

Structural and morphological characterization of tea-waste-derived carbon/TiO₂ (AT–TiO₂) composites prepared by solvent-assisted solid-state dispersion

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Abstract

Tea waste is an abundant agro-industrial residue but its valorization into functional inorganic composites remains largely unexplored. In this study, the waste was torrefied at 230 °C and combined with commercial TiO₂ by a solvent-assisted solid-state dispersion route followed by calcination at 500 °C, giving a Tea-Waste-Derived carbon/ TiO₂ material denoted AT– TiO₂. A total of 3 AT: TiO₂ mass ratios (9:1, 8:2 and 7:3) were prepared with pure AT and pure TiO₂ controls processed identically, and characterized by XRD and SEM–EDS. XRD results showed that single-phase rutile retained its structure in every composite, with no peak shift and secondary phase. The carbon content was obtained in EDS pattern, due to the effect of using ethanol as a composite solvent. Scherrer analysis of the (110) reflection gave apparent crystallite sizes of 61, 34, 61, and 49 nm for pure TiO₂ as well as the 9:1, 8:2 and 7:3 composites. SEM image analysis of 60 objects per sample, fitted to a log-normal distribution, gave median agglomerate sizes of 11.99 ± 0.51, 2.96 ± 0.32, 9.91 ± 0.74, 5.97 ± 0.66 and 11.00 ± 0.81 µm respectively. The 8:2 composite showed both the smallest median and the narrowest distribution (geometric standard deviation 1.56), indicating the most uniform dispersion. This study can serve as the basis for the development of biomass–inorganic composite materials with the potential to be applied in the fields of environmentally friendly adsorption and photocatalysis.

Keywords: Tea waste, Titanium dioxide, Composite, Rutile, Particle size distribution

1. Introduction

Valorization of agro-industrial residues into functional materials has attracted growing interest, driven by the need for low-cost and sustainable feedstocks. Tea is among the most widely consumed beverages worldwide, with black and green tea accounting for approximately 98% of global production. Spent tea leaves consist mainly of cellulose, hemicellulose, lignin, structural proteins, secondary metabolites and mineral components [1]. Due to this composition, the waste is often rich in carbon, bears oxygen-containing surface functionalities such as –OH and –COOH, and possesses a porous texture that can interact with a range of aqueous pollutants [2]. These features make it a plausible low-cost support for inorganic active phases. Several studies have shown that thermal treatment converts such residues into a disordered, aromatic-rich black carbon whose structure evolves progressively with treatment temperature [3]. Biochars and activated carbons derived from lignocellulosic biomass have the potential to serve as supports and adsorbents in water treatment [4, 5].

Titanium dioxide (TiO₂) is one of the most extensively studied semiconducting metal oxides, valued for its chemical stability, strong oxidizing power, low cost and low toxicity. TiO₂ crystallizes in 3 polymorphs, namely anatase and rutile as tetragonal, and brookite, which is orthorhombic. Rutile is the thermodynamically stable phase, while anatase and brookite are metastable and convert to rutile on heating [6, 7]. The reported band gaps are approximately 3.2 eV for anatase and 3.0 eV for rutile [8, 9]. Despite its widespread use, TiO₂ suffers from a wide band gap that restricts absorption to the ultraviolet region, rapid recombination of photogenerated charge carriers, a pronounced tendency to agglomerate, and practical difficulty of recovery and reuse after treatment [10, 11]. Dispersing TiO₂ on a carbonaceous support has been reported to mitigate agglomeration, increase the accessible surface area, and facilitate recovery of the solid after use [12–14].

The mechanisms by which a carbonaceous phase is held to address these limitations are worth discussing due to their differences, particularly in various composites. According to previous studies, a total of 4 mechanisms are often used. The first is geometric, which involves anchoring the oxide on a support to separate the particles and limits the agglomeration that often covers a large fraction of the surface. This ensures that more oxide remains accessible to both light and solute [12, 13]. The second is adsorptive pre-concentration, where the oxygen-containing surface functionalities and porosity of a biomass-derived carbon helps in binding organic solutes and raising their local concentration in the immediate vicinity of the oxide. This increases the apparent reaction rate without altering the

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intrinsic activity of TiO_2 [4, 14]. The third is electronic, where carbon acts as an acceptor for photogenerated electrons, extending the lifetime of the separated charge carriers and mitigating the rapid recombination that limits TiO_2 . The mechanism is most often credited for the improvements reported in carbon– TiO_2 systems [15, 16]. The fourth is optical, where interfacial Ti–O–C states or carbon incorporation into the lattice can shift the absorption edge toward the visible, partially relieving the constraint imposed by a wide band gap [14]. A fifth, practical rather than mechanistic approach involves supporting the oxide on coarser carbon fragments to produce a solid that settles and filters readily, addressing the recovery problem directly [13, 17].

These mechanisms are not independent and often impose conflicting demands. Adsorptive pre-concentration and electronic charge separation both favor a high carbon fraction, while a high carbon fraction also screens the oxide from incident light. Establishing which mechanisms operate in a given composite requires evidence beyond structural characterization. Photoluminescence spectroscopy is often used for charge separation, diffuse-reflectance spectroscopy for the optical effect, nitrogen physisorption for the adsorptive contribution, and controlled performance testing to separate adsorption from degradation. The present study does not provide the evidence, and the mechanisms above are therefore presented as the rationale drawn from the literature for the approach taken rather than processes demonstrated.

A number of TiO_2 -based composites have been reported using both biomass-derived and synthetic secondary phases, including cellulose acetate [18], activated carbon [19], PMMA [20], CaTiO_3 perovskite [21, 22], Fe_2O_3 [23], reduced graphene oxide [24], Fe_3O_4 [25] and eggshell [17]. Carbonaceous supports have attracted particular attention, with activated carbon [14], biochar [15], and other waste-derived carbons [16] all reported to improve TiO_2 dispersion and recoverability. In a previous study, eggshell/ TiO_2 composites prepared using a solid-state dispersion (SSD) method degraded 95.63% of methylene blue under UV irradiation. SSD was found to be a simple and solvent-lean approach to disperse a pre-formed oxide onto a waste-derived support [17].

The present study extends that approach with the use of torrefied tea waste. The scientific contribution of this study is threefold and goes beyond the substitution of a biomass for another. First, it establishes that a solvent-assisted solid-state dispersion route carried out at 500 °C preserves a single rutile structure without generating any titanium-containing secondary phase such as TiC , Ti_3O_5 or a Ti–Ca mixed oxide. This was achieved despite the carbon-rich support and calcium supplied by tea-waste ash, a combination under which carbothermal reduction or perovskite formation would be plausible. Second, it identifies and quantifies a non-monotonic dependence of agglomerate size on TiO_2 loading, with an optimum near 20 wt% TiO_2 , which defines the loading window for subsequent performance studies. Third, it documents a calcium-bearing crystalline phase carried over from the tea-waste ash that persists in the final composite. This phase is intrinsic to tea waste and is not present in the eggshell or activated-carbon systems reported previously. Therefore, it must be accounted for in any subsequent interpretation of surface chemistry or catalytic behavior.

