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Magnetically guidable single TiO_2 nanotube photocatalyst: structure and photocatalytic properties

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Abstract

The influence of annealing temperature, the crystallinity, textural properties of magnetically guidable anodic TiO_2 nanotubes in form of single tube powders on the photocatalytic decomposition of model organic dye is investigated for the first time. The powders were prepared from self-organized anodic TiO_2 nanotube layers (grown on Ti) by etching in piranha solution, detaching them from the Ti substrate, and annealing in a wide range of temperatures (400 – 900 °C). The nanotubular shape was preserved up to 800 °C. Powders annealed up to 800°C did not contain any detectable rutile phase, which is unique among other TiO_2 nanomaterials at this temperature. Part of the obtained TiO_2 ST-NT powders was decorated with Fe_3O_4 nanoparticles using an oleic acid-based synthesis. The TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders were characterized in terms of morphology, crystallinity, and specific surface area. Finally, all materials were exploited for the photocatalytic decomposition of a model dye. The best photocatalytic performance of TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders were obtained at annealing temperatures of 600 and 700 °C, respectively. The synergy resulting from annealing, crystallite size, and specific surface area enhances the photocatalytic activity of TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders under UV light. This approach goes beyond the classical Kasuga alkaline hydrothermal approach, enabling the preparation of large quantity of TiO_2 nanotubes without any impurities (such as e.g. Na or Ca content resulting from the Kasuga approach).

Keywords: TiO_2 nanotube powders, TiO_2 single nanotubes, Fe_3O_4 nanoparticles, Photocatalysis.

1. Introduction

Within the last two decades, TiO_2 nanotube (TiO_2 NT) layers formed by electrochemical anodization of Ti foil have attracted considerable scientific interest due to their unique combination of morphology, structure, and properties [1]. In addition, their synthesis turned out also to be easier and faster than the TiO_2 hydrothermal route pioneered by Kasuga et al. [2]. By varying mainly the applied potential anodization time, and the concentration of fluoride ions in the electrolyte, the geometry of anodic TiO_2 NT layers can be changed, including the nanotube diameter and thickness [3–5]. TiO_2 NT layers possess a high surface area, catalytically active sites, corrosion resistance, very good light absorption and charge transport, among other features. The combination of these properties allows TiO_2 NT layers to be used in a variety of applications, including photocatalysis [6], chemical compound sensing [7], and medical devices [8–10].

As anodized TiO_2 NT layers possess an amorphous structure [6,11]. To obtain crystalline phases of TiO_2 NT layers and improve their chemical stability, annealing can be performed. As the temperature is raised during the annealing of TiO_2 NT layers, their amorphous phase becomes crystallized into anatase, and the percentage of anatase increases on TiO_2 NT layers with increasing the temperature and time at a particular temperature. With further increased annealing temperatures of more than 500 °C, the transformation of anatase to rutile begins to appear, increasing the number of morphological defects and phase transformations [6,11]. Additionally, the TiO_2 NT layers are gradually densified, and as a result, the surface area is reduced, and gradually the tube structure disappears. The nanotube collapse for TiO_2 NT layers on Ti substrates was reported to occur from an annealing temperature of ~800 °C [12]. However, it has also been demonstrated that a robust free-standing TiO_2 NT membrane with anatase /

rutile mixed crystalline structure preserves its nanotubular integrity even at 850 °C [13,14]. A significant improvement of the thermal stability of TiO_2 NT layers preserving the nanotubular shape up to 850 °C was also achieved by coating the TNT layer with thin Al_2O_3 coating using Atomic Layer Deposition [15].

In general, TiO_2 NT layers can be produced in aqueous and nonaqueous electrolytes with a certain concentration of fluoride ions. However, the TiO_2 NT layers produced in ethylene glycol-based electrolytes present a double-walled structure with an outer wall composed of pure TiO_2 and an inner wall composed of TiO_2 contaminated with carbon and fluoride species [16,17]. The inner wall can be selectively removed by an etching procedure in piranha solution, leaving the single wall TiO_2 NT layers composed of pure TiO_2 [18,19]. According to recent studies, single-walled TiO_2 NT layers are more photo-electrochemically efficient than double-walled nanotubes, due to a selective etching of the inner wall of the TiO_2 NTs removing contaminations [20,21].

