Highly-Pure Titanium Dioxide nanopowders Synthesized by Eco-Friendly Solvothermal Method

Doha M. Challoob [1]
Mohammed Y. Khdiar [1]
Oday A. Hammadi [2]

[1] Department of Biology, College of Education, Al-Iraqia University, Baghdad, IRAQ
[2] Department of Physics, College of Education, Al-Iraqia University, Baghdad, IRAQ

In this study, titanium dioxide nanopowders were synthesized by solvothermal method using banana peels as a source for plant extract and titanium isopropoxide as a precursor. The structural characteristics confirmed that the synthesized nanopowders have tetragonal crystalline structure containing both anatase and rutile phases of titanium dioxide. These nanopowders showed high structural purity as no materials other than titanium dioxide was found according to the x-ray diffraction (XRD) patterns and Fourier-transform infrared (FTIR) spectroscopy. As well, no elements other than titanium and oxygen were found according to the energy-dispersive x-ray spectroscopy (EDX). The minimum particle size in the synthesized samples was 53.48nm. The spectroscopic characteristics showed that the prepared nanopowders have reasonable absorption in the UV region of electromagnetic spectrum (<375nm) and very low absorption in the visible region. The solvothermal method used in this work can be described by low complexity, simple assembly, low cost and high purity production.

Keywords: Titanium dioxide; Nanoparticles; Solvothermal method; Green synthesis
Received: 13 January 2024; **Revised:** 19 February, **Accepted:** 26 February 2024

1. Introduction

Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology. Their unique size-dependent properties make these materials superior and indispensable in many areas of human activity [1]. Nanomaterials could be defined as a set of materials where at least one dimension is less than approximately 100 nanometers [2]. Nanomaterials are of interest because at this scale, unique optical, magnetic, electrical, and other properties emerge. These properties have the potential for reasonable impacts in photonics, electronics, medicine, and many other fields [2]. Two approaches; bottom–up and top–down, are generally used to synthesize the nanopowders. The bulk materials are divided into small particles by top–down methods. Small particles are aggregates and form nanoscale range crystals throughout bottom–up methods [3]. Top-down methods include high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc. [4]. The bottom–up approach starts from the atomic level and leads to the formation of nanostructures with further self-assembly of the atoms/molecules, whose growth and self-assembly as building blocks leads to the formation of nanomaterials with well-defined size, morphology, and chemical composition. This approach includes chemical, physical and biological methods [5,6]. Chemical methods often allow synthesis of nanoparticles in large quantities. Moreover the possibility of controlling particle size even at nanometer scale is also possible during chemical synthesis of nanoparticles [7]. The chemical methods include oraganometallic chemical route, revere-micelle route, sol-gel synthesis, colloidal precipitation, and hydrothermal synthesis. Physical route or mechanism includes different methods, e.g., gas-phase deposition, electron beam lithography, pulsed-laser deposition or ablation, laser-induced pyrolysis, powder ball milling, reactive sputtering, thermal evaporation, electrodeposition, and aerosol [6]. The biological route includes different methods, e.g., fungi mediated, algae, bacteria mediated, yeast mediated, etc. Nanoparticles made by a biogenic enzymatic process are significantly superior to those made by chemical methods in various aspects. Even though the latter methods can produce large quantities of nanoparticles with a defined size and shape during short time, they are complicated, outdated, expensive, and inefficient, and they generate hazardous toxic wastes that are harmful not only to the environment but also to human health [6] .

Among the many semiconductor materials, titanium dioxide or titania (TiO_2) has been regarded as one of the most relevant for photocatalytic purposes, owing to its exceptional optical and electronic properties. Its high level of photoconductivity, ready availability, low toxicity, inertness (biologically and chemically) and low cost, resistance to photocorrosion, high photocatalytic activity, and biological compatibility [8]. However, the effectiveness of TiO_2 as photocatalyst depends on its crystal phase, impurities, particle size, surface area, crystallinity and other physicochemical parameters that strongly influence charge recombination and electron/hole trapping [9].

