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Structural, Optical, Photocatalytic, and Dielectric properties of Biosynthesized, Sol-Gel, and Simple Precipitated TiO₂ nanoparticles

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Abstract

TiO₂ (titanium dioxide) nanoparticles in anatase form were synthesized through three different methods: lemon peel-assisted green synthesis (TBio), sol-gel (TSol), and simple chemical precipitation (TPre). X-ray diffraction (XRD) and Williamson-Hall analysis demonstrated all samples contained phase-pure anatase. Crystallite sizes calculated using XRD were 4.3 nm (TBio), 6.5 nm (sol-gel) and 5.5 nm (precipitation) with TBio exhibiting the most micro-strain. Scanning electron microscopy (SEM) revealed almost spherical particles with average sizes of 32.45±14.13 nm (TBio), 45.22±12.14 nm (TSol), and 32.64±5.61 nm (TPre); therefore, lemon peels phytochemicals are effective in controlling particle growth. All three samples exhibited Ti-O-Ti lattice vibrations confirmed by Fourier transform infrared (FTIR) spectroscopy, and hydroxyl groups, organic species and other residues are most intense in TBio, moderate in TSol, and low in TPre. Ultraviolet-visible (UV-Vis) and Tauc analyses yielded indirect band gaps of 3.15 eV (TBio), 3.22 eV (TSol), and 3.16 eV (TPre). Slight band gap narrowing for TBio and TPre resulted from defect-induced band tailing. Methylene blue photodegradation results revealed pseudo-first-order kinetics under UV light, with photocatalytic activity decreasing in the order of TPre > TSol > TBio, correlating well with their relative crystallinity and lower rates of electron and hole recombination in precipitated nanoparticles. Dielectric measurements (20 Hz to 20 MHz) revealed significant Maxwell-Wagner interfacial polarization. TSol and TPre had lower losses and more moderate permittivity values than TBio, which had the highest low-frequency dielectric permittivity ($\epsilon' \approx 351$ at 20 Hz) and loss; TBio > TPre > TSol (about 351, 100, and 71 at 20 Hz, respectively). The Nyquist plots of TSol and TPre consisted of single depressed semicircles dominated by grain boundary effects, whereas TBio resolved into two overlapping arcs corresponding to distinct grain and grain-boundary relaxation processes; consistently, TBio exhibited the lowest overall impedance and the highest AC conductivity through defect-assisted hopping, although these same defect and interfacial states act as recombination centers that limit its photocatalytic activity. These findings demonstrate that the lemon peel assisted green route is an environmentally friendly method that maximizes interfacial polarization and low-frequency permittivity, albeit with higher

dielectric loss and reduced photocatalytic activity, while precipitation derived TiO₂ offers the most effective combination of photocatalytic performance and balanced dielectric behavior, and sol-gel TiO₂ displays an intermediate multifunctional capability.

Keywords: TiO₂ nanoparticles, Green synthesis, Lemon peel extract, Photocatalytic activity, Dielectric properties.

1. Introduction

Nanoparticles represent significant instruments within nanotechnology and are under investigation due to their diverse applications in sensing, optical, biomedical, photocatalytic, and electronic devices [1]. Nanomaterials' distinct features, particularly the quantum confinement effect and the effects of minimal gravitational force, their overall large surface area, and the predominance of electromagnetic forces over other forces, play a critical role in altering how materials behave on a nanoscale [2]. Metal oxide nanoparticles are advantageous compared to larger particles (bulk materials) due to the unique properties of metal oxides at the nanometer level, including magnetic, electrical, and optical properties [3]. Titanium dioxide (TiO₂), a transition metal oxide, is a perfect semiconducting material because it is inexpensive, nontoxic, easy to use, and resistant to chemical and photochemical degradation [4]. Although titania is a material that is widely acknowledged for its biocompatibility, lack of side effects and stability [5]. Recent new synthesis methods have been developed recently to produce titania nanostructures, including hydrothermal, solvothermal, sol-gel, chemical vapour deposition (CVD), electro-deposition, direct oxidation, "green" synthesis and precipitation methods [6], [7], [8], [9], [10]. The synthesis method for TiO₂ nanoparticles plays a crucial role in determining their crystalline phases, which strongly affect their structural characteristics, optical performance, antibacterial effectiveness, and electrical properties [11].

The crystalline phase, particle size, and defect density of TiO₂ nanoparticles are determined by the synthesis route [12]. In the conventional sol-gel synthesis of titanium dioxide nanoparticles, metal alkoxides, such as titanium isopropoxide, undergo hydrolysis and polycondensation. This process forms a network of Ti-O-Ti bonds, leading to the formation of a titanium oxide sol that subsequently transforms into a gel [13], [14]. The nucleation and growth rates of TiO₂ can be controlled by adjusting the water-to-alkoxide ratio, pH, and aging or calcination conditions, including temperature. This control enables the formation of high-crystallinity anatase TiO₂ with narrow size distributions and well-defined morphologies following drying and heat treatment [15] [16]. In contrast, precipitation relies on the simultaneous precipitation of titanium precursor species, typically Ti⁴⁺ salts, through the addition of a base. This method results in rapid nucleation and subsequent growth of an amorphous or poorly crystalline precipitate, which is then converted to crystalline TiO₂ through calcination [17]. The particle size and defect density in this approach are influenced by the precipitation pH, temperature, and aging time [16]. Green synthesis utilizes naturally occurring phytochemicals, including phenolics, organic acids, flavonoids, polyphenols,

and organosulfur compounds derived from plants. These compounds function as reducing, complexing, or capping agents [18]. By complexing Ti^{4+} ions with these biomolecules and applying controlled heating, TiO_2 nanocrystal nucleation occurs within the organic matrix. Subsequent calcination decomposes the organic matrix, yielding TiO_2 nanoparticles with bio-derived surface functionality and typically smaller crystallite sizes [19].

Comparative studies of sol-gel synthesized titanium dioxide (TiO_2) and TiO_2 produced via direct precipitation indicate that sol-gel methods yield highly crystalline TiO_2 with a well-defined anatase structure. This structure demonstrates efficient ultraviolet light absorption, rendering it suitable for photocatalytic and optoelectronic applications [12], [17]. Although both material types exhibit high conductivity and can be adapted for dielectric or impedance applications, TiO_2 prepared through simpler methods typically shows greater defect-mediated conductivity and a more dispersed conduction response due to a higher density of grain-boundary states [12],[17].

Titanium dioxide synthesized using green methods, utilizing agricultural waste such as citrus peel and onion/garlic peel, offers advantages including reduced toxicity, lower synthesis temperatures, and enhanced antibacterial and antioxidant properties, while maintaining competitive photocatalytic and dielectric performance [18],[19]. Compared to sol-gel and precipitation methods, green synthesis generally results in smaller crystallite sizes with residual bio-organic components adhering to the particle surface. These surface components increase the density of surface defects and interfacial states, which can improve interfacial polarization and defect-mediated conductivity. However, they may also function as charge trapping and recombination centers, potentially reducing photocatalytic efficiency [20], [21]. In contrast, TiO_2 derived from sol-gel and precipitation routes typically exhibits higher crystallinity, reduced microstrain, and fewer grain-boundary defect states, leading to more effective charge separation and lower dielectric loss [12], [14], [17].

Drawing upon these findings, the present research involves the synthesis of anatase TiO_2 nanoparticles through sol-gel and precipitation methods, alongside a green protocol that employs an extract from dried lemon peel as a renewable reducing and capping agent [21]. The resulting powders undergo systematic characterization to ascertain the impact of these three synthesis routes on the microstructure and multifunctional properties of the TiO_2 nanoparticles.

