Research article

Structure, light absorption properties and photocatalytic activity of carbon-containing titania nanocomposites synthesized via a facile sol–gel method

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ABSTRACT

Facile and green sol–gel method was used to synthesize carbon-containing titania nanopowder, and diethanolamine (DEA) was used as the in situ carbon source. The titania gel was heat treated at temperatures ranging from 300 to 700 °C. X-ray diffraction (XRD), thermal analysis, and Raman spectroscopy reported no crystalline phase at <325 °C. Crystallization of the anatase phase with traces of brookite phases was observed at T > 325 °C, followed by a transformation to anatase/rutile in the range of 400 °C < T ≤ 650 °C. Finally, the complete phase transformation to the rutile phase occurs at temperatures of T > 650 °C. High-resolution electron microscopy (HREM) micrographs confirm the coexistence of anatase and rutile nanocrystals and amorphous carbon clusters in the composite samples. Chemical element analysis via X-ray photoelectron spectroscopy (XPS) indicated non-stoichiometry in the O/Ti ratio, the presence of (Ti3+) oxidation state, and elemental carbon. Thermogravimetric (TG) measurements are the most accurate method to measure the carbon content in samples. UV-vis spectroscopy demonstrated considerable enhancement in the optical absorption properties and electronic structure of prepared samples compared to the pure anatase and rutile. This enhancement is strongly correlated with the structure and composition of prepared samples and consequently depends on the preparation method as well as conditions. Innovative features such as self-cleaning action was demonstrated in carbon containing titaneate nanocomposite.

1. Introduction

The naturally occurring TiO2 contains four polymorphs: anatase, brookite, rutile, and bronze TiO2 (B). Although all of these polymorphs comprise TiO6 octahedra, their edge and corner-sharing are different from each other. The tetragonal crystal structures of the anatase and rutile polymorphs have space groups I41/amd and P42/mnm, respectively. However, brookite and bronze polymorphs have orthorhombic and monoclinic crystal systems with Pnca and C2/m space groups, respectively [1]. Anatase and rutile TiO2 are the most thermodynamically stable phases in the TiO2 nanostructure. However, depending on the size and morphology of the nanostructured TiO2, the phase transition can prolong to temperatures as high as 1200 °C. In general, the irreversible phase transformation shift from anatase to rutile happens when heated at a temperature of >600 °C in air [2].

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TiO2 is used in multiple technological applications because of its advantageous properties such as abandoning, low cost, non-toxicity, high chemical and thermal stability, and excellent optical/electronic properties, including paintings and coatings; wastewater treatment; water splitting; hydrogen production; batteries; solar energy harvesting materials; and electronics-, memristors-, and biomedical-related applications [3, 4, 5, 6, 7, 8]. TiO2’s significant bandgap (3 eV), which only permits the material to exploit the absorption of UV light (4 %–5 % of the solar spectrum energy), limits some viable uses. This results in low solar energy utilisation efficiency and a high rate of electron-hole recombination [9].

Numerous methods, including as doping, have been devised to increase the TiO2 efficiency when exposed to visible light. with different metal and nonmetal elements [10, 11, 12, 13, 14, 15], semiconductor coupling [16, 17, 18], and surface modifications by which oxygen

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vacancies and self-doped (Ti$^{3+}$) are incorporated on the surface of nanostructured TiO$_2$ [19]. The TiO$_2$ surface can be modified by different methods such as wet-chemical reduction methods, including hydrothermal and microwave-assisted hydrothermal methods [20, 21], annealing in a vacuum or an oxygen-deficient environment [22, 23, 24], and annealing under hydrogen gas [25].