The intended application of this material is stated explicitly, because adsorption and photocatalysis impose different requirements on a composite and both must not be pursued interchangeably. The target of this line of study is the photocatalytic degradation of organic dyes in aqueous media, continuing the approach validated for eggshell/ TiO_2 in an earlier study [17]. Adsorption by the carbon material fraction is regarded as a supporting function and its role is to concentrate the pollutant around the oxide surface and aid recovery of the solid without transferring the pollutant to another phase. The distinction matters for how the material must be optimized, and it also determines the evidence required before any performance claim can be made.

This study is deliberately restricted to the structural and morphological characterization that precedes any such evaluation. *X-Ray Diffraction* (XRD) was used to identify the crystalline phases present and to estimate apparent crystallite size and micro-strain, while *Scanning Electron Microscopy* with *Energy-Dispersive X-ray Spectroscopy* (SEM–EDS) was used to examine surface morphology, agglomerate size distribution and elemental composition. Optical properties, textural properties, and catalytic performance were not measured in this study and no claims were made. The characterization required to support such claims is specified below.

2. Materials and methods

2.1 Materials

Spent black tea leaves were collected locally and used as the biomass precursor. The inorganic phase was a commercial titanium dioxide powder (Merck KGaA, Darmstadt, Germany) in single-phase *Rutile*. Another material used was ethanol 98% as a solvent and distilled water (H_2O). The composite synthesis method of tea waste (AT)- TiO_2 was used as the Solvent-Assisted Solid-State Method (SA-SSD). The composite samples used variations in mass composition between tea waste (AT) and TiO_2 powder which consisted of AT- TiO_2 (7:3), AT- TiO_2 (8:2), and AT- TiO_2 (9:1). In addition, pure AT and pure TiO_2 samples were also used as controls.

2.2 Preparation of the tea-waste-derived carbon (AT)

Tea leaves were steeped in hot water and the spent leaves were recovered by filtration, then washed repeatedly under running water until the filtrate ran clear. The washed residue was treated in a laboratory oven at 230 °C for 1 h. This step was a mild torrefaction rather than simple drying; at 200 to 300 °C, the hemicellulose fraction of lignocellulosic biomass decomposed and part of the cellulose began to depolymerize. As a result, the treatment removed moisture and light volatiles, lowered the hygroscopicity of the solid, embrittled it and thereby improved grindability, yielding a more thermally stable and more uniform precursor for the subsequent processing steps [26, 27]. Comparable thermal pre-treatments were routinely applied to lignocellulosic residues before conversion into carbon materials [5]. The choice of 230 °C placed the treatment at the lower end of the torrefaction window, where mass loss remained moderate while the grinding benefit was already realized [26]. The torrefied solid was ground in a blender, further reduced with a mortar and pestle and sieved through a 200-mesh screen, and the resulting powder was denoted AT.

Because AT was subsequently calcined at 500 °C, the final carbonaceous component of the composite was a char rather than an intact lignocellulosic matrix. The terminology used throughout this manuscript was revised accordingly. AT denoted a tea-waste-derived carbonaceous residue. This assignment was supported by the elemental data, showing that carbon remained the dominant element (38–46 at%) in all composites after calcination, the solid was a carbon-rich char and not an ash. Part of this carbon originated from the tea waste and part from residue of the ethanol dispersion medium, which the 500 °C calcination did not remove completely, the 2 contributions were not separated by EDS alone.

2.3 Preparation of AT-TiO₂ composites

AT and TiO₂ were combined at AT:TiO₂ mass ratios of 9:1, 8:2 and 7:3, with a total mass of 5.0 g per batch. The corresponding masses were given in Table 1. Pure AT and pure TiO₂ controls were prepared at the same total mass of 5.0 g and were carried through the identical processing sequence as the composites: each was dispersed in 100 mL of ethanol, stirred for 1 h, allowed to settle for 12 h, dried at 110 °C for 12 h and calcined at 500 °C for 1 h. No step was omitted for either control. Consequently, the controls and the composites shared the same solvent exposure and thermal history, any difference was attributable to composition alone. This also suggested that the pure TiO₂ control was not simply the as-received Merck powder: it was that powder after ethanol dispersion and calcination, and it was the appropriate reference against which the composites must be compared.

Each mixture was transferred to a beaker containing 100 mL of ethanol and stirred for 1 h until visually homogeneous, then left to settle for 12 h. The sediment was dried in an oven at 110 °C for 12 h to evaporate the ethanol, and finally calcined at 500 °C for 1 h to give the AT–TiO₂ powder. A schematic of the procedure was shown in Figure 1.

Table 1 Mass composition of the samples

Sample	AT (g)	TiO ₂ (g)	Total (g)	TiO ₂ (wt%)
Pure AT	5.0	–	5.0	0
Pure TiO ₂	–	5.0	5.0	100
AT–TiO ₂ (9:1)	4.5	0.5	5.0	10
AT–TiO ₂ (8:2)	4.0	1.0	5.0	20
AT–TiO ₂ (7:3)	3.5	1.5	5.0	30

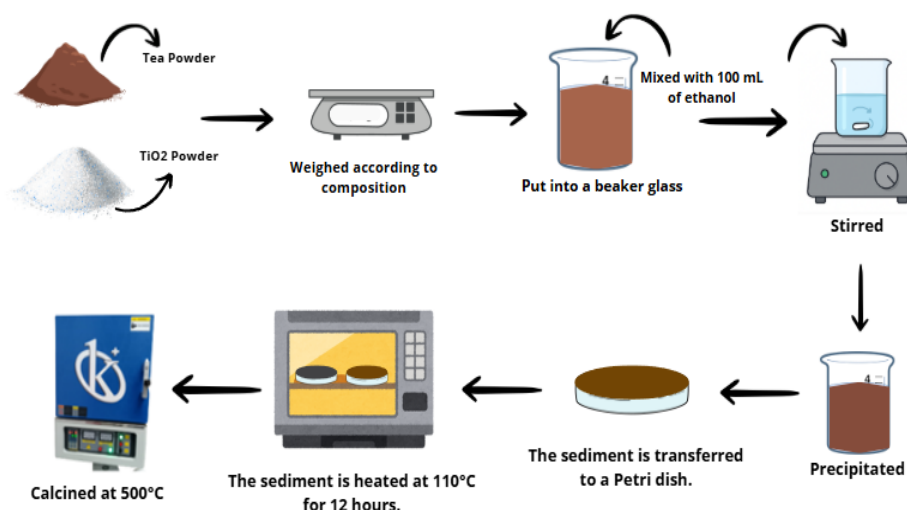


Figure 1 Schematic of the preparation of AT–TiO₂ composites by solvent-assisted solid-state dispersion

AT/TiO₂ composite was placed in a measuring cup and mixed with 100 mL of ethanol [17]. The mixture was stirred using a stirrer until homogeneous for 1 hour. Subsequently, the mixture was left to settle for 12 hours. The precipitate obtained was dried using an oven at a temperature of 110°C for 12 hours. The next stage was the calcination process, which required heating at a temperature of 500°C for 1 hour to produce the final material in the form of tea waste/TiO₂ powder ready for use.

