

# CNT/TiO<sub>2</sub> Hybrid Nanostructured Materials: Synthesis, Properties and Applications



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**Abstract** The study of semiconductor photocatalysts is essential to achieve sustainable solutions for application in energy generation and treatment of environmental pollution. Titanium dioxide (TiO<sub>2</sub>) is one of the most researched photocatalysts because of its abundance and non-toxicity, but its low efficiency, when deployed as a photocatalyst, can sometimes hinder its potential for these applications. Combining nanostructured TiO<sub>2</sub> with carbon nanotubes (CNTs) to form hybrid materials can help overcome some of the metal oxide limitations, such as a large band-gap and a high electron–hole recombination rate. This chapter summarizes some of the CNT/TiO<sub>2</sub> nanostructured materials that have been reported in the last years and outlines their morphologies, methods of synthesis, and applications.

**Keywords** TiO<sub>2</sub> · CNTs · Nanocomposites · Photocatalysts · Semiconductor

## Abbreviations

1D	One-dimensional
AC	Alternating current
ALD	Atomic layer deposition
BET	Brunauer-Emmett-Teller
CNT	Carbon nanotube
CO	Carbon monoxide
Co-TiO <sub>2</sub>	Cobalt doped titanium dioxide
CVD	Chemical vapor deposition
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
DSSC	Dye-sensitized solar cell
EDL	Electric double-layer capacitor

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EDS	Energy dispersive X-ray spectroscopy
FE-SEM	Field emission scanning electron microscopy
FF	Fill factor
FT-IR	Fourier transform infrared spectroscopy
H <sub>2</sub>	Hydrogen gas
HCl	Hydrochloric acid
HNO <sub>3</sub>	Nitric acid
J <sub>SC</sub>	Short circuit current density
KOH	Potassium hydroxide
LIB	Lithium-ion battery
MAO	Micro-arc oxidation
MWCNT	Multi-walled carbon nanotube
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Sodium thiosulfate
NO	Nitric oxide
NP	Nanoparticle
PAN	Polyacrylonitrile
PCE	Power conversion efficiency
PP	Plasma polymer
PVP	Poly(vinyl pyrrolidone)
SEM	Scanning electron microscopy
SiO <sub>2</sub>	Silicon dioxide
SWCNT	Single-walled carbon nanotube
TBT	Titanium butoxide
TEM	Transmission electronic microscopy
TGA	Thermogravimetric ananalysis
TiO <sub>2</sub>	Titanium dioxide
TNR	Titania nanoribbon
TTIP	Titanium isopropoxide
UV	Ultraviolet
V <sub>OC</sub>	Open circuit voltage
XRD	X-ray diffraction

## 1 Introduction

Titanium dioxide is the naturally occurring oxide of titanium and can be found in nature in its three primary crystalline forms: anatase, rutile, and brookite [1]. Due to its low cost, non-toxicity, and strong oxidizing power [2, 3], TiO<sub>2</sub> is a promising material to be used in applications such as photocatalysis [4], dye-sensitized solar cells (DSSC) [5], and H<sub>2</sub> production via water splitting [6]. However, its relatively high band-gap (3.2 eV for the anatase phase) and high charge carrier recombination rate limit its solar photoconversion [7]. The three main ways this can be overcome is by band-gap tuning, which can be achieved using dopants [8] or by synthesizing

oxygen-rich titania [9], suppressing the electron–hole recombination [10], and by improving surface reactions [11]. Carbon nanotubes (CNT) present a high surface area, high-quality active sites, and high electronic conductivity [12, 13], therefore allowing it to enhance the photocatalytic activity of TiO<sub>2</sub> through all of these routes.

Since their discovery by Iijima in 1991 [14], CNTs have attracted attention because of their unique properties. They can be either single-walled (SWCNTs), which consists of a single graphite sheet wrapped into a cylindrical tube, or multi-walled (MWCNTs), which are an arrangement of multiple concentric SWCNTs [7]. The SWCNTs have a surface area of 400–900 m<sup>2</sup> g<sup>-1</sup>, while MWCNTs have a surface area of 200–400 m<sup>2</sup> g<sup>-1</sup>, which means that they can provide a large reactive surface area that is comparable to activated carbon. According to Woan et al. [15], TiO<sub>2</sub> and CNTs may form a Schottky barrier similar to metal–semiconductor junctions, which results in the CNTs having an excess negative charge and the TiO<sub>2</sub> an extra positive charge. In addition, they may accept photo-induced electrons in CNT/TiO<sub>2</sub> hybrid materials, thus increasing the recombination time.

The formation of CNT/TiO<sub>2</sub> heterostructures was reported by Banerjee and Wong in the early 2000s [16]. Thenceforth, a variety of TiO<sub>2</sub>/CNTs hybrid nanomaterials have been researched [7], including TiO<sub>2</sub> nanoparticles on the CNTs surface [17], TiO<sub>2</sub> coated with CNTs [18], and CNTs grown on TiO<sub>2</sub> nanotubes [19].

## 2 Synthesis and Morphology

As mentioned above, both the CNTs and the TiO<sub>2</sub> used in the hybrid nanostructures can present different morphologies. The titanium dioxide can be synthesized in the form of nanoparticles [17], nanotubes [19, 20], nanorods [21, 22], nanofibers [23], or thin films [24]. Regarding the methods employed for the synthesis of these hybrid nanostructures, some widely performed techniques can be mentioned: mixture in solution with pre-functionalized surfaces [4, 25], sol–gel [26, 27], hydrothermal [28, 29], chemical vapor deposition (CVD) [19], and atomic layer deposition (ALD) [17]. This section summarizes some of the main synthesis routes and promising nanostructures that have been studied recently.

