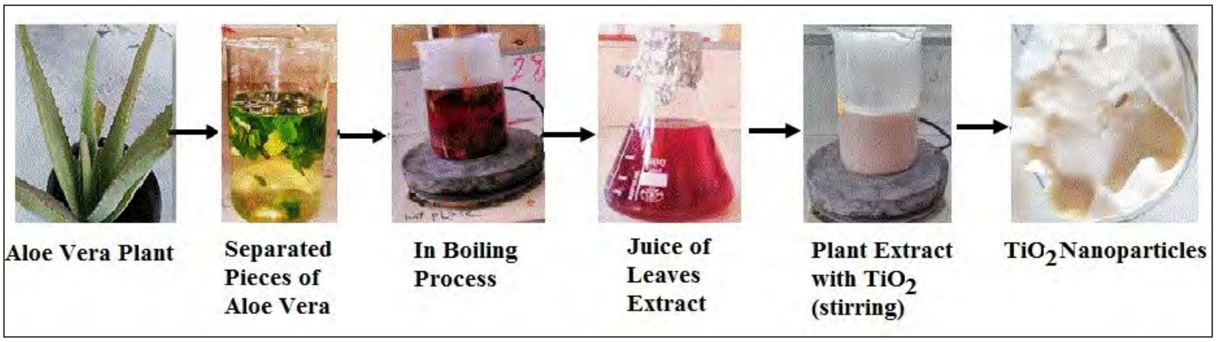

Fig. 1 Diagrammatic scheme for green synthesis of TiO_2NPs using Aloe era leaves extract

Characterization of TiO_2NPs

Formation of TiO_2NPs under acidic, neutral and basic pH values was assessed by UV-visible spectrophotometry which used to characterize the optical properties of the prepared particles. It was carried out using a double beam spectrophotometer (Ray Leigh UV-2601, USA) in the range of 200-600 nm. X-ray diffraction (XRD, Philips analytical) was applied to the three prepared samples in order to identify the crystal phase and to estimate the average particle size as well. It was done using CuKα-radiation (λ=0.154 nm), 2θ in the range of 10°- 80°. The morphology of the prepared particles was examined by high-resolution transmission electron microscopy (HR-TEM AR-TEM, Tecnai G20, FEI, Nether land). Diluted samples were wetted on a carbon-coated copper grid and left to dry before the analysis. Fourier transform infrared (FTIR) spectra were carried out in wave number range of 4000 to 400 cm^{-1} using IR spectrometer [JASCO model (FT/IR–4100 type A)] to record chemical bonds and the functional groups of the synthesized nanoparticles.

RESULTS AND DISCUSSION

UV-visible spectrophotometry

The absorption spectra of the acidic, neutral and basic TiO_2NPs showed maximum absorption in the UV region at 318, 326 and 320 nm as illustrated in Fig. 2 A, B, and C, respectively. Several previous studies have reported that the maximum absorption of TiO_2NPs was at UV region but at different wavelengths. The maximum absorption of TiO_2NPs that synthesized using *Trigonella Foenum* leaves extract was at 400 nm (Subhapriya and Gomathipriya, 2018), while those synthesized using *Echinacea purpurea* Herba extract showed maximum absorption at 280 nm (Dobrucka, 2016). These differences may be attributed to the sensitivity of the UV spectrum to many factors such as shape, size, and agglomeration of the particles.