Recently, there has been a lot of interest in the surface modification of nanostructured TiO$_2$ by carbon or carbonaceous species. Recently, there has been a lot of interest in the surface modification of nanostructured TiO$_2$ by carbon or carbonaceous species. Carbon materials have high conductivity and electron storage capacity. They act as surface sensitizers and can efficiently increase the charge transfer rate [26, 27, 28]. Surface modifying carbon and carbonaceous species are innovative means by which surface disorder states are incorporated to narrow the bandgap of nanostructured TiO$_2$, suppress the electron-hole recombination rate, and increase visibility and near-infrared (Vis–NIR) light absorption [3, 9]. To overcome the challenges of a multi-step synthesis for large-scale production of the material, or for using affordable facilities, or to synthesize conditions in the modification process, the realisation of a truly facile, fast, and green synthetic method for preparing highly active carbon modified TiO$_2$ nanocomposites remains a challenge.

This study reports a fast, facile, and green sol–gel method for synthesizing carbon-containing titania nanopowder with enhanced optical absorption properties in solar energy applications.

2. Experimental and methods

2.1. Materials and sample preparation

Titanium tetraisopropoxide (TTIP 98% Arcos) and diethanolamine (DEA, 99%) were used as starting materials, and anhydrous ethanol was used as a solvent. Commercial TiO$_2$ anatase and rutile (99.8% Aladdin Industrial Corporation) were used as reference materials.

Mis Spinning and Weaving Co., El Mahalla El Kubra, Egypt, supplied the textiles utilised, consisting of viscose, linen, viscose, 100% cotton, and cotton/PET 50:50 blends. Aldrich-supplied 3-Glycidyloxy propyl trimethoxy silane (GPTMS). Hydrochloric acid, acetic acid, nitric acid, and isopropanol were used without additional purification because they were of analytical quality.

Note that 7.25 g (25 mmol) of TTIP was mixed with 2.65 g of DEA and 20 ml ethanol to produce solution A, and 9 ml bidistilled water was mixed with 11 ml ethanol to produce solution B. Then, solution B was poured into solution A with vigorous stirring. The final solution was reported to be basic with pH ~ 10 rather than the commonly used acidic solution in titania gel preparation. The hydrolysis and gelation processes were completed at room temperature after mixing for a few minutes. The molar ratio of TTIP: DEA: H$_2$O: ethanol was 1:1:20:20. The gel obtained was dried in a 150 °C oven for 12 h. The dried gel was heat treated in static air for 2 h at different temperatures from 300°C to 700°C. Each sample is labeled as TDx where x represents the calcination temperature.

2.1.1. Treatment of cotton fabrics with carbon containing titania nanocomposites

Linen, viscose, 100% cotton, and cotton/PET fabrics were soaked for 5 min in a finishing solution comprising 200 ml of hydrolyzed 3-Glycidoxy propyl trimethoxy silane (GPTMS) and 0.25 g of carbon-containing titania nanocomposites. After 20 min, a few drops of N-methylimidazole were added as a catalyst, and the samples were dried at room temperature before being cured at ninety degrees Celsius for 20 min. The samples were then rinsed twice with distilled water and dried at room temperature [29].

2.1.2. Self-cleaning action of carbon containing titania nanocomposites loaded cotton fabrics

By exposing samples containing adsorbed Methylene blue (MB) to sunlight, the self-cleaning effect of the Carbon-containing Titania nano-composites was determined. One half of each stain was exposed to sunlight for 12–48 h, while the other half was covered with black paper to avoid exposure to sunlight. The exposed portion of the stain was compared to the covered portion in terms of its ability to clear itself. The colour strength, as defined by the K/S value, of untreated and Carbon-containing Titania nanocomposites-loaded fabric samples was determined. K/S values are directly proportional to the dye concentration on the substrate. The decline in K/S values is a direct result of the dye stain degradation [30], according to equation [1]:

\[
\text{Extent of discoloration(\%)} = \left( \frac{K/S_a}{K/S_b} \right) \times 100
\]  

(1)

where (K/S)$_a$ represents the colour intensity immediately after being exposed to daylight and (K/S)$_b$ represents the colour intensity just before being exposed to daylight.

