

The effect of synthetic routes on the physicochemical properties and optical response of N-doped titania–oxidized carbon nanotube nanohybrids

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ABSTRACT

This work systematically evaluates the effect of synthetic routes on the physicochemical and optical properties of nitrogen-doped titania (NTiO₂) nanohybrids supported on oxidized carbon nanotubes (oxCNTs). A series of NTiO₂–oxCNT nanohybrids consisting of 0–5 wt.% oxCNTs and NTiO₂ were synthesized using either a hydrothermal treatment technique or a solgel synthetic route under controlled conditions. A fair and comprehensive assessment of the effect of the two synthetic methods on the properties of NTiO₂–oxCNT nanohybrids was carried out for the first time. Fourier transform infrared spectroscopy confirmed the formation of a chemical bond between N and Ti as well as between NTiO₂ and CNTs, and X-ray photoelectron spectroscopy confirmed the incorporation of N (~at.1%) and the formation of the Ti–C linkage between NTiO₂ and oxCNTs into the nanohybrids. Significant Raman shifts due to TiO₂ and CNT scattering suggested strong electrostatic interactions between N-doped TiO₂ and oxidized CNTs. Microscopic investigations indicate that solgel-synthesized nanohybrids have smaller particles (11–16 nm) as opposed to the large, cuboidal NTiO₂ nanoparticles of the hydrothermally synthesized nanohybrids (11–25 nm). An increase in the CNT content led to a decrease in NTiO₂ aggregation and reduced the particle sizes of the nanohybrids produced. The 100% anatase nanohybrids thus showed that an increase in oxCNT content significantly reduces the crystalline sizes of NTiO₂. The solgel-synthesized nanohybrids were found to be more thermally stable degrading in the range 550–640 °C compared with 470–630 °C for hydrothermally synthesized nanohybrids. Hydrothermally synthesized nanohybrids were found to exhibit lower energy band gaps (as low as 2.0 eV) and displayed higher visible light absorption. The hydrothermally synthesized nanohybrids had lower electron–hole (e_{cb}^-/h_{vb}^+) recombination rates than the nanohybrids produced via the solgel method. This comparative work clearly demonstrates that NTiO₂–oxCNT nanohybrids exhibit diverse optical, chemical, and surface properties depending on the production technique.

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1. Introduction

In a quest to improve the performance of semiconductor photocatalysts, particularly under visible light, a wide range of strategies for the synthesis of titania (TiO₂)-based photocatalysts has been developed. TiO₂ nanohybrids with carbon nanotubes (CNTs), for example, have shown low electron–hole (e_{cb}^-/h_{vb}^+) recombination rates and hence improved photocatalytic activities [1,2]. The versatility of CNTs and TiO₂ has given rise to a new continuum of possible

applications for their hybrids even beyond photocatalysis; i.e. fuel cells, oxygen reduction, electrocatalysis, and sensors [3]. However, the application of TiO₂ and its modified forms are still predominantly in photocatalysis. Indeed, a good photocatalyst should necessitate a fine balance between particle size, morphology, energy band gap (E_g), e_{cb}^-/h_{vb}^+ recombination rate, and photosensitization.

To improve the photoresponse of TiO₂, popular modification strategies of TiO₂ photocatalysts have been applied including the use and modification of catalyst supports, doping and co-doping with foreign atoms [4,5]. Doping and co-doping of TiO₂ provide access to modified photocatalysts that are capable of absorbing ultraviolet (UV) light and a large portion of the visible light. These improvements are due to dopants narrowing the E_g and

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lowering the e_{cb}^-/h_{vb}^+ recombination rate [6]. Whereas doping of semiconductors with non-metallic elements only introduces mid-band gap states between the valence band (VB) and the conduction band (CB) of the semiconductor crystals, metal doping creates an electron channel where electrons that have been excited to the CB are sequestered away so that they do not fall back to the VB [2,7]. Previous research has also shown that nanohybrids of Eu^{3+} -doped TiO_2 with CNTs (Eu^{3+} - TiO_2 -CNT) and graphene oxide (Eu^{3+} - TiO_2 -GO) synergize the effect of metal doping and hybridizing with carbonaceous materials to promote electron withdrawal from TiO_2 , resulting in the enhancement of visible light photocatalysis [8,9]. Unfortunately, metal doping can potentially result in the leaching of the metal, which is a serious concern particularly in the application of the metal semiconductors in water treatment. It is for this reason that non-metallic doping has been touted as being safer and more suitable for environmental applications [10]. Of the various known non-metallic TiO_2 dopants, elemental N has, for many reasons, been found to be the most suitable dopant for TiO_2 .

Another viable approach for enhancing the photoresponse of TiO_2 is the use of carbon supports to form TiO_2 nanohybrids, a technique which is currently being investigated. Carbon-based TiO_2 nanohybrids have led to improvements in the photocatalytic activity of TiO_2 , brought about by factors such as the reduction of the e_{cb}^-/h_{vb}^+ recombination rate, photosensitization of the TiO_2 , increase in the active photocatalytic surface area, and provision of electrons for the reductive breakdown of organic pollutants [1,5]. To this end, TiO_2 nanohybrids of CNTs, carbon nanofiber, carbon nanospheres, graphene, and amorphous carbon have been synthesized. However, these nanohybrids often possess poor absorption capacities in the visible light, which emanates from the wide E_g associated with TiO_2 [11]. Recent research interests in nanohybrids composed of N-doped and N-co-doped TiO_2 supported on carbon nanomaterials have given rise to nanocomposites that possess a combination of the narrowed TiO_2 E_g (as low as 2.3 eV) and reduced e_{cb}^-/h_{vb}^+ recombination rate [12,13].

While doping of TiO_2 can be achieved effectively through both *ex situ* and *in situ* approaches, the *in situ*-based methods have so far been found favorable for the synthesis of doped TiO_2 -CNT nanohybrids [12,14]. Owing to the chemical stability of TiO_2 and the inertness of CNT surfaces, it has become crucial to maximize the incorporation of N onto the TiO_2 lattice while improving the surface coverage of CNTs by the doped TiO_2 nanoparticles. In enhancing the distribution and surface coverage of TiO_2 onto CNTs, other methods such as layer-by-layer deposition, biomimetic deposition, pulsed laser deposition, chemical vapor deposition, hydration-dehydration, solgel, hydrothermal or alcohothermal, and electrostatic attraction-based methods have been used [15,16]. Each of these methods has its merits and demerits with respect to energy input, efficient usage of raw materials, safety, reproducibility, economic viability, doping efficiency, and ease of scaling up.

In general, the hydrothermal and the solgel methods are the most commonly used techniques for the doping of TiO_2 and synthesis of TiO_2 -CNT nanohybrids [17]. In addition, the hydrothermal method is favored for its use of lower temperatures to achieve good particle crystallinity with less defects, which results from the high pressure generated inside the reaction vessel [18]. This method also offers additional control over particle size, facet growth, and crystalline phase by controlling the temperature and duration of the hydrothermal treatment [19,20]. Although each of these methods has its own unique advantages, a direct and logical comparison of hydrothermal and solgel synthesis and their effects on the physicochemical properties of TiO_2 -CNT nanohybrids is still lacking. In the few reports that exist, the syntheses were carried out under diverse conditions, and conflicting conclusions were drawn. Researchers previously used TiCl_3 as the TiO_2 source and demonstrated that the solgel-prepared nanohybrid outperforms the hydrothermally

synthesized TiO_2 -CNT nanohybrids in the photocatalytic activity [21]. In a separate study, the solgel procedure yielded TiO_2 -CNT nanohybrids with high photocatalytic activity compared with the hydrothermally synthesized nanohybrids when titanium butoxide and TiOSO_4 were used as TiO_2 sources, respectively [22]. On the contrary, other workers found that hydrothermally synthesized TiO_2 -CNT nanohybrids had better photocatalytic performance than solgel-synthesized nanohybrids [23].

It is worth noting that in the few reports discussed previously, the hydrothermal procedure consisted of crystallizing the TiO_2 -CNT hybrid in two steps, i.e. the precursor suspension was heated in an autoclave and then calcined at elevated temperatures [23,24,26]. In this way, the hydrothermally prepared nanohybrids were subjected to two heating steps leading to the promotion of crystal growth while the solgel-prepared nanohybrids were subjected to high-temperature calcination only [21,22,24]. Elsewhere, it has been shown that TiO_2 crystal sizes and phases are dependent on heating temperature and duration; longer heating times and high temperatures accelerate crystal growth and formation of the rutile phase, whereas short heating times and low temperatures limit the growth of the TiO_2 nanoparticles and promote anatase phase formation [24,26]. It has also been demonstrated that TiO_2 -CNT nanohybrids prepared via the hydrothermal route without subsequent calcination yield nanohybrids with good attachment of perfectly crystalline TiO_2 nanoparticles onto CNTs [18,25,27]. These uncalcined nanohybrids had photocatalytic activities comparable to the nanohybrids prepared via the solgel method with subsequent calcination. As such, there remains a need to compare the hydrothermal and solgel routes where there is no subsequent calcination in the hydrothermal route to minimize crystal growth while maintaining standard working conditions. Whereas the synthesis of NTiO_2 -CNT nanohybrids has been reported in a previous study, to the best of our knowledge, a comparative analysis of the two methods for the synthesis of NTiO_2 -CNT nanohybrids under similar conditions has not been reported. In addition to this, while the hydrothermal method without post calcination has been utilized for the synthesis of CNT/phosphorous-doped TiO_2 (PTiO_2 -CNT) and TiO_2 -CNT nanohybrids, a similar procedure has not been applied to the synthesis of NTiO_2 -CNT nanohybrids [25,28]. It is expected that the differences in atomic radii between N and P atoms will likely introduce significant differences in the physicochemical properties of TiO_2 -CNT nanohybrids. N-doping of the TiO_2 is envisaged to enhance the visible light absorption of the NTiO_2 -CNT nanohybrid by creating additional inter-band states between the VB and the CB of the NTiO_2 nanoparticles.

In this work, a systematic study to compare the effect of synthetic routes on the structural morphology and optical response of nanohybrids formed between N-doped TiO_2 and acid-oxidized CNTs (oxCNTs) is undertaken. We also explore the synergistic effects of N-doping and anchoring of oxCNTs on TiO_2 to determine its effect in enhancing the surface and structural properties and optical response of NTiO_2 . Therefore, NTiO_2 nanohybrids containing a range of oxCNT wt.% were synthesized by the modified hydrothermal and solgel methods while eliminating high-temperature sintering in the hydrothermal method to enable a comprehensive and objective analysis on their effects on the photocatalytic activity of the nanohybrids.

2. Materials and methods

2.1. Materials

Titanium isopropoxide (TTIP) 97%, ammonium hydroxide (NH_4OH) 25%, sulfuric acid (H_2SO_4) 98%, nitric acid (HNO_3) 65%, ethanol (95%), propanol (99.5%) and anatase TiO_2 (25 nm, 99% purity)

were all supplied by Sigma Aldrich (Germany) and were used without any further purification. Commercial anatase TiO_2 was purchased from Sigma Aldrich (Germany). Pristine multiwalled CNTs of outer diameter ~15–40 nm (Sigma Aldrich, Germany) were purified by acid treatment before use as outlined in the next section.

2.2. Functionalization of CNTs

Commercial CNTs were dispersed in an $\text{H}_2\text{SO}_4\text{:HNO}_3$ mixture of 3:1 v/v composition. This suspension was ultrasonicated under a fume hood for 1 h at 30 °C using an Elma S3H ultrasonicator [15]. The resultant suspension was washed through repeated dilution with deionized water (DI) and subsequent centrifuging in a Hettich Universal 320R Centrifuge until it reached pH = 7. The oxCNTs obtained were then dried in an oven at 70 °C for 24 h and thereafter stored in a desiccator for further use.