As a result of an extensive etching procedure, TiO_2 ST (single tube)-NT powders were synthesized in our previous work [22]. This recently developed material is unique, not only by the synthetic approach used and practically also by ultra-high TiO_2 purity (thanks to impurities being etched away), but because its entire whole surface can be used for photocatalytic applications. This is in strong contrast to classical TiO_2 NT layers, where diffusional and light penetrations limits apply. In addition, this material opens a door for a wide range of application opportunities either alone, or upon further modifications by doping, decoration, and modification with different materials such as superparamagnetic Fe_3O_4 nanoparticles. The pioneering work by Shrestha et al. revealed the potential of TiO_2 nanotubes to be magnetically movable photocatalysts, when loaded

with commercial magnetic nanoparticles [23]. Same materials were used in the pioneering papers on selective enrichment of proteins [24].

Our previous work [22] was the first one to show the decoration of Fe_3O_4 nanoparticles (NPs) on TiO_2 ST-NT powders, achieved through an oleic acid-based synthesis, to facilitate their use as magnetically guided photocatalysts [22]. The method for magnetic particles had to be optimized in that work, as the commercial nanoparticles did not adhere well, and it was not possible to load them homogeneously all over the surface. The oleic acid-based synthesis turned out to be a very good one for this purpose. However, the crystalline structure of the used TiO_2 ST-NT powders was not optimized or investigated anyhow in detail in that study, but it deserves attention, as the annealing process and crystallization transition could be completely different thanks to the absence of underlying Ti substrates. In addition, the different annealing temperatures (and crystallinity) must have an impact on the photocatalytic properties of the material, and this was also not exploited so far neither for pure TiO_2 nanotubes nor for modified ones by magnetic particles.

Therefore, herein we report a complex study aiming on the exploitation of the photocatalytic performance of TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders annealed at different temperatures. The latter ones are very effective magnetically guidable photocatalysts. To obtain this goal, two batches of TiO_2 ST-NT powders were annealed at different temperatures (from 400 to 900 °C) in an oxidative atmosphere. The first batch was photocatalytically tested as such. The second batch was modified with Fe_3O_4 NPs using an oleic acid-based synthesis as previously published [22]. Detailed scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

analysis were used to evaluate the morphology, composition, and decoration of TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders. The resulting crystal structure, specific surface area, and pore size distribution were analyzed through X-ray diffraction (XRD) and N_2 adsorption/desorption isotherms measurements. Finally, the photocatalytic activities were evaluated by the degradation of methylene blue as a model dye.

2. Material and methods

2.1. Synthesis of TiO_2 ST-NT powders

The synthesis is composed of a sequence of steps that are schematically depicted in Fig. 1 along with the materials involved. In particular, the synthesis consists of following steps:

2.1.1. Anodization towards TiO_2 NT layers

For TiO_2 NTs growth, Ti foils with a thickness of 0.127 mm (99.7% purity, Sigma Aldrich) with 1 cm^2 area were used. Before anodization, Ti foils were cleaned in acetone and isopropanol in an ultrasonic bath for 1 min, respectively, and then dried in a N_2 jet. The anodization process was performed at room temperature using a high-voltage potentiostat (PGU-200 V, IPS Elektroniklabor GmbH) at 100 V for 4 h in ethylene glycol-based electrolyte containing 10% water and 0.15 M NH_4F [25]. Afterwards, the samples were soaked in isopropanol, sonicated for 5 min, and dried at room temperature.

2.1.2. Etching of TiO_2 NT layers

As-prepared TiO_2 NT layers were pre-annealed at 135 °C for 1 h in air using a heating rate of 15 °C min^{-1}. Subsequently, the samples were soaked in piranha solution (H_2SO_4:H_2O_2 = 3:1) for 16 min at 70 °C. After etching, the samples were cleaned with distilled water and soaked in isopropanol for 24 h. A longer etching period was used in this work (16 min) compared to previous work (10 min) [22] to ensure the achievement of single nanotubes powders after the next step, which is sonication.

2.1.3. Sonication of TiO_2 NT layers

Firstly, Ti foils were bent to remove the TiO_2 NT layers from the substrate. Subsequently, TiO_2 NT layers were sonicated (FB11203, Fisherbrand) for 5 h at 37 kHz and 100 % power to obtain TiO_2 ST-NT powders. The last step to separate the TiO_2 ST-NT powders from the isopropanol was ultra-centrifugation (Optima MAX-XP, Beckman Coulter) at 25000 g force for 10 min at 25 °C using a fixed angle rotor MLA-50.