2.4 Characterization

2.4.1 X-Ray Diffraction

The XRD test was conducted to determine the crystal structure of the synthesized tea waste material and the AT/TiO₂ composite. Samples that had undergone calcination were analyzed using XRD. This process aims to identify the crystal phase, crystallite size, and degree of structural order of the material, as presented in Table 2. The XRD data was in the form of a diffractogram pattern showing the intensity against the 2θ angle. Data were collected over the range $2\theta = 20\text{--}60^\circ$ in continuous scan mode. This pattern was compared with standard data using *DiffraC Eva Software* to confirm the presence of the TiO₂ crystal phase and other compounds of composites.

2.4.2 Scanning Electron Microscopy with EDS

SEM-EDS testing was conducted to observe the surface morphology and elemental composition of the synthesized tea waste material and AT/TiO₂ composite. Subsequently, the prepared samples were analyzed using SEM. High-energy electron beams were fired at the sample surface to produce secondary electron signals and backscattered electrons that formed high-magnification images to observe the morphological shape, particle size, porosity, and texture of the material. Meanwhile, EDS analysis was used to assess the elemental composition through the detection of characteristic X-rays emitted due to the excitation of atoms by the electron beam, resulting in a spectrum showing the type of elements and their mass percentages. The combination of SEM morphological images and EDS element mapping allowed verification of the presence and distribution of TiO₂ in tea waste composites, thereby providing information about the surface structure of each sample.

2.4.3 Calculation of crystallite size

The volume-weighted mean crystallite size D was calculated from the Scherrer equation show in equation 1 and the average microstrain (ϵ) using equation 2.

$$D = \frac{K\lambda}{(\beta \cos \theta)} \quad (1)$$

$$\epsilon = \frac{\beta}{(4 \tan \theta)} \quad (2)$$

where $\lambda = 1.5406 \text{ \AA}$ is the Cu $K\alpha$ wavelength, θ is the Bragg angle and β is the full width at half maximum of the reflection expressed in radians. The shape factor was taken as $K = 0.9$, the value conventionally adopted for crystallites of approximately spherical habit.

This was an assumption rather than a measured quantity, and a different assumed morphology could rescale all reported sizes by a common factor. A total of 3 assumptions were stated explicitly, binding the interpretation of the results. First, the calculation attributed all peak broadening beyond the instrumental contribution to crystallite size in the case of D , and to lattice strain in the case of ϵ . D and ϵ were each upper limits on the contribution of their respective mechanism and could not be summed, because the 2 effects were not separated by a Williamson–Hall or Rietveld treatment here. Second, instrumental broadening had not been deconvoluted, so the reported D values were lower bounds and the reported ϵ values were upper bounds. Third, the calculation was applied only to the (110) reflection, which was the most intense and best resolved rutile peak in every pattern. The results of this study were reported in Table 3.

2.4.4 Agglomerate size distribution

Agglomerate sizes were measured from the SEM micrographs using ImageJ. For each sample, 60 discrete objects were measured, and the resulting size histograms were fitted with a log-normal distribution. All values reported in this work derive from a single synthesis batch and a single measurement per sample; independent synthesis replicates were not prepared. Consequently, the differences between composite ratios were described here as observed trends and were not tested for statistical significance.

3. Results

3.1 XRD analysis

The diffraction patterns of pure TiO_2 , pure AT and the 3 composites were shown in Figure 2, also the extracted peak parameters were listed in Table 2. All patterns were collected over $2\theta = 20\text{--}60^\circ$.

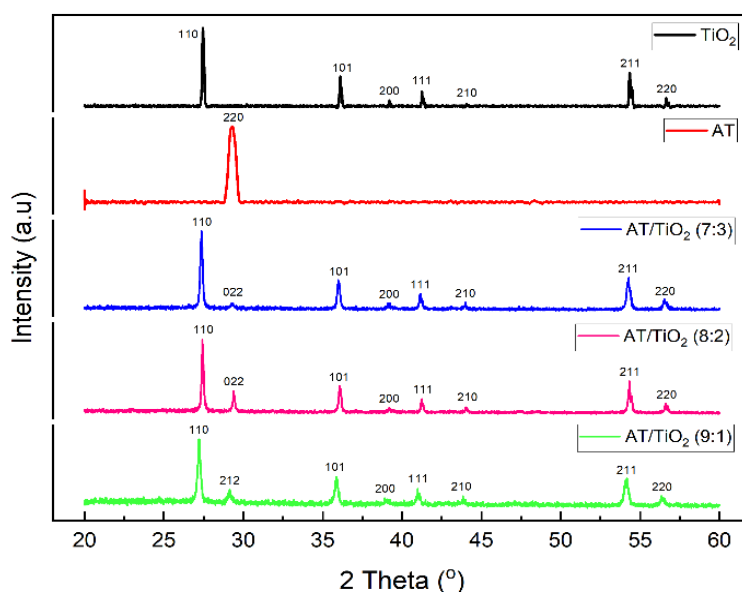


Figure 2 XRD Analysis of Pure TiO_2 , Pure AT and AT- TiO_2 Composites (7:3, 8:2, 9:1)

Pure TiO_2 exhibited sharp, well-defined reflections at $2\theta = 27.45, 36.09, 39.20, 41.25, 44.05, 54.34$ and 56.64° , which indexed completely to the (110), (101), (200), (111), (210), (211) and (220) planes of tetragonal rutile (JCPDS 21-1276). No anatase (101) reflection at $2\theta \approx 25.3^\circ$ and no brookite reflection were detected, confirming that the starting oxide is phase-pure rutile.