2.2. Characterisation

XRD patterns were recorded in the range of 20°–80° at a scan rate of 4°/min using the Pananalytic X’pert diffractometer with CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). The Rietveld refinement method was implemented to calculate the microstructure and weight fraction of phases using FullProf [31]. All patterns were simulated with a model including the three TiO$_2$ polymorphs. The crystallographic parameters used to conduct the structural refinement for each phase were determined using the crystallographic information files (CIF) of anatase, rutile, and brookite phases [32, 33, 34]. The Tompson–Cox–Hastings pseudo-Voigt function with axial asymmetry is considered to be fitted with the measured data [35]. The refinement is evaluated using the weighted profile and expected R-factors: (R$_{wp}$) and (R$_{exp}$) [36, 37]. The goodness-of-fit or $\chi^2$ is the $R_{wp}/R_{exp}$ ratio, which should be ~1.

Equation [2] is used to determine the weight fractions (W$_i$) of the phases found in the powder:

\[
W_i = \left\{ \frac{S_i Z_i M_i V_i / \lambda_i}{\sum S_i Z_i M_i V_i / \lambda_i} \right\}
\]  

(2)

where $M_j$ is the mass of the formula unit, $V_j$ is the volume of the unit cell, $S_j$ is the scaling factor, $Z_j$ is the number of formulas per unit cell, and $\lambda_j$ is the Brindley particle absorption contrast factor for the phase $j$ [38]. Through the use of the Williamson-Hall (W–H) equation, the crystallite size is determined from equation (3) [39].

\[
\frac{\beta \cos(\theta_{hk0})}{\lambda} = \frac{K}{D} + 4\varepsilon \sin(\theta_{hk0})
\]  

(3)

where $\theta_{hk0}$ is the peak position, $\beta$ is the broadening (FWHM), $\lambda$ is the wavelength, $K$ is a constant, which is generally considered 0.9, $\varepsilon$ is the strain, and the crystallite size $D$ is calculated from the intercept of the straight line ($W$–$H$ plot) with the $\left( \frac{\beta \cos(\theta_{hk0})}{\lambda} \right)$ axis [40].

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a NETZSCH SAT449 F5 thermo-gravimetric (TG) analyzer, and measurements were conducted in a temperature range from 40°C–1000°C with a heating rate 10°C/min in air.

Raman spectra were recorded at room temperature from 100 to 1000 cm$^{-1}$, and the samples were excited with a 785-nm-sized laser beam. HRTEM images of samples were obtained using a Tecnai G$^2$ F30 high-resolution transmission electron microscope with an attached EDAX unit.

The surface chemical composition of samples was evaluated using Kratos AXIS.

ULTRA DLD X-ray photoelectron spectroscopy (XPS). XPSPeak41 free was used for photoelectron peaks fitting.
temperature of complete transformation from anatase to the rutile phase occurs at a temperature range from 400°C to 700°C. TD700 has been observed as a pure rutile phase. These observations of rutile phase (JCPDS card no. 00-21-1276). However, the sample of the other samples are reported to be crystalline and have the characteristics of anatase A (101) (JCPDS card no. 00-21-1272) and R (110) peaks. Sample TD300 is amorphous, no crystalline phases are detected, while sample TD700 is a mixture of anatase (98%) and brookite trace (2%) with a crystallite size of 62.52 nm. All samples are measured pro heat treated at temperatures from 425°C to 700°C and the thermal behavior of titania gel derived from the TTIP–DEA–H₂O-ethanol system was examined using simultaneous TG–DSC thermal analysis. Figure 3 shows the resulting TG, DTG, DSC, and DDSC for titania dried gel.

3. Results and discussion

The hydrolysis and condensation of titanium tetra isopropoxide in aqueous media can be used to generate titanium dioxide nanoparticles (TiO₂NPs) using the sol-gel method.

In the presence of water, alkoxides are hydrolyzed and then polymerized to create a three-dimensional oxide network. The following diagram can be used to represent these reactions.