2.3. Synthesis of $\text{NTiO}_2\text{--oxCNT}$ nanohybrid catalysts

2.3.1. Precursor preparation of $\text{NTiO}_2\text{--oxCNT}$ nanohybrids

The preparation of the precursor was carried out via *in situ* doping of TiO_2 and condensation-based deposition of the NTiO_2 nanoparticles onto oxCNTs. A previously published procedure was adopted with minor modifications in the precursor preparation step [12]. In addition to varying the aging time, HNO_3 was substituted with NH_4OH to act as both a hydrolyzing agent and a N-source for TiO_2 doping (Fig. 1 and Fig. A1 Appendix data). A beaker containing a solution of TTIP (10 mL) in 2-propanol (90 mL) was labeled solution A and was immediately covered with parafilm and sealed to reduce chances of the TTIP being hydrolyzed by the moisture in air. A second solution (solution B) was prepared by dissolving NH_4OH (13 mL) in a 1:1 mixture of 2-propanol (20 mL) and deionized water (20 mL). The volume of the NH_4OH was calculated such that N wt.% was 3% relative to the mass of Ti. Solution B was also covered with parafilm and sealed to reduce the rate of evaporation of the NH_4OH solution. A calculated mass of oxCNTs were dispersed in ethanol (30 mL) and sonicated at room temperature for 30 min. The resultant suspension was placed in a 500 mL beaker and stirred at 400 rpm at room temperature. After pouring the alkaline NH_4OH solution, solution A (TTIP solution) was added drop-wise into the resulting mixture. Various $\text{NTiO}_2\text{--oxCNT}$ precursor suspensions with different wt.% of oxCNTs were prepared (Table 1).

2.3.2. Hydrothermal synthesis of $\text{NTiO}_2\text{--oxCNT}$ nanohybrid catalysts

The precursor suspension (45 mL) was transferred into a teflon-lined stainless-steel autoclave. After placing in an oven and heating for 36 h at 200 °C, the autoclave was left in the oven to cool to ca 80 °C and thereafter placed in a fume hood and unscrewed to release the pressure. The resultant dark gray suspension was centrifuged at 3000 rpm for 20 min, and the supernatant solvent was decanted off. The remaining precipitate was washed with a 1:1 v/v deionized water (DI): ethanol solvent until the solution was neutral. After drying the precipitate at 100 °C for 24 h, the resultant solid was crushed using a mortar and pestle and stored in a desiccator. The $\text{NTiO}_2\text{--oxCNT}$ nH nanohybrids (where “n” is the wt.% of oxCNTs and H denotes the hydrothermal method of synthesis) obtained were isolated as powdered catalysts (see Table 1).

2.3.3. Solgel synthesis of $\text{NTiO}_2\text{--oxCNT}$ nanohybrid catalysts

The precursor suspension (45 mL) was stirred to evaporate the solvent until a thick gel was formed. The gel was dried in an oven at 100 °C for 24 h to form a precursor xerogel, which was crushed to a fine powder using a mortar and pestle, transferred to a crucible and calcined in air at 450 °C for 2 h using a muffle furnace. The temperature of the furnace was ramped up at 10 °C/min to 450 °C. The furnace was allowed to cool to 100 °C before taking out the

crucibles. The resultant powders were crushed again using the mortar and pestle and then stored in a desiccator. For the solgel synthetic method, the $\text{NTiO}_2\text{--oxCNT}$ (nS) (where “n” refers to the wt.% of oxCNTs and S denotes the solgel method of synthesis) were isolated as powdered catalysts (Table 1). Commercial anatase TiO_2 was used for comparison purposes.

2.4. Characterization of $\text{NTiO}_2\text{--oxCNT}$ nanohybrid catalysts

Fourier transform infrared (FTIR) spectroscopic analysis (Perkin Elmer Frontier FTIR spectrometer) was carried out to investigate the bonding between NTiO_2 and the oxCNTs. For transmittance measurements, each sample was ground with KBr and pressed to be a semi-transparent pellet before running the scans. To determine the crystalline phase and investigate the bonding configuration between NTiO_2 and oxCNTs, Raman spectroscopic analysis was undertaken using Witec's Alpha 300RA AFM/Raman combined system. A double-sided, transparent tape was spread onto a microscope glass slide, and ca 5 mg of the nanohybrid powder was pasted onto the tape. Measurements were taken using the Raman 532 nm module at an integration time of 0.6 s. Particle size measurements and structural morphology investigations were carried out using a transmission electron microscope (TEM) (Jeol TEM 201 operated at 200 kv). Approximately 5 mg of the nanohybrid powder was dispersed in 10 mL ethanol by ultrasonication at room temperature using an Elmasonic 5H ultrasonicator. Two drops of the colloidal suspension were spread onto a copper grid that had been previously sputter coated with ~5 nm carbon. X-ray photoelectron spectroscopy (XPS) analysis were carried out on an Axis TM X-ray photoelectron spectrophotometer to determine the chemical state of the elements in the nanohybrids and to determine the bonding configurations of each element. Analysis was carried out on pellets of each sample, pressed using a Retsch PP 25 hydraulic pellet presser. All data, unless otherwise specified, were collected as csv files and plotted and analyzed using the software Origin 8 Pro. version. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Trios TGA 5500 equipped with a high-temperature furnace. For these analyses, ca 10 mg of each nanohybrid was placed and spread onto a platinum high-temperature pan before inserting into the high-temperature furnace. A ramp rate of 10 °C min⁻¹ under a 25 mL min⁻¹ N_2 and air flow were used separately to determine the thermal stability profile in the temperature range 30–850 °C.

The specific surface area and pore volumes were determined through the Brunauer-Emmett-Teller (BET) analysis technique using a Micromeritics TriStar II analyzer. The samples were degassed by first heating at 90 °C under a N_2 gas flow followed by heating at a temperature of 350 °C and maintaining this temperature for 3 h. The analysis bath temperature was kept at –195 °C. X-ray diffraction (XRD) analysis was carried out using a Rigaku SmartLab X-Ray diffractometer. Approximately 1.0 g of the nanohybrid powder was spread on a glass slide, and the rays passed over the sample. Each nanohybrid sample was scanned from 2θ 5–90°. Data were processed using the SmartLab XRD software. The full width at half maximum height, for the lattice spacing, peak positions, and length of each face of the crystal were determined by the software using the Scherrer equation. The ultraviolet-visible (UV–vis) absorbance spectra were collected from a Perkin Elmer Lambda 650 S UV–vis spectrometer equipped with a tungsten and deuterium lamp in the range 180–800 nm. All the scans were done at a rate of 266 nm min⁻¹, and all samples were scanned as powders. Photoluminescence (PL) spectroscopy was carried out using a Horiba Fluorolog FL3 spectrophotometer equipped with a xenon lamp in a scan range 200–750 nm. The nanohybrids were excited at 350 nm, and the emission spectra were collected in the range 270–600 nm.

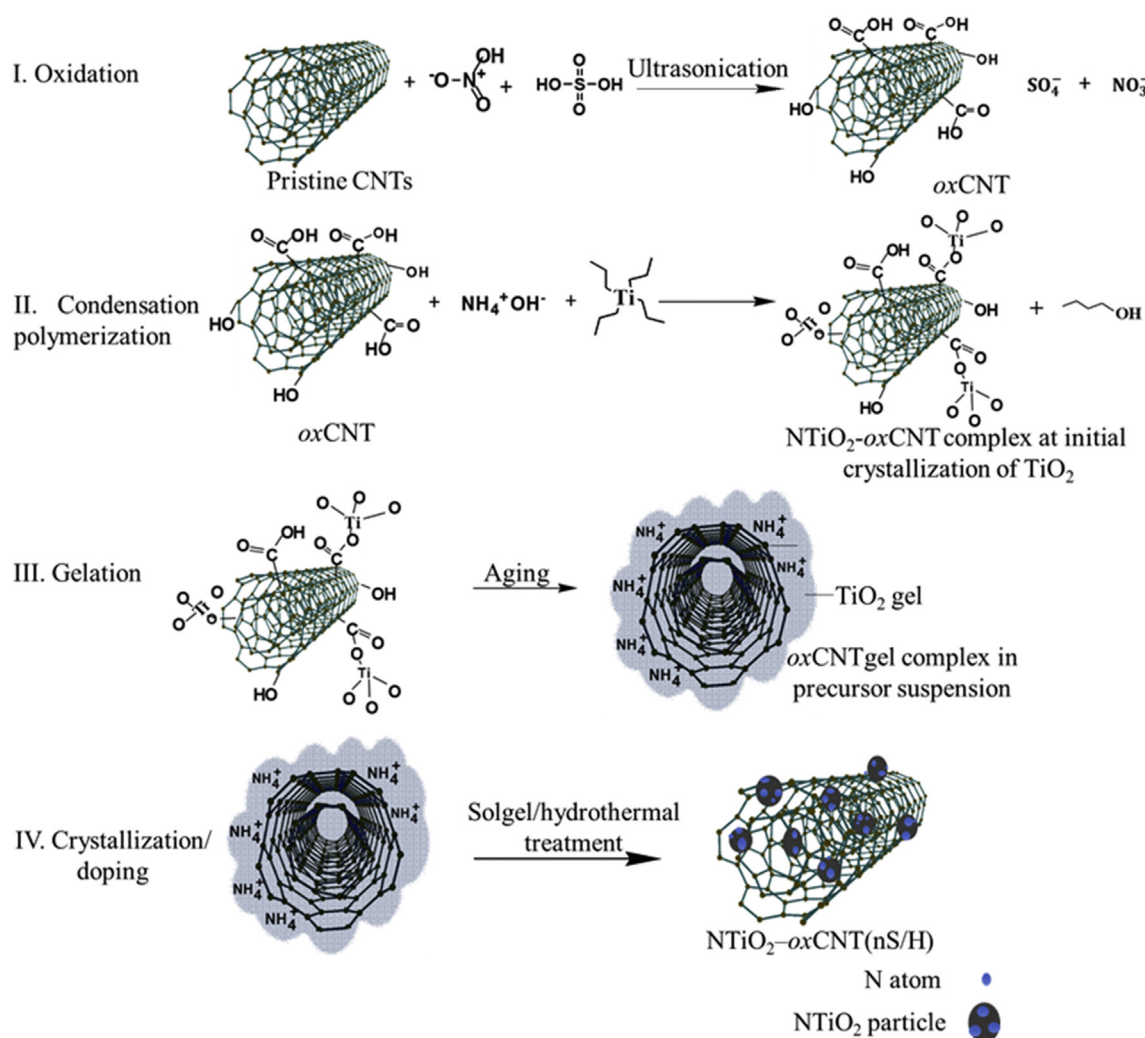


Fig. 1. Scheme for the synthesis procedure and mechanism of formation for NTiO₂-oxCNT nanohybrid catalysts. NTiO₂, nitrogen-doped titania; oxCNT, oxidized carbon nanotube.

Table 1
Summary of nanohybrid catalysts synthesized by the hydrothermal and solgel methods.

Synthetic method	^a Wt.% oxCNT	Nanohybrid catalyst code name	Nanohybrid code	Mass of catalyst (mg)	Physical appearance
Solgel	0	NTiO ₂ -oxCNT 0%	0S	1325	Yellow
	1	NTiO ₂ -oxCNT 1%	1S	886	Yellow-gray
	2	NTiO ₂ -oxCNT 2%	2S	1135	Yellow-gray
	3	NTiO ₂ -oxCNT 3%	3S	1163	Gray
	4	NTiO ₂ -oxCNT 4%	4S	1443	Gray-black
Hydrothermal	5	NTiO ₂ -oxCNT 5%	5S	1625	Black
	0	NTiO ₂ -oxCNT 0%	0H	925	White
	1	NTiO ₂ -oxCNT 1%	1H	1236	Gray
	2	NTiO ₂ -oxCNT 2%	2H	1389	Gray
	3	NTiO ₂ -oxCNT 3%	3H	1320	Gray-black
	4	NTiO ₂ -oxCNT 4%	4H	1512	Black
	5	NTiO ₂ -oxCNT 5%	5H	1578	Black

NTiO₂, nitrogen-doped titania; oxCNT, oxidized carbon nanotube.

^a Wt.% oxCNT calculated from the total mass of Ti in the precursor.