2. Methodology

METHODOLOGY: SYNTHESIS OF TiO₂ NANOPARTICLES

Green Synthesis, Sol-Gel and Precipitation Methods

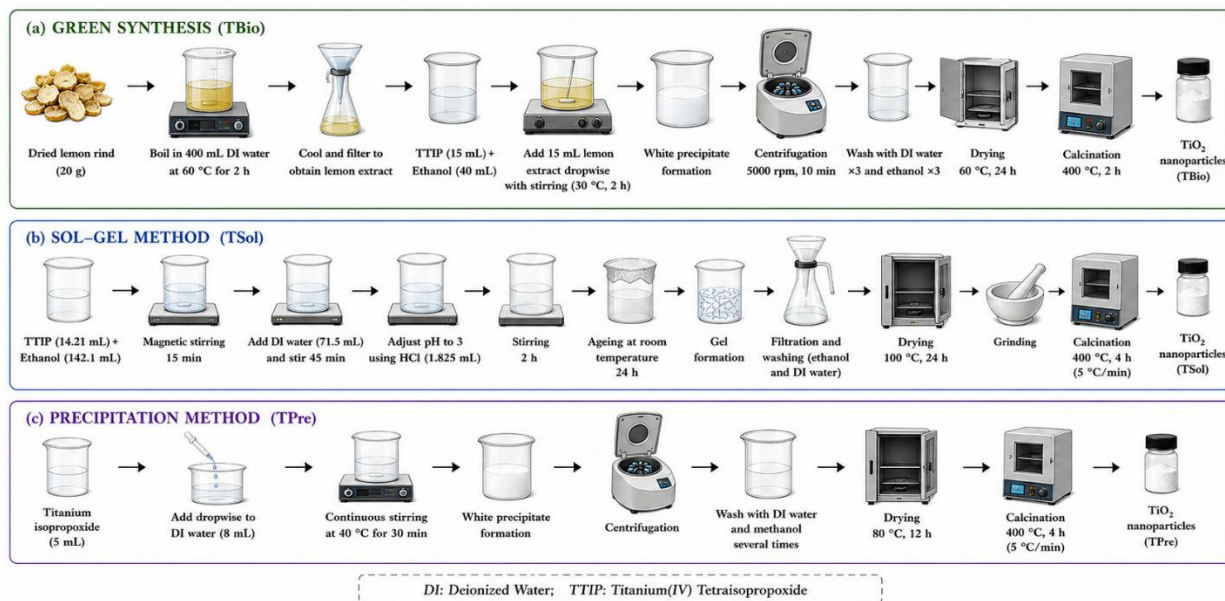


Fig. 1. Synthesis Methods of TiO₂ NPs

2.1 Biosynthesis Method

The dried and crushed Lemon rind was used to make lemon rind extract for TiO₂ nanoparticle production. This extract was produced by boiling 20 gm of dried lemon rind in 400 ml of distilled water at 60°C for 2 hours before cooling and filtering it to generate a clear extract. To prepare the TTIP-ethanol solution, 15 ml of titanium tetraisopropoxide (TTIP) was mixed with 40 ml of ethanol and agitated until a homogeneous mixture was achieved. Following this, 15 ml of filtered lemon extract was added dropwise to the TTIP/ethanol solution, with constant stirring, after which the solution was kept at 30°C for 2 hours. The TiO₂ NPs biosynthesized, indicated by the appearance of a white precipitate, were then collected by centrifuging at 5000 rpm for 10 minutes before being rinsed with distillate and ethanol three times each. The resultant precipitate was dried at 60°C for 24 hours before being subjected to heat treatment at 400°C for 2 hours to produce crystalline anatase-phase TiO₂ NPs.

2.2 Sol-Gel Method

The onset of the sol-gel process occurs when the Ti-OR groups are removed and replaced with Ti-OH groups, initiating the hydrolysis phase of the sol-gel transformation. Then, the second stage is condensation, where either Ti-O-Ti bonds are created through "oxolation" or Ti-OH-Ti bonds are formed using "olation." In the preparation of a 1M TTIP precursor solution, 14.21 mL of titanium tetraisopropoxide (TTIP), 142.1 mL of ethanol, 71.5 mL of distilled water, and 1.825 mL of HCl were combined. The TTIP was dissolved in the ethanol solution using a magnetic stirrer for 15

minutes. The addition of distilled water began to form ions and the mixture was stirred for an additional 45 minutes. After adjusting the pH to 3 with HCl (1M), the sol was stirred for 2 hours and then left at room temperature for 24 hours to age. After aging the gel was filtered, washed in both ethanol and distilled water, and dried in an oven at 100°C for 24 hours. Finally, the material was ground into a fine powder and calcined in a furnace for 4 hours at 400°C, with a heating rate of 5°C/minute.

2.3 Precipitation Method

The starting material for producing TiO₂ powders was titanium isopropoxide. In this process, titanium isopropoxide (5 mL) was added to 8 mL of deionized water in a dropwise fashion. This process caused the titanium isopropoxide to hydrolyze and form a hydrated titanium oxide precipitate [5]. The mixture was continuously stirred at 40°C for 30 minutes. After mixing completely, the white TiO₂ NP precipitate had formed at the bottom of the beaker. To complete the precipitation process, the TiO₂ NP precipitate was collected via centrifugation, washed several times with deionized water and methanol, and dried at 80°C for 12 hours. The resulting material was calcined at 400°C for four hours, with an average heating rate of 5°C/minute.

2.4 Pellet preparation

Pellets of the TiO₂ NPs were created for electrical property analysis. Each 1 g sample of nanoparticles was combined with a polyvinyl alcohol binder and compressed under 2.5 tonnes of pressure into 13 mm-diameter disk-shaped pellets. The formed pellets were then sintered at 750 °C in ambient air.

2.5 Characterization

The crystallographic structure of TiO₂ nanoparticles was analyzed utilising a SHIMADZU LabX XRD-6100 apparatus (Japan). The Williamson–Hall (UDM) study of peak broadening was conducted in Python 3.x utilizing NumPy and SciPy, incorporating FWHM values, Cu K α radiation with a shape factor $K=0.9$ and wavelength $\lambda=0.15406$ nm and linear least squares fitting of $\beta hkl \cos\theta$ against $4\sin\theta$. Field emission scanning electron microscopy (FESEM) was utilised to examine the surface morphology of the TiO₂ nanoparticles, utilising a JEOL JSM-7600F apparatus from Germany. The ImageJ software was employed to evaluate the average particle size and distribution from the FESEM pictures. The UV–vis absorption spectrum of TiO₂ nanoparticles was recorded with a Shimadzu UV-2600i spectrophotometer (Japan) across wavelengths ranging from 250 to 800 nm. An Ethanol suspension containing the nanoparticles was used when measuring how well the NPs photocatalytically degraded MB under UV irradiation with an intensity of 120 $\mu\text{W}/\text{cm}^2$, and the absorbance spectra of the dye solution were recorded over the 450 to 800 nm

range at time intervals of 0, 15, 30, 45, 60, 75, 90, 105, and 120 min. The dielectric characteristics of the synthesized TiO₂ nanoparticle pellets were characterized using a standard parallel plate capacitor method throughout a frequency range of 20 to 20,000 kHz using an Agilent 4294A Precision Impedance Analyzer.

3. Result and discussion

3.1 Structural Characteristics

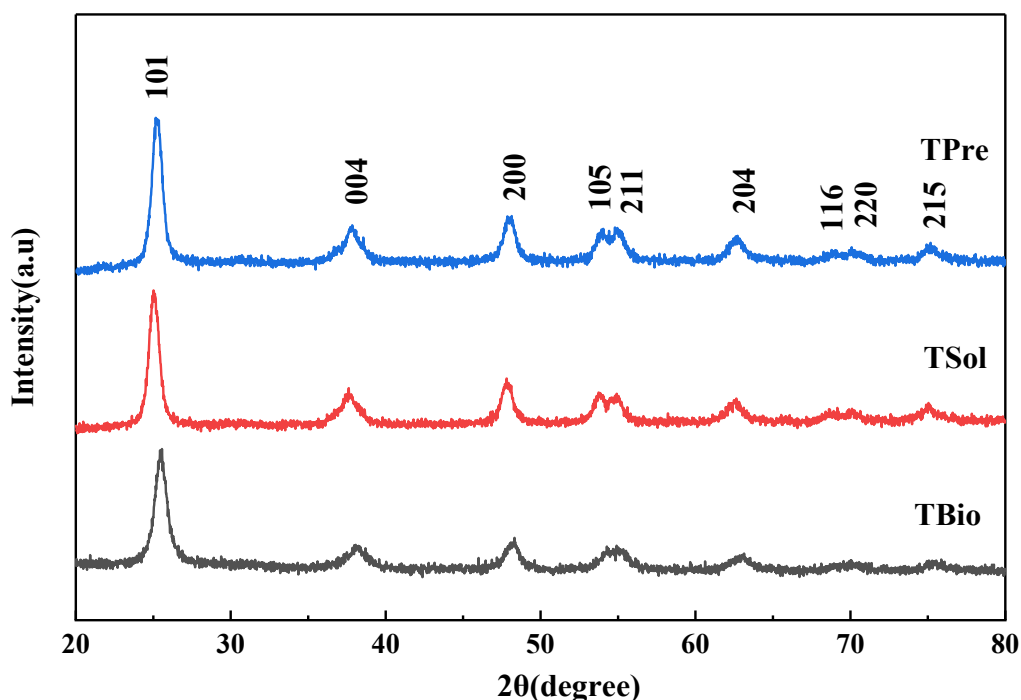


Fig. 2. XRD patterns of TiO₂ NPs

The X-ray diffraction spectra shown in Fig. 2 demonstrate that TBio, TSol and TPre samples have clear diffraction patterns and the peaks correspond to the following crystallographic planes found in tetragonal anatase TiO₂ according to JCPDS Card No. 01-073-1764 - (101), (004), (200), (105), (211), (204), (116), (220), and (215) respectively. The lack of secondary diffraction maxima associated with rutile or brookite phases signifies that all three samples crystallize exclusively in a singular anatase phase with elevated structural purity. Table 2 indicates that the experimental peak positions for TBio, TSol, and TPre closely align with the conventional anatase reflections, affirming that the coordination environment of Ti⁴⁺ is mostly characterized by corner-sharing TiO₆ octahedra with trigonal planar O–Ti–O connections [22]. Inter-planar spacing between atoms (*d* spacing) of each catalyst was calculated using the Bragg's equation,

$$n\lambda = 2d \sin\theta \quad (1)$$

Scherrer's equation was used to calculate the crystallite size of the TiO₂ NPs based on the significant diffraction peak that corresponds to the (101) plane which is expressed as:

$$d = \frac{0.89\lambda}{\beta \cos\theta} \quad (2)$$

where θ represents Bragg diffraction angle, β denotes the full width at half maximum (FWHM), d represents the crystallite size (nm), and λ is the X-ray wavelength (nm) [23]. For the TSol, TBio, and TPre samples, the estimated crystallite sizes were around 5.2 nm, 4.2 nm, and 6.3 nm respectively. These numbers are fairly similar to those seen in published literature [24], [25].