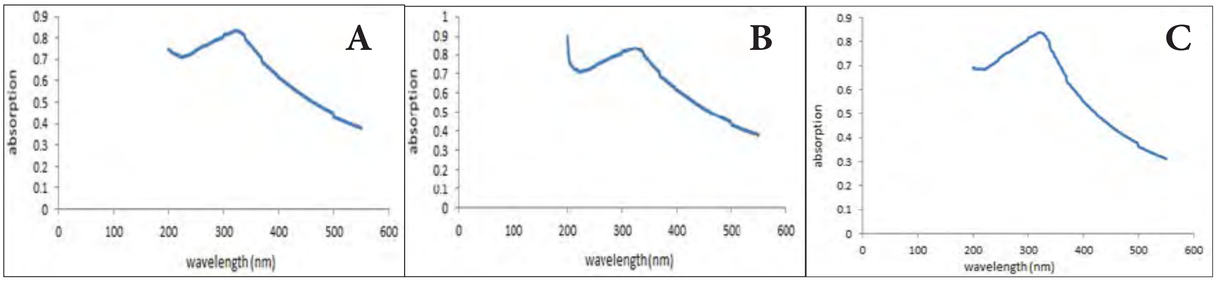

Fig. 2 UV-visible spectrum of TiO_2NPs: A) synthesized at acidic pH, B) synthesized at neutral pH, C) synthesized at basic pH

X-Ray Diffraction (XRD)

XRD pattern of TiO_2NPs prepared by green synthesis using *Aloe Vera* leaves extract at acidic, neutral and basic pH are illustrated

Fig. 3A, B and C, respectively. It is obvious that the pattern of acidic TiO_2NPs exhibited eight distinct sharp diffraction peaks (marked with A) at 25.4°, 37.98°, 48.06°, 54.03°, 55.19°, 62.84°, 68.89°, and 75.23° of the tetragonal anatase phase of TiO_2 (Anatase XRD JCPDS card number No.78-2486). These peaks dominated over the rutile phase (a weak diffraction peak at 2θ=27.45° and marked with R) and brookite phase (a weak diffraction peak at 2θ=31.93° and marked with B). XRD pattern of neutral TiO_2NPs (Fig. 3B) exhibited intense eight diffraction peaks at 25.08°, 25.33°, 37.88°, 48.05°, 53.84°, 55.08°,62.50°, and 75.09° of the tetragonal anatase phase of TiO_2 (Anatase XRD JCPDS card number No.84-1285) and a weak diffraction peak of rutile phases at 2θ=36.86. XRD pattern of basic TiO_2NPs (Fig. 3C) showed only six diffraction peaks at 25.26°, 36.98°, 48.98°, 53.88°, 54.95°, and 62.62° of the tetragonal anatase phase of TiO_2. XRD measurements revealed that the prepared TiO_2NPs were characterized by high purity as indicated by the sharpness of the peaks and the absence of unidentified peaks.

The average particle size was calculated by Scherrer's equation on the anatase phase (the most intense peaks), brookite and rutile phases (weak diffraction peaks) as following:

$D=K\lambda/(\beta \cos \theta)$ (Oskam *et al*., 2003)

Where D is crystalline size, λ is the wavelength of X-ray (1.54 Å), β is full-width half maxima, θ is diffracting angle, and K is shape factor (0.9). The average size estimated for acidic, neutral and basic TiO_2NPs was 22.86±0.85, 15.83±0.902, and 13.3±0.68 nm, respectively (data are represented as mean ± standard deviation, n=3). It is clear that as the pH increases the particle size decreases. In all pH values, the TiO_2NPs exhibited nanoparticle size that is favorable for biomedical applications.

Based on XRD measurements, basic TiO_2NPs exhibited the smallest size and composed of only one crystalline phase (anatase phase) while acidic and neutral TiO_2NPs were composed of a mixture of phases. Few previous studies have studied the effect of pH on the green synthesis of TiO_2NPs. Dobrucka (2016) studied the effect of pH on green synthesis of TiO_2NPs from *Echinacea purpurea* Herba leaf extract, and reported that basic pH has facilitated the formation of TiO_2NPs.