Green synthesis employs a clean, safe, cost effective and environmentally friendly process of synthesizing nanomaterials. Microorganisms such as bacteria, yeast, fungi, algae species and certain plants act as substrates for the green synthesis of nanomaterials [10]. Molecules in plants and microorganisms, such as proteins, enzymes, phenolic compounds, amines, alkaloids and pigments perform nanoparticle synthesis by reduction [11-17]. The plant extracts including leaves, roots, flowers, and parks are said to contain many secondary metabolites which act as reducing, stabilizing, and capping agents for the bioreduction reactions in the synthesis of nanomaterials [18-21].

In traditional chemical and physical methods; reducing agents involved in the reduction of metal ions, and stabilizing agents used to prevent undesired agglomeration of the produced nanoparticles carry a risk of toxicity to the environment and to the cell. Besides, the contents of the produced nanoparticles are thought to be toxic in terms of shape, size and surface chemistry. In the green synthesis method in which nanoparticles with biocompatibility are produced, these agents are naturally present in the employed biological organisms [22].

In this work, titanium dioxide nanopowders were synthesized by an eco-friendly solvothermal method using a plant extract (banana peels) and titanium isopropoxide as a precursor. The structural and spectroscopic characteristics of the synthesized nanopowders were determined.

2. Experimental Part

The banana peels and titanium isopropoxide were used as a reference for the plant extract and precursors, respectively. Fresh bananas were taken from the local market and banana peels were cut into small pieces, washed three times with distilled water to remove any contaminants and excrement and dried with drying paper. Then, an 80g of the dried peels were put in a beaker containing 150 mL of deionized water. The mixture was heated up to boiling temperature (100°C) for 20 min. Then, the boiled mixture was filtered twice using filter paper (Whatman No. 1).

An aqueous solution was prepared by solving 1ml of titanium isopropoxide ($C_{12}H_{28}O_4Ti$) in 10ml of deionized water. The aqueous solution is placed on the hotplate stirrer (40°C) for 10 min. Then, 50 ml of the extracted solution of banana peels was added to the aqueous solution as drops while keeping stirring for one hour. The mixture was filtered twice using filter paper (Whatman No. 1) to separate the formed nanopowder. These filtered nanopowder were washed twice with distilled water to remove any residuals from the previous mixing process and reaction step. The separated nanopowder was dried by heating up to 100 °C for 24 hours and bleaching by using (KOH) to remove organic residues stuck on the nanopowders during the preparation process. Figure (1) shows schematically the experimental procedure.

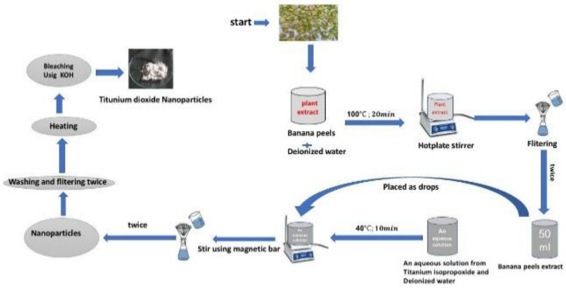


Fig. (1) The experimental procedure used in this work to synthesize TiO_2 nanopowder

The structural characteristics of the synthesized nanopowders were determined by x-ray diffraction (XRD) patterns using a Bruker D2 PHASER XRD system (Cu-Kα x-ray tube with λ=1.54056Å), the surface morphology was determined by an Inspect F50 field-emission scanning electron microscope (FE-SEM), the elemental constitution was determined by energy-dispersive x-ray spectroscopy (EDX), the formation of molecular bonds and their vibrations were determined by Fourier-transform infrared (FTIR) spectroscopy using a SHIMADZU FTIR-8400S instrument, and the absorption spectra were recorded using a K-MAC Spectra Academy SV2100 spectrophotometer in the range of 300-800 nm as the synthesized nanopowder was immersed in a transparent viscous host as a reference.