3. Results and discussion

3.1. Physical features of NTiO₂-oxCNT nanohybrid catalysts

The synthesis procedure for NTiO₂-oxCNT nanohybrids entailed acid functionalization of the CNTs in aqua regia followed by deposition of TiO₂ sol NH_4^+ ions onto the CNTs and subsequent

gelation of the TiO₂ through stirring at room temperature (Fig. 1). The resultant gel was then subjected to either hydrothermal treatment or solgel treatment with subsequent calcination. The nanohybrid 0S powder obtained was yellow in color, while its oxCNT counterparts showed a blend of yellow, gray and black colors (Fig. 2). The yellow color was overshadowed first by the gray and ultimately the black color when oxCNT content was increased from

1 to 5 wt.% (Table 1 and Fig. 2). The yellow color in solgel-synthesized nanohybrids is an indication of successful N-doping as well as the formation of oxygen (O) vacancies in the TiO_2 lattice [29–31]. The doping of TiO_2 with N is further indicated by the Urbach tail appearing in the UV–vis spectra of 0S, 1S, 2S, and 3S (to be discussed in latter sections). The target hydrothermal nanohybrids, on the other hand, did not display the ordinary yellow color; instead they changed from their deep black color before hydrothermal treatment to a gray color after hydrothermal treatment thus suggesting an interaction between TiO_2 and oxCNTs (Fig. 2). However, the nanohybrid 0S maintained its white color before and after hydrothermal treatment. This lack of yellow coloration in hydrothermally synthesized N-doped TiO_2 is consistent with findings from previous studies where the presence of N species in TiO_2 was confirmed via XPS measurements [32]. Typically, TiO_2 nanocrystals bond onto CNTs through dative coordination between Ti^{6+} in the nanocrystals and π electrons on the C skeleton. TiO_2 nanocrystals also bonded onto oxCNTs through electrostatic forces and dative covalent coordination between the Ti^{6+} and the surface $-\text{COOH}$ and $-\text{OH}$ groups [33].

An increase in the wt.% of oxCNTs led to an increase in the yield of the nanohybrids (Table 1), suggesting that CNTs are efficient in anchoring NTiO_2 nanoparticles to form stable nanohybrids. This is further confirmed by the degree of attachment of the NTiO_2 nanoparticles from our microscopic data as discussed in subsequent sections.

3.2. FTIR spectroscopic analysis of the nanohybrids

Hydrothermally prepared nanohybrids have stronger $-\text{OH}$ bending and stretching peaks in the region $3000\text{--}3500\text{ cm}^{-1}$ and at 1641 cm^{-1} , respectively. These intense peaks are a combined contribution of surface-adsorbed $-\text{OH}$ functional groups on both the NTiO_2 and oxCNTs . This is because both NTiO_2 and oxCNTs are renowned for their tendency to have a high proportion of $-\text{OH}$ functional groups. The hydrothermally synthesized nanohybrids have a stronger $-\text{OH}$ intensity because of their relatively high oxCNT abundance compared with the solgel-synthesized nanohybrids where a large portion of the oxCNTs are oxidized during the sintering. The abundance of $-\text{OH}$ groups suggests that the hydrothermally synthesized nanohybrids have stronger affinity for organic pollutants in water and H_2O molecules hence make good generators of $\cdot\text{OH}$ radicals [13,34].

The FTIR spectra of commercial anatase TiO_2 was compared with those of N-doped TiO_2 (also prepared by the solgel technique), and the results are shown in Fig. A2 Appendix data. The spectrum of the N-doped TiO_2 shows peaks in the range $1170\text{--}1050\text{ cm}^{-1}$, which are attributed to the translational modes of O--Ti--N and Ti--N hence establishing that our method results in successful doping of TiO_2 with N.

The FTIR spectra of the hydrothermally synthesized nanohybrids show two strong peaks at 1212 and 1146 cm^{-1} , which are

attributed to surface-adsorbed CO_3^- ions and CO_2 , respectively [35]. It has been shown elsewhere that TiO_2 has a high adsorption capacity for CO_2 , and once the CO_2 has been adsorbed, it can undergo reduction to form the CO_3^- species [36]. The exclusive presence of these groups in the hydrothermally synthesized nanohybrids could be attributed to non-volatilization of the residual organic species from the precursors due to the elimination of the post calcination step in the hydrothermal synthesis process. The presence of these groups in the hydrothermally prepared nanohybrids is likely to enhance the adsorption of organic pollutants during photocatalytic processes. The peaks are absent in the FTIR spectra of the solgel-synthesized nanohybrids because organic residues that could have formed these groups were completely volatilized during the sintering step.

All the nanohybrids show broad peaks in the region $1110\text{--}400\text{ cm}^{-1}$, which are attributed to the combined bending and stretching modes of O--Ti--O bonds [34,37] (Fig. 3(a) and (b)). This broad peak becomes narrower with an increase in the nanohybrids' wt.% oxCNTs . The narrowing is first through the appearance of a shoulder peak in the range $1060\text{--}1025\text{ cm}^{-1}$ in the spectra of nanohybrids 0H, 1H, and 0S. With further increase in oxCNTs from 2 to 5 wt.% the shoulder peak transforms to distinct peaks in the same region and extending to 900 cm^{-1} . These peaks are attributed to the translational modes of O--Ti--C and O--C--Ti [38]. Previous models have shown that when Ti^{4+} ion is deprotonated from its organic precursor, it adopts the Ti^{6+} oxidation state and thus is able to bond with four neighboring O atoms and still form a bidentate coordinate bond with the C atoms of CNTs. The interaction of the $-\text{OH}$ groups located on the walls of oxCNTs and the $-\text{OH}$ groups located on NTiO_2 results in a condensation reaction such that TiO_2 forms a Ti--O--C bond [39]. The Ti^{6+} can also interact with $-\text{COO}^-$ thereby binding onto the CNT surface leading to the formation of a Ti--O--C-- bonding configuration.

Sintering N-doped TiO_2 at temperatures in the range $300\text{--}500\text{ }^\circ\text{C}$ has been reported to be effective in enhancing substitutional doping [34]. The peak at 1634 cm^{-1} tails toward the lower wavenumbers in all the hybrids (Fig. 3). This tailing can be due to the contribution of the peaks at 1503 and 1612 cm^{-1} , which are attributed to the deformation of NH_2 . This shows that N is coordinated to the Ti center as NH_2 in both the solgel and hydrothermally synthesized nanohybrids. There are also peaks appearing at 2923 cm^{-1} and 2844 cm^{-1} , which are due to alkane $-\text{C--H}$ and $-\text{C--O}$ stretch, respectively. These are obviously due to the presence of oxCNTs on the photocatalytic hybrid [40]. The intensity of these peaks decreases when TiO_2 is introduced thus suggesting a chemical bond between TiO_2 and oxCNTs .

3.3. Microscopic investigations of nanohybrid photocatalysts

TEM images show that NTiO_2 nanoparticles are coated onto the oxCNTs for nanohybrids with 1–5 wt.% oxCNTs (oxCNTs are marked with arrows in Figs. 4 and 5). This further confirms that the red

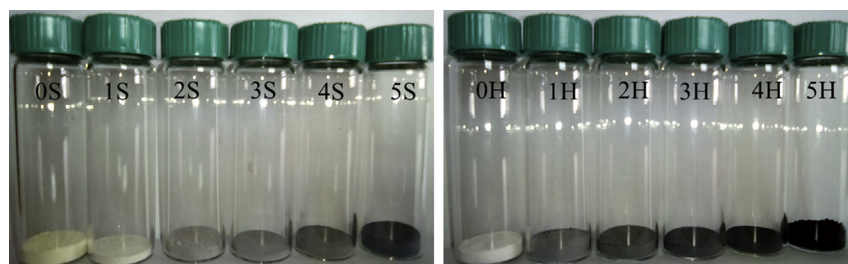


Fig. 2. A comparison of the color variations between solgel-synthesized (S) and hydrothermally synthesized (H) nanohybrids (the nanohybrids are arranged from left to right in order of increasing wt.% oxCNT). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

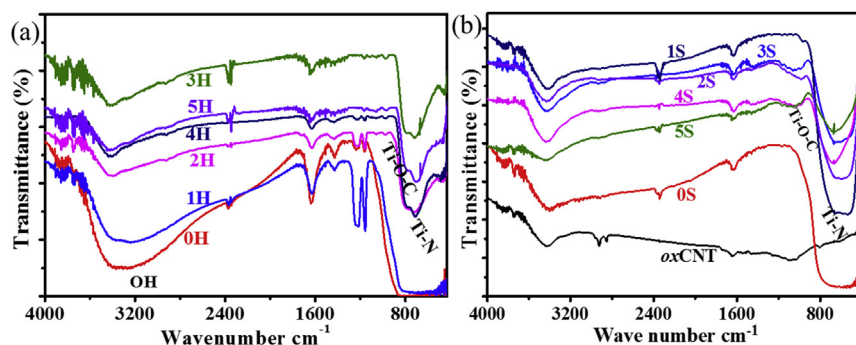


Fig. 3. Fourier transform infrared spectra of (a) hydrothermally synthesized nitrogen-doped titania–oxidized carbon nanotube nanohybrids (OH, 1H, 2H, 3H, 4H, and 5H); and (b) solgel-synthesized nanohybrids (0S, 1S, 2S, 3S, 4S, and 5S).

shifts of the NTiO_2 E_g band observed in the Raman spectra were due to the interaction between NTiO_2 nanoparticles and oxCNTs . The average NTiO_2 particle size range was determined to be 20–25 nm. The smaller particles tended to get attached to the oxCNTs , and while the larger particles formed aggregates.

Although the two synthetic routes were capable of producing both the cuboidal and cube-shaped NTiO_2 nanoparticles (marked with a circle in Fig. 4 OH), the former shape predominantly occurred in the hydrothermal samples. The hydrothermal synthesis method produced three types of NTiO_2 nanoparticles namely (i) rice-grained nanorods (marked with an ellipsoid in Fig. 4 1H), (ii) nanorods with regular edges and well-defined corners, and (iii) regular cube-shaped particles. The occurrence of rice-grained nanorods increased with the incorporation of oxCNTs from 0 to 3 wt.% (Fig. 4 1H and 2H and Fig. 5 3H). At 4 wt.% oxCNTs , the NTiO_2

nanoparticles became predominantly cuboidal, and at 5 wt.%, they became irregular (Fig. 5 4H and 5H). In short, under hydrothermal conditions, it was found that:

- (i) without oxCNTs , a blend of rice-grained, regular nanorods and cuboidal nanoparticles was promoted,
- (ii) the incorporation of 1, 2 and 3 wt.% oxCNTs promoted the growth of rice-grained NTiO_2 nanoparticles,
- (iii) the presence of 4 wt.% oxCNTs promoted the growth of cuboidal NTiO_2 nanoparticles,
- (iv) the presence of 5 wt.% oxCNTs resulted in the formation of irregularly shaped NTiO_2 and
- (v) the combined influence of oxCNTs and N atoms promoted the formation of cuboidal and nanorod-shaped NTiO_2 , which is in contrast with the synergistic influence of P and oxCNTs

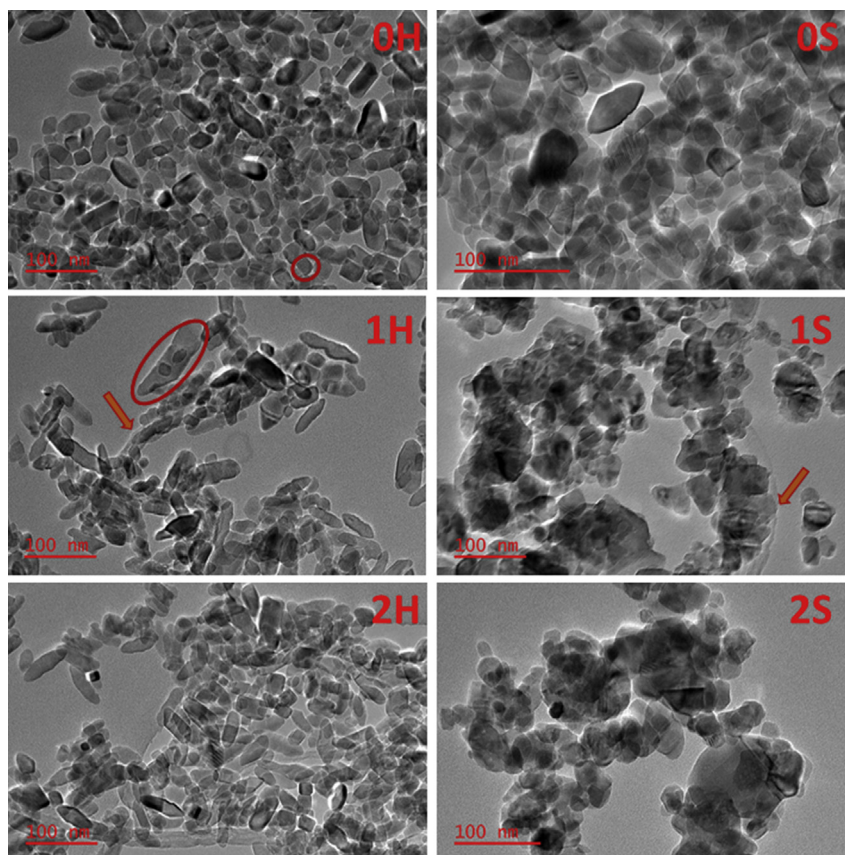


Fig. 4. TEM images for nitrogen-doped titania–oxidized carbon nanotube OH, 1H, 2H, OS, 1S and 2S nanohybrids.