The sol-gel synthesized TiO₂ (TSol) exhibits significant and intense reflections, signifying a crystallinity of 78.57%, comparable to values recorded for well-ordered sol-gel anatase nanomaterials. The biosynthesized TiO₂ (TBio) exhibits somewhat larger peaks, resulting in a crystallinity of 73.78%, in accordance with other studies indicating that plant-mediated methods produce smaller crystallites and significantly diminished long-range order due to organic residues from the extract. Conversely, the co-precipitated sample (TPre) exhibits the highest crystallinity at 78.98%, characterized by the most pronounced (101) reflection, indicating enhanced crystal formation and diminished lattice strain under co-precipitation conditions. Table 1 shows the comparison among the samples and Table 2 shows the crystallographic parameters. The close correspondence of all diffraction characteristics with conventional anatase TiO₂ indicates that the synthesis methods affect crystallinity without altering the fundamental tetragonal phase [26].

The Williamson–Hall plots indicate that XRD peak broadening results from contributions of crystallite size and microstrain, as typically seen in anatase TiO₂ nanostructures (Fig. 3). Linear fitting produces average crystallite sizes of approximately 4.3 nm (TBio), 5.5 nm (TPre), and 6.5 nm (TSol), all of which are within the 3–10 nm range documented for green synthesised and sol-gel TiO₂. The pronounced slope for TBio signifies the maximum lattice strain, whilst TSol exhibits the minimal microstrain, aligning with the anticipated higher defect density associated with plant-mediated synthesis and the enhanced strain relaxation in optimised sol-gel processes [27], [28].

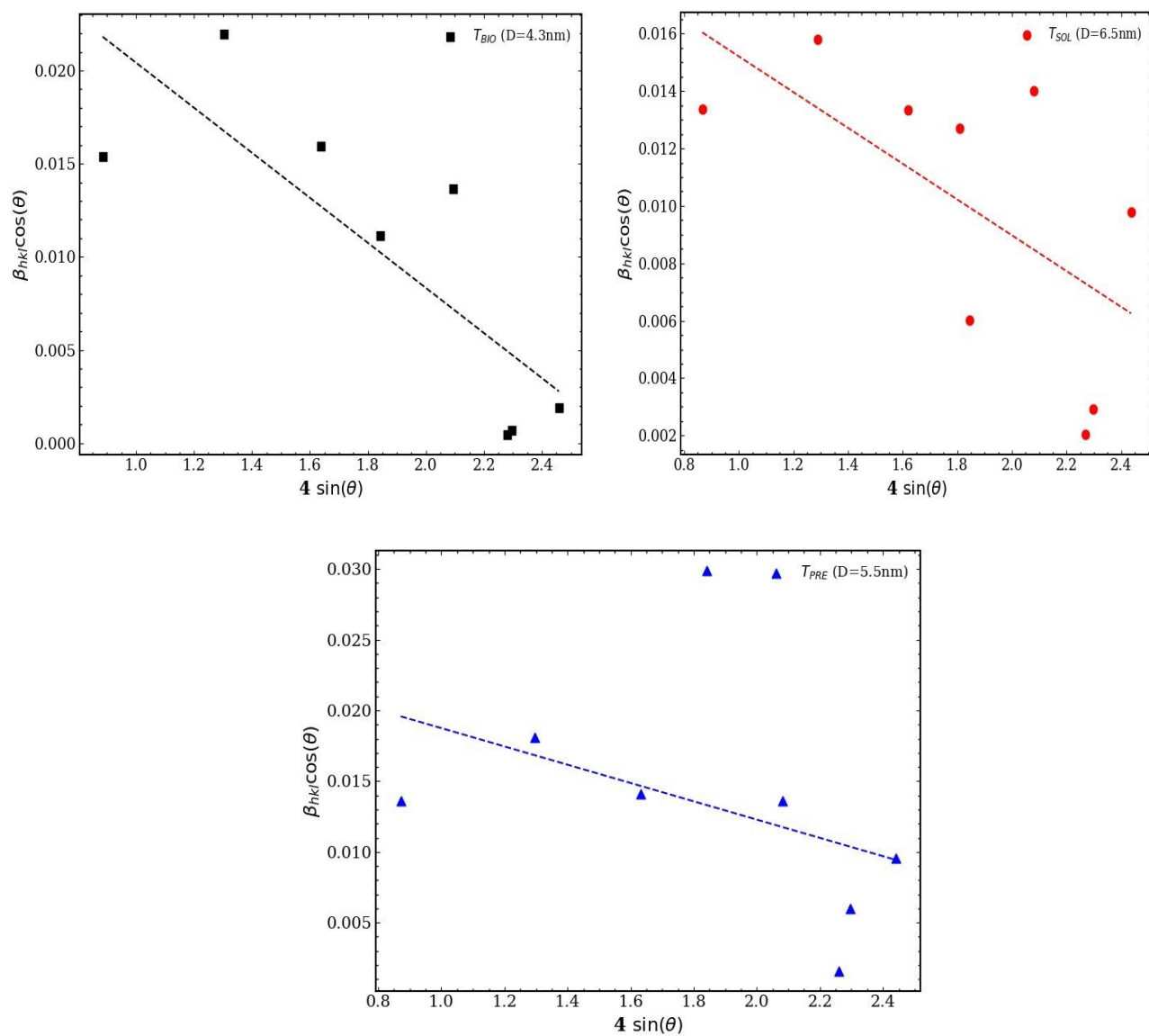


Fig. 3. Williamson-Hall plots of TiO₂ NPs

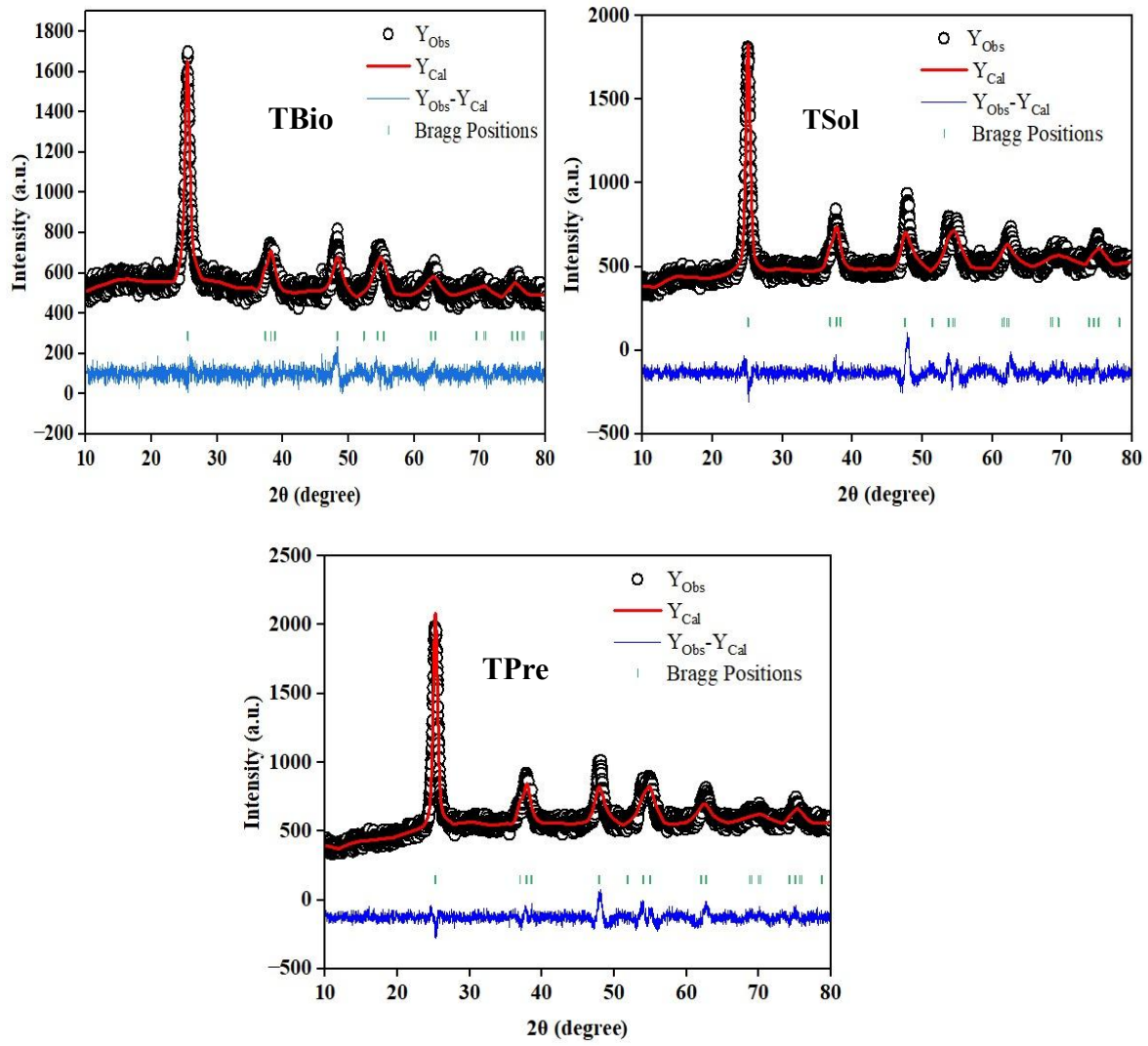


Fig. 4. Rietveld refinement plots of TiO₂ NPs

Table 1: Comparison of XRD data of TiO₂ Nanoparticles

Miller Plane(hkl)	TBio		TSol		TPre	
	FWHM	D Space	FWHM	D Space	FWHM	D Space
101	1.76963	3.49360396	1.42771	3.543792	1.84083	3.523168
004	1.76961	2.36124093	1.42767	2.383354	1.84091	2.375113
200	1.76962	1.890019201	1.42766	1.898088	1.84085	1.892532
105	1.76965	1.685032933	1.42761	1.701931	1.84091	1.697572
211	1.76967	1.662455358	1.42761	1.670412	1.84083	1.666612

204	1.76963	1.474763341	1.42769	1.484253	1.84083	1.479346
116	1.76967	1.359159545	1.42761	1.365519	1.84083	1.3641
220	1.76969	1.330869061	1.42762	1.338029	1.84087	1.335557
215	1.76966	1.257265371	1.42772	1.264626	1.84083	1.262484

Table 2: NPs crystallographic Parameters

Crystallographic Parameters		TBio	TSol	TPre
Cell Volume		133	139.627	137
Lattice parameters	a = b	3.76553	3.82604	3.79816
	c	9.42477	9.53834	9.49669
Crystallinity		73.78%,	78.57%	78.98%
R-factors	Rp	50.1	4.51	38.3
	Rwp	34.2	5.89	28.3
	Rexp	29.98	4.31	21.44
Density		3.970 g/cm ³	3.799 g/cm ³	3.872 g/cm ³

The integrated W–H plot (Fig. 3) further emphasises the inverse relationship between crystallite size and microstrain across the three samples, consistent with prior investigations of TiO₂ nanopowders utilising Williamson–Hall and analogous size–strain models.