3. Results and Discussion

Figure (2) shows a photograph of TiO_2 nanopowder sample synthesized in this work by solvothermal method and figure (3) shows the XRD pattern of this sample. Obviously, 21 peaks are seen, which belong all to the TiO_2; 15 of them for anatase (A) phase and 6 for rutile (R) phase. This is why the TiO_2 nanopowder referred to as mixed-phase and tetragonal crystalline structure [23,24]. The formation of rutile phase cannot be avoided even much more care is considered during the formation of nanopowder as heating steps are necessarily required. The crystallite size (D) was determined for all peaks, as shown in table (1), by Scherrer's equation as [24]:

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

where λ is the wavelength of x-rays (1.54Å), 0.9 is a constant, β is the full width at half-maximum (FWHM), which was given by the software of the XRD instrument

Fig. (2) Photograph of TiO_2 nanopowder synthesized by solvothermal method

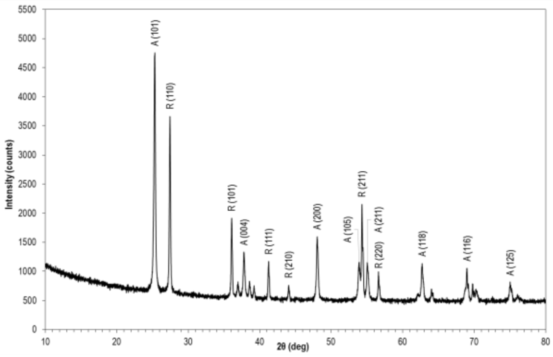


Fig. (3) XRD pattern of synthesized TiO_2 nanopowder

Table (1) Determination of crystallite size for the synthesized mixed-phase TiO_2 nanopowder

Peak no.	2θ (deg)	D (nm)	Phase
1	25.2723	1.23	A
2	27.4066	1.71	R
3	36.0501	1.91	A
4	36.9171	1.29	R
5	37.7662	1.22	A
6	38.5467	1.6	A
7	39.1683	1.85	A
8	41.2124	1.94	A
9	44.0255	2.05	R
10	48.016	1.32	R
11	53.8677	1.11	A
12	54.2986	2.11	R
13	55.0386	1.33	A
14	56.6053	18.6	R
15	62.681	1.23	A
16	64.0264	2.07	A
17	68.9473	1.21	A
18	69.7733	1.99	A
19	70.254	1.06	A
20	75.0219	1.19	A
21	76.0538	0.96	A

Figure (4) shows the FE-SEM image of TiO_2 nanopowder synthesized in this work. The nanopowder sample clearly contains different sizes and the smallest particle size is 53.48 nm, but the difference is not big enough. The sample is considered to be non-uniform. As well, aggregation is apparent, which is unavoidable in any preparation method or technique that includes formation processes based on thermally-activated chemical reactions [23].