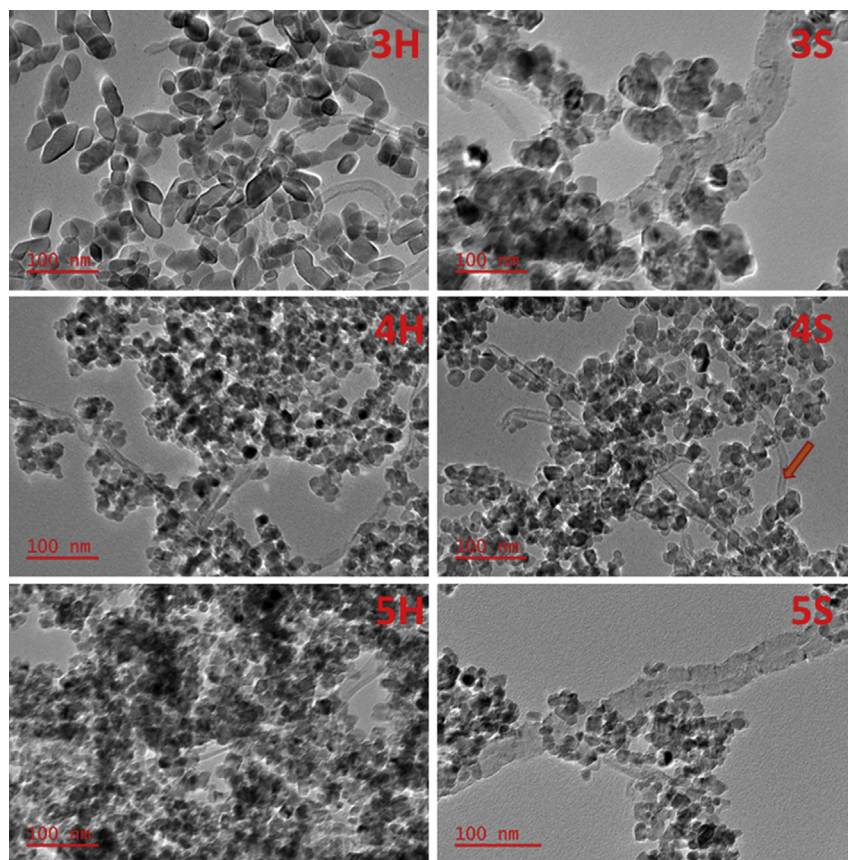


Fig. 5. TEM images for nitrogen-doped titania–oxidized carbon nanotube 3H, 4H, 5H, 3S, 4S, and 5S nanohybrids.

previously observed to promote spherical PTiO_2 nanoparticles [25].

The occurrence of rice-grain–shaped TiO_2 nanorods has previously been shown to favor electron transfer between the nanoparticles because of the predominant exposure of the 110 facet on the nanorods [41]. This phenomenon of increased electron transfer rate was further found to favor charge separation thus promoting photocatalytic reactions [42]. Exposed cuboid-shaped TiO_2 nanoparticles have been found to enhance predominantly high energy 001 and 100 facets which have been reported to induce high chemical activity [20]. Among the solgel-synthesized nanomaterials, only NTiO_2 without oxCNTs (0S) has nanoparticles with well-defined edges (Fig. 4 0S). The nanoparticles in nanohybrid 0S are predominantly nanorods with a small number of cuboid-shaped nanoparticles. The nanohybrids 1S, 2S, 3S, 4S, and 5S have irregularly shaped nanoparticles. Therefore, the solgel method demonstrates poor control over the NTiO_2 particle shape and shape distribution.

It is also shown that the hydrothermally prepared nanohybrids are less aggregated compared with the solgel-synthesized nanohybrids. The least aggregation was observed in the 4H nanohybrid. The nanohybrid 4H also shows a higher degree of attachment of NTiO_2 nanoparticles onto oxCNTs , which explains the low e_{cb}^-/h_{vb}^+ recombination shown by the PL spectrum (Fig. 14 (b)). For the solgel-synthesized nanohybrids, the nanoparticle aggregation followed the trend: 0S > 2S > 4S.

These micrographs reveal that an increase in the amount of oxCNT wt.% increases the dispersion of NTiO_2 particles in both the hydrothermal and solgel-synthesized nanohybrids. On the other hand, while the solgel-fabricated nanohybrids showed greater

NTiO_2 nanoparticle aggregation, there is denser attachment of the NTiO_2 nanoparticles onto the oxCNTs as observed by the more uniform distribution of NTiO_2 nanoparticles around the oxCNTs in 4 wt.% oxCNT solgel-fabricated nanohybrid. This could be due to the fact that annealing NTiO_2 samples at high temperatures better enhances the formation of bonds between TiO_2 nanoparticles at the crystal boundaries and between CNTs thus resulting in aggregated nanocrystals [43]. The hydrothermally prepared nanohybrids also have larger NTiO_2 particle sizes than solgel-prepared samples (Fig. 4 2H versus 2S). This is as a result of the high pressure in the hydrothermal reactor preventing the dispersion of NTiO_2 nanoparticles during the crystal growth process as observed by others [22].

3.4. Raman spectroscopic analysis of the nanohybrids

As shown in Fig. 6, both solgel-synthesized and hydrothermally synthesized NTiO_2 – oxCNT nanohybrids show the TiO_2 anatase E_g ,¹ B_{1g} and A_{1g} peaks. In all the target nanohybrids, there is a significant red shift of the E_g peak toward higher wavenumbers compared with the solgel-synthesized and hydrothermally synthesized nanohybrids synthesized without oxCNTs . A red-shift of the E_g peak in TiO_2 – CNT nanohybrids provides evidence for the interaction of TiO_2 with a material such as CNTs that sequesters electrons [44,45]. A withdrawal of electrons from TiO_2 nanoparticles tends to decrease the bond strength within the nanocrystal such that the O–Ti–O or O–Ti–N bonds are weakened in the process allowing their Raman

¹ Note that the usage of the notation E_g with reference to energy band gap is italicized to differentiate it from the Raman notation, E_g , for TiO_2 peaks.

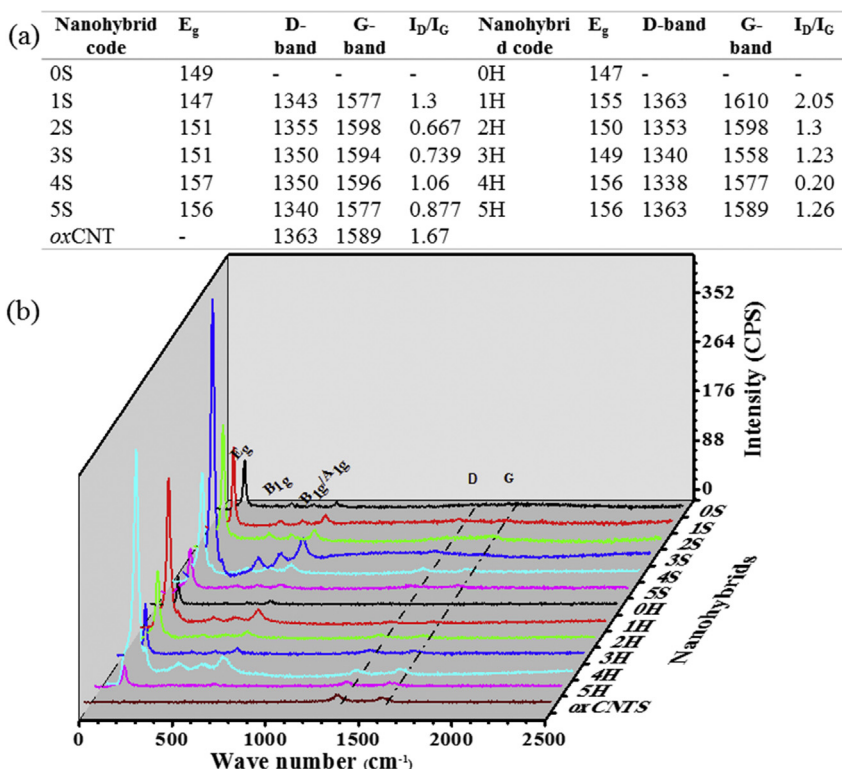


Fig. 6. Raman data for the nanohybrids (a) shifts in the anatase nitrogen-doped titania E_g and carbon nanotube D-/G-bands, (b) spectra for solgel-synthesized (0S–5S), hydrothermally synthesized (0H–5H) nitrogen-doped titania–oxidized carbon nanotube n % nanohybrids and oxidized carbon nanotubes.

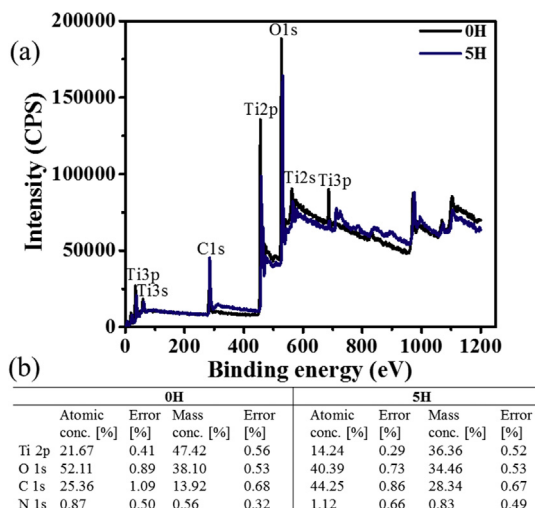


Fig. 7. X-ray photoelectron spectroscopy data of the nanohybrids 0H and 5H (a) the wide spectrum and (b) an overall elemental composition of the elements.

activity to be induced by longer, low energy wavelengths [44]. CNTs are known to sequester electrons from TiO_2 and NTiO_2 because, in as much as CNTs have surface electron density due to the π system, the ratio of π electrons to C is low; ~ 1 π electron for every 6 C atoms [1,46]. Solgel-synthesized NTiO_2 – α CNT 0% (0S) displayed the E_g peak at 149 cm^{-1} , and this E_g peak shifted toward higher wave-numbers when the wt.% α CNTs was increased in 1S, 2S, 3S, 4S, and 5S (Fig. 6(a)). Hydrothermally synthesized NTiO_2 – α CNT 0% (0H) has the E_g peak that appears at 147 cm^{-1} , and as shown in Fig. 6(a) a red shift of the E_g peak was noted in 1H, 2H, 3H, 4H, and 5H when the wt.% α CNTs was increased.

In both the hydrothermally synthesized and the solgel-synthesized nanohybrids, a blue shift of the D-band and a red shift of the G-band were observed (Fig. 6(a)). These shifts are due to the weakening of the resonant force constant of the C–C vibrations in the α CNTs caused by the movement of electrons from the NTiO_2 to the α CNT skeleton [45,47]. These Raman shifts of the anatase E_g band and the α CNT D- and G-bands suggest the formation of the Ti–C interfacial bond between the α CNTs and the NTiO_2 . This interaction was further confirmed by our TEM micrographs which showed that the NTiO_2 particles are either directly or laterally attached to the α CNTs (Figs. 4 and 5). Both direct and lateral attachment allow the sequestration of electrons from the CB of NTiO_2 to the α CNTs to occur [2].