Rietveld refinement of the TBio, TSol, and TPre XRD patterns shown in Fig. 4 represent excellent agreement between observed and calculated profiles, confirming a single tetragonal anatase phase for all samples with no detectable secondary phases, in line with reported nanocrystalline TiO₂ systems. The refined lattice parameters and low R-factors indicate that the different synthesis routes primarily influence crystallite size and micro strain.

3.2 Morphological Characteristics

FESEM

Figs. 5 and 6 represent the SEM and EDX micrographs of TiO₂ nanoparticles synthesized via green (TBio), sol–gel (TSol), and chemical precipitation (TPre) routes, along with their particle-size histograms.

The TBio sample consists of nearly spherical nanoparticles forming relatively loose aggregates, with a homogenous size distribution and an average particle size of 32.45 ± 14.13 nm, confirming that phytochemicals from the lemon-peel extract act as effective stabilizing and capping agents

that limit particle evolution. The TSol nanoparticles appear as compact assemblies of uniformly shaped grains with a broader distribution (45.22 ± 12.14 nm), characteristic of sol-gel derived TiO_2 in which hydrolysis-condensation and subsequent thermal treatment promote cluster formation. The TPre sample shows well-defined spherical grains organized into dense clusters, exhibiting an intermediate and comparatively narrow size distribution (32.64 ± 5.61 nm), consistent with homogeneous nucleation and growth during controlled hydrolysis of titanium isopropoxide [22], [29], [30].

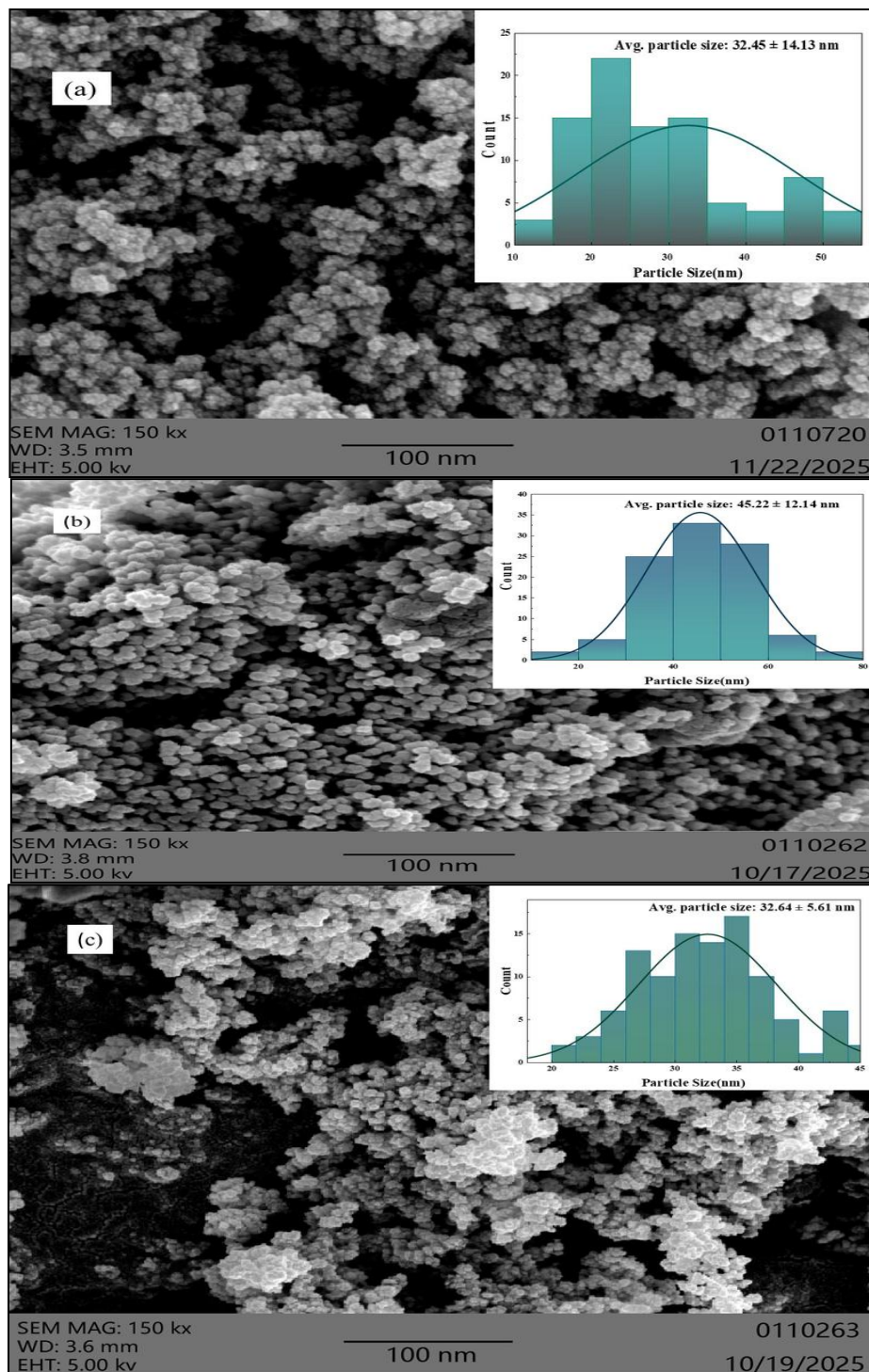


Fig. 5. FESEM micrographs of (a) TBio, (b) TSol and (c) TPre, with insets representing particle size distribution

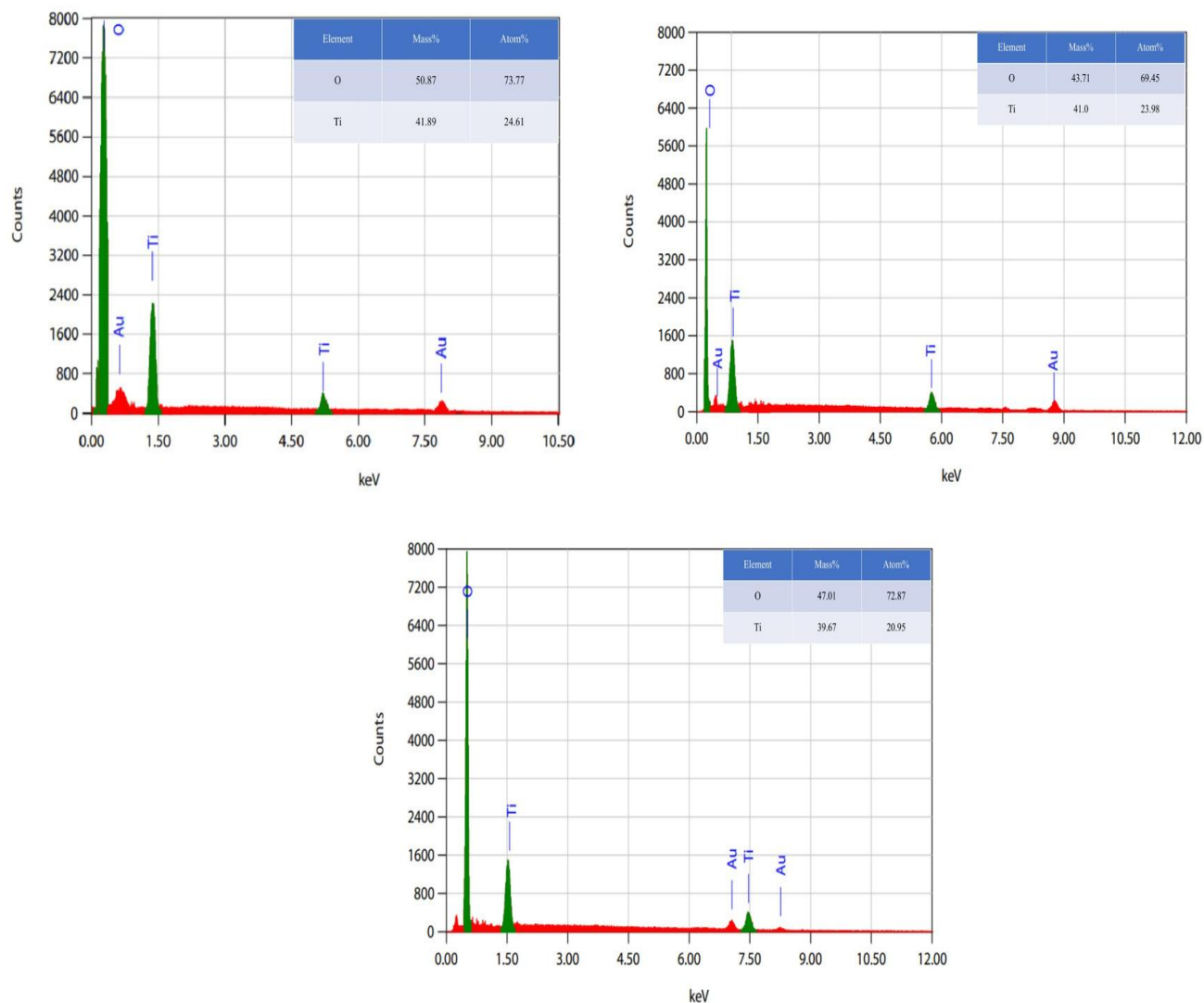


Fig. 6. EDX spectra of (a) TBio, (b) TSol and (c) TPre

Fourier Transform Infrared (FTIR) Spectroscopy:

The FTIR spectra (Fig. 7) of TBio, TSol, and TPre TiO_2 nanoparticles, recorded in the $4000\text{--}500\text{ cm}^{-1}$ range, exhibit a broad band at $3800\text{--}3550\text{ cm}^{-1}$ attributed to O–H stretching vibrations of

surface hydroxyl groups and adsorbed water, aligning with other studies on TiO₂ nanomaterials. Weak spectral characteristics between approximately 2350–2050 cm⁻¹ and 1750–1600 cm⁻¹ result from CO₂ and residual C=O and C–O vibrations of organic moieties derived from the precursor or plant extract, with greater intensity observed in the green-synthesized TBio sample [31]. A pronounced absorption in the low wavenumber range ($\approx$ 800–500 cm⁻¹) is indicative of Ti–O–Ti lattice vibrations, hence confirming the formation of the TiO₂ framework across all three synthesis methodologies [32], [33].

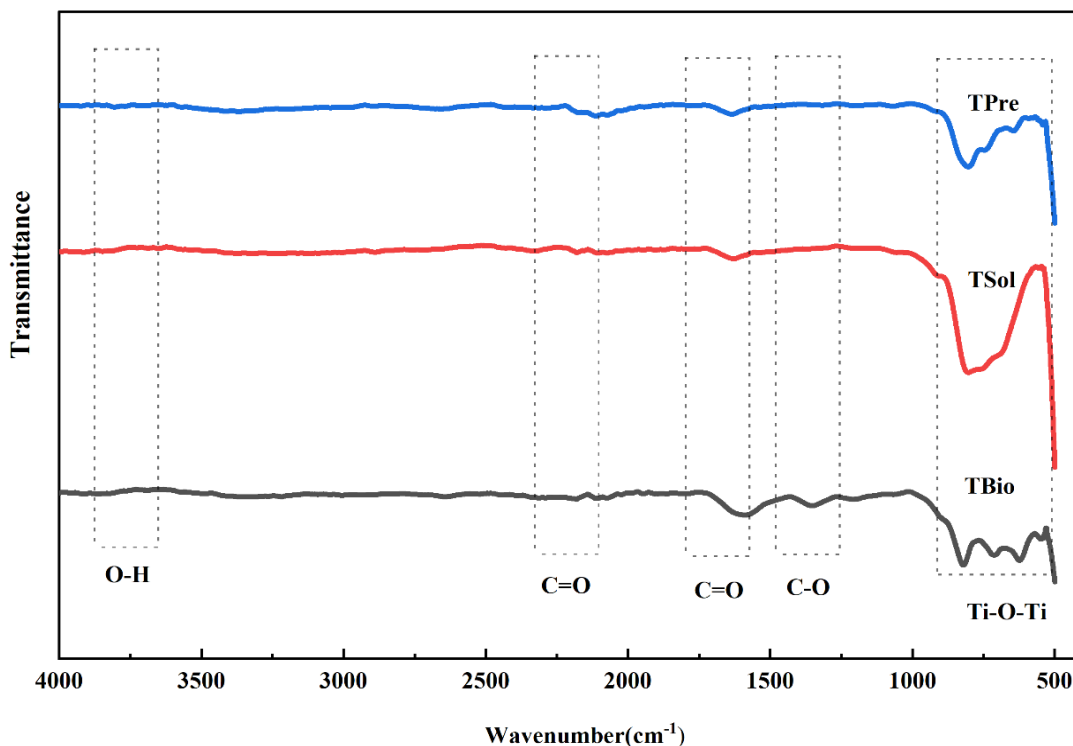


Fig. 7. FTIR spectra of (a) TBio, (b) TSol and (c) TPre

3.3 Optical Property

The UV-Visible absorption spectral response (Fig. 8a) of TBio, TSol, and TPre TiO₂ nanoparticles were measured in the 250–800 nm range, revealing a pronounced absorption edge in the near UV region at approximately 290.6, 292.1, and 288.4 nm, respectively. This phenomenon is ascribed to charge transfer transitions in anatase TiO₂ and aligns with values documented for sol–gel and green synthesized TiO₂ nanostructures [34]. In comparison to bulk TiO₂, all samples demonstrate a pronounced blue shift of the absorption threshold, affirming the nanoscale characteristics of the particles. The marginally increased absorbance and slight blue shift of the edge noted for the co-

precipitated sample (TPre) suggest enhanced crystallinity and diminished defect density, while the smoother edge of TBio illustrates the impact of surface organic compounds from the plant extract and minor size/disorder effects resulting from the green synthesis method.