1. Hydrolysis step: 
   
   \[ \text{Ti(OH)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4 \text{ROH} \]

2. Condensation step: 
   
   \[ \text{Ti(OH)}_4 \rightarrow \text{TiO}_2 \cdot x\text{H}_2\text{O} + (2-x)\text{H}_2\text{O} \]

Where R is isopropyl group

3.1. XRD analysis

Figure 1 shows the XRD patterns of certain selected samples heated at different temperatures from 300°C to 700°C. The figure shows that the sample TD300 is amorphous, no crystalline phases are detected, while the other samples are reported to be crystalline and have the characteristic peaks of anatase A (101) (JCPDS card no. 00-21-1272) and R (110) of rutile phase (JCPDS card no. 00-21-1276). However, the sample TD700 has been observed as a pure rutile phase. These observations report that the anatase phase is formed at a temperature of >300°C. The rutile phase is then formed at temperature 400°C < T < 425°C, and the complete transformation from anatase to the rutile phase occurs at a temperature of >650°C.

The acquired Rietveld refinements for all samples heat treated at temperatures from 400°C to 700°C agree with the experimentally measured profiles (Rwp < 10%, Rexp < 9%, and 1 < χ² < 2). Because of refinement, the sample TD400 is reported not to be a pure anatase phase; however, it is a mixture of anatase (98%) and brookite trace (2%) with crystallite sizes of 9.50 and 8.25 nm, respectively. The sample TD700 is a pure rutile phase with a crystallite size of 62.52 nm. All samples heat treated at temperatures from 425°C to 650°C are mixtures of anatase and rutile phases. Figure 2 shows the Rietveld refinement of sample TD550 and shows the process for all the described samples.

Table 1 shows the data of refined lattice parameters, the refined weight fraction of phases present, and crystallite size calculated by the W–H plot and Debye–Scherrer’s equation. As shown in Table 1, there is no noticeable change in lattice parameters in both phases (anatase and rutile) because of the effect of heat treatment at different temperatures. The crystallite sizes calculated using the W–H plot were larger than those calculated from Scherrer’s equation. The reason is that the former method does not consider broadening because of the strain effect. Figure 2(a) shows the crystallite sizes calculated with a W–H plot as a function of temperature, thus showing an increase in crystallite size of both phases with temperature from 12.41 to 38.45 nm for the anatase phase and from 29.61 to 62.52 for the rutile phase.

Figure 2(b) shows the weight fractions of rutile and anatase phases calculated using the Rietveld refinement method as functions of temperature, demonstrating that the desired anatase/rutile ratio in titania nanocomposite can be easily controlled with changing temperature in a lower temperature range.

3.2. (TG–DSC) analysis

The UV-vis absorbance and diffuse reflectance spectra (DRS) in the range from 200 nm to 800 nm were recorded using a spectrophotometer.

The following diagram shows the UV–vis absorbance and diffuse reflectance spectra (DRS) in the range from 200 to 800 nm were recorded using a spectrophotometer.

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The UV-vis absorbance and diffuse reflectance spectra (DRS) in the range from 200 to 800 nm were recorded using a spectrophotometer. The thermal behavior of titania gel derived from the TTIP–DEA–H₂O-ethanol system was examined using simultaneous TG–DSC thermal analysis. Figure 3 shows the resulting TG, DTG, DSC, and DDSC for titania dried gel.

The TG curve shows a total mass loss of 44.52% in two marked steps, the first step with a mass loss of 23.6% in the temperature range from 40°C to 454.8°C, the second step with a mass loss of 20.72% in the range from 454.8°C to 1000°C. The DTG curve represents the mass loss rate, it shows two peaks corresponding to the two mass loss regions in TG curve, the first peak has maximum mass loss rate at 307.9°C, and the second peak has a maximum rate at 516.1°C. The DSC curve has one endothermic peak with sharp maximum at 516.1°C, this complex peak resulted from superposition of several exothermic peaks of different thermal processes over a wide range of temperature. To understand this thermal behavior,

![Figure 1. XRD patterns for titania powder heat treated at temperatures from 300°C to 700°C: (a) 300°C, (b) 350°C, (c) 400°C, (d) 425°C, (e) 475°C, (f) 525°C, (g) 550°C, (h) 575°C, (i) 650°C and (j) 700°C.]

![Figure 3. TG, DTG, DSC, and DDSC for titania dried gel.]