As evidenced by the relatively high I_D/I_G values, Raman analysis of the nanohybrids revealed more distortion in the α CNTs. Although the distortion is present in both the nanohybrids and the α CNTs, it is much more pronounced in the α CNTs (Fig. 6). This distortion in the α CNTs is due to the defects on the graphitic walls and the etching of the –COOH and –OH groups during the acid treatment process [48,49]. Sonication or refluxing of CNTs in HNO_3 or HNO_3 : H_2SO_4 etch the CNT outer walls thus producing surface defects. As a result, the decrease in distortion in the nanohybrids is proof of the formation of the Ti–C interfacial bonds between the NTiO_2 and the α CNTs.

As illustrated in Fig. 6(b), the hydrothermally synthesized nanohybrids showed α CNT peaks with stronger intensity than solgel-synthesized nanohybrids. The low intensity of the D- and G-bands in the spectra solgel-synthesized nanohybrids is interpreted to suggest a low wt.% α CNTs due to the α CNTs being oxidized in air when the precursor xerogel was sintered during the high-temperature calcination. The higher α CNT content in the hydrothermally synthesized nanohybrids serves to increase the photocatalytic efficiency of the hydrothermal nanohybrids in that the α CNTs act as

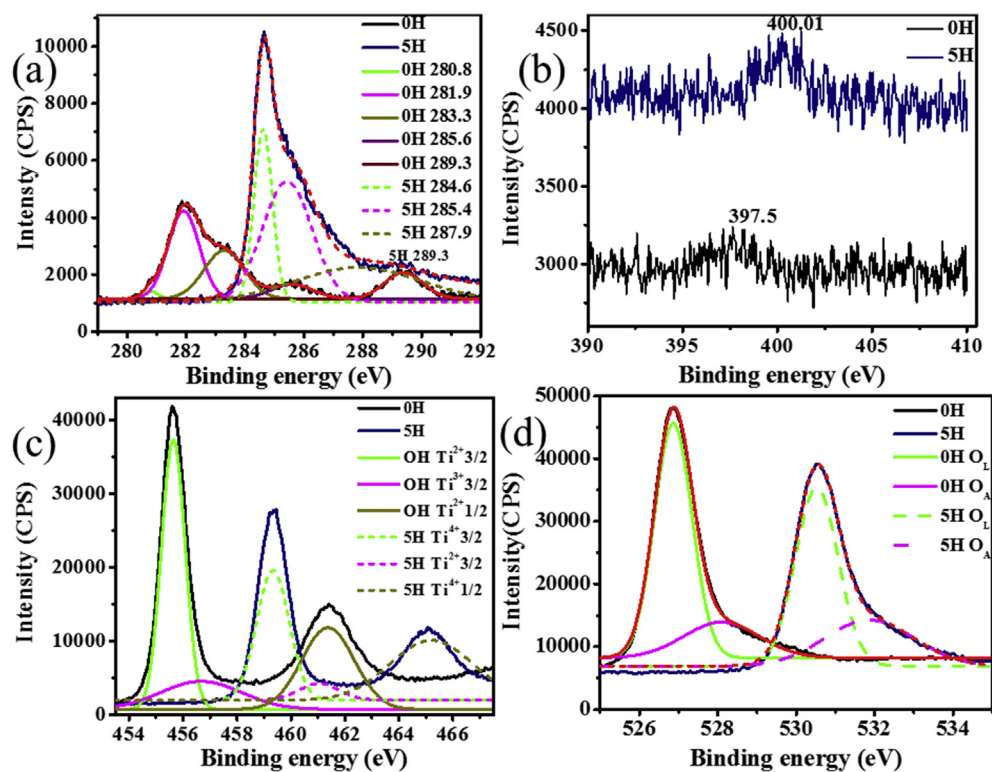


Fig. 8. A comparison of the (a) C1s, (b) N1s, (c) Ti2p, and (d) O1s X-ray photoelectron spectrophotometer spectra for the nanohybrids 0H and 5H.

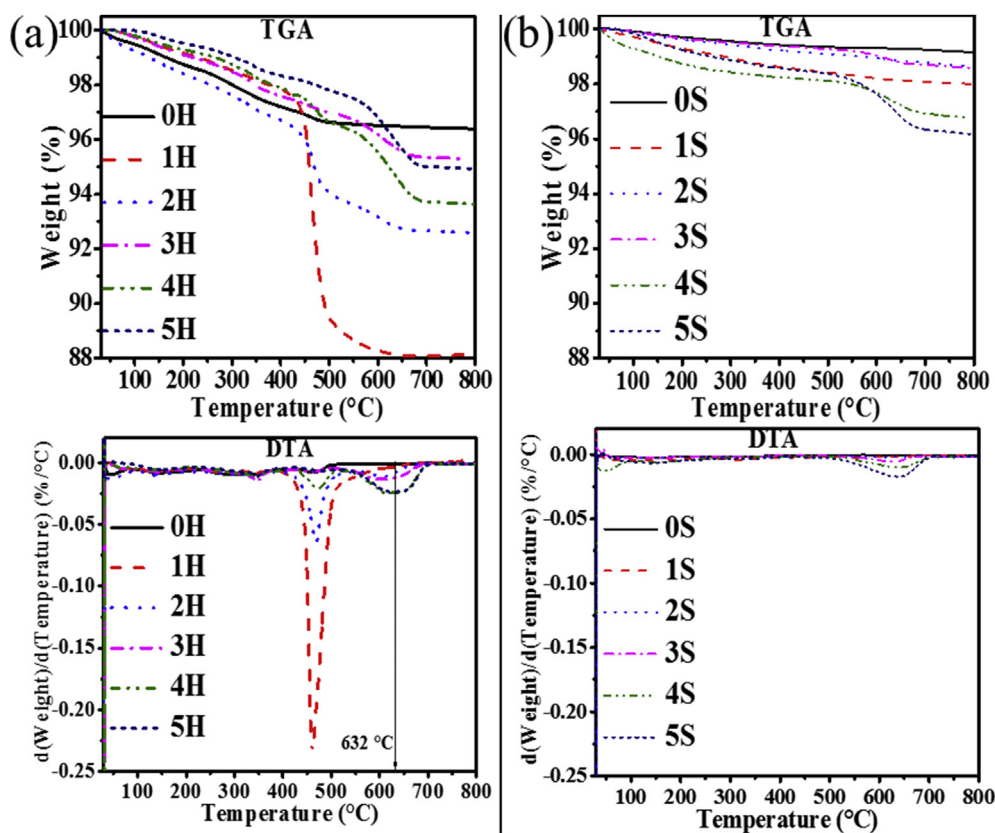


Fig. 9. Thermogravimetric analysis and differential thermal analysis curves for (a) hydrothermally synthesized nanohybrid (H) and (b) sol-gel-synthesized nanohybrids (S) run under atmospheric air conditions.

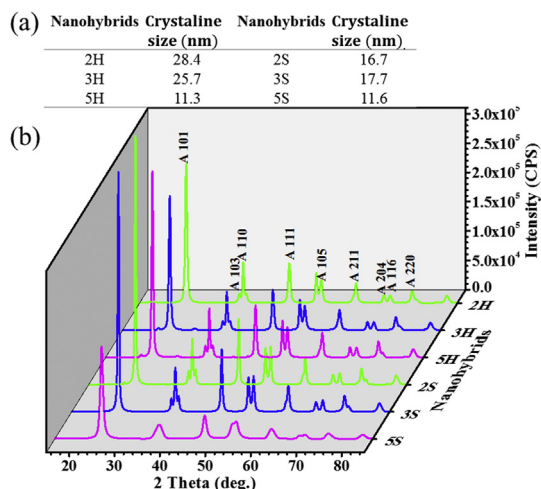


Fig. 10. A comparative X-ray diffraction analysis of the (a) crystalline sizes and (b) spectra for solgel-prepared (S) and hydrothermally prepared (H) nanohybrids.

crystals and by extension the surface area available for the adsorption of organic molecules during photocatalytic processes.

The hydrothermally synthesized nanohybrids generally showed a higher I_D/I_G ratio than the solgel-synthesized nanohybrids. This confirms that the oxCNTs in the hydrothermally synthesized nanohybrids have a higher distortion of the graphitic wall than the solgel-synthesized nanohybrids. This excessive distortion is likely due to the higher degree of $-\text{COOH}$ and $-\text{OH}$ group attachment. The solgel-synthesized nanohybrids have low I_D/I_G ratios due to the removal of the $-\text{COOH}$ and $-\text{OH}$ groups and the amorphous carbon residue in the oxCNTs during calcination at 450°C . The stronger intensity of the D-band is attributed to structural defects such as etching of the CNTs, formation of non-hexagonal rings, introduction of non-carbonaceous atoms due to the presence of $-\text{COOH}$ and $-\text{OH}$ groups and presence of amorphous residue produced by the acid treatment of the CNTs with HNO_3 is known to produce amorphous carbon, and the amount of amorphous carbon produced increases with increased treatment times [52]. The presence of H_2SO_4 during the acid-functionalization process, however, stabilizes the acid functionalization and reduces the formation of amorphous carbon. The presence of amorphous

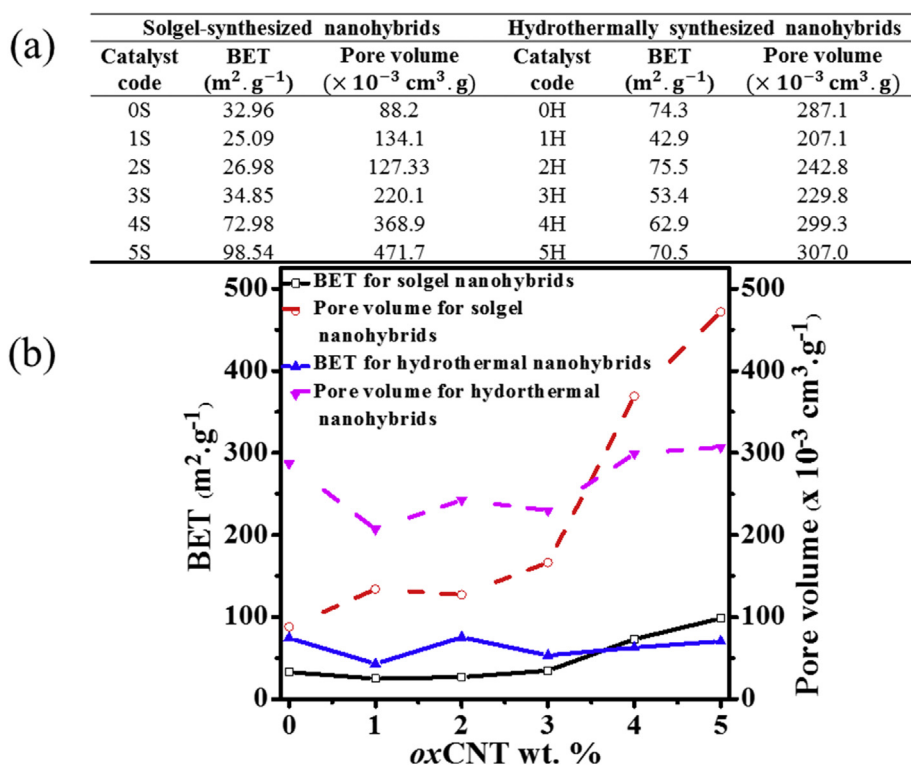


Fig. 11. A comparison of the Brunauer-Emmett-Teller surface area and pore volume variation with increasing wt.% oxCNT for solgel-synthesized and hydrothermally synthesized nanohybrids in (a) table form and (b) graphical illustration. BET, Brunauer-Emmett-Teller; oxCNT, oxidized carbon nanotube.

electron channels for photo-excited electrons in the NTiO_2 CB and thus slow down the e_{vb}^-/h_{cb}^+ recombination rate in NTiO_2 [50].

The formation of the NTiO_2 -oxCNT nanohybrids increased the crystallinity of the NTiO_2 . The intensity of the E_g peak for solgel-synthesized NTiO_2 (0S) was recorded at 81 cps, while that of NTiO_2 -oxCNT (1S) was at 133 cps. Similarly, the E_g peak for hydrothermally synthesized NTiO_2 (0H) was 48 cps and that of NTiO_2 -oxCNT (1H) was found to be 252 cps. In general, the hydrothermally synthesized nanohybrids were found to possess better crystallinity compared with the solgel-synthesized nanohybrids and as confirmed by the TEM studies (Figs. 4 and 5), crystallinity can be an indication of the surface uniformity on the NTiO_2

carbon in both solgel-synthesized and hydrothermally synthesized nanohybrids is corroborated by the early onset thermal decomposition of the oxCNTs as discussed in the section covering TGA and DTA studies (Section 3.6). Thus, the strong $-\text{OH}$ peaks in these hydrothermally synthesized nanohybrids is due to the attachment of the $-\text{OH}$ onto NTiO_2 and onto the surfaces of the oxCNTs.