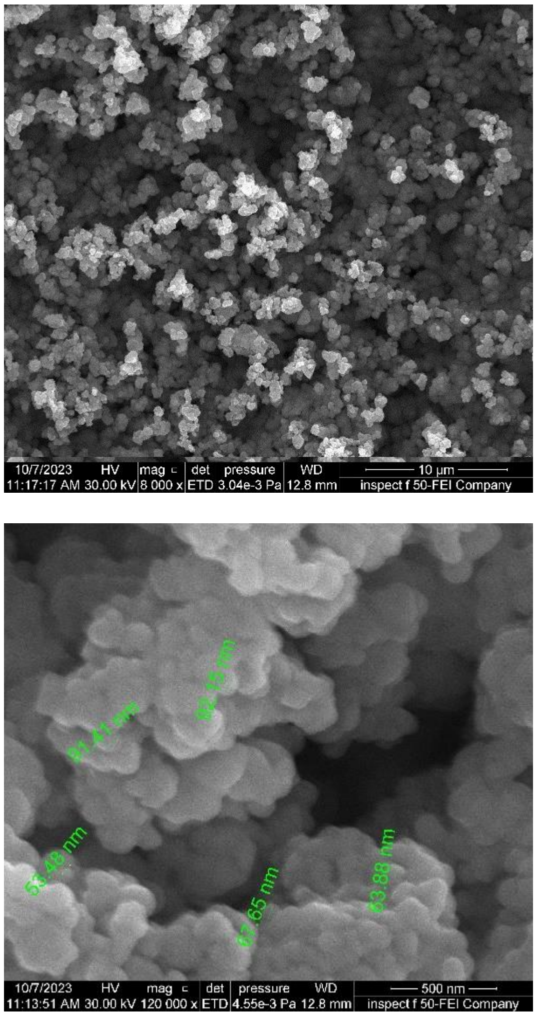
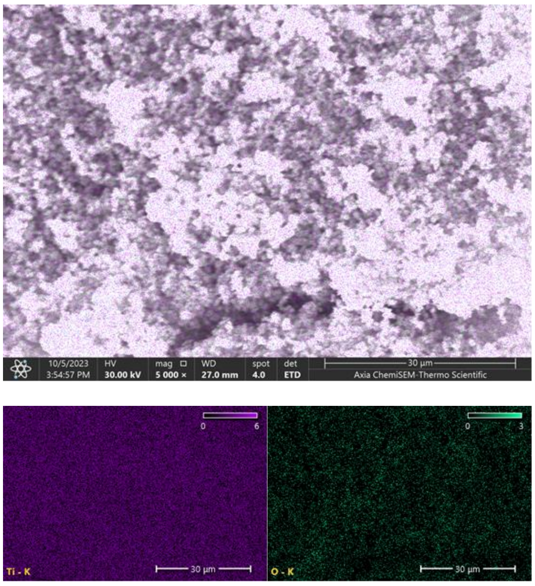


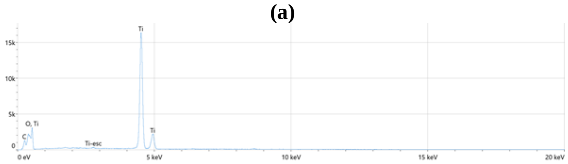
Fig. (4) FE-SEM images of synthesized TiO_2 nanopowder with two different magnification powers

Figure (5) shows the EDX results of the TiO_2 nanopowder synthesized in this work. The color mapping images (Fig. 3a) show that the volume density of Ti atoms is higher than that of O, which is confirmed by the elemental weight analysis (56.7% Ti vs 34.7% O). This can be attributed to the difference in atomic radius between titanium and oxygen. Furthermore, the atomic percentages of both elements (Ti and O) are comparable (29% and 53%, respectively). These results show that the synthesized nanopowder certainly contains stoichiometric TiO_2 compound.

Figure (6) shows the FTIR spectrum of the TiO_2 nanopowder synthesized in this work. There are three distinct peaks centered at 409, 447 and 667 cm^{-1} belonging to the vibrations of the TiO_2 molecules in the TiO_2 lattice; bending, asymmetric and symmetric modes, respectively [25]. As well, two bands at 1620 and 3450 cm^{-1} are clearly seen and they are attributed to the vibration modes of O-H bond. The two possible sources for the OH molecules are (1) the aqueous solution included in the synthesis route, and (2) adsorption of water molecules from the environment when the synthesized sample is exposed to the atmosphere [24,26].