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DDSC curve was derived, it exhibits 6 transition temperatures over the range from 200 to 650 °C, the 1st is at 247.2 °C assigned to decomposition of DEA molecules, the 2nd and 3rd transition points are at 322.5 and 401.5 °C the second point representing the formation of crystalline anatase and brookite, the formation of Brookite phase is attributed to the decomposition of titanium-organic complexes [41]. The third transition point represents transition from unstable brookite to stable rutile phase [42, 43]. The 4th transition temperature at 516.1 °C is assigned to decomposition of titanium-organic residues mainly TTIP-DEA complexes and associated species [44], the 5th transition point at 570.8 °C may represent oxidation of residual carbon structures and release of CO2 gas, the last transition point at 604.5 °C may represent the removal of oxygen vacancies formed on the surface of due to decarbonization.

Carbon content was estimated by measuring the thermogram (TG) for all samples heat treated from 400 to 700 °C and the weight fraction of carbon (MW%) in titania nano powder as given in Table 2. It is clear that, the carbon content decreases with increasing calcination temperature till vanish at high temperatures T ≥ 700 °C.

### 3.3. Raman spectroscopy

All three TiO2 crystal structures have the same fundamental structural unit [TiO6] octahedron but with different arrangements and links, consequently having different characteristic Raman modes. Anatase has six (1A1g + 2B1g + 3Eg) Raman-active modes, while rutile has four (A1g + B1g + B2g + Eg) modes [45]. However, Brookit has predicted 36 (9A1g + 9B1g + 9B2g + 9B3g) Raman-active modes [46]. The Eg mode is assigned to the symmetrical stretching vibration of O-Ti-O bonds in TiO2. B1g mode corresponds to a symmetrical bending vibration of O-Ti-O and A1g mode refers to the anti-symmetric bending of O-Ti-O bonds [47].

Figure 4 shows the Raman spectra of certain selected titania composite samples and pure commercial anatase and rutile powder ranging from 100 to 200 cm⁻¹ and from 300 to 750 cm⁻¹.
As shown in Figure 4, curve (a) shows a strong sharp peak representing the characteristic Raman active mode of the pure anatase phase at 143.1 cm\(^{-1}\) with FWHM = 14.5 cm\(^{-1}\), and three peaks positioned at 393.3 cm\(^{-1}\) (B1g), 513.4 cm\(^{-1}\) which is the result of two components A1g and B1g of the anatase phase [48], and 635.3 cm\(^{-1}\) (Eg). Curve (g) shows the weak B1g and the characteristic modes Eg and A1g modes of the pure rutile phase at 142.3, 442.8, and 608.3 cm\(^{-1}\), respectively. Raman spectra of carbon-containing titania samples; curves from (b to f) show movement in a position toward higher energy (blue shift) and change in peak broadening, particularly the characteristic peak of the Eg mode compared to the pure anatase phase. Curve (b) represents the Raman spectrum of sample TD400 fired at 400°C. The characteristic anatase Eg is convoluted with the strong characteristic A1g (153 cm\(^{-1}\)) of the brookite phase (confirmed with XRD) [39], thus resulting in a peak located at 148.3 cm\(^{-1}\) with FWHM equals 18.5 cm\(^{-1}\). Some other brookite Raman active modes such as B1g (320 cm\(^{-1}\)), B2g (366, 463, 584 cm\(^{-1}\)), and B3g (545 cm\(^{-1}\)) appear. In curves from c to f, the anatase Eg (143.1 cm\(^{-1}\)) is convoluted with the Rutile B1g (142.3 cm\(^{-1}\)) and the resulting peak is blue-shifted to higher energy at 146.8 cm\(^{-1}\). The blue shifts of Raman bands in C/TiO\(_2\)-nanocomposites could be attributed to stress caused by probably nonstoichiometric oxygen deficiency [49] and/or lattice mismatch between different phases present in composites such as carbon/brookite/anatase in the sample TD400 represented by curve b, and carbon/rutile/anatase in samples represented by curves from (c to f). The FWHM for each sample was less than that of pure anatase, and it declines as the calcination temperature rises. The change in peak broadening is attributed to the size effect where broadening is inversely proportional to the crystallite size [50].