3.5. Elemental composition and bonding configuration of NTiO_2 -oxCNT nanohybrids

XPS studies were carried out on the as-synthesized nanohybrids to investigate the chemical state of the elements and bonding

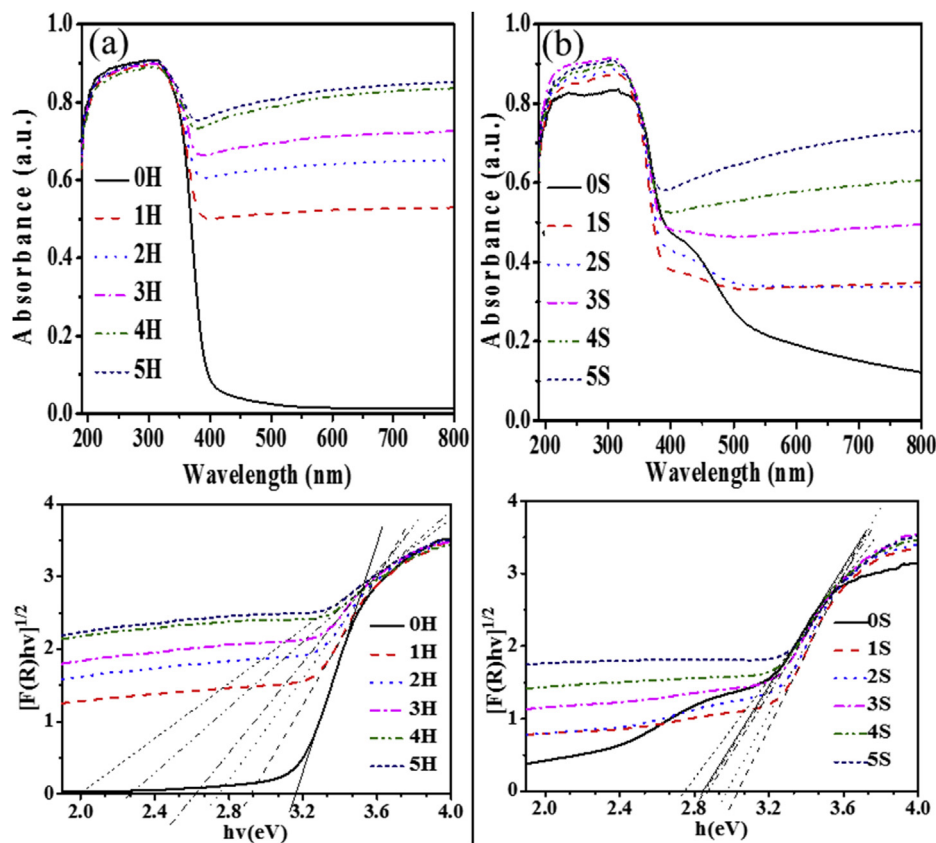


Fig. 12. Ultraviolet–visible spectra (top) and corresponding Tauc plots (bottom) for (a) hydrothermally synthesized (H) and (b) sol-gel-synthesized (S) nanohybrids.

configuration of the NTiO_2 with αCNTs . It is an established fact that the yellow coloration of NTiO_2 is evidence of incorporation of N into TiO_2 hence the physical characteristics, FTIR, Raman spectra and the TEM micrographs were enough to conclude that N was doped into TiO_2 and that the resultant NTiO_2 was covalently attached onto the αCNTs . The hydrothermally-synthesized nanohybrids, however, did not have the yellow coloration. Therefore, a particular focus was paid to the hydrothermally synthesized nanohybrids 0H and 5H to investigate the effect of eliminating the post calcination step on the doping configuration of N and the attachment of NTiO_2 onto the αCNTs .

The broad spectrum and the elemental composition confirmed the incorporation of N into TiO_2 (Fig. 7) for both nanohybrids studied. The nanohybrid 5H had a higher at.% C (44.25) than 0H (25.36) and hence confirming the incorporation of αCNTs into the nanohybrid 5H. The presence of C in the nanohybrid 0H is due to organic residue remaining in the nanohybrid because of the elimination of the post calcination step during the synthesis process. The nanohybrid 5H also had higher N at.% (1.12) than 0H (0.87) hence suggesting that the αCNTs also play a role in the assimilation of N into the nanohybrid.

The N1s, Ti2p, C1s, and O1s were deconvoluted to determine the species and the bonding configurations of each element (Fig. 8). The nanohybrid 5H shows relatively symmetric $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$ peaks at 459.3 and 465 eV, respectively, accounting for 93.3% of the Ti in the nanohybrid (Fig. 8 (c)). The formation of dative covalent bonds between TiO_2 and CNTs has been shown to be preceded by the oxidation of Ti^{3+} and Ti^{2+} in TiO_2 precursors to Ti^{4+} . Therefore, the predominance of the Ti^{4+} species indicates the degree of the formation of the Ti–C– bond between NTiO_2 and αCNTs . A $\text{Ti}^{2+} 2p_{1/2}$ accounting for 6.8% is also observed at

461.0 eV and has been indexed to the –O–Ti–N– bonding configuration [53]. The incorporation of N into TiO_2 is also confirmed by the appearance of the N1s peak which, upon integration, shows that the nanohybrid has 1.12% N by atomic composition (Fig. 8 (b)). The N1s peak maxima at ~401 eV further suggests N to be predominantly interstitially doped into TiO_2 as –N–H and –N–O– [54]. The C1s spectra for the nanohybrid 5H show an intense peak at ~284.6 eV with a shoulder peak centered at 285.4 eV which are indexed to sp^3 and sp^2 hybridized C in the αCNT skeleton, respectively (Fig. 8 (a)). These binding energies are due to the –C=C– and –C–C– in the αCNT skeleton. The peaks at 287.9 and 289.3 eV are indexed to the –Ti–C– and –O–C=O– bonding configurations, respectively, thus confirming the attachment of NTiO_2 onto the αCNTs through the configuration O–Ti–C– and oxidation of the CNTs [55,56]. A broad peak also occurs in the range 283–293 eV with the strongest intensity at 287 eV. The region of strongest intensity is indexed to the –C=N– and –C–N– bonds, suggesting that NTiO_2 nanoparticles are etched onto the surfaces of αCNTs through molecular N configuration –C=N–Ti– and lattice N configuration –C–N–Ti– [57]. The O1s spectra of the nanohybrid are similar to that of 0H in that both spectra indicate the predominance of lattice O (O_L) and adsorbed O (O_A) (Fig. 8 (a)). The occurrence of O_A indicates the presence of surface –OH functional groups which enhance photocatalytic applications of the nanohybrids [58]. Adsorbed O is at a ~ at.% 35 (higher) in 5H and only at.% 23.4 in the nanohybrid 0H and thus indicating an enhanced adsorption capacity for the nanohybrid 5H.

The Ti 2p spectra of the nanohybrid 0H show a $\text{Ti}^{2+} 2p_{3/2}$ peak at 455.6 eV and a $\text{Ti}^{2+} 2p_{1/2}$ at 528.1 eV, which are obviously at lower binding energies than those of the nanohybrid 5H. These

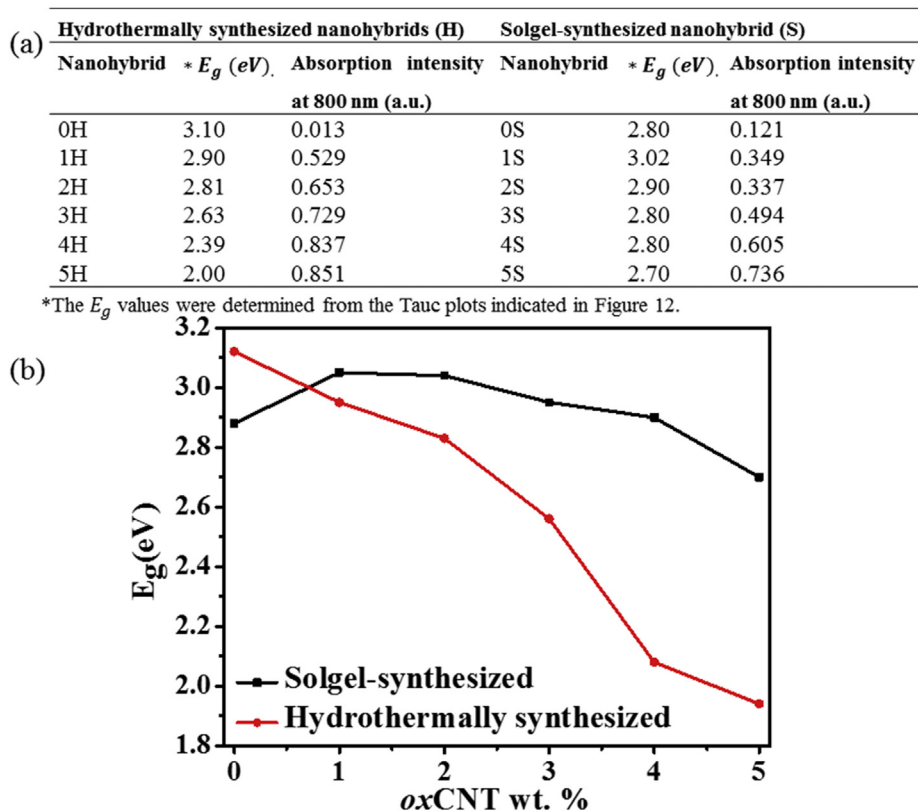


Fig. 13. A summary of the optical properties of NTiO_2 - oxCNT nanohybrids in the form of (a) a table showing the E_g and maximum visible light absorption intensities for hydrothermally synthesized (H) and solgel-synthesized (S) nanohybrids and (b) a graphical comparison of the variation of E_g with oxCNT for the two methods. NTiO_2 - oxCNT , nitrogen-doped titania-oxidized carbon nanotube.

peaks at low binding energies have been observed for N-doped TiO_2 and have been indexed to the $-\text{O}-\text{Ti}-\text{N}-$ configuration hence suggesting lattice N [40,45]. The $\text{C}1\text{s}$ spectra for 0H shows peaks at 281.9 and 283.4 eV, which are indexed to the $-\text{Ti}-\text{C}-$ bond in TiC (Fig. 8 (a)). Peaks corresponding to the $-\text{Ti}-\text{C}-$ bond are also observed in the $\text{Ti}2\text{p}$ spectra at 455.6 eV [59]. The peak at 289.3 eV is indexed to TiCO_3 [60]. The broad peak occurring in the range 284–286 eV is due to $-\text{C}=\text{C}-$ and $-\text{C}-\text{O}-$ bonds [57]. The $\text{N}1\text{s}$ peak appearing in the range 394–401 eV suggests that there is more than one type of N incorporation. This range covers the

binding energy at 399.5 eV, which is assigned to substitutional doping of TiO_2 by anionic N existing in the form $-\text{N}-\text{Ti}-\text{O}-$ and to a lesser extent the binding energy at 401.7 eV which is due to interstitial N [54,61]. The peak at binding energy 397.5 eV is the most intense and is due to substitutional N as $-\text{Ti}-\text{N}-$ [62]. An integral of the $\text{N}1\text{s}$ peak indicates that there is ~ at.% 0.87 of N atoms in the nanohybrid.