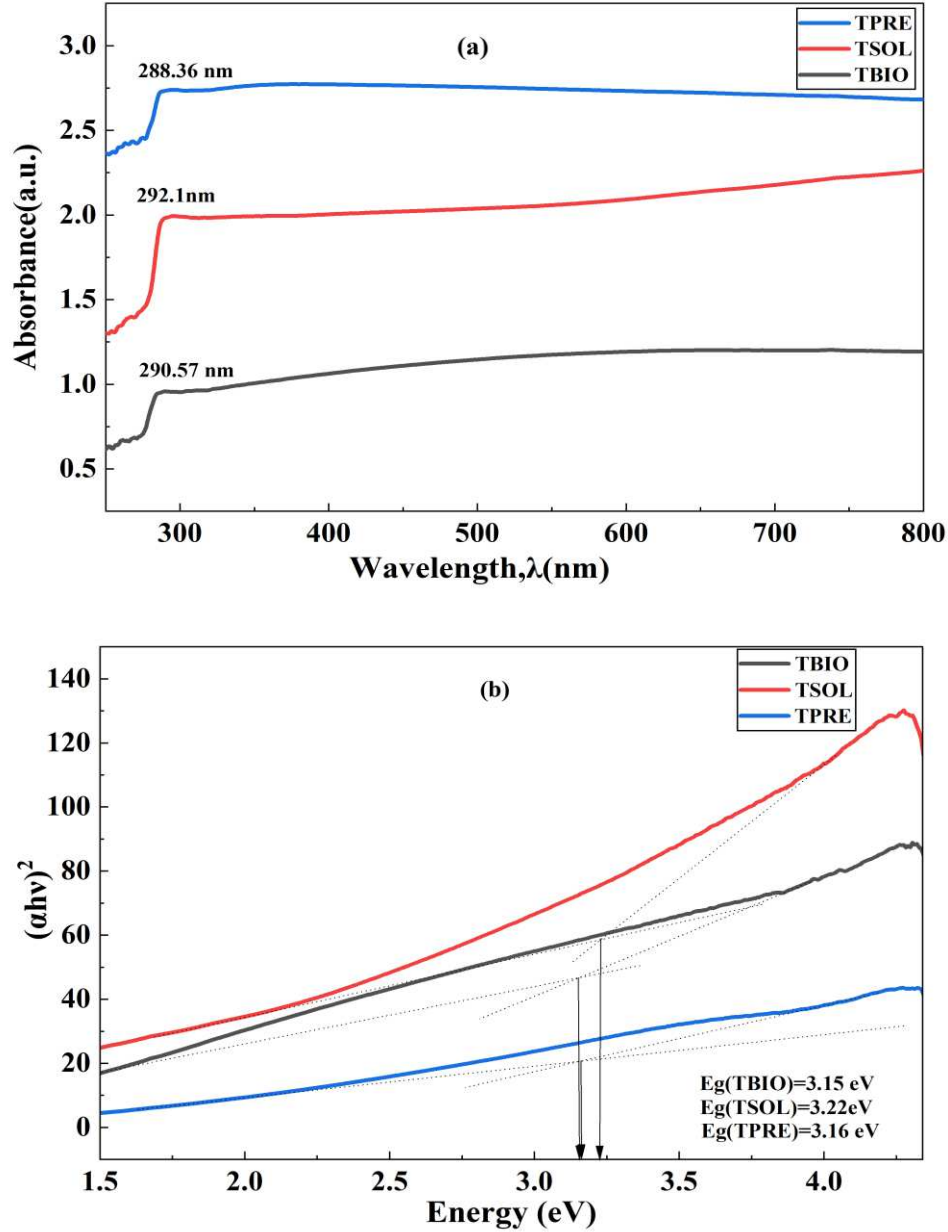


Fig. 8. (a) UV–vis absorption spectrum and (b) the Tauc plot of TiO₂ NPs

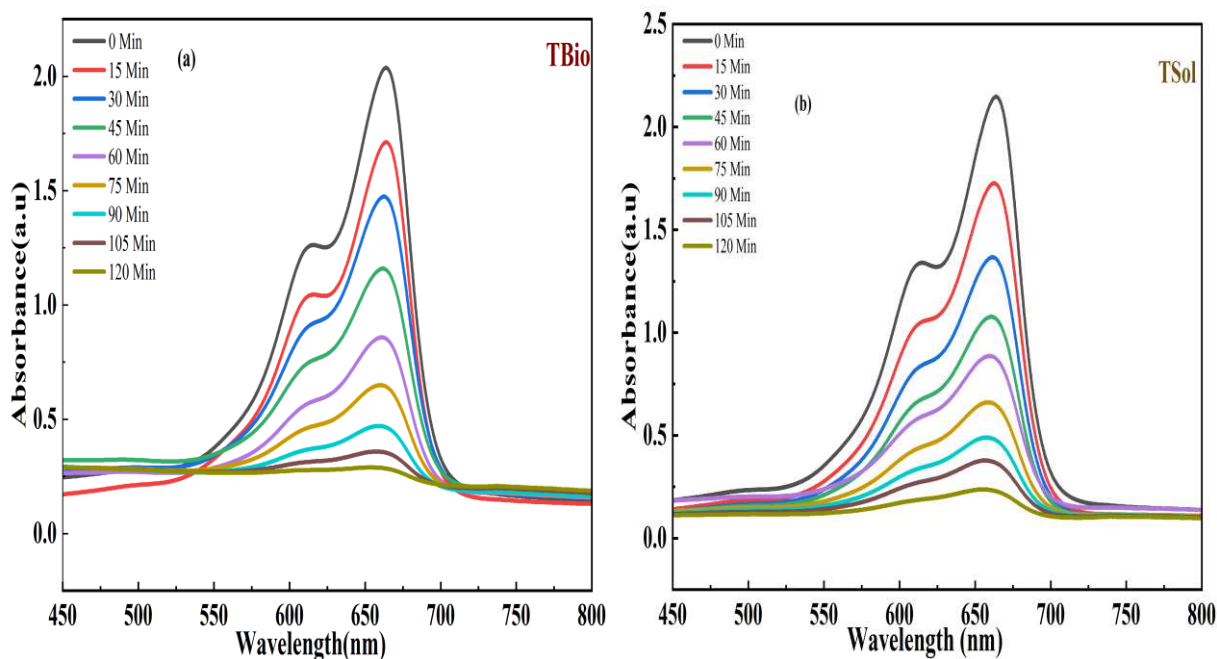
The optical band gaps (Fig. 8b) were ascertained using Tauc, presuming an indirect allowed transition for anatase TiO₂. The predicted band gap energies are 3.15 eV for TBio, 3.22 eV for TSol, and 3.16 eV for TPre, which laid within the typical range of 3.1–3.3 eV reported for anatase TiO₂ synthesized using sol–gel, co-precipitation, and green techniques, and are proximate to the nominal 3.2 eV energy gap of bulk anatase. The marginally reduced gaps of TBio and TPre

compared to TSol can be attributed to defect and surface states linked to organic capping (TBio) and lattice disorder induced by precipitation (TPre), resulting in band tailing and increased visible light absorption, a pattern consistent with previous optical investigations on plant-mediated and chemically precipitated TiO₂ nanoparticles. The results indicate that simple precipitation and green synthesis methods produce TiO₂ nanoparticles with superior optical properties for photocatalytic and UV shielding applications compared to traditional sol-gel produced materials [35], [36].

3.4 Photocatalytic Activity

The photocatalytic efficacy of TBio, TSol, and TPre TiO₂ nanoparticles was characterized through methylene blue (MB) degradation under UV light exposure for 120 minutes, as illustrated in Fig. 9(a–c). A gradual reduction in the distinctive MB absorption band at approximately 664–668 nm with extended irradiation duration signifies the ongoing photodecomposition of the dye molecules on the TiO₂ surface. The significant reduction in peak intensity, together with the slight blue shift of the maximum, can be ascribed to successive N-demethylation and opening of the MB molecular ring, finally resulting in mineralization into H₂O, CO₂, and inorganic ions [37], [38], [39].

Upon activation by UV light, TiO₂ produces pairs of holes and electrons, with the photo-excited charge carriers (holes) oxidizing surface-anchored water or hydroxide ions to yield hydroxyl radicals $h^+ + H_2O \rightarrow \cdot OH$, [40][41] while the conduction band electrons convert dissolved oxygen reduction yielding superoxide species $e^- + O_2 \rightarrow O_2^{\cdot -}$. These potent oxidising agents interact with the MB chromophore along the pathway $MB + \cdot OH / \cdot O_2^- \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O + SO_4^{2-} + NO_3^-$ [42]. The temporal progression of the absorbance spectra indicates that the degradation adheres to pseudo-first-order kinetics for MB concentration, a phenomenon frequently reported in TiO₂-based photocatalytic systems [43], [44].



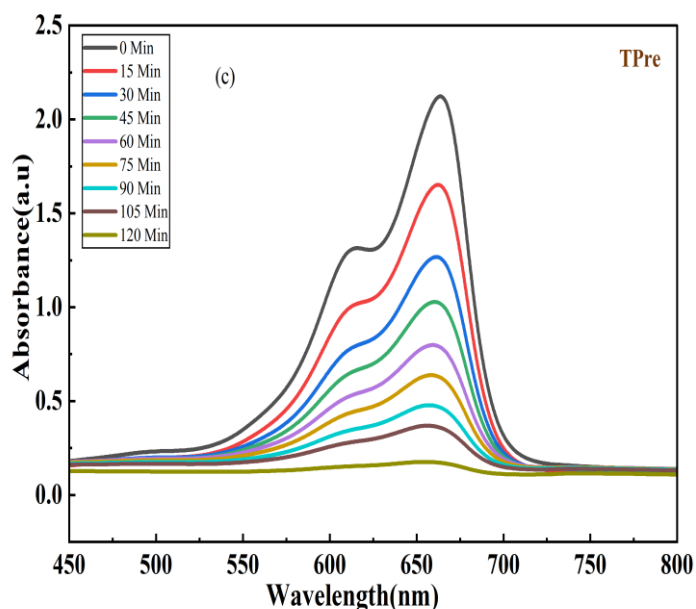
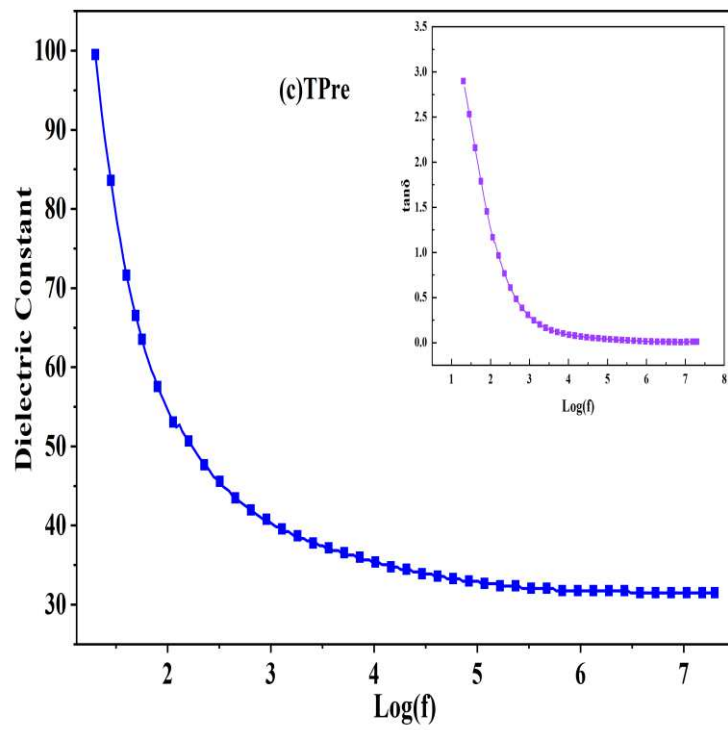
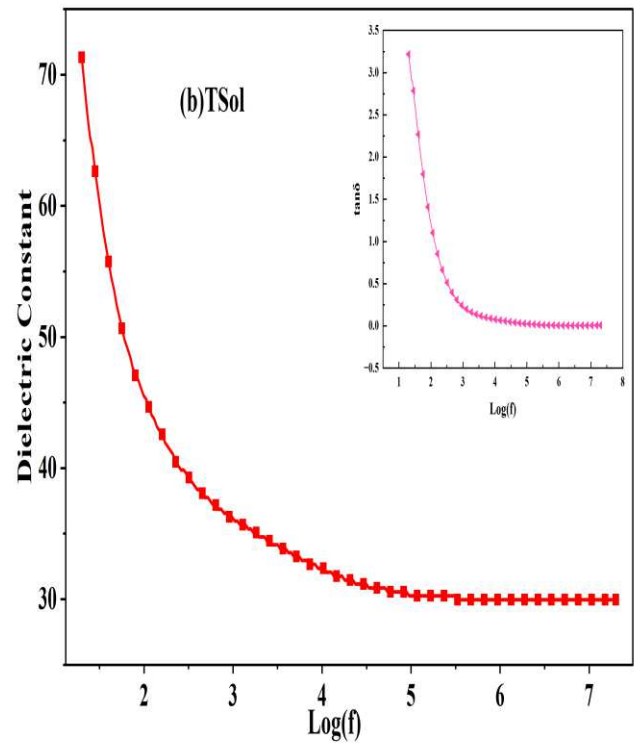
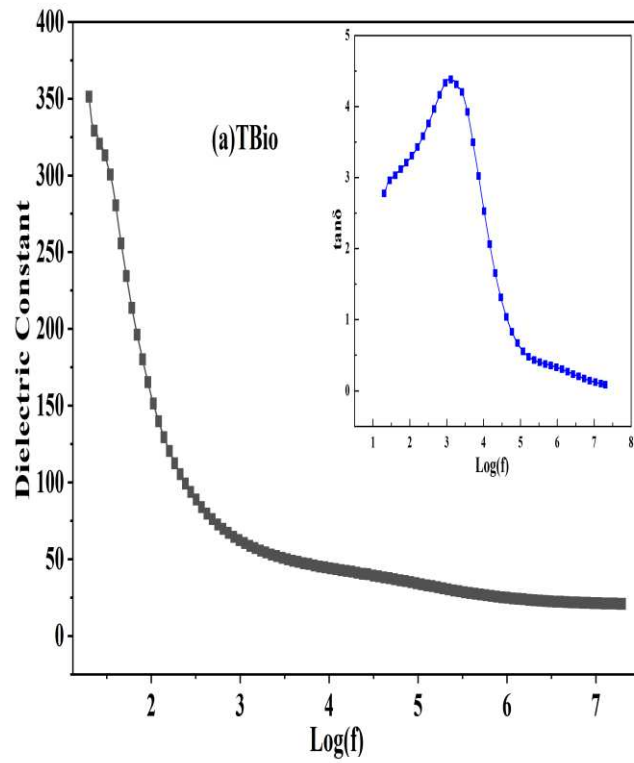