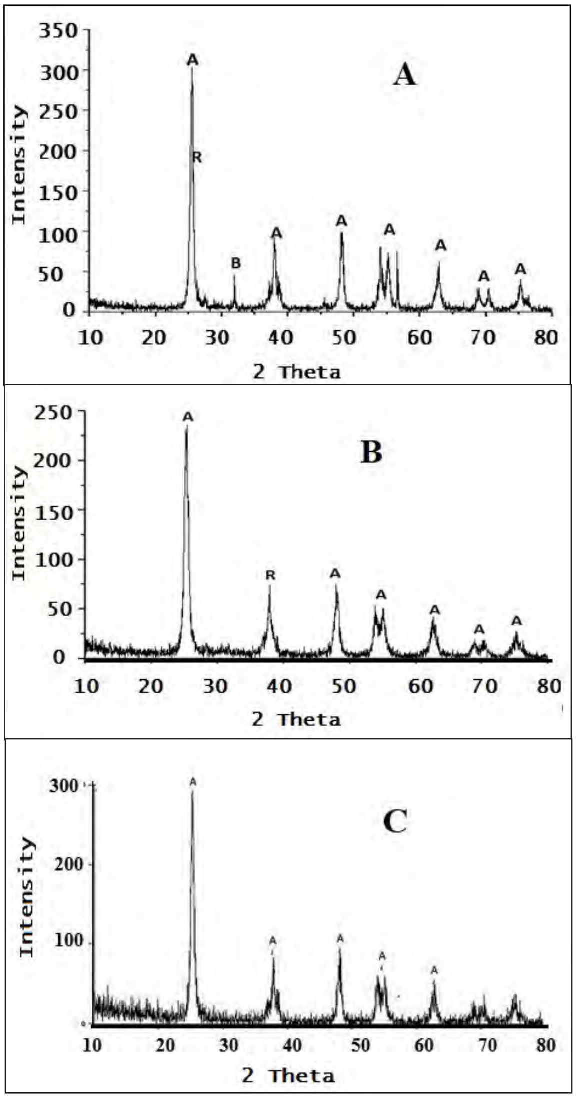

Fig. 3 XRD patterns of TiO_2NPs: A) synthesized at acidic pH, B) synthesized at neutral pH, C) synthesized at basic pH.

High-resolution transmission electron microscope (HR-TEM)

The morphology, structure arrangement and diameter of the particles were observed by HR-TEM. TEM images of acidic, neutral, and basic TiO_2NPs were illustrated in Fig. 4A, B, and C, respectively. The TEM image revealed spherical particles with no aggregates. The average particle size estimated for acidic, neutral, and basic TiO_2NPs was about 22.615.8±0.826 ,1.81±, and 13.3±0.351 nm, respectively which is in a good agreement with XRD results.