The pattern of pure AT was essentially featureless across most of the measured range, with a low, flat background consistent with a predominantly amorphous carbonaceous solid, and a single discrete reflection centered near $2\theta \approx 29.4^\circ$ ($d \approx 3.04 \text{ \AA}$). In the original version of this manuscript this feature was reported at 22.5° and indexed as a (220) plane. Based on the results both assignments were corrected. A reflection at 22.5° was not present in the measured pattern, and the index (220) did not correspond to any plane of cellulose I, whose principal reflection lied near 22.5° and was conventionally indexed as (200). The observed d -spacing of approximately $3.04 \text{ \AA}$ together with the calcium detected by EDS in both pure AT and all composites (Figure 3) was most consistent with a calcium-bearing mineral phase, plausibly calcite, carried over from the tea-waste ash; the (104) reflection of calcite occurs at $2\theta = 29.4^\circ$ with $d = 3.035 \text{ \AA}$.

Table 2 XRD peak positions, interplanar spacings, and sample phase

Sample	2 θ (°)	D-Spacing (Å)	(hkl)	FWHM (°)	Phase
AT	22.5	3.95	(220)	2.80	Amorphous
TiO ₂	27.45	3.25	(110)	0.135	Rutile TiO ₂
	36.09	2.49	(101)	0.135	
	39.20	2.30	(200)	0.155	
	41.25	2.19	(111)	0.145	
	44.05	2.05	(210)	0.279	
	54.34	1.69	(211)	0.207	
	56.64	1.62	(220)	0.228	
AT- TiO ₂ (9:1)	27.43	3.25	(110)	0.238	Rutile TiO ₂
	36.09	2.30	(101)	1.170	
	39.20	2.19	(200)	0.279	
	41.25	2.05	(111)	0.724	
	44.05	1.69	(210)	0.373	
	54.34	1.62	(211)	0.517	
	56.64	1.20	(220)	0.238	
AT- TiO ₂ (8:2)	27.44	3.25	(110)	0.135	Rutile TiO ₂
	36.09	2.30	(101)	1.170	
	39.20	2.19	(200)	0.197	
	41.25	2.05	(111)	0.580	
	44.05	1.69	(210)	0.197	
	54.34	1.62	(211)	0.259	
	56.64	1.48	(220)	0.135	
AT- TiO ₂ (7:3)	27.45	3.25	(110)	0.166	Rutile TiO ₂
	36.09	2.30	(101)	0.693	
	39.20	2.19	(200)	0.217	
	41.25	2.05	(111)	0.373	
	44.05	1.69	(210)	0.259	
	54.34	1.62	(211)	0.331	
	56.64	1.48	(220)	0.166	

All 3 composites reproduced the full set of rutile reflections at essentially unchanged positions (the (110) peak lies at 27.43, 27.44 and 27.45° for the 9:1, 8:2 and 7:3 samples respectively, i.e. within $\pm 0.02^\circ$ of pure TiO₂), together with the same $\approx 29.4^\circ$ reflection seen in pure AT. No titanium-containing secondary phase was detected, and there was no evidence of anatase, of titanium carbide, of a reduced Ti–O phase such as Ti₃O₅, or of CaTiO₃ perovskite, any of which could be expected to produce reflections outside the rutile set. The relative intensity of the rutile reflections decreased and the background rose as the AT fraction increased from 7:3 to 9:1, which was the expected dilution of a crystalline phase by an amorphous matrix.

3.2 Crystallite size and micro-strain

Quantitative Scherrer analysis was performed on the most intense rutile reflection (110), for pure TiO₂ and for each composite. The apparent crystallite size *D* was obtained from Eq.1 and the average microstrain ϵ was estimated from Eq.2. This treatment followed standard practice for TiO₂ materials [28]. The results were given in Table 3.

Table 3 Scherrer crystallite size and microstrain from the rutile (110)

Sample	2 θ (°)	FWHM (°)	β (rad)	<i>D</i> (nm)	ϵ (%)
Pure TiO ₂	27.45	0.135	2.36×10^{-3}	60.6	0.241
AT–TiO ₂ (9:1)	27.43	0.238	4.15×10^{-3}	34.4	0.426
AT–TiO ₂ (8:2)	27.44	0.135	2.36×10^{-3}	60.6	0.241
AT–TiO ₂ (7:3)	27.45	0.166	2.90×10^{-3}	49.3	0.297

Based on this study, 2 points must be emphasized. First, the narrowest measured widths (0.135°) were close to the resolution limit of a conventional laboratory diffractometer, and the corresponding crystallite sizes were lower bounds and the true values could be considerably larger. Second, and more importantly, the trend was not monotonic: the 8:2 composite returned exactly the same width, and the same apparent crystallite size, as pure TiO₂, while the 9:1 sample, the one with the least TiO₂ and the poorest signal-to-noise ratio, showed the largest apparent broadening. The claim made in the previous version of this manuscript, that compositing with tea waste reduced the crystallite size and increased the microstrain of TiO₂, was not supported by the data. The correct interpretation was that the rutile crystallite size was unchanged within the uncertainty of the measurement, which was entirely consistent with a physical dispersion route in which pre-formed TiO₂ particles were not chemically altered. The apparent broadening in the 9:1 pattern was most plausibly an artefact of the weak diffracted intensity from the most dilute sample.

3.3 Surface morphology and elemental composition

Secondary-electron micrographs recorded at 1500x magnification were presented in Figure 3. Pure AT consisted of irregular, angular fragments of widely varying size, with visible voids and a rough, layered surface texture characteristic of a ground char. Pure TiO₂ consisted of markedly finer, more equiaxed particles that were clustered into loose aggregates. In the composites, the fine TiO₂ population was visible decorating the surfaces of the coarser AT fragments. The coverage appeared sparse and uneven at the 9:1 ratio,

most uniform at 8:2, and at 7:3 the excess TiO₂ formed discrete clusters that were not attached to AT surfaces. The morphological structure of the composite sample was analyzed using *Scanning Electron Microscopy* (SEM) with *Energy Dispersive Spectroscopy* (EDS). The SEM-EDS characterization results were shown in Figure 3.

Across the 3 composites the titanium content increased with TiO₂ loading, from 3.46 at% (10.84 wt%) at 9:1 to 3.71 at% (11.65 wt%) at 8:2 and 5.92 at% (17.53 wt%) at 7:3, while the carbon content ranged between 44.77 and 38.09 at%. Both trends were in the expected direction and confirmed that the intended compositional gradient was achieved. Calcium, aluminum, magnesium, silicon, potassium and iron were present at low levels in pure AT and, at correspondingly diluted levels, in the composites. These were ash-forming elements native to tea leaves rather than contaminants introduced during processing, and the calcium content in particular supports the phase assignment. Carbon was detected in every sample, including the pure TiO₂ control, which was expected because all samples were dispersed in ethanol before calcination.