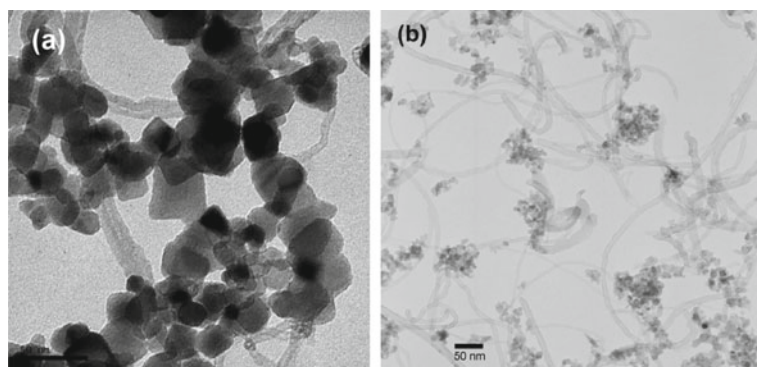
### 2.1 CNT/TiO<sub>2</sub> Nanoparticles

Hybrid nanostructures of CNTs and TiO<sub>2</sub> nanoparticles can be obtained through multiple routes, such as hydrothermal synthesis [28], modified microwave method [30], and ALD [17]. However, sol–gel is the most employed technique [7]. Sol–gel is a relatively low-cost method that presents good controllability of the synthesis conditions [31]. In addition, it has the advantage of using precursors in a liquid state, which allows good dispersion of the filler phase when producing composites [32]. However, because CNTs present strong van der Waals interactions, they tend

to form agglomerates, which requires a functionalization step to be dispersed in an aqueous solution [33]. Thus, the synthesis is divided into two significant steps, one organic and one inorganic. The CNTs are functionalized in the organic step, and surfactants are used to disperse them in the inorganic step. The composite materials are formed during the gelification process of the condensed sol, and the porous sol–gel can encapsulate nanoparticles and carbon nanotubes. In addition, sol–gel synthesis provides the prospect of adding CNTs alongside the precursors, allowing for a better connection between the carbon and the nanotubes and providing a uniform mesoporosity throughout the material [31].

Da Dalt et al. [4] produced CNT@TiO<sub>2</sub> composites by a modified sol–gel method using commercial MWCNT (Baytubes®), titanium propoxide, nitric acid, isopropyl alcohol, and deionized water. Different heat treatment temperatures for the obtained sol were evaluated. The authors synthesized spherical-shaped TiO<sub>2</sub> nanoparticles (NPs) aggregated on the CNT surface, as shown in Fig. 1. The TiO<sub>2</sub> NPs presented an average diameter smaller than 30 nm. The photocatalytic activity of the composites was evaluated and compared to commercial TiO<sub>2</sub> (AEROXIDE®—P25) and its combination with MWCNT. The CNT@TiO<sub>2</sub> composites performed better than pure TiO<sub>2</sub> nanoparticles when the catalyst concentration in the dye solution increased. The authors concluded that the CNT/TiO<sub>2</sub> heterojunctions formed reduced the recombination rate of photo-induced electron–hole pairs.

Yao et al. [18] synthesized anatase/CNTs composite materials. Anatase nanoparticles with diameters of 5 and 100 nm were added to different proportions of commercially SWCNTs and MWCNTs. First, the CNTs were functionalized with nitric acid and dispersed in water. Then, they were combined with the composite structures by simple evaporation and drying process. The photocatalytic activity for the degradation of a solution containing phenol was tested. The TiO<sub>2</sub>/SWCNTs composites presented a lower electron–hole recombination rate than TiO<sub>2</sub>/MWCNTs composites, probably because of the attachment area of the nanotubes on the surface of the nanoparticles.



**Fig. 1** TEM images of the CNT@TiO<sub>2</sub> composites using. **a** P25. **b** Sol–gel obtained nanoparticles. Edited and reprinted with permission of Da Dalt et al. [4]

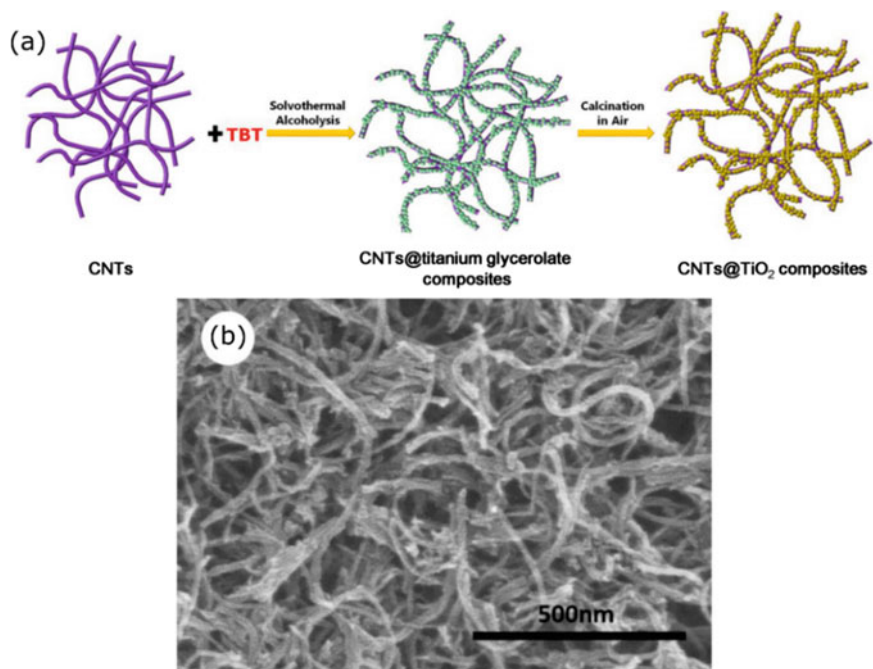
Banerjee and Wong [16] synthesized heterostructures by oxidizing raw SWCNTs bundles using acidic potassium permanganate solution and hydrochloric acid and then etched the nanotubes using HNO<sub>3</sub>. This procedure removed most of the amorphous carbon and the metal catalysts from the nanotubes. Next, the TiO<sub>2</sub> nanoparticles were synthesized by slow hydrolysis of titanium tetraisopropoxide in the presence of an alcoholic solution of 11-aminoundecanoic acid. Finally, in order to achieve TiO<sub>2</sub>/CNTs heterostructures, solutions containing the nanoparticles and the oxidized SWCNTs were sonicated for 24 h in a dimethylformamide (DMF) solution. After filtering, washing, and drying, the authors confirmed the formation of the heterostructures by Transmission Electronic Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), and Fourier Transform Infrared Spectroscopy (FT-IR). In addition, the FT-IR analysis indicated that charge transfer from nanotube to nanoparticles had been achieved.