### 3.4. High-resolution transmission electron microscopy

The microstructures and morphology of titania nanopowder samples were characterized using HRTEM. Figure 5 shows the obtained microstructures for the sample TD550. The particle size of the rutile phase and the large particles in Figures 5a and b are comparable to those calculated using the W–H equation; however, the particle size of the anatase phase looks smaller. Figure 6(b) and (c) with scale bar nm show a higher resolution micrograph demonstrating rutile phase particles and anatase grain clusters cemented with amorphous carbon on the surface, respectively. Figure 6(d) shows the chemical compositions of the samples examined using EDAX attached to the HRTEM. The ratio O/Ti was < 2, indicating that titania nanopowders are nonstoichiometric. This can be explained because the surface area subjected to the electron beam is extremely small, and the electron beam may encounter an area with a high concentration of oxygen vacancies or have TiO\(_2\) atomic planes with a lower O/Ti ratio. The carbon content is relatively larger than that estimated by TG measurement, which may be attributable to higher carbon density on the sample grid. It is thus subjected to an electron beam beside the carbon content.

### 3.5. X-ray photoelectron spectroscopy analysis

Figure 7(a) shows the XPS survey spectrum for the composite samples, revealing the characteristic photoelectron peaks C1s, O1s, and Ti 2p of carbon, oxygen, and titanium with binding energies of 284.8, 458.5, and 529.7 eV, respectively. The characteristic photoelectron peak of nitrogen N1s was not detected to indicate that nitrogen is not incorporated in the chemical composition. XPS C1s are fitted with three peaks and shown in Figure 8(b); binding energy values of the main peak at 285.05 eV are attributed to the C–C bond with the sp\(^2\) orbital, revealing the presence of elemental carbon, while the other peaks at 286.5 and 289 eV corresponds to the C = O and O=C–O bonds, which reveals the presence of surface carbonates and/or structural fragments such as Ti–O–C and Ti–OCO [51, 52]. The binding energies at 281.9 and 290.7 eV corresponding to carbide (C–Ti bond) and graphitic carbon, respectively, are not detected in all samples, indicating that carbon is not incorporated as a dopant element in the TiO\(_2\) lattice and that there are no graphitic carbon structures formed on the surface of TiO\(_2\) particles, with amorphous carbon being the only pure carbon structure present [10, 14].

Figure 7(c) shows the O 1s peak as fitted into four peaks centered at 530.07, 530.7, 532.23, and 533.9 eV. The lower energy peak at 530.07 eV