(a)



(b)

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
O	53.2	1.9	34.7	1.2
Ti	29.0	0.1	56.7	0.2
C	17.7	0.4	8.7	0.2

Fig. (5) EDX result of synthesized TiO_2 nanopowder (a) color map distribution, (b) EDX spectrum and elemental analysis table

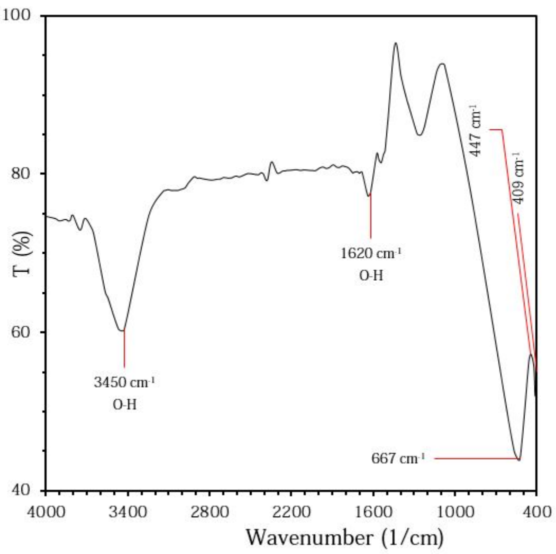


Fig. (6) FTIR spectrum of synthesized TiO_2 nanopowder

Figure (7) shows the UV-visible spectrum of the synthesized TiO_2 nanopowder in the spectral range of 300-800 nm. It is clear that the sample exhibits high absorption in the UV region (<375nm) and very low absorption in the visible and near-infrared (NIR) regions. Such behavior is a characteristic of TiO_2 as its photocatalytic activity is induced by the absorption of UV radiation. Figure (8) shows the determination of energy band gap (E_g) of the TiO_2 nanopowder sample synthesized in this work. The value is about 3.14 eV, which lies in the range of energy band gap of mixed TiO_2 structures (3.0-3.2eV).

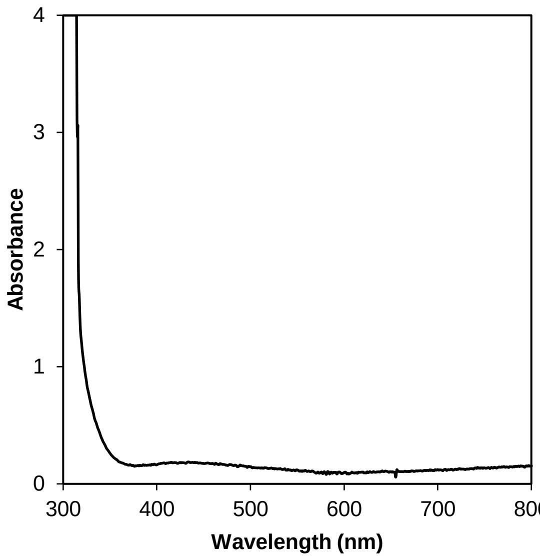


Fig. (7) UV-visible spectrum of synthesized TiO_2 nanopowder

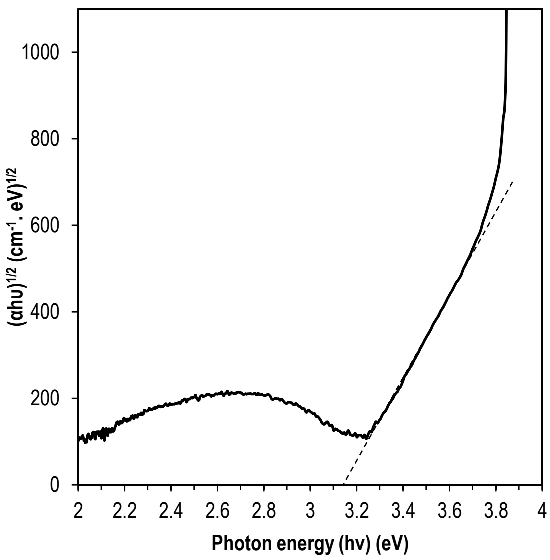


Fig. (8) Determination of energy band gap of the synthesized TiO_2 nanopowder sample