2.1.4. Annealing

The TiO_2 ST-NT powders were annealed at 400 – 900 °C for 1 h in static atmosphere of air in a laboratory muffle oven, the heating rate to reach each particular temperature was 2.1 °C min^{-1}.

2.2. Preparation of Fe_3O_4 NPs

The preparation of Fe (III) oleate was carried out according to the procedure proposed in our previous work [22]. The reagents $FeCl_3 \cdot 6H_2O$ (≥99%), oleic acid and 1-octadecene (both technical grade, 90%), methanol and heptane (both for HLPC ≥99%) were delivered from Sigma Aldrich. NaOH (98 %) was received from Lach-Ner, s.r.o.

The obtained solution of Fe (III) oleate in 1-octadecene was used as the precursor for magnetite nanoparticles (Fe_3O_4 NPs). The synthesis of Fe_3O_4 NPs was carried out similarly as in [22,26]. 0.4 ml of the prepared Fe (III) oleate solution was stirred with 20 ml of 1-octadecene (400 rpm) and then ultrasonicated (37 kHz; 100% power) at 65 ℃ for 10 min to obtain a homogeneous solution. Oleic acid of 0.08 ml was added to the latter and treated with stirring and ultrasonication in the same manner. The orange-brown muddy solution was purged with gaseous nitrogen for 30 min to displace air to avoid oxidation of reagents. The final solution was introduced in 30 mL glass vial sealed with a snap cap comprising silicone septum. The filled vial was enclosed into a synthesis reactor (Monowave-400, Anton-Paar). The reactor was heated to the temperature of 240 °C for 45 min with dwelling time of next 45 min under magnetic stirring rate of 600 rpm. The obtained light brown solution was considered as a micellar solution of Fe_3O_4 NPs.

2.3. Decoration of TiO_2 ST-NTs@Fe_3O_4NPs

Since TiO_2 NTs is a strong oxidizer that can react with reagents used during the Fe_3O_4 NPs preparation or even convert the final product of Fe_3O_4 to Fe_2O_3 at elevated temperatures, decoration process for TiO_2 NTs was carried out separately. Decoration of TiO_2 NTs with the previously prepared Fe_3O_4 NPs was carried out at room temperature. That is different compared to the one-step decoration process used previously in [22], where decoration process was done directly during Fe_3O_4 NPs preparation at 240 °C. The prepared solution of Fe_3O_4 NPs (5 ml) was ultrasonicated with heptane (5 ml) in a 12 ml plastic tube to obtain the dispersion of Fe_3O_4 NPs. 3 mg of TiO_2 ST-NT powder annealed at different temperatures (400 up to 700 °C) were added to the dispersion and

again stirred and ultrasonicated to get a homogeneous mixture between TiO_2 ST-NT and Fe_3O_4 NPs. Subsequent centrifugation at 5000 rpm for 20 min resulted in a good separation of solid and liquid. The heptane washing procedure was repeated 3 times to dissolve the rest of oleic acid and 1-octadecene and resulted in a light brown magnetic powder that was finally washed with isopropanol to remove residual inorganic chemicals ($FeCl_3$, NaOH, and H_2O) using the same ultrasonication and centrifugation procedures. The TiO_2 ST-NT powder decorated with Fe_3O_4 NPs was dried at 100 °C overnight to completely remove isopropanol.

2.4. Characterization

A field-emission scanning electron microscope (FE-SEM, JEOL JSM7500F) was used for morphological characterization of all the samples. The quantitative EDX measurements were performed using a scanning electron microscope (LYRA3, Tescan) equipped with EDX analyzer AZtec X-Max 20 (Oxford Instruments) at an acceleration voltage of 20 kV. TEM analyses of TiO_2 ST-NT powders and TiO_2 ST-NT@Fe_3O_4NPs were carried out using a Titan Themis 60 – 300 (Thermo Fisher Scientific) instrument operated at 300 kV and equipped with a monochromator, a spherical aberration corrector of objective lens for TEM imaging, a high-angle annular dark-field (HAADF) detector for scanning TEM (STEM) imaging and Super-X detector for STEM energy dispersive X-ray (EDX) spectroscopy. The crystallography of single TiO_2 nanotubes was analyzed by TEM selection area electron diffraction (SAED) and the crystallography of Fe_3O_4 NPs was analyzed by high-resolution TEM (HR-TEM) and Fast Fourier Transformation (FFT).