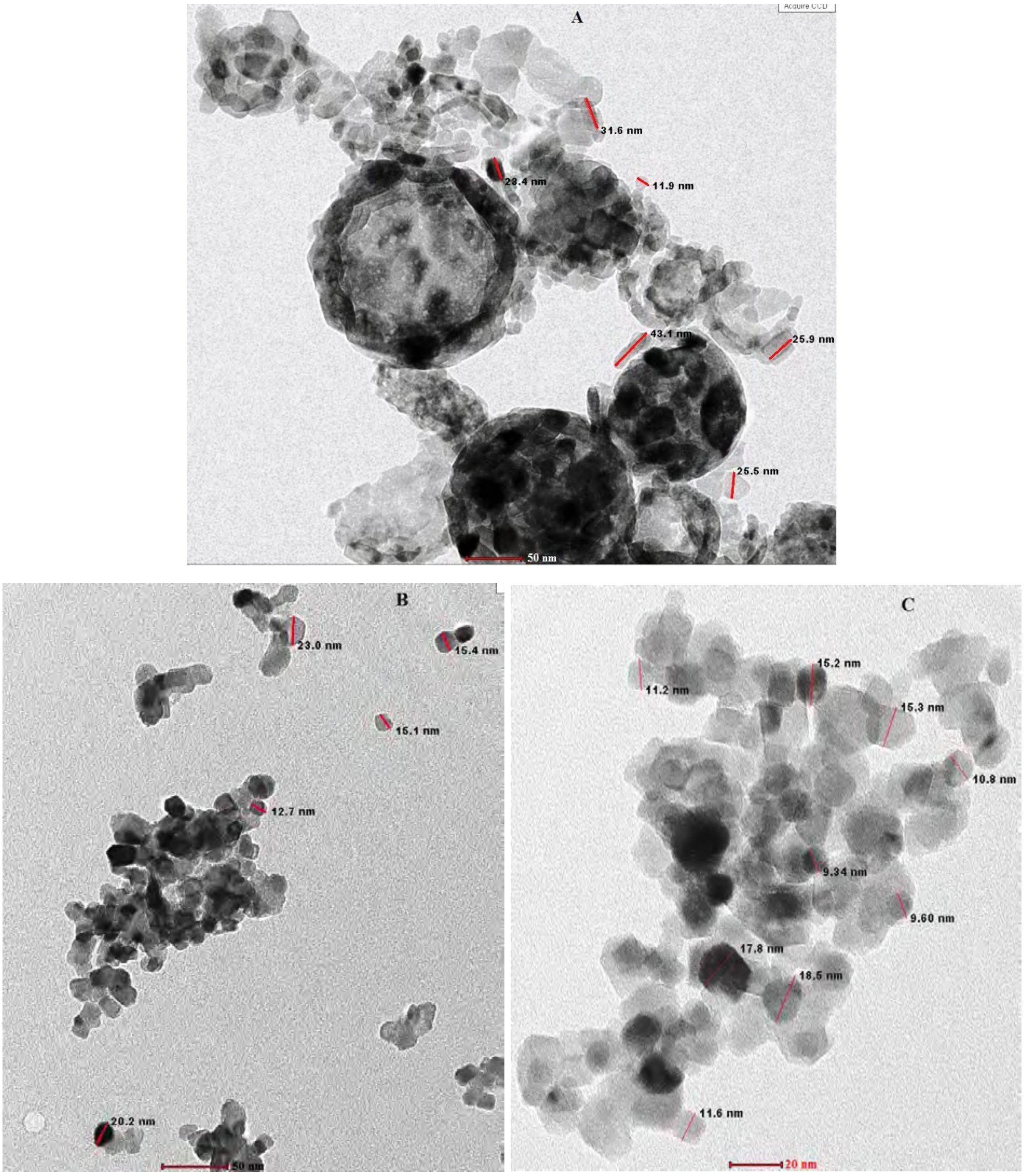

Fig. 4 TEM images of TiO_2NPs: A) synthesized at acidic pH, B) synthesized at neutral pH, C) synthesized at basic pH.

Fourier Transform Infrared (FTIR) Spectroscopy

The infrared spectrum of the basic TiO2 NPs (Fig. 5) showed peak at 555 cm^{-1} which is characteristic of Ti-O stretching vibration that confirms the formation of metal oxygen bonding. The peak at 1383 cm^{-1} is characteristic to the stretching vibrations of Ti-O-Ti. The peaks centered at 3435 cm^{-1} and 1631 cm^{-1} are the characteristic of the stretching and bending vibration of hydroxyl groups and the adsorbed water molecules on