Zhao et al. [34] deposited TiO<sub>2</sub> on the surface of CNTs by solvothermal reaction. To achieve that, the authors functionalized commercial-grade CNTs with HNO<sub>3</sub>, which was later dispersed in an ethanol and glycerol solution. Titanium butoxide (TBT) was added dropwise to this solution, and the formed liquid was heated at 110 °C for 24 h. Finally, the products were dried and then calcinated at 350 °C for 2 h. Figure 2a shows a schematic illustration of the experimental procedure adopted and Fig. 2b presents the scanning electron microscopy (SEM) image of the CNT@TiO<sub>2</sub> morphology obtained, in which can be noticed the TiO<sub>2</sub> grains on the surface of CNTs. The SEM analysis showed that composites with a CNT content of 42 wt% maintained the original morphology of tangled CNTs, and EDS analysis showed that the TiO<sub>2</sub> nanoparticles were connected and coated on the surface of the CNTs.

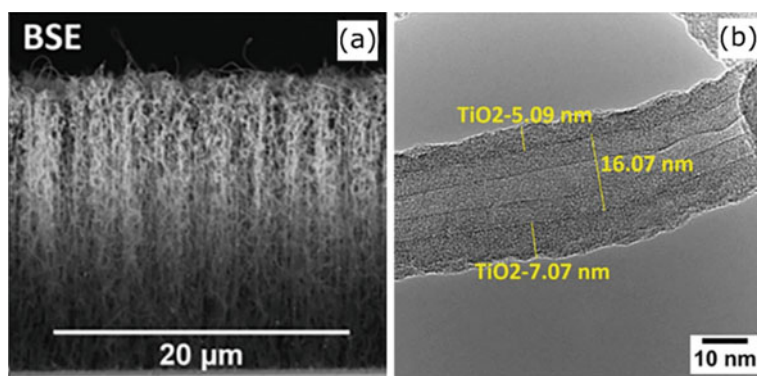
MWCNT forests coated with TiO<sub>2</sub> films via Atomic Layer Deposition (ALD) were obtained by Kaushik et al. [35]. Two types of layer configuration were obtained: (1) MWCNT with TiO<sub>2</sub> films and (2) MWCNT with a coating of carboxyl plasma polymer (PP) and TiO<sub>2</sub> films. Figure 3a presents the SEM image of the lateral view of the MWCNTs forest after 400 cycles of ALD. It can be seen that the tips of the forests are brighter, which means that TiO<sub>2</sub> film was not deposited uniformly on CNTs, only on the surface of the forests. The region selected at TEM analysis (Fig. 3b) shows a uniform TiO<sub>2</sub> film covering a MWCNT. The carboxyl coating created more nucleation sites for the deposition of TiO<sub>2</sub>, thereby producing a more uniform layer.

## 2.2 CNT/TiO<sub>2</sub> Fibers

One-dimensional (1D) nanoarchitectures attract attention because of their length-to-diameter ratio, which can enhance their chemical and optic properties when compared to nanoparticles [36]. That may occur because TiO<sub>2</sub> nanoparticles have reduced electron mobility caused by the contact between the particles, which enhances the scattering of free electrons [5]. Nevertheless, when employed as a photoanode, structures such as nanofibers present some limitations caused by their



**Fig. 2** **a** Schematic illustration of the experimental procedure for the synthesis of CNTs@TiO<sub>2</sub> composites. **b** SEM image of the CNTs@TiO<sub>2</sub> composite with 42 wt% of CNT. Edited and reprinted with permission of Zhao et al. [34]



**Fig. 3** **a** Backscattered electrons (BSE) SEM image of the lateral view of the MWCNTs forest coated with TiO<sub>2</sub>. **b** TEM image of the TiO<sub>2</sub>-coated MWCNT. Reprinted with permission of Kaushik et al. [35]