The first was genuine and followed directly from the preparation route. Every sample in this study, including the pure TiO₂ control, was dispersed in ethanol before drying and calcination. Therefore, carbon was expected in the control rather than absent from it, and the elemental balance was consistent with a residue of this origin, subtracting the oxygen bound to titanium as TiO₂ ($2 \times 2.74 = 5.48$ at%) leaves 27.27 at% oxygen associated with 64.51 at% carbon, an O:C ratio of 0.42 against 0.50 for ethanol itself. A carbonaceous residue derived from incompletely combusted ethanol was compositionally plausible, and its presence must be acknowledged rather than treated as contamination.

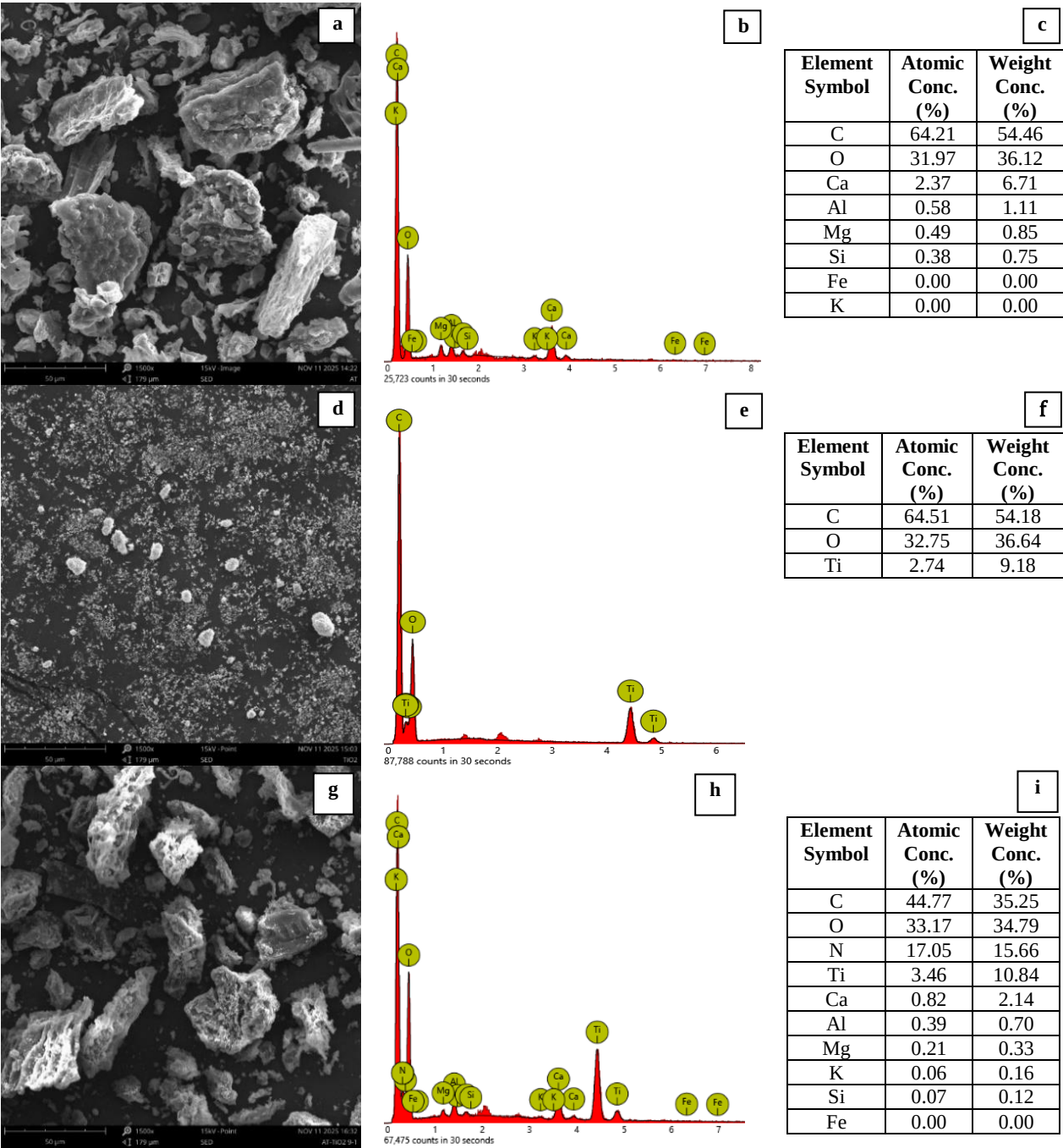


Figure 3 Morphological structure using SEM with 1500x magnification, EDS Spectra and quantitative elemental analysis by EDX (a-c) Pure AT; (d-f) Pure TiO₂; (g-i) AT-TiO₂ (9:1); (j-l) AT-TiO₂ (8:2); and (m-o) AT-TiO₂ (7:3)