| Sample | Carbon Fraction (%) | Anatase Fraction (%) | O/Ti | Abs. Edge (eV) | Rutile Fraction (%) | O/Ti | Abs. Edge (eV) |
|--------|---------------------|---------------------|-----|--------------|---------------------|-----|--------------|
| TD400  | 10.7                | 87.5                | 1.95| 3.16         |                      |     |              |
| TD425  | 6.71                | 89                  | 1.9 | 3.15         | 4.52                | 1.95|              |
| TD450  | 5.96                | 88.5                | 1.9 | 3.11         | 5.33                | 1.9 |              |
| TD475  | 5.21                | 75.11               | 1.9 | 3.07         | 19.68               | 1.9 | 2.93         |
| TD500  | 4.66                | 64.34               | 1.85| 3.05         | 35.66               | 1.85| 2.9          |
| TD525  | 4.05                | 40.82               | 1.75| 2.82         | 55.13               | 1.8 | 2.7          |
| TD550  | 3.3                 | 31.81               | 1.8 | 2.9          | 64.89               | 1.85| 2.87         |
| TD575  | 2.35                | 16.85               | 1.85| 2.9          | 80.8                | 1.9 | 2.9          |
| TD600  | 1.83                | 5.44                | 1.93| 2.9          | 92.73               | 1.93| 2.93         |
| TD625  | 1.45                | 1.15                | 1.95| 2.9          | 97.4                | 1.95| 2.94         |
| TD650  | 1.11                | 1.05                | 2   | 2            | 97.85               | 1.95| 2.94         |
| TD700  | x                   | x                   | x   | x            | 100                 | 2   | 3            |
is attributed to O 1s in the Ti–O linkages of TiO2. In comparison, the smaller peak at 530.7 eV is attributed to Ti(3+–O) linkage as that of Ti2O3, the peak at −532.23 eV is attributed to OH groups, and the weak peak at 533.9 eV is attributed to covalent oxygen resulting from incomplete oxidation of carbon sources [53, 54]. The Ti2p photoelectron spectrum is fitted with five peaks centered at 458.1, 458.7, 459.7, 463.3, and 464.4 eV, respectively, as shown in Figure 7(d). The peaks located at 458.1 and 463.3 eV are attributed to Ti3+ 2p3/2 and Ti3+ 2p1/2, respectively; however, the peaks at 458.7 and 464.4 eV are typical of 2p3/2 and Ti 2p1/2. The difference between them was 5.7 eV, which corresponds to the normal state of Ti4+ in TiO2 [55]. Other researchers have identified a weak peak centered at 459.7 eV because of deconvolution and fitting. Sarkar et al. attributed the 459.7 eV peak on the Ti2p spectrum to (Ti3+ 2p1/2), indicating the presence of oxygen vacancies and related defects on the surface of H2Ti3O7 nanowires [56], while Ekemena et al. suggested that this peak might be attributed to Ti–C bond on the surface [3, 57].

3.6. UV-vis spectroscopy

UV-vis absorption and diffuse reflectance spectra (DRS) were conducted to evaluate the optical properties of prepared samples compared to the commercial pure anatase and rutile powders. Figure 9 shows the absorption spectra of carbon-containing titania samples calcined at different temperatures, anatase, and rutile powders.

All samples show absorption in both the UV and visible light regions higher than that of anatase and rutile. The sample TD400 heat-treated at 400 °C has the highest absorption, while the sample TD650 has the lowest. The sample TD700 shows the optical characteristics typical of commercial rutile. Generally, the absorption of light by C/TiO2 decreases as the calcination temperature of the prepared samples increases. The absorption edge is shifted to higher wavelengths (redshift) towards the visible light region. The relatively higher absorption in the visible region is attributed to the presence of amorphous carbon structures [3, 58] where its fraction composition decreases with increase in calcination temperature.

The bandgap energies were calculated using the diffuse reflectance (DR) data converted to the Kubelka–Munk function \( F(R)/h\nu^n \), where \( F(R) = \frac{(1-R)^2}{2R} \), \( n = 0.5 \) and 2 for direct and indirect bandgap transitions, respectively [59], from the intercept of the tangent to the curve with energy axes in the region where \( F(R)/h\nu^n \) linearly changes with photon energy \( (h\nu) \). Figure 8 shows \( F(R)/h\nu^n \) as a function of absorbed photon energy by certain selected composite samples, pure anatase and rutile powders.

Figure 4. Characteristic Raman-active modes for commercial anatase (a), carbon containing composite samples; (b) TD400, (c) TD 475, (d) TD500, (e) TD550, (f) TD600, and commercial rutile (g).
Table 2 contains the calculated bandgap energy values. The bandgap energies of commercial anatase and rutile are 3.3 and 3.0 eV, respectively. Bandgap energies are lower in samples heat treated at different temperatures from 400 °C to 650 °C than in reference materials. The lowest bandgap energy is recorded for the sample TD525 (42.54% A, 57.46% R), which is 2.695 and 2.829 eV for the rutile and anatase fractions, respectively. The change in bandgap energy is attributed to the change in fractional composition, oxygen vacancies, and trapped states of (Ti^{3+}) [10, 38].

Figure 5. (a) HRTEM image for sample TD550, (b) Image of a large particle with rutile phase, (c) cluster of grains with anatase structure, and (d) chemical compositions with EDAX. The scale bar is 50 nm for (a) and 5 nm for (b and c).