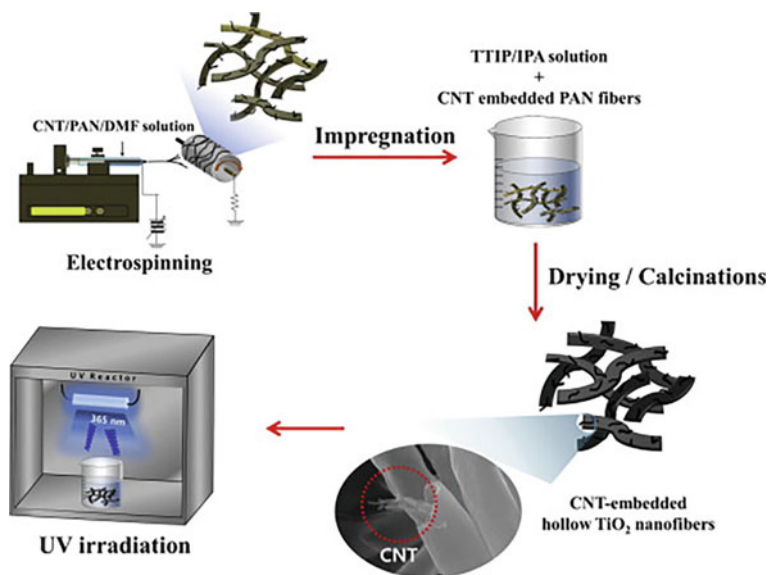
reduced surface area, which can be surpassed by using nanoparticles decorated on their surface [37]. Another innovative way to overcome these limitations is by using CNTs combined with 1D nanostructures.

One versatile and simple method to produce ultrathin TiO<sub>2</sub> fibers is the electrospinning technique [38]. It requires a relatively simple basic setup that involves electrifying a liquid droplet to generate a jet, which is stretched into a fiber. The droplet is deformed into a Taylor cone due to the electrostatic repulsion among the surface. Initially, the formed jet is stretched through a straight line before whipping due to electrostatic instability, and finally, the thinner jet solidifies and is deposited into an electrified collector [39].

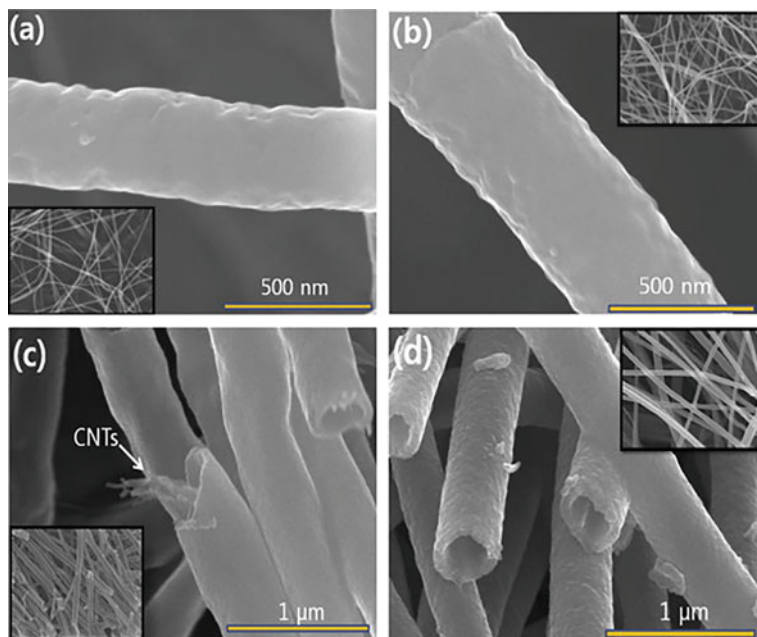
Macdonald et al. [40] fabricated a TiO<sub>2</sub> nanofiber-CNTs composite to be applied as a photoanode in a DSSC. To achieve that, the authors synthesized SWCNTs by arc discharge and TiO<sub>2</sub> nanofibers by electrospinning. First, they electrospun a sol-gel containing titanium n-butoxide, poly(vinyl pyrrolidone) (PVP), and glacial acetic acid in absolute ethanol. Next, the fiber mats were subject to pyrolysis at 500 °C to remove the PVP. The remaining TiO<sub>2</sub> nanofibers were then sonicated in an SWCNT/ethanol solution until a uniform TiO<sub>2</sub> nanofibers/CNTs mixture was formed. Finally, the mixture underwent rotary evaporation to remove the ethanol. The inclusion of CNTs in the mixture was confirmed by Raman spectroscopy, which showed the disorder-induced D-band at 1345 cm<sup>-1</sup> and the G-band at 1575 cm<sup>-1</sup> for the samples containing SWCNTs. Following, the authors fabricated DSSC using TiO<sub>2</sub> nanofibers and TiO<sub>2</sub> nanofibers/SWCNT photoanodes and applied J-V curves to characterize the photovoltaic activity. The solar cells composed of TiO<sub>2</sub>/CNTs photoanodes presented J<sub>SC</sub> of 12.65 mA cm<sup>-2</sup>, V<sub>OC</sub> of 0.72 V, FF of 0.53, and PCE of 4.83%. The addition of SWCNTs improved the efficiency of the solar cells by 67%, probably due to the CNTs contributing with additional charge-transfer channels which ultimately increased the diffusion coefficient.

Jung et al. [41] synthesized hollow TiO<sub>2</sub> nanofibers with embedded CNTs through electrospinning and impregnation. To achieve that, they electrospun a solution containing polyacrylonitrile (PAN), DMF, and MWCNTs. The as-spun fibers were then impregnated using a solution containing 0, 1, 5, and 10 wt% titanium isopropoxide (TTIP)/ isopropyl alcohol for 5 h, dried, and later calcinated at 550 °C for 1 h. The characterization was made by field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and the surface area was calculated via Brunauer-Emmett-Teller (BET) method. Finally, the adsorption and photocatalytic capability of the obtained materials were investigated by adding the photocatalyst in a solution containing methylene blue under magnetic stirring in a dark room for 30 min before exposing the solution to UV light at 365 nm for 70 min. For comparison, the authors also prepared hollow TiO<sub>2</sub> nanofibers without the presence of CNTs. A schematic representation of the experimental procedure is shown in Fig. 4. The obtained CNT-embedded hollow TiO<sub>2</sub> fibers (Fig. 5) had a diameter that ranged from 430 to 550 nm, and the CNTs were aligned with the fibers. The authors attributed this variation in diameter to the irregular distribution of CNTs within the nanofiber. They suggested that the alignment of the CNTs could be due to the electric field lines during the injection.