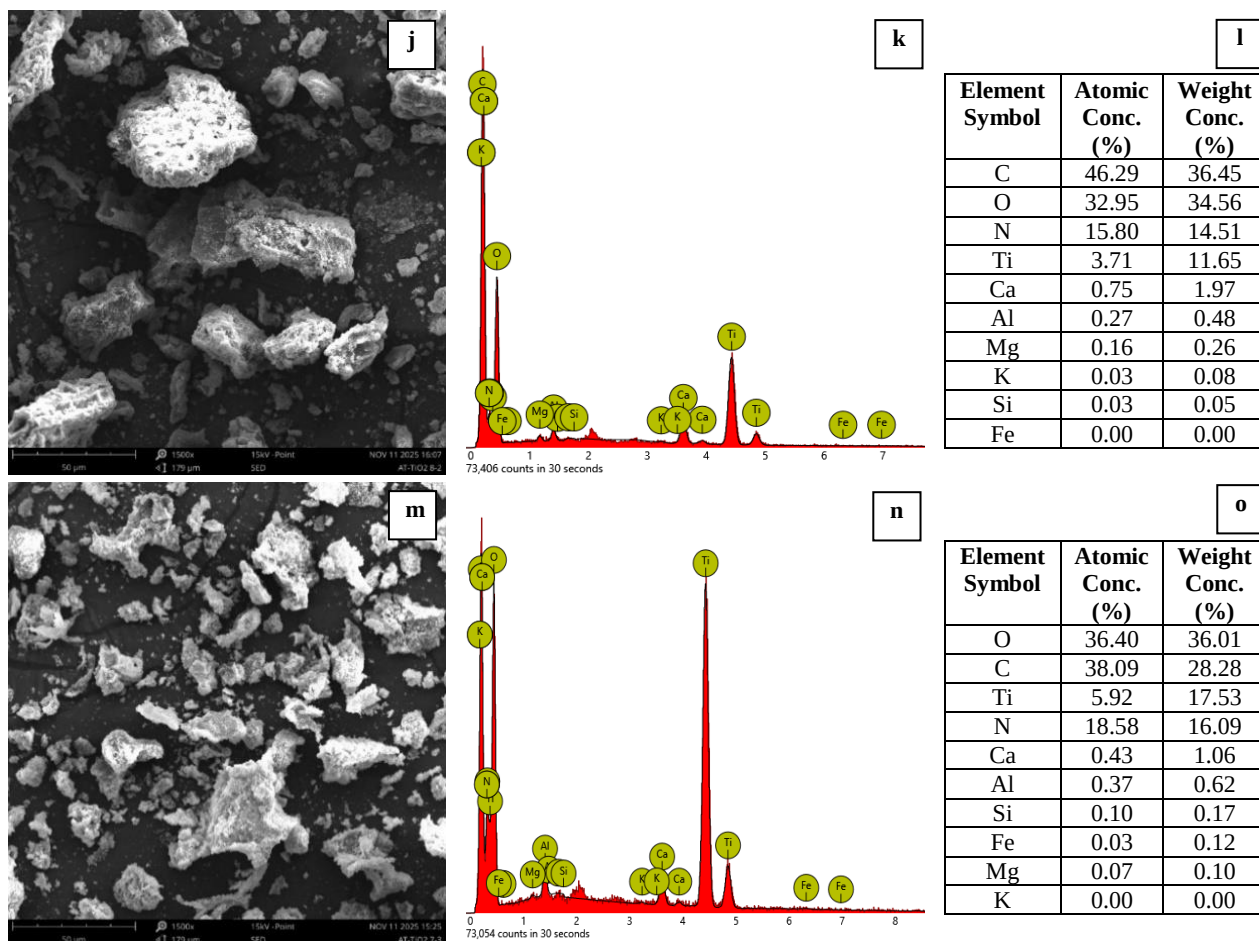


Figure 3 (continued) Morphological structure using SEM with 1500x magnification, EDS Spectra and quantitative elemental analysis by EDX (a-c) Pure AT; (d-f) Pure TiO₂; (g-i) AT-TiO₂ (9:1); (j-l) AT-TiO₂ (8:2); and (m-o) AT-TiO₂ (7:3)

The second contribution was not attributed to ethanol and must be stated plainly. The measured titanium content corresponded to only 15 wt% TiO₂ within the analyzed volume, accounting for the remaining 85 wt% as ethanol-derived carbon could require approximately 28 g of residue from the 79 g of ethanol used, a carbon yield of about 35%, which was not attainable for ethanol calcined in air. More decisively, the pure TiO₂ control contained 3.3 times more TiO₂ than the 7:3 composite yet returned a titanium signal 2.2 times lower, a discrepancy of roughly sevenfold in the wrong direction. Since all samples received the same ethanol treatment, no explanation that applied uniformly across the series could account for this ordering. The carbon and oxygen contents of the pure TiO₂ control (64.51 and 32.75 at%) were also almost identical to those of pure AT (64.21 and 31.97 at%), which pointed to a common carbon-rich background dominating both spectra. The most probable cause was that the analyzed volume in the pure TiO₂ measurement was dominated by the mounting medium rather than the specimen, or that the acquisition was made on an unrepresentative area. The spectrum was retained in Figure 3 for completeness but was excluded from all quantitative comparison in this study.

4. Discussion

4.1 Structural analysis of composite AT-TiO₂

In AT-TiO₂ composites with ratios of 7:3, 8:2, and 9:1, all diffraction patterns continued to show characteristic Rutile peaks at the same 2θ position as pure TiO₂, particularly the highest peak with the (110) crystal plane as the main peak. This showed that the composite process carried out using the SA-SSD method did not cause changes in the TiO₂ crystal structure or the formation of new phases. However, there was a decrease in relative intensity and an increase in the amorphous background as the AT mass fraction increased, showing the dilution effect of the crystalline phase by the biomass matrix (tea waste). Furthermore, the absence of peak shift showed that there was no significant ionic substitution or lattice distortion in the Rutile structure, suggesting that the interaction formed was physical in nature through dispersion and surface interaction mechanisms [29].

Overall, the 3 composite samples used in this study showed that the rutile crystal structure of TiO₂ remained stable after being composited with tea waste, while AT acted as an amorphous supporting matrix. With increasing AT composition (7:3 → 9:1), the contribution of the amorphous phase became more dominant and the relative crystallinity decreased. This showed that the AT-TiO₂ composite was formed as a heterogeneous system in which rutile particles were dispersed in an amorphous lignocellulose matrix, a characteristic that structurally supported the combination of the adsorptive properties of biomass and the photocatalytic activity of anatase TiO₂, as reported in several studies on biomass-TiO₂ composites.

Based on the data in Table 2, the XRD analysis results showed that the pure AT sample was amorphous with a broad peak at 2θ ≈ 22.5° and a large FWHM value (2.80°), showing low crystallinity. However, pure TiO₂ exhibited sharp peaks with small FWHM (0.135–0.279°) indexed as the tetragonal rutile phase, characterized by a main peak at 27.45° (crystal plane (110)). All AT-TiO₂

composite samples (9:1, 8:2, and 7:3) showed that the peak positions remained consistent with the rutile phase without significant shifts. This showed that the crystal structure of TiO_2 did not change during the mixing process with tea waste (AT) and no new phases were formed. However, the FWHM values in several crystal planes in the composite samples increased, showing a decrease in crystallite size or an increase in microstrain due to interaction with the amorphous biomass matrix [28]. The XRD peak parameter data confirmed that the composite formed was a 2-phase system, namely crystalline rutile dispersed in an amorphous lignocellulose matrix, without any transformation of the basic TiO_2 structure.

The invariance of the rutile peak positions across all 3 composites (Table 2) showed that no ionic substitution into the rutile lattice and no measurable lattice distortion occurred during processing. Taken together with the absence of any titanium-containing secondary phase, this showed that the association between TiO_2 and the carbonaceous matrix was physical, such as dispersion and surface contact, rather than the formation of a new compound. This was the expected outcome for a route in which a pre-formed, thermodynamically stable oxide was dispersed over a support and heated to a temperature well below that required for solid-state reaction. Comparable behavior, in which a dispersed oxide phase remained structurally distinct from its support, was reported for other supported TiO_2 systems [29].