4. Conclusions

The mixed-phase titanium dioxide nanopowders were synthesized by an eco-friendly solvothermal method. The structural characteristics confirmed that the synthesized nanopowders have tetragonal crystalline and contains anatase and rutile phases of titanium dioxide. The minimum particle size is 53.48nm with inevitable aggregation of the nanoparticles. The prepared nanopowders have reasonable absorption in the UV region of electromagnetic spectrum (<375nm) and very low absorption in the visible region. The energy band gap of the synthesized samples was determined to be 3.14eV, which agrees with the standard range of energy band gap of mixed-phase TiO_2 structures (3.0-3.2eV). The solvothermal method used in this work can be described by low complexity, simple assembly, low cost and high purity production.

References

[1] O. V Salata, "Applications of nanoparticles in biology and medicine," *J. Nanobiotechnology*, vol. 2, no. 1, pp. 1–6, 2004.
[2] H. H. M. Darweesh, "Nanomaterials: classification and properties-Part I," *Nanoscience*, vol. 1, no. 1, pp. 1–11, 2018.
[3] P. Nikolaidis, *Analysis of green methods to synthesize nanomaterials*, no. September 2020. 2020. doi: 10.1002/9781119576785.ch5.
[4] N. Baig, I. Kammakakam, and W. Falath, "Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges," *Mater. Adv.*, vol. 2, no. 6, pp. 1821–1871, 2021.
[5] Z. Vaseghi and A. Nematollahzadeh, "Nanomaterials: types, synthesis, and characterization," *Green Synth. Nanomater. bioenergy Appl.*, pp. 23–82, 2020.
[6] S. S. Salem, E. N. Hammad, A. A. Mohamed, and W. El-Dougdoug, "A comprehensive review of nanomaterials: Types, synthesis, characterization, and applications," *Biointerface Res. Appl. Chem*, vol. 13, no. 1, p. 41, 2022.
[7] A. Mageswari, R. Srinivasan, P. Subramanian, N. Ramesh, and K. M. Gothandam, "Nanomaterials: classification, biological synthesis and characterization," *Nanosci. Food Agric. 3*, pp. 31–71, 2016.
[8] Y. A. Shaban, M. A. El Sayed, A. A. El Maradny, R. K. Al Farawati, and M. I. Al Zobidi, "Photocatalytic degradation of phenol in natural seawater using visible light active carbon modified (CM)-n-TiO_2 nanoparticles under UV light and natural sunlight illuminations," *Chemosphere*, vol. 91, no. 3, pp. 307–313, 2013.
[9] M. Tomás-Gamasa and J. L. Mascareñas, "TiO_2-Based Photocatalysis at the Interface with Biology and Biomedicine," *ChemBioChem*, vol. 21, no. 3, pp. 294–309, 2020.
[10] M. Huston, M. DeBella, M. DiBella, and A. Gupta, "Green synthesis of nanomaterials," *Nanomaterials*, vol. 11, no. 8, p. 2130, 2021.
[11] M. Shah, D. Fawcett, S. Sharma, S. K. Tripathy, and G. E. J. Poinern, "Green synthesis of metallic nanoparticles via biological entities," *Materials (Basel).*, vol. 8, no. 11, pp. 7278–7308, 2015.
[12] H. Nadaroglu, H. Onem, and A. Alayli Gungor, "Green synthesis of Ce_2O_3 NPs and determination of its antioxidant activity," *IET nanobiotechnology*, vol. 11, no. 4, pp. 411–419, 2017.
[13] H. Nadaroglu, A. A. Gungor, S. Ince, and A. Babagil, "Green synthesis and characterisation of platinum nanoparticles using quail egg yolk," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 172, pp. 43–47, 2017.
[14] S. Cicek, A. A. Gungor, A. Adiguzel, and H. Nadaroglu, "Biochemical evaluation and green synthesis of nano silver using peroxidase from Euphorbia (Euphorbia amygdaloides) and its antibacterial activity," *J. Chem.*, vol. 2015, 2015.
[15] K. B. Narayanan and N. Sakthivel, "Biological synthesis of metal nanoparticles by microbes," *Adv. Colloid Interface Sci.*, vol. 156, no. 1–2, pp. 1–13, 2010.
[15] Z.H. Zaidan, K.H. Mahmood and O.A. Hammadi, "Using Banana Peels for Green Synthesis of Mixed-Phase Titanium Dioxide Nanopowders", Iraqi J. Appl. Phys., 18(4) (2022) 27-30
[17] N. K. Mukhopadhyay and T. P. Yadav, "Some aspects of stability and nanophase formation in quasicrystals during mechanical milling," *Isr. J. Chem.*, vol. 51, no. 11-12, pp. 1185–1196, 2011.
[18] N. M. Noah and P. M. Ndangili, "Green synthesis of nanomaterials from sustainable materials for biosensors and drug delivery," *Sensors Int.*, vol. 3, p. 100166, 2022.
[19] S. Rajeshkumar and L. V Bharath, "Mechanism of plant-mediated synthesis of silver nanoparticles–a review on biomolecules involved, characterisation and antibacterial activity," *Chem. Biol. Interact.*, vol. 273, pp. 219–227, 2017.
[20] K. Vijayaraghavan and T. Ashokkumar, "Plant-mediated biosynthesis of metallic nanoparticles: A review of literature, factors affecting synthesis, characterization techniques and applications," *J. Environ. Chem. Eng.*, vol. 5, no. 5, pp. 4866–4883, 2017.
[21] Z.H. Zaidan, O.A. Hammadi and K.H. Mahmood, "Effect of Preparation Method on Crystalline Structure of Titanium Dioxide Nanoparticles", Iraqi J. Appl. Phys. Lett, 6(2) (2023) 11-14.
[22] I. Hussain, N. B. Singh, A. Singh, H. Singh, and S. C. Singh, "Green synthesis of nanoparticles and its potential application," *Biotechnol. Lett.*, vol. 38, pp. 545–560, 2016.
[23] H. E. Swanson, *Standard X-ray diffraction powder patterns*, vol. 25. US Department of Commerce, National Bureau of Standards, 1953.