**Fig. 4** Schematic representation of the experimental procedure to obtain hollow TiO<sub>2</sub> nanofiber embedded with CNTs. Reprinted with permission of Jung et al. [41]



**Fig. 5** SEM images of the **a** PAN-CNT fibers, **b** impregnated PAN-CNT fibers, **c** CNT embedded hollow TiO<sub>2</sub> fibers, and **d** hollow TiO<sub>2</sub> fibers. Reprinted with permission of Jung et al. [41]



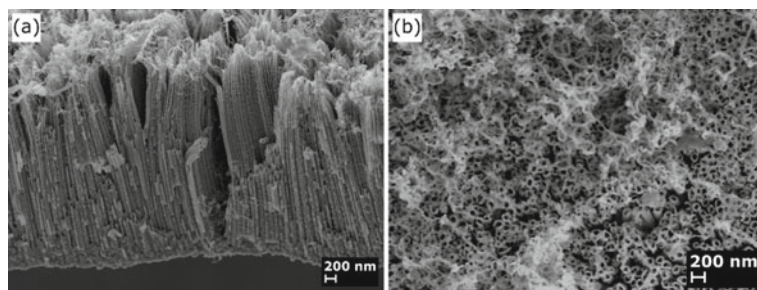
Furthermore, the addition of CNTs improved the adsorption capability of the TiO<sub>2</sub> nanofibers. The photocatalytic activity was highest for the sample impregnated in the solution containing 5 wt% TTIP concentration, and the CNT-TiO<sub>2</sub> photocatalysts more efficiently degraded the methylene blue compared to the pure TiO<sub>2</sub> nanofibers. The authors proposed that the CNTs might have introduced photogenerated electrons into the conduction band of the TiO<sub>2</sub> fibers, contributing to the enhancement of the photocatalytic capability of the TiO<sub>2</sub> fibers.

### 2.3 TiO<sub>2</sub> as Catalyst for CNT Synthesis

Carbon nanotubes can be synthesized by three main methods: the laser deposition method, electric arc method, and CVD [42]. The latter is the most employed method to synthesize nanomaterials and to mass-produce CNTs. When employed to synthesize CNTs, CVD has the advantage of requiring a lower temperature (550–1000 °C). Moreover, the method allows the control of the morphology and structure of the nanotubes and the growth of CNTs with the desired alignment [43].

In order to produce CNTs, the CVD method involves employing a carbon-bearing precursor over a substrate in the presence of a catalyst [43]. This catalyst has the function of decomposing and nucleate the carbon source in the form of nanotubes. The most common catalysts are transition metals such as Fe, Ni, and Co. Hydrocarbons such as methane or acetylene are commonly used as carbon sources. As for the substrates, the most common are Ni, SiO<sub>2</sub>, Cu/Ti/Si, glass, and stainless steel [44]. Lately, a particular type of substrate (doped TiO<sub>2</sub>) has been researched, where the doping atoms act as a catalyst for the CNTs [19].

Recently, Guaglianoni et al. [45] investigated the influence of CVD parameters on synthesizing CNTs using cobalt doped TiO<sub>2</sub> nanotubes (Co-TiO<sub>2</sub>) as catalyst. For that, the authors produced Co-TiO<sub>2</sub> nanotubes via a one-step anodization process using titanium foil as substrate. Instead of performing the traditional heat treatment to transform the amorphous titania to anatase, they used the as-synthesized metal oxide as catalyst to produce MWCNTs. They employed hexane as the carbon source and studied the synthesis temperatures of 700 and 800 °C, as well as different synthesis times (10, 20, and 30 min). The Co-TiO<sub>2</sub>/CNT structures were characterized by X-ray diffraction (XRD), Raman spectroscopy, SEM, and TEM. The Raman spectra showed the characteristic modes for CNTs in all synthesized samples. The presence of CNTs on the surface of the TiO<sub>2</sub> nanotubes was also confirmed by SEM (Fig. 6). By comparing the intensity between the D and the G bands ( $I_D/I_G$ ), the authors found out that the CNTs obtained in longer synthesis times are more defective. Linear voltammetry essays showed that the combination of CNTs and Co-TiO<sub>2</sub> developed a photocurrent density 65 times greater than the Co-TiO<sub>2</sub> nanotubes.



**Fig. 6** **a** Lateral, **b** top-view FE-SEM images of connected Co-TiO<sub>2</sub> nanotubes and CNTs obtained by CVD with synthesis temperature of 700 °C