4.2 Morphological analysis of composite AT- TiO_2

SEM characterization was performed using 1500x magnification. The SEM morphological results obtained generally showed non-homogeneous shape and size characteristics. The pure Tea Waste (AT) sample showed the formation of fragments with non-homogeneous shapes and sizes and visible voids, showing a porous nature. Meanwhile, the Pure TiO_2 sample showed smaller particle sizes compared to AT. The AT- TiO_2 (9:1), AT- TiO_2 (8:2), and AT- TiO_2 (7:3) composite samples showed a combined morphology of tea waste and TiO_2 with varying shapes and sizes depending on the mass composition ratio. In this SEM image, the particles had various sizes and shapes that are not uniform. Coarse particles with surfaces that appeared brittle and fragmented were observed, showing that the composite samples consisted of more brittle materials or had porosity. Some particles appeared larger and more defined, while others appear finer or as small fragments.

This showed variation in the distribution of particle sizes formed during the composite manufacturing process. The rough and uneven particle surface indicated that this composite had many pores or textures that could increase the surface area. This rougher structure was very useful in photocatalytic applications, as it increased the interaction between the material surface and substances that must be oxidized or degraded, such as organic pollutants [14, 15].

EDS results provided information on the percentage of chemical elements present in a sample by monitoring the intensity of X-ray signals emitted by the elements when the sample was exposed to electron beams. Each peak visible in the spectrum represented a specific element present in the sample. These peaks showed the quantitative amount of elements present in the sample based on the detected X-ray signal intensity [16]. The results showed that carbon and oxygen dominated the elements detected in this sample. This was consistent with the biomass components of tea waste and possibly other organic compounds. Titanium (Ti) found at a peak of around 4.5 keV was a clear indication of the presence of TiO_2 in the composite, which was used as a photocatalyst in this study. Potassium, Calcium, Magnesium, Aluminum, Silicon, and Iron originated from additional materials or mineral impurities required in the sample preparation or characterization process. Higher peaks showed a greater number of atoms of that element in the sample. Carbon and oxygen clearly dominated, reflecting the main composition of organic materials in the composite.

The EDS results demonstrated a clear compositional trend with increasing TiO_2 content from the 9:1 to 7:3 ratios. The Ti atomic concentration increased systematically from 3.46% to 5.92% from 9:1 to 7:3 composite. Meanwhile, carbon content decreased progressively (44.77 → 38.09%), reflecting the reduced dominance of the organic AT matrix at higher TiO_2 loading. The increasing Ti weight percentage was more pronounced than the atomic percentage due to the higher atomic mass of Ti, confirming effective inorganic phase incorporation. When correlated with SEM morphology, the 9:1 sample, having the lowest Ti content, exhibited broader particle size distribution and greater heterogeneity, due to insufficient TiO_2 coverage on the AT surface, promoting biomass aggregation. The 8:2 ratio showed a more balanced elemental composition and moderate Ti presence, corresponding to a relatively narrower particle distribution and improved dispersion observed in SEM. Meanwhile, the 7:3 composite, with the highest Ti concentration, displayed increased inorganic contribution which enhanced surface coverage but also introduced potential TiO_2 - TiO_2 interactions, consistent with the slight broadening of particle distribution observed morphologically. Overall, the combined SEM-EDS analysis confirmed that compositional variation directly influenced dispersion behavior, particle aggregation, and microstructural uniformity in the AT- TiO_2 composite system, with intermediate ratios providing a more homogeneous distribution of both phases.

4.3 Agglomerate size distribution

Agglomerate size distribution analysis was performed by measuring the diameter of the particles. Size distributions obtained from the SEM micrographs were shown in Figure 4 and the fitted log-normal parameters were detailed in Table 4. In this study, the quantity measured here was described throughout as the agglomerate or fragment size and not as the primary AT- TiO_2 composite particle size. The objects resolved at 1500x magnification span roughly 1–58 μm , which was 2 to 3 orders of magnitude larger than the crystallite dimensions obtained from XRD (34–61 nm, Table 3), and were biomass fragments and aggregates of TiO_2 crystallites, not individual TiO_2 particles. The terminology was revised accordingly in the text, in the table headings and in the figure captions.

The distribution showed a significant difference between pure Tea Waste (AT) and pure TiO_2 samples. The AT sample exhibited its highest distribution peak at approximately 11.99 μm , showing that most particles were centered around this relatively large size, with the distribution extending broadly toward larger sizes (up to ~40 μm), reflecting a wide and heterogeneous particle size range. However, the pure TiO_2 sample showed its maximum distribution at approximately 2.96 μm , demonstrating that the dominant particle size was much smaller and concentrated within a narrower range (approximately 1–8 μm). This comparison clearly showed that AT particles were about 4 times larger than TiO_2 particles at their respective distribution maxima. Furthermore, AT presented a broader and more dispersed size distribution, suggesting higher variability and possible agglomeration, while TiO_2 exhibited a finer and more uniform particle size distribution, which was typically associated with higher surface area and better dispersion potential in composite applications. These results confirmed that pure TiO_2 possessed a finer and more uniform microstructure compared to the biomass-derived AT sample.