X-ray diffraction patterns were measured on Panalytical Empyrean in Bragg-Brentano geometry, equipped with Cu Kα radiation. The measurement range was 5 ° up to 65 °. The crystalline structure and evaluation of anatase peaks were identified by HighScore software with ICDD PDF4 database.

The specific surface area and pore size distribution of TiO_2 ST-NT powders at different annealing temperatures (from 400 up to 700 °C) were calculated from N_2 adsorption-desorption isotherms by MicroActive software (Micromeritics). Using an ASAP 2020 instrument (Micromeritics), the isotherms were acquired. The TiO_2 ST-NT powders were degassed before adsorption measurement at 200 °C under dynamic vacuum to allow a quantitative removal of the pre-adsorbed H_2O. Beginning at room temperature, the powders were degassed at 110 °C (heating rate 0.5 °C min^{-1}) until the residual pressure of 1 Pa was attained. After further soaking at 110 °C for 1 h, the temperature was increased (1 °C min^{-1}) to 200 °C. The TiO_2 ST-NT powders were degassed at this temperature under a turbomolecular pump vacuum for 8 h. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area [27]. Mesopore and external surface areas were calculated by t-plot using the Harkins-Jura equation. The BJB methodology employing Harkins-Jura equation determined the pore volume and pore size distribution.

The photocatalytic activities of all powders (i.e. TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders annealed at different temperatures) were evaluated by using the photocatalytic degradation of methylene blue solution (MB; initial concentration = 1×10^{-5} M). To achieve the dye adsorption/desorption equilibrium, 2 mg of all the powders were soaked in the MB solution (3.5 ml) in the dark for 1 h under constant

stirring of 600 rpm. After the equilibrium was reached, all powders were irradiated with a LED-based UV lamp (10 W, λ= 365 nm) and the absorbance of the MB solution was periodically measured (5 or 10-min steps) using a visible light spectrophotometer (S-200, Boeco) at a wavelength of 670 nm to monitor degradation rates. To separate TiO_2 ST-NT powders from the MB solution, a high-speed centrifuge (Fisherbrand, HSE09225) at 12000 rpm for 1.5 min at 25 °C was used before absorbance measurements. A magnetic force in combination with a high-speed centrifuge was used to separate the TiO_2 ST-NT from MB solution, 2 min and 1 min at 12000 rpm at 25 °C, respectively. A pyranometer (SUSS MicroTec, MvL-D-0113-3) was used for measurement of the power density (P) of the incident light. The influence of the scavengers on the photodegradation of MB was investigated adding 10^{-2} M CH_3OH (Lach-Ner, s.r.o) to the MB solution.

3. Results and discussion

3.1. Characterization

Fig. 2 shows SEM and TEM images of TiO_2 ST-NT powders annealed at 400, 500, 600, and 700 °C. As one can see from these images, the nanotube walls are preserved at all these temperatures without any collapse. The TiO_2 ST-NT powders annealed at 400 °C (Fig. 2a) exhibit rippled surfaces. At 500 and 600 °C, distinct grain boundaries begin to appear on the TiO_2 NT surfaces (Fig. 2b and c). As a result of crystallization at 700 °C, the TiO_2 NT surface becomes deformed, and the ripples disappear from the surface (Fig. 2d). Additional SEM images of the TiO_2 ST-NT powders annealed at 800 and 900 °C are shown in **Fig. S1**. At 800 °C the surface of the nanotubes shows distorted shapes

with large crystal boundaries, whereas at 900 °C the nanotubes are completely collapsed and lose their nanotubular shape. Insets in Fig. 2 show SAED patterns from the corresponding TEM images. All SAED patterns reveal the polycrystalline structure of the nanotubes annealed at different temperatures. In particular, by detailed inspection of numerous spots on the nanotube bodies and analyses of resulting SAED diffraction patterns, it was found out, that the nanotubes consist solely of anatase phase. No detectable traces of rutile or brookite or even an amorphous phase were revealed.