Fig. 9. Photocatalytic activity of (a) TBio, (b) TSol and (c) TPre NPs

The simple-precipitated TiO_2 (TPre) demonstrates the most rapid decline of the MB absorption band and the lowest residual intensity after 120 minutes, indicating a superior apparent rate constant compared to the sol-gel (TSol) and green-synthesized (TBio) samples. This improved performance comes from having a higher crystalline structure and lower amount of electron-hole pair recombination of the TPre nanoparticles, allowing for effective creation and utilization of reactive oxygen species [45]. The TSol catalytic activity is moderate, consistent with literature reports that highly crystalline anatase produced via sol-gel routes degrades methylene blue effectively. The TBio sample, however, has a lower degree of effectiveness than TSol as a result of the presence of organic material at its surface as well as having a smaller size of crystal particles that possibly functions as areas for recombination [46], [47].

3.5 Electrical Property



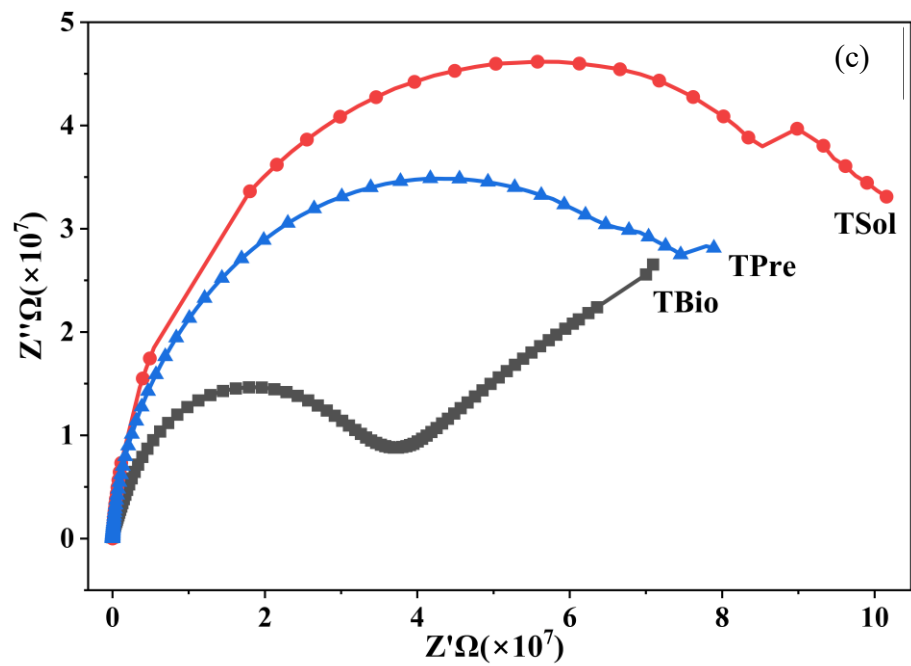
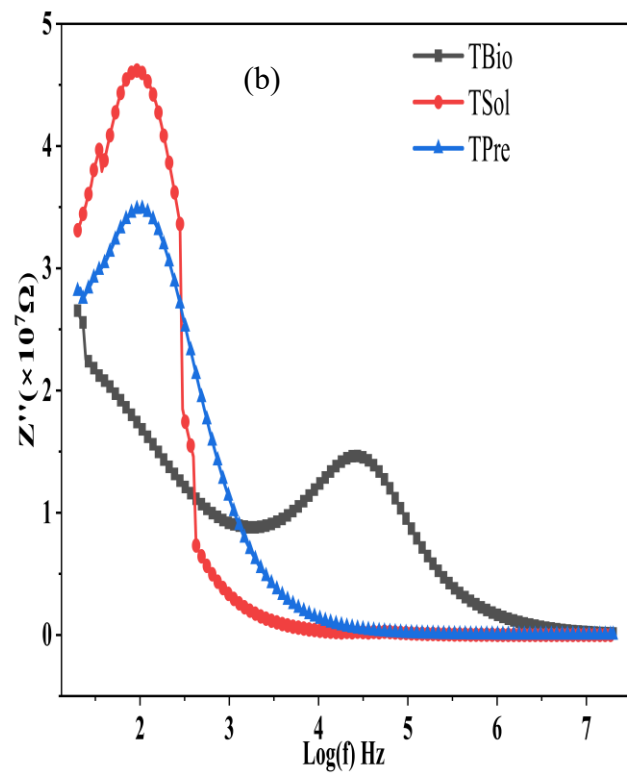
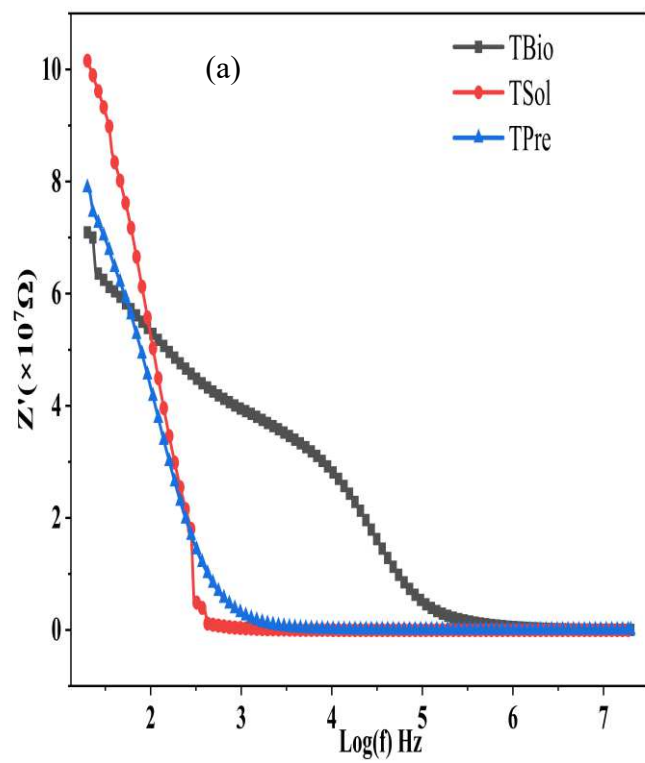


Fig. 11. (a) Real part of impedance, (b) imaginary part of impedance (c) Nyquist plot of TBio, TSol and TPre NPs