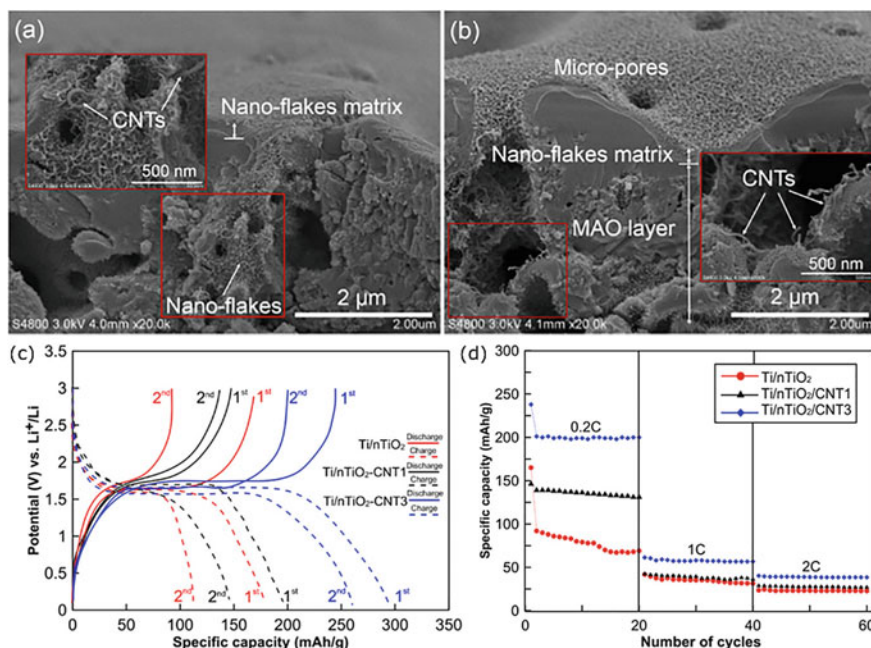
### 3 Applications

#### 3.1 Lithium-Ion Batteries

TiO<sub>2</sub> is a promising material to be employed as anode for lithium-ion batteries (LIBs) because of its stability, non-toxicity, low cost, high theoretical capacity and low volume expansion during the charging/discharging processes (<4%) [34, 46]. However, the electrochemical performance of this semiconductor is hindered by its poor electronic conductivity and low lithium-ion diffusivity [25, 34, 47]. A strategy to surpass these limitations is the formation of composites with carbonaceous materials, such as carbon nanotubes (CNTs).

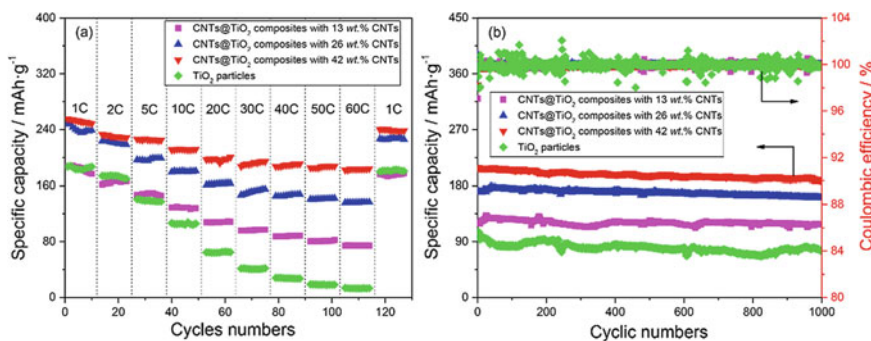
Lo et al. [48] reported the application of TiO<sub>2</sub>-CNT layers deposited on titanium thin plate as anodes for LIBs. The composites (Fig. 7a, b) were obtained using a micro-arc oxidation (MAO) process with different CNT quantities in the electrolyte. The charge–discharge behavior (Fig. 7c) was evaluated between 0.1 and 3.0 V (vs. Li/Li<sup>+</sup>) at a current rate of 0.2 C. The sample without CNTs (Ti/nTiO<sub>2</sub>) presented charge–discharge capacities of 176 and 170 mAh g<sup>-1</sup> in the initial cycle. The formation of the CNT composite greatly increased the charge–discharge capacities. For instance, the capacities were 292/248 mAh g<sup>-1</sup> for the sample with higher CNT content (Ti/nTiO<sub>2</sub>-CNT3). Thus, the presence of CNTs provided electrons to the TiO<sub>2</sub> nanostructure and promoted the Li-ion incorporation. Additionally, the discharge capacity of the Ti/nTiO<sub>2</sub> decreased to 69 mAh g<sup>-1</sup> at the 20th cycle (Fig. 7d), probably due to changes in the anode surface generated by the Li-ion insertion/extraction. On the other hand, the TiO<sub>2</sub>-CNT composites showed high cycle stability and discharge capacities. The discharge capacities of the Ti/nTiO<sub>2</sub>-CNT3 sample at discharge rates of 0.2 C, 1 C, and 2 C were 201, 53 and 38 mAh g<sup>-1</sup>, respectively. The authors attributed the enhancement of electron transport and discharge capacity observed for the composites to the conductive CNT network that supported the TiO<sub>2</sub> nano-flaky structures.

Another interesting TiO<sub>2</sub>/CNT configuration that produced outstanding results for application as anode material for LIBs was obtained by Zhao et al. [34]. TiO<sub>2</sub>



**Fig. 7** FE–SEM cross-sectional images of **a** Ti/nTiO<sub>2</sub>-CNT1 and **b** Ti/nTiO<sub>2</sub>-CNT3 composites. **c** Charge–discharge curves for Ti/nTiO<sub>2</sub>, Ti/nTiO<sub>2</sub>-CNT1, and Ti/nTiO<sub>2</sub>-CNT3 anodes. **d** Cycling performance of Ti/nTiO<sub>2</sub> and Ti/nTiO<sub>2</sub>-CNT composites at discharge rates of 0.2 C, 1 C, and 2 C. Edited and reprinted with permission of Lo et al. [48]

nanoparticles connected to the surface of the CNTs were obtained. The samples had their specific capacities tested at different current densities (Fig. 8a) and their cyclic performances were evaluated at 10C (Fig. 8b). The composites exhibited superior performance than the TiO<sub>2</sub> alone for all current densities tested. The sample with



**Fig. 8 a** Specific capacities at different current densities and **b** cyclic performances of the CNTs@TiO<sub>2</sub> composites. Reprinted with permission of Zhao et al. [34]