To further investigate the structure of TiO_2 ST-NT powders annealed at different temperatures, XRD analyses were carried out as shown in **Fig. 3**. All diffractograms revealed anatase phase (ICSD: 154603). The average crystallite size was calculated by the Scherrer equation [28] for (101) crystal orientation and the values are in **Table 1**. As shown in **Fig. S2**, for an annealing temperature of 800 °C still only anatase phase was revealed, which is unique among any known TiO_2 nanomaterials. However, at an annealing temperature of 900 °C rutile and anatase phases were found in TiO_2 ST-NT powders. This is very surprising and clearly shows that TiO_2 ST-NT powders detached from the Ti substrate undergo a different crystallization pathway (i.e. with pure anatase phase obtained at even very high temperatures) than TiO_2 NT layers attached to Ti substrates, where rutile is usually observed at 500°C [11,29]. The driving factor seems to be the absence of the Ti substrates. For TiO_2 NT layers attached to the Ti substrate, the annealing leads to the formation of thin rutile thermal oxide layer at the metal/oxide interface starting at 350 °C. And from this interface, the rutile phase starts to appear in the XRD patters of the crystalline structure of the TiO_2 NTs, apart of anatase that is formed within TiO_2 tube walls. By increasing the temperature, the fraction of rutile increases on behalf of anatase.

In TiO_2 ST-NT powders, the situation is quite different. The Ti substrate is not present during the annealing (because it is disconnected by etching from NT layers). Therefore, the rutile nucleation is prevented at temperatures, where one would expect it. During the annealing of TiO_2 ST-NT powders, the crystallization proceeds predominantly to the anatase phase (in the range from 400 to 800 °C) and only at temperatures above, the rutile starts to form. Most likely, this is because it is thermodynamically not so favourable (or not as easy) to nucleate rutile crystals in the already readily crystalline network of anatase crystals in the nanotube walls.

The N_2 adsorption-desorption isotherms of TiO_2 ST-NT powders annealed at different temperatures are depicted in **Fig. S3**. The corresponding textural parameters and specific surface areas obtained from N_2 isotherms by Brunauer-Emmett-Teller (BET) method are summarized in Table 1. The BET data are in good accord with the morphological differences seen by SEM (Fig. 2) and in XRD (Fig. 3). More specifically, the specific surface area, pore volume and the overall roughness apparent from SEM images decrease with the increase of the annealing temperature, while the crystallite size increases. The highest specific surface area (SBET) was achieved for TiO_2 ST-NT powders annealed at 400 °C (SBET = 36.9 m^2/g) which is ~2 times higher than the one of the TiO_2 ST-NT powders annealed at 700 °C (SBET = 18 m^2/g). The pore volume values for TiO_2 ST-NT powders annealed at 400, 500, and 600 °C were almost constant, while for the TiO_2 ST-NT powders annealed at 700 °C a strong decrease was observed. It is worth mentioning that the isotherm-derived pore information relates to the mesopores in the tube walls and not to the NT diameter. The pore diameters of TiO_2 ST-NT powders annealed at 400, 500, and 600 °C were in the mesopore range (5-20 nm). However, for TiO_2 ST-NT powders annealed at 700 °C, the

curve does not provide any clear pattern of specific porosity (Fig. S3b), which means that the wall of the tubular structure begins to densify reducing the specific surface area.

The SEM images of TiO_2 ST-NT@Fe_3O_4NPs powders annealed at 400, 500, 600, and 700 °C are shown in **Fig. 4**. Since the annealing was carried out in the same way as for the blank TiO_2 ST-NT powders, one can observe the same morphological trends as on blank TiO_2 ST-NT powders (i.e. the emergence of grain boundaries). More importantly, one can see from the SEM images of all TiO_2 ST-NT@Fe_3O_4NPs powders, that Fe_3O_4 NPs are homogeneously distributed on the TiO_2 ST-NT surface. Illustrative HR-TEM images of TiO_2 ST-NT@Fe_3O_4NPs annealed at different temperatures are also depicted in Fig. 4. The HR-TEM images in Fig. 4 show examples of Fe_3O_4 NPs attached to the surface of a nanotube and the insets are FFT patterns corresponding to the white dashed rectangles showing the crystallinity of the Fe_3O_4 NPs. The STEM-EDX elemental mapping provided confirmation of uniform and homogeneous distribution of Ti and O elements and also of Fe_3O_4 NPs all along TiO_2 ST-NT@Fe_3O_4NPs (**Fig. S4**). Quantitatively, EDX measurements of bulk powders (using EDX detector within SEM) revealed that the content of Fe on the TiO_2 ST-NT@Fe_3O_4NPs powders annealed at different temperatures is between 2 – 3 atomic %.