Figure 6. High-resolution XPS survey (a) C1s (b) O1s (c) Ti2p, and (d) photoelectron peaks of the sample TD550.
3.7. Self-cleaning action of fabrics loaded with titanate nanocomposite

Figure 9 illustrates how the photocatalytic destruction of titanium dioxide can be used to explain the self-cleaning behaviour of samples that have absorbed methylene blue (MB) stain [60, 61]. Table 3 displays the K/S values for the exposed and untouched regions of the samples throughout the course of 12–48 h. The self-cleaning capabilities of control samples and coated samples have been compared under the same testing conditions. The decrease in K/S percentage values of the exposed sample section compared to the unexposed sample portion was determined to evaluate the self-cleaning impact. The K/S values for the exposed and untouched regions of the samples throughout the course of 12–48 h. The self-cleaning capabilities of control samples and coated samples have been compared under the same testing conditions. The decrease in K/S percentage values of the exposed sample section compared to the unexposed sample portion was determined to evaluate the self-cleaning impact.

The MB stain fades quickly within the first 12 h of exposure, according to Table 3. The surface formation of reactive oxidation species is the basis for the self-cleaning ability of cellulose-based fabrics treated with TiO2NPs. When the sample is exposed to visible light, an excited methylene blue dye (MB) molecule adhering on the surface transfers an electron to the TiO2NPs’ conduction band. As a result, the photocatalytic degradation of MB stain is caused by a reactive oxidation species produced by the electron caught by molecular oxygen on the surface of TiO2NPs.

\[
\text{MB stain} + \text{reactive Oxygen species (OH}, \text{OH}_2, \text{H}_2\text{O}_2, \text{etc})
\]

Here, the presence of TiO2 nanoparticles determines which titanate nanocomposite is responsible for the discoloration of MB. This is explained by an increase in the band gap of irradiated TiO2 nanocomposite. A positive hole (h+) is left behind when the electron is stimulated from the valence band to the conduction band. The reduction and oxidation reactions are brought on by the electrons (e-) in the conduction band and the positive holes (h+) in the valence band, respectively (Figure 5). This causes the reactive oxygen O2 and OH species to develop, which can react with hazardous organic compounds and break them down into less harmful byproducts [62].

4. Conclusion

Nonstoichiometric carbon containing titania nanocomposites has been successfully synthesized via a facile, fast, and green sol–gel route. The sol–gel method allows the regulation of the crystallite size, the weight fraction of each crystalline phase, and carbon content. Diethanolamine (alkanolamine) is an essential in situ carbon source and its functions as a stabilizer for (Ti4+) cations and a pH modifier. The phase transformation from amorphous to rutile phase over a short range of temperatures occurs stepwise from amorphous to (anatase/brookite), to (anatase/rutile), and then to the pure rutile phase. The increase in calcination temperature indicates that the amorphous carbon content decreases and completely transforms into a pure rutile phase. Significant

Figure 7. Absorbance spectra of certain selected samples and commercial anatase and rutile powders.

Figure 8. Bandgap energy calculations using the plot of the Kubelka-Munk function versus the photon energy of light absorbed by certain selected samples and commercial anatase and rutile.

Figure 9. TiO2 nanocomposite photocatalytic degradation and photoexcitation to produce reactive oxidation species, and self-cleaning of MB stain.
improvement in the electronic and optical absorption properties of titania nanocomposites compared to ordinary titania nanopowder was observed, making it more effective in many technological applications; this improvement is strongly correlated with structure, composition, defects, and impurities. The synthesized titanate nanocomposite sol-gel method shows higher photocatalytic activity (self-cleaning effect). Titanate nanocomposite-treated fabrics show promise as a potential application for both industrial and medical uses.

**Declarations**

**Author contribution statement**

Ibrahim Moussa, Hassan Ibrahim, El-Amir M. Emam, and Tawfik M. Tawfik: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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**Data availability statement**

Data will be made available on request.

**Declaration of interests statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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