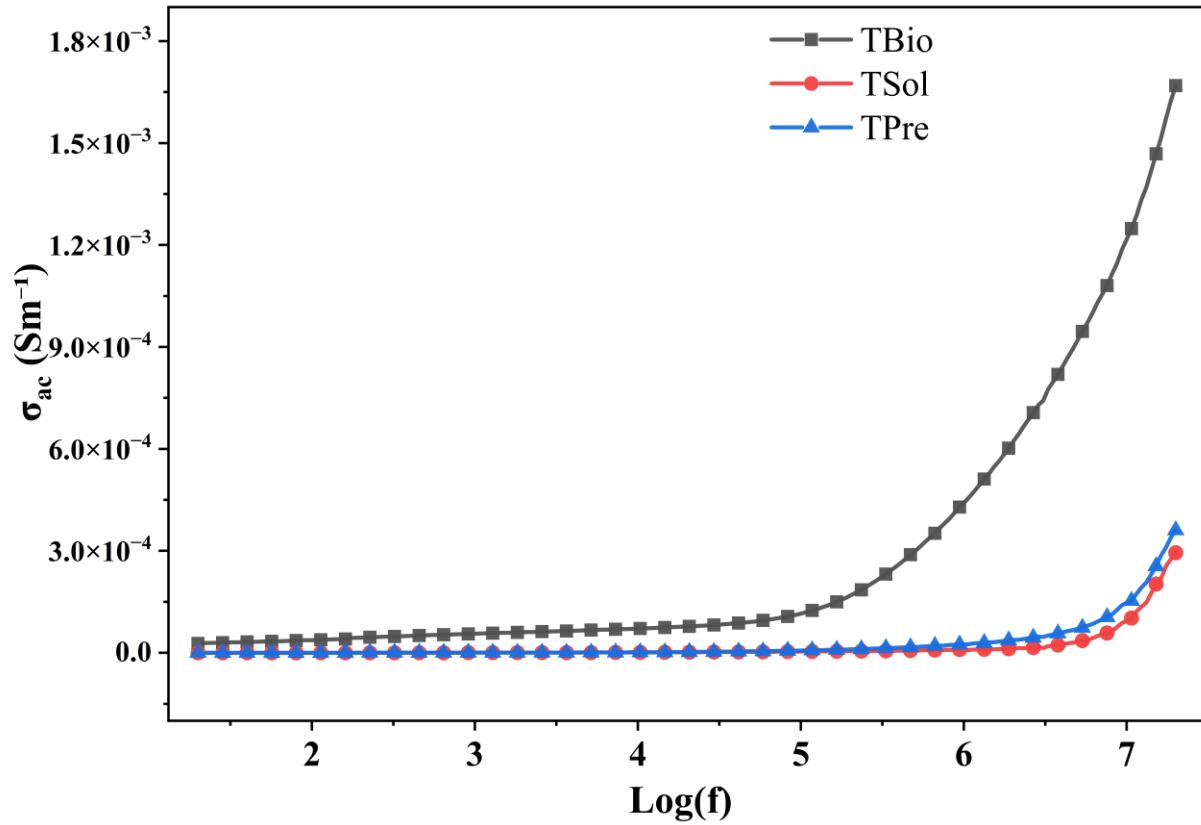


Fig. 12. AC conductivity of TiO₂ NPs

The frequency dependence of the dielectric constant (ϵ') and loss tangent ($\tan \delta$) of TBio, TSol and TPre were determined at room temperature in the frequency range of 20 Hz to 20 MHz, shown in Fig. 10(a–c). The three samples show high dielectric dispersion with the highest value of ϵ' at the lowest frequency, a sharp drop to around 1 kHz, and then a more or less flat value with a weak frequency dependence. The increased low-frequency permittivity is due to the combined effect of electronic, ionic, orientational, and space-charge polarization, and the reduction with frequency is related to the universal dielectric dispersion observed in disordered solids [48] and is consistent with that predicted by the Maxwell-Wagner model of interfacial polarization [49] and the Koops model of conducting grains separated by grain boundaries of higher resistance [50]. At high frequency, TBio saturates at the lowest level (about 21) compared to TPre (about 31) and TSol (30), as the interfacial polarization which contributes to TBio's large low-frequency response becomes "frozen" when the frequency of the field oscillation exceeds the frequency at which the carrier relaxes. At 20 Hz, the order is ϵ' (TBio) greater than ϵ' (TPre) greater than ϵ' (TSol); this order

changes at a high frequency as the interfacial polarization, which is responsible for the large low-frequency response of TBio, becomes 'frozen' when the field oscillation frequency exceeds the carrier relaxation frequency. The loss spectra further distinguish the samples: TBio has a well-defined relaxation peak, increasing from 2.8 at 20 Hz to 4.4 at $\log f = 3.1$ and then decreasing below 0.2 at $\log f > 100$ kHz, whereas the losses of TSol and TPre decrease monotonically from initial values of 3.2 and 2.9, respectively, without any relaxation peak, leading to the loss order $\tan \delta(\text{TBio}) > \tan \delta(\text{TSol}) > \tan \delta(\text{TPre})$. The peak-free monotonic decay of TSol and TPre suggests that predominant losses are of conduction-type, whereas the discrete relaxation in TBio suggests that losses are governed by a Debye-type process associated with charge carriers trapped at grain boundaries and at surfaces with residual organic species. The results of the enhanced low-frequency permittivity, higher overall loss, and discrete relaxation found in TBio suggest a significantly higher concentration of interfacial and space-charge polarization centers in the green-synthesized sample, which is attributed to its smaller crystallite size, higher microstrain, and surface-bound organic residue revealed by XRD, Williamson-Hall, and FTIR analysis [19][17]. In general, green-synthesized and co-precipitated TiO_2 nanostructures show a comparable enhancement of the low-frequency dielectric response due to interfacial polarization, whereas TiO_2 nanostructures prepared by sol-gel and controlled precipitation routes, possessing higher crystallinity and fewer grain-boundary defect states, exhibit lower permittivity and reduced dielectric loss [12] [17].

The charge transport and relaxation nature of the TBio, TSol and TPre samples were analyzed by complex impedance spectroscopy techniques in the frequency range of 20 Hz to 20 MHz (Fig. 11a–c). The real part of the impedance (Z') monotonically decreases with frequency for all samples, merging towards a common low value for frequencies higher than ~ 100 kHz, which is typical of semiconducting oxide ceramics and corresponds to the decrease of the barrier to charge transport with the increase of frequency and possible release of space charge[51][52]. At the lowest measured frequency, Z' shows the same trend as the AC conductivity results, with the green-synthesized sample being the least resistive, followed by the TPre sample and then the TSol sample. The imaginary parts of the impedance Z'' are unambiguous evidence of the underlying relaxation processes: the impedance of TSol and TPre shows only single broad relaxation peaks around 100 Hz characteristic of a single dominant charge-transport process, while the impedance of TBio is characterized by two clearly separated relaxation features, a low frequency contribution and a distinct peak near 25 kHz, reflecting two different relaxation processes with different time constants. In the Nyquist representation (Fig. 11c), TSol and TPre follow single depressed semi-circular arcs, while TBio resolves into two arcs (overlapping), normally considered as the sum of grains and grain boundaries as serially connected RC elements with different relaxation times[51][53]. The grain boundary response in TBio is more pronounced, which is consistent with its smaller crystallite size and larger microstrain and residual surface organic species revealed by the XRD, Williamson-Hall and FTIR analysis, resulting from high density of interfacial states.

Although these interfacial and defect states increase the electrical conductivity of TBio, they are also trapping and recombination centers for the photogenerated carriers, which is responsible for the lower photocatalytic activity of TBio compared to its electrical conductivity. The single-relaxation response and higher impedance of TSol and TPre are attributed to their more homogeneous and well-crystallized microstructures which contain fewer interstitial defect state, resulting in their higher efficiency for methylene blue degradation.

All three samples show a low-frequency plateau in the frequency-dependent AC conductivity (σ_{ac}) with a sharp dispersive increase at high frequencies, shown in Fig. 12, as expected from Jonscher's universal power law, $\sigma(\omega) = \sigma_{dc} + A\omega^s$, where the hopping mechanism between localized states [52] is responsible for the charge transport. The high conductivity of TBio throughout the entire frequency range is in line with its higher density of defects and interfacial states due to the smaller crystallite size and residual surface organics of the green synthesis route, which offers an abundant hopping pathway [19]. The greater frequency dispersion of TBio further supports the conduction taking place mostly as defect-assisted carrier hopping instead of long-range band transport[52] [50].

4. Conclusion

A successful demonstration was carried out for the synthesis of anatase TiO₂ nanoparticles using three different methods to synthesize them with a clear correlation among the methodologies used in producing microstructures and the methods used in creating functional properties. These methods included lemon-assisted green precipitation (TBio), sol-gel (TSol), and chemical precipitation (TPre). Both XRD and Williamson-Hall measurements confirmed that all samples were composed of single phase anatase. TSol and TPre had higher crystallinities and lower microstrains than TBio, while the green synthesis method yielded the smallest crystallite sizes. SEM observations revealed nearly spherical nanoparticles in all cases; the lemon peel phytochemicals restricted particle growth and promoted good dispersion in TBio, whereas the sol-gel route produced larger aggregates. FTIR and UV/Vis spectroscopic analyses verified that TBio and TPre nanoparticles (represented by the two different types of prefabricated TiO₂) formed distinctly sized Ti-O-Ti networks, showed clear peaks produced at corresponding energy intervals of 3.15 eV to 3.22 eV with a progressive narrowing of energy gap for both TBio and TPre due to defects and surface state induced band tailing; this has extended the optical absorption of both nanoparticles toward the visible region. A series of photocatalytic tests for methylene blue led to an established order of catalyst activity: TPre, TSol followed by TBio due to TPre exhibiting the highest crystallinity, and lowest recombination rate of carriers. In terms of dielectric and impedance properties, the most significant interfacial polarization at low frequencies was measured with TBio based on the Maxwell-Wagner model, which provided TBio with the highest

low frequency permittivity and loss, together with the highest AC conductivity and lowest overall impedance arising from defect-assisted hopping conduction, its Nyquist response resolving into two overlapping arcs associated with distinct grain and grain-boundary relaxations. Conversely, TPre and TSol both exhibited balanced dielectric properties with lower loss, and their impedance spectra showed single depressed semicircular arcs characteristic of a single dominant charge-transport process. Therefore, the combined results demonstrate that the lemon peel-assisted route is an environmentally friendly method that maximizes interfacial polarization and low-frequency permittivity, although at the cost of higher dielectric loss and reduced photocatalytic activity. Finally, while precipitation of TiO₂ provides the best performance for both photocatalytic and dielectric applications requiring the highest level crystalline structure, and sol-gel provides a compromise between the two with reasonable performance to enable multi-functional device integration.

Credit authorship contribution statement

Shah Sadia Rahman Joya: Writing original draft, Methodology, Conceptualization, Project administration, Supervision.

Sadia Samanta: Writing original draft, Methodology, Visualization, Formal analysis, Investigation.

Harunur Rashid: Writing original draft & review.

Md. Lutfor Rahman: Investigation, Data curation.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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