3.2. Photocatalytic characterization

The photocatalytic activities of TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders were explored by the photodegradation of MB as an organic model dye under UV light (λ= 365 nm). The photodegradation kinetic curves of all powders are depicted in **Fig. 5**. The linear relation between ln C/C_o and irradiation times implies the first-order kinetics of the MB photodegradation [6]. As one can see in **Table 2** the highest

photodegradation rate was obtained for TiO_2 ST-NT powders annealed at 600 °C (k = 0.248 min^{-1}) and the lowest rate was achieved at 400 °C (k = 0.054 min^{-1}). Even though the highest specific surface area (S_{BET}) was achieved at 400 °C (36.9 m^2/g), the value of photodegradation rate was the lowest from all samples investigated. This can be related to the fact that TiO_2 ST-NT powders annealed at 400 °C have a small crystallite size which can affect the photocatalytic behavior by limiting the active area exposed to UV light. According to previous works [6,30–33], the crystallite size and the crystalline phase are important factors that influence photocatalytic activity of nanotubes. But the same applies also for other, non-nanotubular morphologies of TiO_2 [34,35].

In general, the transformation of TiO_2 from amorphous to anatase phase within anodic nanotubes takes place at around 280 °C [36]. Complete crystallization is usually guaranteed after annealing at 400 °C, at which all the TiO_2 material crystallizes into anatase phase as shown by XRD in Fig. 3. The TiO_2 ST-NT powders annealed at 600 °C show the best photocatalytic performance (k = 0.248 min^{-1}) although their specific surface area is slightly smaller compared to the one achieved upon annealing at 400 °C (Table 1) TiO_2 ST-NT powders annealed at 600 °C have crystallite size sufficiently large, providing the best photocatalytic rate despite the decrease in specific surface area after annealing. With a further increase of the annealing temperature to 700 °C, the specific surface area (S_{BET} = 18 m^2/g) was significantly decreased. However, the crystallite size (817 Å) was 1.5 times increased compared to that at 600 °C (534 Å) resulting in a decrease of the photocatalytic activity at this temperature as is shown in Table 1. Overall, the results indicate that photocatalytic activity is influenced not only by the crystalline phase but also by crystallite size and specific surface area. Clearly,

there must be a synergy between crystallite size and specific surface area, which becomes evident for TiO_2 ST-NT powders annealed at different temperatures.

Additional photocatalytic experiments were carried out also with TiO_2 ST-NT powders annealed at 800 and 900 °C and the photodegradation rate were 0.009 and 0.008 min^{-1} respectively (**Fig. S5**). Annealing at higher temperatures than 700 °C diminishes the photocatalytic properties. To determine the influence of the NT mass on the photocatalytic rate constants, TiO_2 ST-NT powder annealed at 600 °C, was subjected to a set of photocatalytic experiments with different weights (1, 2, 4, 8 mg) as shown in **Fig. S6**. For 1 mg the photocatalytic activity was 0.23 min^{-1}. For 2 mg the photocatalytic performance increased (0.25 min^{-1}). Nevertheless, for higher TiO_2 ST-NT powder amounts than 2 mg, the performance decreased (0.12 and 0.09 min^{-1} for 4 and 8 mg, respectively). Therefore, the best photocatalytic performance for the particular photocatalytic setup used was achieved for 2 mg of TiO_2 ST-NT powder. Although the weight increases, the photoactivity rates decrease, since the TiO_2 ST-NT are shading each other from irradiation with UV light.

In the case of TiO_2 ST-NT@Fe_3O_4NPs depicted in Fig. 5b, the highest photodegradation rate was obtained for TiO_2 ST-NT powders annealed at 700 °C (k = 0.110 min^{-1}). The value is ~2 times smaller compared to best archived for TiO_2 ST-NT powders (k = 0.248 min^{-1}, 600 °C). In this case, the presence of Fe_3O_4 NPs on the TiO_2 NT surface caused shading effect of the incident UV light [22,37,38], thus reducing the overall photoactive area for TiO_2.