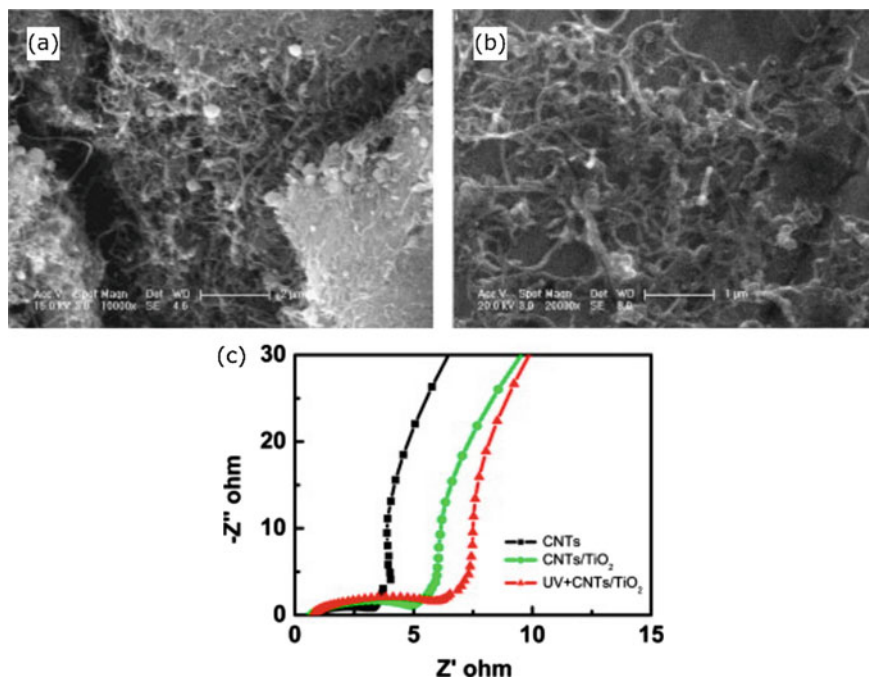
higher CNT content (i.e., 42 wt%) showed an increased specific capacity (approximately  $200 \text{ mAh g}^{-1}$ ), with a discharge capacity almost 2.5 times that of pure  $\text{TiO}_2$  after 1000 cycles (Fig. 8b). These results indicate that the CNTs provided a prompt pathway for the electrons and ions movement throughout the composites.

### 3.2 Supercapacitors

Originated from the patent applied by Becker in 1954 [49], supercapacitors or ultracapacitors are electrochemical energy storage devices that present high power-density in discharge and recharge, basically combining the capabilities of batteries and capacitors [50, 51]. The supercapacitors can be divided into three categories based on their charge storage mechanism: (1) electric double-layer capacitors (EDL); (2) pseudocapacitors; and (3) hybrid capacitors [52].

Due to their high surface area, high chemical stability, and low electric resistance, CNTs are promising materials to be used as an electrode of supercapacitors [53]. To further enhance the CNTs performance for this application, methods such as modifying the nanotubes with transition metal oxides or conductive polymers are often used [54, 55].

Zhang et al. [56] produced a  $\text{CNT/TiO}_2$  composite via hydrothermal method and enhanced its capacitance by pretreating the material with UV light irradiation. To achieve this, the authors placed commercial-grade CNTs, titanium sulfate, and urea in an autoclave and baked it at  $150 \text{ }^\circ\text{C}$  for two hours. The remaining product was centrifuged and later dried. Electrodes were manufactured with the composite to test the electrochemical properties by cyclic voltammetry, chronopotentiometry, and AC impedance method. Finally, the UV light pretreatment was made by placing the  $\text{CNT/TiO}_2$  electrode in a black-box-type analyzer and irradiated it for 1 h under 254 and 365 nm UV light. In addition, pristine CNT electrodes were used for comparison. The SEM analysis (Fig. 9a–b) revealed that the  $\text{TiO}_2$  nanoparticles and dispersed evenly and well-mixed with the CNTs. The AC impedance analysis (Fig. 9c) showed that the  $\text{CNT/TiO}_2$  electrodes pretreated with UV light presented the largest polarization resistance. The authors attributed the results to the oxygen-containing groups on the  $\text{TiO}_2$  surface and its larger Faradic pseudo capacitance from the oxidation–reduction reaction of  $\text{TiO}_2$ . In addition, the calculated impedance derived from the AC impedance method was  $10.7 \text{ F g}^{-1}$  for the UV-irradiated  $\text{CNT/TiO}_2$  electrode and  $4.1 \text{ F g}^{-1}$  for the pristine CNT electrode.

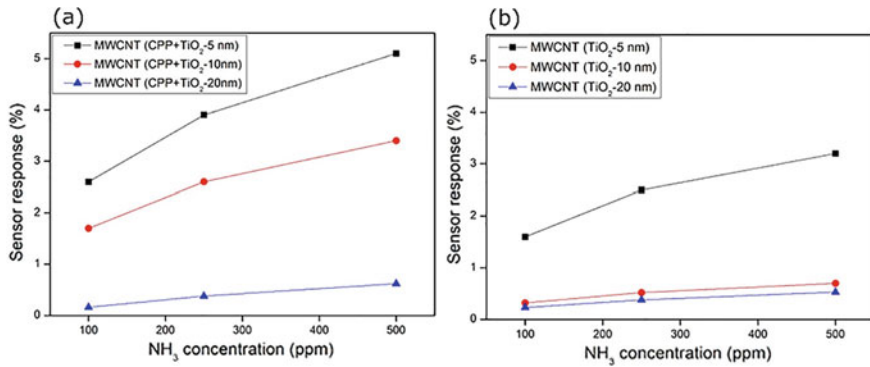


**Fig. 9** a–b SEM images of the CNT/TiO<sub>2</sub> electrodes. c AC impedance analysis performed on the CNT, CNT/TiO<sub>2</sub> and UV-irradiated CNT/TiO<sub>2</sub> electrodes. Reprinted and edited with permission of Zhang et al. [56]

### 3.3 Gas Sensors

TiO<sub>2</sub>/CNT composites have been studied as gas sensors for detection of ammonia, toluene, hydrogen, oxygen, NO, CO, among other gases [35, 57–60]. The TiO<sub>2</sub>/CNT hybrid materials present enhanced sensing performance, when compared to sensors made by the single constituents, due to the formation of p-n junctions, facilitated electron transfer and increased surface area [61, 62].