Comparing the two nanohybrids, 0H and 5H reveal the role of oxCNT s in enhancing the optical properties of the nanohybrids in several ways. The following considerations can be noted:

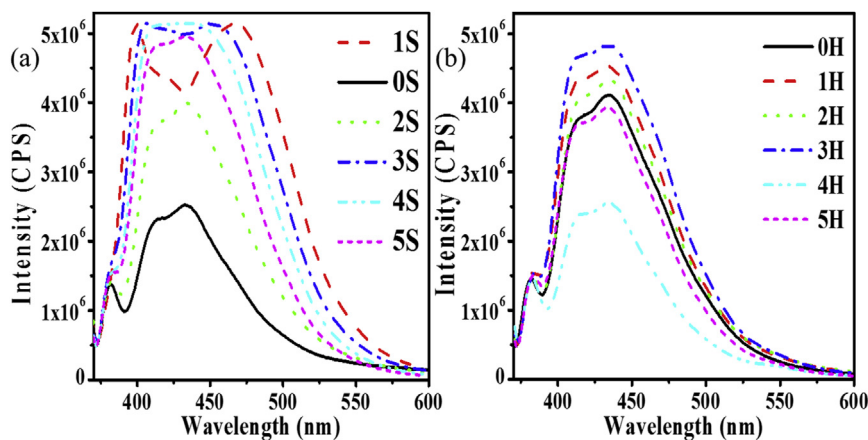


Fig. 14. Photoluminescence spectra of (a) solgel- (S) and (b) hydrothermally synthesized nanohybrids (H). NTiO_2 , nitrogen-doped titania; oxCNT , oxidized carbon nanotube.

- (i) The presence of *oxCNTs* enhances the incorporation of N atoms into TiO_2 , and this is hypothesized to be due to the *oxCNTs* promoting the oxidation of Ti ions in the precursors to higher oxidation states and enabling faster coordination of the N atoms to the Ti center.
- (ii) Carbon is also found in the nanohybrid 0H. We attribute this to a combination of factors including the presence of C residue from the precursors and solvents in the ultimate product. This can be in the form of CO and CO_2 as suggested by the FTIR spectra of the nanohybrid 0H. The occurrence of C is also hypothesized to be due to adventitious C.

3.6. Thermal stability of NTiO_2 –*oxCNT* nanohybrids

TGA analysis of the nanohybrids and *oxCNTs* was carried out under atmospheric air conditions to determine the degradation temperatures and actual wt.% *oxCNTs* in each nanohybrid (Fig. 9). The TGA and DTA profiles reveal significant differences in thermal stabilities between the solgel-synthesized and hydrothermally synthesized nanohybrids. Solgel-synthesized nanohybrids are more thermally stable than the hydrothermally synthesized nanohybrids as illustrated by the low wt.% loss (Tables 2 and 3) and the high residue at 850 °C (Fig. 9). Hydrothermally synthesized nanohybrids also show a significant wt.% loss in the temperature range 450–480 °C as illustrated by the DTA peaks in Fig. 9 (a). This is attributed to the detaching of surface –OH groups [63]. Of the hydrothermally synthesized nanohybrids, the nanohybrid with 1 wt.% *oxCNTs* shows the highest wt.% loss in this region; 10.2% (Fig. 9 (a) and Table 3).

Hydrothermally synthesized nanohybrids also show higher wt.% loss in the temperature range 558–650 °C. This temperature range is the region for the thermal degradation of the *oxCNTs* as shown by the TGA profile of the *oxCNTs* (Fig. A4 Appendix data). Therefore, this is the region from which the actual wt.% of the *oxCNTs* can be determined. As expected, the wt.% *oxCNT* increases from 1.04% in nanohybrid 2H to 2.6% in nanohybrids 4 and 5H. Nanohybrids 0H and 1H do not show a significant wt.% loss in this region. For nanohybrid 0H, it confirms the absence of *oxCNTs*, and for nanohybrid 1H, the wt.% loss is insignificant because it is overshadowed by the wt.% loss due to organics and surface adsorbed H_2O . Solgel-synthesized nanohybrids similarly show a gradual increase in wt. loss % in the temperature range 558–650 °C (Table 3 and Fig. 9(b)).

The temperatures at which *oxCNT* thermal degradation is at its maximum are higher for the solgel-synthesized nanohybrids than the hydrothermally synthesized nanohybrids. For example, the *oxCNTs* in nanohybrids 4S and 5S degrade at 637 and 639 °C, respectively; whereas for 4H and 5H, the *oxCNTs* degrade at 622 and

623 °C, respectively. This suggests that the *oxCNTs* in solgel-synthesized hybrids attain higher thermal stability due to the strong attachment of the NTiO_2 nanoparticles. This also suggests that the solgel-synthesized nanohybrids have a denser covering of NTiO_2 nanoparticles, and this high-density coverage imputes higher thermal stability on the *oxCNTs* [64]. For comparison, we carried out a TGA analysis under an inert atmosphere to determine the thermal behavior of the nanohybrids (Appendix data A3). The results indicate that the incorporation of the *oxCNTs* into the nanohybrid increases the presence of surface groups such as the –COOH and –OH. These groups are essential for the enhancement of adsorption and the overall photocatalytic efficiency of the nanohybrids.

3.7. XRD spectroscopic analysis of nanohybrids

Both solgel-synthesized and hydrothermally synthesized nanohybrids were found to consist of the anatase phase, as evidenced by the appearance of 101, 103, 110, 111, 105, 211, and 204 XRD 2θ peaks at 25.2°, 36.9°, 37.7°, 47.9°, 53.9°, 54.9°, and 62.6°, respectively [41]. The CNT peak, which appears at 24°, was also not observed because it was overshadowed by the strong intensity of the anatase TiO_2 peak appearing at 24.8° [55]. A sharp decrease in the intensity of the 101 peak when the wt.% *oxCNTs* was increased was observed for the solgel-synthesized nanohybrids (Fig. 10(b)). The decrease in the intensity of the 101 peak suggests that an increase in wt.% *oxCNTs* decreases the crystallinity of the solgel-synthesized nanohybrids.

Hydrothermally synthesized nanohybrids have smaller crystalline sizes than their solgel-synthesized counterparts. For example, the average crystalline size for 2H is about 16.7 nm, while that of 2S is ~28.4 nm (Fig. 10(a)). However, at higher wt.% *oxCNTs*, the contribution of *oxCNTs* toward the regulation of the crystalline size is significantly increased. For example, the average crystalline sizes for 5S and 5H (both 5 wt.% *oxCNTs*) are 11.3 and 11.6 nm, respectively.

3.8. BET surface area and pore volume analysis

At low wt.% *oxCNTs* (1–3%), the hydrothermally synthesized nanohybrids showed higher specific surface area and pore volumes than their solgel counterparts with the same composition. The solgel-synthesized nanohybrids that contain 0–3 wt.% *oxCNTs* exhibit low surface area and pore volumes, particularly those with low *oxCNT* composition (32.96 $\text{m}^2 \text{g}^{-1}$ for 0S, 25.09 $\text{m}^2 \text{g}^{-1}$ for 1S, 26.98 $\text{m}^2 \text{g}^{-1}$ for 2S and 34.85 $\text{m}^2 \text{g}^{-1}$ for 3S). Their hydrothermally synthesized counterparts 0H, 1H, 2H and 3H have higher BET surface areas of 74.3, 42.9, 75.5 and 53.4 $\text{m}^2 \text{g}^{-1}$ respectively (Fig. 11).

Table 2
Thermogravimetric analysis profile breakdown for hydrothermally synthesized nanohybrids.

Catalyst	Catalyst code	Region of degradation	Onset–offset within region	Max degradation temp.	Wt.% loss per region	Wt.% loss total
NTiO_2 – <i>oxCNT</i> 0%	0H	A	278–359	309	1.75	3.6
		B	460–485	459	0.693	
NTiO_2 – <i>oxCNT</i> 1%	1H	A	448–487	457	10.2	10.2
NTiO_2 – <i>oxCNT</i> 2%	2H	A	331–356	344	0.922	4.88
		B	452–481	469	2.76	
		C	584–640	606	1.04	
NTiO_2 – <i>oxCNT</i> 3%	3H	A	324–357	345	1.2	4.8
		B	464–478	460	0.6	
		C	558–657	607	1.662	
NTiO_2 – <i>oxCNT</i> 4%	4H	A	293–359	341	1.37	6.5
		B	458–488	471	1.24	
		C	576–674	622	2.9	
NTiO_2 – <i>oxCNT</i> 5%	5H	A	310–364	346	1.06	5.2
		B	577–675	623	2.9	

NTiO_2 , nitrogen-doped titania; *oxCNT*, oxidized carbon nanotube.

Table 3
Thermogravimetric analysis profile breakdown for the solgel-synthesized nanohybrids.

Catalyst	Catalyst code	Region of degradation	Onset–offset within region	Max degradation temp.	Wt.% loss per region	Wt.% loss total
NTiO ₂ –oxCNT 0%	0S	A	30–192	145	0.400	1.06
		B	303–354	326	0.216	
		C	684–855	791	0.259	
NTiO ₂ –oxCNT 1%	1S	A	30–174	134	0.334	2.07
		B	575–640	612	0.238	
		C	461–571	560	0.503	
NTiO ₂ –oxCNT 2%	2S	A	322–361	347	0.594	1.68
		B	452–481	469	2.76	
NTiO ₂ –oxCNT 3%	3S	A	583–651	627	1.2	1.68
		B	733–802	760	0.220	
NTiO ₂ –oxCNT 4%	4S	A	573–648	637	1.62	3.17
NTiO ₂ –oxCNT 5%	5S	A	566–674	639	2.33	4.03

NTiO₂, nitrogen-doped titania; oxCNT, oxidized carbon nanotube.

The difference in the BET surface area and pore volume patterns is attributed to the hydrothermally synthesized nanohybrids having good dispersion of the NTiO₂ nanocrystals compared with the solgel-synthesized nanohybrid at low wt.% CNTs. For both synthetic procedures, the presence of ox-CNTs at low wt.% decreased the specific surface area and pore volume (Fig. 11(a)). This could be due to oxCNTs increasing aggregation of the NTiO₂–oxCNT nanohybrids. At 4 and 5 wt.% oxCNTs, the specific surface area and pore volume of the solgel-synthesized nanohybrids are higher than those of their hydrothermally synthesized counterparts. The nanohybrids 4S and 5S have BET surface areas at 72.98 and 98.54 m² g^{−1}, respectively, whereas 4H and 5H have BET surface areas of 62.9 and 70.5 m² g^{−1}, respectively (Fig. 11(a)). In this regard, the impact of the oxCNTs toward the enhancement of the pore volume and surface area is only realized at wt.% oxCNT > 2 in solgel-synthesized nanohybrids.

While the hydrothermally synthesized nanohybrids show high surface area and high pore volume at low wt.% oxCNTs, at high wt.% oxCNTs, they are surpassed by the solgel-synthesized nanohybrids, particularly in the range 4 and 5 wt.% oxCNTs. In addition, the solgel-synthesized nanohybrids, 4S and 5S, have BET and pore volumes that are higher than that of commercial TiO₂ (Fig. 11(a)). A similar pattern was observed in the crystalline sizes of the NTiO₂ when determined by XRD spectroscopy (Fig. 10(a)). The drastic increase in the pore volume and the BET surface area at 4 and 5 wt.% oxCNT loading in the solgel-synthesized nanohybrids makes them suitable materials for photocatalysis. This is because in photocatalysis, the surface area plays a key role in the adsorption of the pollutants before they are degraded, and the adsorption step is the rate determining step.

3.9. Optical response of nanohybrids

The optical response for the nanohybrids was evaluated using UV–vis and PL spectroscopy techniques. The E_g , degree of photosensitization and degree of Urbach tailing were determined from UV–vis spectra. Variations in e_{cb}^-/h_{vb}^+ rates of the nanohybrids and the presence (or absence) of defects in NTiO₂ were determined from PL spectra.

3.9.1. UV–vis spectroscopic analysis of nanohybrids

The strong UV absorbance in the range 190–380 nm is typical of TiO₂ nanocrystals. The effect of N-doping on the photosensitization of NTiO₂ was first evaluated by comparing the UV–vis spectra of hydrothermally synthesized NTiO₂ (0H) with that of commercial anatase TiO₂ (Fig. A1 (b) Appendix data). It was found that while N-doping enhances the optical properties of NTiO₂ by shifting the absorption into the visible range, the incorporation of oxCNTs

further increased the photosensitization and further shifted the absorption edge of the nanohybrids into the visible region for both solgel-synthesized and hydrothermally synthesized nanohybrids. This is supported by UV–vis (Fig. 12) and spectral data, which indicate that an increase in the wt.% oxCNT enhances absorbance in the visible region.