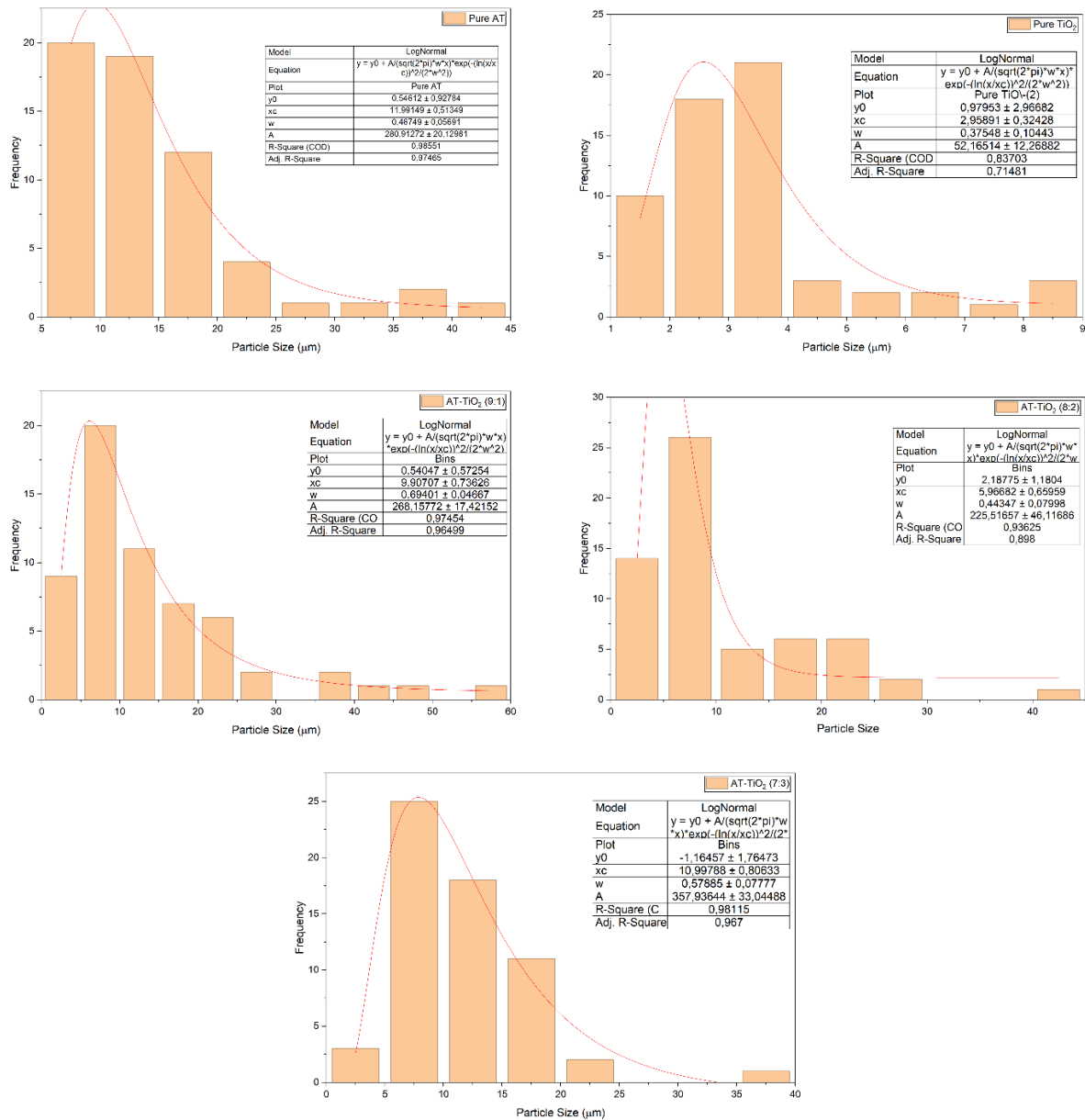


Figure 4 Particle Size Distribution from SEM Images on Pure AT, Pure TiO₂, and AT-TiO₂ Composites (9:1, 8:2, and 7:3) Respectively

The particle size distribution of the AT– TiO₂ composites revealed a clear influence of TiO₂ composition on the dominant particle size. The AT–TiO₂ (9:1) sample showed its maximum distribution at approximately 9.91 μm, showing that the particle size was still largely governed by the coarse AT component. When the TiO₂ content increased to the 8:2 ratio, the dominant particle size decreased significantly to approximately 5.97 μm, suggesting that the addition of finer TiO₂ particles improved particle packing and reduced the overall effective particle size. However, further increasing the TiO₂ composition to 7:3 shifted the dominant size back to a larger value of approximately 10.99 μm, which could be attributed to particle agglomeration and increased interparticle interactions at higher TiO₂ loading. This trend showed that moderate TiO₂ addition refined the particle distribution, while excessive addition promoted aggregation and broadening of the size range. Therefore, the 8:2 sample could be considered to exhibit the most favorable particle size distribution among the 3 composites, as it presented the smallest dominant particle size and a more concentrated distribution, reflecting better dispersion and reduced agglomeration compared to the 9:1 and 7:3 compositions.

Table 4 Log-normal fit parameters of the agglomerate size distributions (n = 60 objects per sample)

Sample	Range Size (μm)	Most Dominant Particle Size (μm)	R ²
Pure AT	2–42	11.99	0.986
Pure TiO ₂	1–8.5	2.96	0.837
AT–TiO ₂ (9:1)	1–58	10.99	0.975
AT–TiO ₂ (8:2)	1–43	5.97	0.936
AT–TiO ₂ (7:3)	1–39	9.91	0.981

The observed variation in particle size distribution among the composite ratios were associated with the dispersion mechanism of TiO₂ within the AT matrix. At the 8:2 composition, the relatively narrower and more concentrated distribution suggested a more effective dispersion of TiO₂ particles on the surface of AT, leading to reduced agglomeration and improved interfacial interaction. The presence of sufficient TiO₂ facilitated surface coverage and limited direct AT–AT aggregation, resulting in a more homogeneous microstructure. However, at the higher AT content (9:1), the reduced TiO₂ fraction appeared insufficient to uniformly coat or anchor onto the biomass surface, promoting particle clustering and broader size distribution. The 7:3 ratio containing higher TiO₂ content could induce partial TiO₂–TiO₂ interactions that slightly broadened the distribution. These results showed that an optimal balance between inorganic TiO₂ and organic AT was essential to achieve uniform dispersion and controlled particle growth within the composite system.

5. Conclusions

In conclusion, composites of tea-waste-derived carbon and TiO₂ are prepared at AT:TiO₂ mass ratios of 9:1, 8:2 and 7:3 by a solvent-assisted solid-state dispersion route, and their structure and morphology are characterized by XRD and SEM–EDS. The TiO₂ retains a single tetragonal rutile structure in every composite, with peak positions unchanged to within $\pm 0.02^\circ$ and no titanium-containing secondary phase detected, showing that the association between the oxide and the carbonaceous matrix is physical rather than chemical. Scherrer analysis of the (110) reflection provide apparent crystallite sizes between 34 and 61 nm. The rutile crystallite size is best regarded as unchanged within experimental uncertainty, because these widths approach the instrumental resolution and the trend across compositions is not monotonic. A reflection at $2\theta \approx 29.4^\circ$, present in both pure AT and all composites and accompanied by calcium in the EDS data, is attributed to a calcium-bearing mineral phase inherited from the tea-waste ash.

SEM image analysis showed that the median agglomerate size varies non-monotonically with TiO₂ loading, passing through a minimum of $5.97 \pm 0.66 \mu\text{m}$ at the 8:2 ratio, which also provide the narrowest size distribution of the three composites. This defines an optimum loading near 20 wt% TiO₂ for uniform dispersion under the conditions used here. EDS confirmed that the titanium content increases and the carbon content decreases across the series as intended.

These results establish the structural and morphological baseline for the AT–TiO₂ system and identify the composition most suitable for further study. The intended application of the material is the photocatalytic degradation of organic dyes in water, with adsorption by the carbonaceous fraction serving a supporting rather than a primary role. That application is not demonstrated here. The material is carbon-dominated because titanium accounts for at most 5.92 at% of the composites, and any future dye-removal measurement must separate adsorption from photocatalytic degradation by means of dark equilibration, matched controls and mineralization data rather than decolorization alone. The optical characterization required to support a photocatalytic claim, diffuse-reflectance spectroscopy for the band gap and photoluminescence for recombination behavior, and the nitrogen physisorption required to establish surface area and porosity remain to be performed. These measurements, together with the spectroscopic work needed to determine whether an interfacial interaction exists, form the subject of ongoing study.

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