MWCNT forests coated with TiO<sub>2</sub> films via ALD were employed as ammonia gas sensors [35]. The samples synthesized were exposed to different concentrations (100, 250, and 500 ppm) of ammonia gas, as shown on Fig. 10. The sensors with the thinnest TiO<sub>2</sub> layers, nominal thickness of 5 nm, presented the best response for ammonia detection. TiO<sub>2</sub> layers with greater thicknesses may have reduced the diffusion of charge carriers, which decreased the sensitivity of the sensor. Regarding the type of layer configuration, the sensors formed by TiO<sub>2</sub>-coated MWCNTs with carboxyl PP film had the higher response. According to Kaushik et al. [35], this result can be attributed to the formation of a conduction path for charge carriers that facilitated the charge transfer between the MWCNTs and the TiO<sub>2</sub>. The authors proposed that the improved sensing behavior of the TiO<sub>2</sub>/CNT composites is due to the formation of



**Fig. 10** Sensor response for ammonia detection of the MWCNTs-TiO<sub>2</sub> sensors (a) with and (b) without carboxyl PP layer. Reprinted with permission of Kaushik et al. [35]

two p-n junctions: (1) between the MWCNTs (p-type semiconductor) and the TiO<sub>2</sub> (n-type semiconductor); (2) the TiO<sub>2</sub> surface.

### 3.4 H<sub>2</sub> Production via Water Splitting

Hydrogen (H<sub>2</sub>) is a promising compound used as an energy source in the replacement of petroleum because of its low molecular weight and high-power density. It can be produced by steam reforming of natural gas; however, it can be harnessed more environmentally friendly way. A greener alternative to using fossil fuels is to reduce water to hydrogen using semiconductor and solar energy, but the high charge carrier recombination of these materials is a limiting factor [63]. Fujishima and Honda [6] were the first to publish a report on splitting water using solar radiation. For that, they used an n-type TiO<sub>2</sub> coupled with a Pt counter electrode. The relatively high band-gap of the TiO<sub>2</sub> (3.2 eV) makes only ultraviolet light excite the semiconductor, hindering the TiO<sub>2</sub> application. Thus, solutions to this limitation have been widely researched.

The photocatalytic activity of TiO<sub>2</sub> can be enhanced in numerous ways. One that is commonly researched is the use of dopants, such as metal ions, to decrease the band-gap and better the optical response to sunlight [64, 65]. The most popular dopants are transition metals since their incorporation in the TiO<sub>2</sub> lattice can form a new energy level near the conduction band [66]. The use of CNTs combined with TiO<sub>2</sub> can also increase the photocatalytic activity of the semiconductor. Carbon Nanotubes can promote charge transfer because of their high electrical conductivity and high surface area [67–69].

Recently, Ahmed et al. [70] managed to combine hydrothermal synthesis and CVD to produce a nanoribbon-shaped TiO<sub>2</sub> and CNT hybrid material with a lower band-gap than commercially available TiO<sub>2</sub>. They evaluated the hybrid nanomaterial



using different electrolytes (KOH, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and HCl) and prepared two configurations of electrodes, one using the titania nanoribbons (TNRs) and other using CNT@TNRs. They found a substantial increase in current density voltage from the CNT@TNRs electrode compared with the TNRs electrode under the same configuration. The authors concluded that this was probably because of the decrease of electron–hole recombination on the CNT@TNRs electrode. Moreover, its large surface area, nanoporous structure, and high optical absorption in the visible region made the electrode suitable for H<sub>2</sub> production. However, the downside of their method was that a long time was required to synthesize the TNRs.

Another interesting configuration is the usage of TiO<sub>2</sub> in the form of nanotubes in combination with CNTs. Because of their 1D structure, nanotubes can present enhanced optical and chemical properties when compared to nanoparticles [36]. For example, Guaglianoni et al. [19] produced cobalt doped titania nanotubes via one-step anodization followed by CVD treatment to grow CNTs on its surface. The method allowed the production of connected arrays of titania nanotubes and CNT. When tested, the Co-TiO<sub>2</sub>/CNT nanotubes presented an improved photocurrent performance compared with the cobalt doped titania nanotubes and CNT and TiO<sub>2</sub> nanoparticles composites reported in literature [71].

## 4 Conclusion

TiO<sub>2</sub> is a widely employed semiconductor, but some of its applications are hindered due to its relatively high band-gap and recombination rate. The addition of CNTs to form hybrid nanomaterials with TiO<sub>2</sub> has been extensively studied for various applications, from photocatalysts to supercapacitors. The unique properties and high specific surface area of the carbon nanotubes allow them to overcome these limitations. CNTs can enhance the photocatalytic activity of the TiO<sub>2</sub> by decreasing the recombination rate of electron-hole pairs and contributing to adsorptive active sites. In addition, TiO<sub>2</sub> may improve the capacitance of carbon nanotubes, thus making it a more suitable material to be used as an anode in supercapacitors. Novel CNT/TiO<sub>2</sub> nanostructures have been reported in recent years, and a better understanding of the mechanisms that cause this synergic effect and the development of reliable, low-cost synthesis would make these materials more suitable for energy and eco-friendly applications.

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