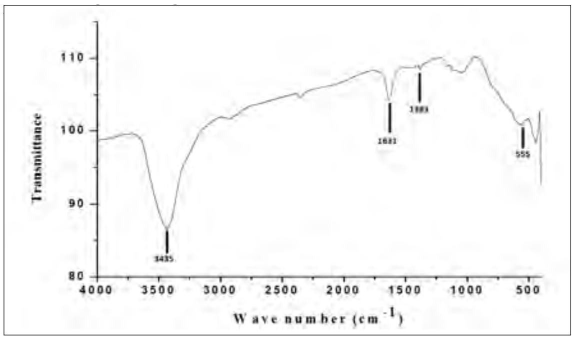

Fig. 5: FTIR spectrum of basic TiO_2NP

CONCLUSION

The TiO_2NPs were successfully synthesized using a green synthesis method at different pH values using *Aloe Vera* leaves extract as a reducing agent and $TiCL_4$ as a starting material. The formation of the nanoparticles was confirmed by UV-spectrophotometry, XRD, and TEM. The influence of pH on the prepared particles was also evaluated. All the prepared particles were characterized by high purity, particle size, and spherical shape with no aggregation. The particle size and crystalline phases of the prepared TiO_2NPs were influenced by the pH of the precursor solution. XRD analysis pointed out that basic pH (pH = 9) is favored for green synthesis of TiO_2NPs using *Aloe Vera* leaves extract, as it resulted in the smallest particle size and the purest crystalline phase. The present work proves that biosynthesis of TiO_2NPs using *Aloe Vera* leaves extract is an environmentally friendly technique that is cost-effective, time-saving, and results in the formation of particles in a nano-size range that can be further used in various biomedical applications.

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تصنيع وتوصيف جسيمات ثنائي أوكسيد التيتانيوم النانومترية بالطريقة الخضراء باستخدام مستخلص أوراق الصبار عند قيم مختلفة من الأس الهيدروجيني

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الملخص

جسيمات ثنائي أوكسيد التيتانيوم النانوية كانت محور العديد من التطبيقات الواعدة نظرًا لخواصها الفريدة، وقلة التكلفة، وتوافرها، وتوافقها الحيوي. في الآونة الأخيرة تمت دراسة استخدام المستخلصات النباتية لإنتاج جسيمات أوكسيد النانو المعدني على نطاق واسع كبديل أكثر أمانًا للطرق الفيزيائية والكيميائية العادية. هذه الدراسة توضح تقنية بسيطة وآمنة ومنخفضة التكلفة وصديقة للبيئة لإنتاج جسيمات ثنائي أوكسيد التيتانيوم النانوية بالطريقة الخضراء. تم تحضير مسحوق جسيمات ثنائي أوكسيد التيتانيوم النانوية البلورية بدرجة حرارة الغرفة باستخدام رباعي كلوريد التيتانيوم كمادة أولية ومستخلص أوراق الصبار كعامل اختزال عند قيم مختلفة من الأس الهيدروجيني (حامضي، متعادل، قاعدي). وتم توصيف الجسيمات النانوية بجهاز الطيف الضوئي المرئي للأشعة فوق البنفسجية لقياس أقصى امتصاص لجسيمات ثنائي أوكسيد التيتانيوم النانوية مختلفة الأس الهيدروجيني (حامضي، متعادل، قاعدي) عند 318 & 326 ,330 نانومتر على التوالي، وجهاز حيود الأشعة السينية لمعرفة التركيب الطوري، والمجهر الإلكتروني النافذ عالي الدقة لدراسة الشكل وترتيب الهيكل وقطر الجسيم. وضحت النتائج أن جسيمات النانو المحضرة كروية الشكل عالية التبلور ونقية. هذا البحث يوضح تأثير الأس الهيدروجيني على الطور والحجم البلوري لجسيمات ثنائي أوكسيد التيتانيوم النانوية. لوحظ أن متوسط الحجم البلوري لجسيمات النانو وفقا للأس الهيدروجيني (حامضي، متعادل، قاعدي) هي 22.86±0.85 & 15.8±0.902 ,13.3±0.68 نانومتر على الترتيب. وجد أن جسيمات ثنائي أوكسيد التيتانيوم في الوسط القاعدي مكونة من الطور البلوري الوحيد (الأناتاس)، بينما في الوسط المتعادل مكونة من (أناتاس، روتايل)، وفي الوسط الحامضي مكونة من (أناتاس، روتايل، بروكيت).

الكلمات المفتاحية: جسيمات ثنائي أوكسيد التيتانيوم النانومترية، الطريقة الخضراء، مستخلص أوراق الصبار.