[23] Z.H. Zaidan, O.A. Hammadi and K.H. Mahmood, "Effect of Structural Phase on Photocatalytic Activity of Titanium Dioxide Nanoparticles" Iraqi J. Appl. Phys., 19(3A) (2023) 55-58.

[22] A. Monshi, M. R. Foroughi, and M. R. Monshi, "Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD," *World J. nano Sci. Eng.*, vol. 2, no. 3, pp. 154–160, 2012.

[23] N. N. Greenwood, E. J. F. Ross, and B. P. Straughan, "Index of vibrational spectra of inorganic and organometallic compounds," *(No Title)*, 1972.

[24] Y. Bouachiba, A. Bouabellou, F. Hanini, F. Kermiche, A. Taabouche, and K. Boukheddaden, "Structural and optical properties of TiO_2 thin films grown by sol-gel dip coating process," *Mater. Sci.*, vol. 32, pp. 1–6, 2014.

[25] F. J. Al-Maliki and N. H. Al-Lamey, "Synthesis of Tb-doped titanium dioxide nanostructures by sol–gel method for environmental photocatalysis applications," *J. Sol-Gel Sci. Technol.*, vol. 81, pp. 276–283, 2017.

[26] Z.H. Zaidan, O.A. Hammadi and K.H. Mahmood, "Plant-Extracted Preparation of Crystalline Titanium Dioxide Nanoparticles", Iraqi J. Appl. Phys. Lett, 6(4) (2023) 23-26.