In addition, hydrothermally synthesized nanohybrids exhibited higher absorption of visible light all the way up to the near infrared region. For example, the absorbance units (a.u.) of nanohybrid 5H, which is black in color, is 0.85 at 800 nm, while that of 5S, which is also black (Fig. 2) is 0.73 a.u. at the same wavelength (Figs. 12 and 13(a)). The hydrothermally prepared nanohybrids generally show higher visible light absorption because they have relatively high wt.% oxCNTs as confirmed by the TGA profiles of the nanohybrids.

The E_g for TiO₂ is calculated from the reflectance derived from the Kubelka–Munk function by as shown in Equation (1) [65,66].

$$[F(R)hv]^n = k(hv - E_g) \quad (1)$$

where $F(R)$ is the reflectance coefficient and an equivalent of the absorption coefficient α ; hv is the photon energy; k is a characteristic constant for each material; E_g is the energy band gap; and n is the order of the inter-band electronic transitions.

TiO₂ is an indirect semiconductor, and the order of the transition has been determined experimentally to be $\frac{1}{2}$. Therefore, the Kubelka–Munk equation for TiO₂ is as follows:

$$[F(R)hv]^{1/2} = k(hv - E_g) \quad (2)$$

$F(R)$ is calculated from the reflectance derived from the Kubelka–Munk function using Equation (3):

$$F(R) = \frac{(1 - R)^2}{2R} \quad (3)$$

A plot of $[F(R)hv]^{1/2}$ vs hv gives the relation between the photon energy and the reflectance coefficient of the material. As shown in Fig. 12, the E_g of the hybrid materials is the value where the extrapolation of the straight part of the plot intersects the photon energy [65,66].

The hydrothermally synthesized nanohybrids show a general decrease in the E_g when the oxCNT content was increased from 0 to 5 wt.%; from 3.01 eV for 0H to 2.00 eV for 5H (Fig. 12). The solgel-synthesized nanohybrids, on the other hand, show an initial increase of the E_g from 2.80 eV for 0S to 3.02 eV for the nanohybrid 1S and a slight decrease to 2.8 eV at 5 wt.% oxCNTs. In overall, for the solgel-synthesized nanohybrids, the increase in wt.% oxCNTs has an insignificant influence on decreasing the E_g (Fig. 12). This implies

that as the wt.% αCNTs increases, there is a corresponding red-shift in the absorption edge of the hydrothermally synthesized nanohybrids. The decrease in the E_g is due to the formation of the Ti–C bond, which creates inter-band energy states from which electrons can be excited [67]. The hydrothermal method is, therefore, proven to be favorable in harnessing the band-gap narrowing effect of αCNTs than the solgel method.

The nanohybrids show enhanced absorption of visible light from the visible to near-infrared region through photosensitization. The photosensitization occurs through the Urbach tailing and the visible light absorption of αCNTs by virtue of their dark color. The Urbach tail indicates the Urbach energy (E_u) contribution which is known to be caused by the presence of impurities, crystal defects, and non-crystalline materials in the nano-powders of semiconductors [68–70]. The Urbach tail intensity and edge is an indication of photosensitization of the material, i.e. the further the tail reaches into the visible spectrum the more intense it is and the greater is its contribution toward the ability of the material to absorb light in the visible spectrum [71].

The solgel-synthesized nanohybrids show enhanced photosensitization due to both Urbach tailing and photosensitization by the darker color of the nanohybrids. The contribution of the E_u toward photosensitization of the nanohybrids is evident in the nanohybrids 0S, 1S, 2S, and 3S. In these solgel-synthesized nanohybrids, the N-doping clearly extends its absorption edge up to 496 nm and thus decreases E_g to as low as 2.50 eV. Since the nanohybrid 0S does not contain αCNTs , the appearance of the Urbach tail can be attributed to N-doping, and the formation of oxygen vacancies. It has previously been shown that substitutional N-doping produces more pronounced Urbach tails than interstitial and surface doping [72]. This suggests that the incorporation of N into TiO_2 is more substitutional for the solgel-synthesized nanohybrids. As the wt.% of αCNTs is increased beyond 3%, however, the absorbance in the visible region due to N-doping in solgel-synthesized nanohybrids gets overshadowed by the absorbance due to the incorporation of αCNTs . Again, here, the αCNTs act as photosensitizers. Fig. 11 shows that the presence of αCNTs in NTiO_2 – αCNT 4 and 5% enhances the photosensitization such that the contribution of the Urbach energy in enhancing visible light absorption is insignificant.

Generally, for the hydrothermally synthesized nanohybrids, the photosensitization effect of the αCNTs in the visible region is greater than in the solgel-synthesized nanohybrids. For example, it is observed that with as little as 1 wt.% of αCNTs in the hydrothermally synthesized hybrids, the absorption in the visible range increases to 0.529 a.u., which is greater than absorption due to Urbach tailing in the solgel-synthesized nanohybrids (Fig. 12). In previous hydrothermal syntheses, it was observed that while the UV–vis spectra did not indicate N-doping, XPS spectra indicated substitutional N-doping into the TiO_2 lattice [37,73]. N has also been found to have been doped as $-\text{NH}_2$ species coordinated to the Ti metal center [74].

3.9.2. Photoluminescence spectroscopic analysis of the nanohybrids

PL intensity indicates the degree to which e_{cb}^-/h_{vb}^+ recombination rate in NTiO_2 has been reduced in a semiconductor nanomaterial. Therefore, a low PL intensity is an indication of a low e_{cb}^-/h_{vb}^+ recombination rate [66]. In this work, hydrothermally synthesized nanohybrids generally had lower PL intensities than solgel-synthesized nanohybrids, thus suggesting that the e_{cb}^-/h_{vb}^+ recombination rate has been significantly lowered (Fig. 14). Correspondingly, the influence of wt.% αCNTs quenching the PL intensity from NTiO_2 is observed among some of the hydrothermally synthesized nanohybrids. In particular, the nanohybrids 4H and 5H have PL intensities lower than that of 0H, with 4H having

the lowest intensity (Fig. 14 (b)). Arranged in order of decreasing PL intensity, the hydrothermally synthesized nanohybrids (that are in agreement with our expectations) are $1\text{H} > 2\text{H} > 5\text{H}$. Therefore, the hydrothermal method is proving to have a better potential in tailoring the e_{cb}^-/h_{vb}^+ recombination rate of NTiO_2 – αCNT nanohybrids.

Although there is currently no consensus with regards to the relationship between the PL peak broadening and the actual particle size, the relationship between PL peak broadening and particle size distribution is widely accepted. Narrow peak broadening suggests a narrow particle size distribution, whereas a larger peak broadening suggests a wider particle size distribution [75,76]. In general, the hydrothermally synthesized nanohybrids show narrow peak broadening than their solgel-synthesized counterparts. This suggests that the hydrothermal method offers better particle size control than the solgel method. With respect to the relationship between particle size and PL peak broadening, the nanohybrids whose crystalline size have been determined to be small, nanohybrids 5S, 5H, 4S, and 4H, have narrower peaks (Fig. 14). As such, there is a direct relationship between particle size and PL peak broadening.

The PL spectra also show that the solgel technique yields NTiO_2 particles with pockets of inter-band energy states. These inter-band energy states are shown by the separation in the emission peaks. These pockets arise from both the intrinsic and extrinsic surface defects [77]. It has previously been shown that annealing TiO_2 at high temperatures creates oxygen deficient defects on TiO_2 crystalline lattice and that these defects act as e_{cb}^-/h_{vb}^+ recombination centers [78]. The introduction of dopants and photosensitizers also increases the occurrence of defects on a crystal lattice, and these defects act as inter-band gap recombination centers below the VB. Since these defects narrow the E_g , when electrons fall from the CB into these inter-band states, low-energy luminescence is emitted. The low-energy luminescence corresponds to the shift of the luminescence toward the visible region [79]. Therefore, when arranged in order of decreasing occurrence of surface defects, the solgel-synthesized nanohybrids are $1\text{S} > 3\text{S} > 5\text{S}$. Since TiO_2 is an indirect semiconductor, the defects enable the transition of electrons from the VB to the CB to be induced by low-energy light [80]. Therefore, defects in TiO_2 are intrinsic. The absence of recombination peaks beyond 500 nm implies that there are no Ti^{3+} defects and that the band at 398 nm is associated with CB–VB transitions. The band at 466 nm is associated with radiationless recombination. This radiationless recombination arises due to Stokes effects, interaction of the emitted quantum yield with the phonons in the crystal lattice resulting in crystallite vibrations and heating up [79].

The role of αCNTs in reducing the e_{cb}^-/h_{vb}^+ recombination rate in these nanohybrids is influenced by the synthesis method. Among the solgel-synthesized nanohybrids, the incorporation of αCNTs (1–5 wt.%) is not effective in reducing the e_{cb}^-/h_{vb}^+ recombination rates. This is because all the nanohybrids 1S–5S have high PL intensities compared with solgel-synthesized NTiO_2 (0S) (Fig. 14 (a)). In the hydrothermally synthesized nanohybrids, however, the nanohybrid 4H has a PL intensity that is lower than hydrothermally synthesized NTiO_2 (0H). The nanohybrid 5H, on the other hand, has a PL intensity that is lower than that of 0H. Therefore, e_{cb}^-/h_{vb}^+ recombination rate for NTiO_2 – αCNT nanohybrids is most effectively reduced through hydrothermal synthesis, and the optimal CNT content is 4%. We, therefore, reveal that the hydrothermal method greatly enhances visible light absorption even if the post calcination step is eliminated. This offers a niche by which the synthesis of NTiO_2 – αCNT nanohybrids and other related nanohybrids can become more economically viable while producing highly photoactive nanohybrids.

4. Conclusion

We have successfully used efficient hydrothermal and the solgel techniques in a facile one-pot production method for photocatalytic NTiO_2 - αCNT nanohybrids where the precursor suspension, synthetic conditions, and αCNT content are constant. We systematically evaluated these two methods to understand their role on the physicochemical properties and optical response of the nanohybrid photocatalysts. The incorporation of αCNTs into the NTiO_2 significantly reduced particle agglomeration, suppressed the growth of rice-grained nanorods and promoted the growth of smaller and regular cuboidal shapes. Our work clearly reveals the influence of N-doping in promoting the growth of rice-grained NTiO_2 nanorods and further demonstrates that the hydrothermal method better enhances the growth of these nanorods than the solgel method. While the hydrothermal method is seen to be generally superior in several aspects, the solgel method offers better control of the NTiO_2 particle size and hence high BET surface area and pore volume than the hydrothermal method. The solgel nanohybrids also have a denser surface coverage of the αCNTs by the NTiO_2 nanoparticles than the hydrothermally synthesized nanohybrids. The solgel-synthesized nanohybrids were found to be more thermally stable and are therefore regarded as better candidates for photocatalytic applications at elevated temperatures. The incorporation of N into NTiO_2 and the formation of covalent bonds between NTiO_2 and αCNTs are possible without the common post calcination step. However, the elimination of the post calcination step promotes the incorporation of C into TiO_2 which further enhances the photocatalytic activity. The results also indicate that αCNTs suppress the formation of TiC in the nanohybrids and increase the density of oxidative surface groups such as $-\text{OH}$ and $-\text{COOH}$, and organic residues such as CO and CO_2 . The presence of these groups and organic residue enhances the adsorption of both charged and neutral pollutants during photocatalytic reactions and thereby making the hydrothermally synthesized nanohybrids better candidates for photocatalysis. Increasing the wt.% αCNTs in the nanohybrids reduces the E_g from 3.01 eV at 0 wt.% αCNT to as low as 2.01 eV at 5 wt.% αCNTs . The αCNTs also enhance the photo-response through increasing the photosensitization and reduction of the $e_{\text{vb}}^-/h_{\text{cb}}^+$ recombination rate of the nanohybrids such that the nanohybrid 4 wt.% NTiO_2 - αCNT nanohybrid had the lowest $e_{\text{vb}}^-/h_{\text{cb}}^+$ recombination rate. Here, the αCNTs served as electron channels for the reduction of $e_{\text{vb}}^-/h_{\text{cb}}^+$ recombination rate.

Conflict of interest

The authors confirm that there is no conflict of interest.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix B. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.mtchem.2018.07.004>.

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