The photocatalytic rate constant achieved after annealing at 400 °C for TiO_2 ST-NT powders was k = 0.054 min^{-1} which is ~5 times higher than the one obtained in our

former work (k= 0.74 h^{-1}, ~0.012 min^{-1}) [22]. In our case, the etching time was extended allowing an enhanced separation of the nanotubes which increased the active area exposed to the MB.

3.3. Apparent quantum yield calculations

The apparent quantum yield (Φ_{app}) was calculated from the photocatalytic degradation of MB for the TiO_2 ST-NT powders annealed at different temperatures with an incident monochromatic wavelength of 365 nm for 10 min. The Φ_{app} is defined by the following Eq. [39].

$$\Phi_{\text{app}}(\%) = \frac{\text{2 x Number of MB molecules degraded in 10 min}}{\text{Number of incident photons}} \times 100\% \quad (1)$$

The number of MB molecules degraded within 10 min (measuring interval during photocatalytic measurements) and the number of incident photos was calculated by using the following equations:

$$Number\ of\ MB\ molecules\ degraded = n_{MB} \times N_A \quad (2)$$

$$Number\ of\ incident\ photons = \frac{E_{total}}{E_{photon}} = \frac{PS\lambda_{in}t}{hc} \quad (3)$$

The Φ_{app} of each TiO_2 ST-NT powder annealed at different temperatures was calculated by inserting Eq. (2) and (3) into Eq. (1):

$$\Phi_{app}\ (\%) = \frac{2n_{MB}N_A hc}{PS\lambda_{in}t} \times 100\% \quad (4)$$

Where, n_{MB} (mol) is the amount of MB degraded over the duration t (10 min) of the incident light exposure, N_A (mol^{-1}) is Avogadro's constant, h is the Planck's constant and c is the speed of light, S is the irradiation area (0.00040 m^2), λ_{in} is the wavelength of

the incident monochromatic light ($3.65x10^{-7}$ m), and *P* is the power density of the incident light (260.4 W m^{-2}) reaching the photocatalyst.

The Φ_{app} values calculated for TiO_2 ST-NT powders annealed at different temperatures are outlined in **Table 3**. During the photocatalytic decomposition of MB, most of the photons in the region at 365 nm are absorbed by TiO_2 due to the large absorption coefficient. However, the values of Φ_{app} are relatively low compared to the literature [40,41]. The same literature explains that the value of Φ_{app} is low when MB is chosen as a pollutant. Due to the radical chain mechanism involved in photocatalytic degradation of MB, it is assumed that during the photocatalytic reaction one photon corresponds to one molecule of MB decomposed, therefore, in the calculation of Φ_{app} the radical chain reaction is not considered [40,41].

3.4. Effect of scavengers

During the photocatalysis process, electron (e−) and hole (h+) pairs are generated and migrate to the surface reacting with water, oxygen, and other molecules at the interface. The effect of scavenger on the photocatalytic degradation of MB dye solution with TiO_2 ST-NT powders annealed at different temperatures was investigated to find out which reactive oxidative species are involved in the surface reaction mechanism. As shown in **Fig. 6**a, the hydroxyl radical ·OH scavenger, methanol (CH_3OH,10^{-2} M) was used for the detection of the involvement of ·OH in the photocatalytic reaction [42–44]. The photodegradation rates were increased in presence of CH_3OH as disclosed in Fig. 6b, in presence of CH_3OH which confirmed the absence of ·OH in the photocatalytic degradation of MB. The enhancement of the kinetic process in presence of CH_3OH could be explained by the formation of the $\cdot O^{2-}$ superoxide radical which further

triggers a chain decomposition reaction that mineralizes and photodegrades the MB more effectively. Hence, the reaction was preceded by the involvement of $\cdot O_2^-$ alone.

4. Conclusions

In summary, the annealing temperature, crystallite size and specific surface area of TiO_2 ST-NT powders and magnetically guidable TiO_2 ST-NT powders annealed at different temperatures play an important role in their photocatalytic performance. The present findings showed that the best agreement between these two parameters was achieved by annealing the powders at 600 °C. XRD patterns of TiO_2 ST-NT powders showed anatase phase even at 800 °C which confirms that nanotubes detached from the Ti substrate crystallize completely differently compared to TiO_2 NT layers attached to a Ti substrate, where rutile is usually observed at ~500 °C. The fact that the TiO_2 ST-NT powders preserved their tubular shape even at 800 °C was also remarkable. The best photodegradation rate of TiO_2 ST-NT@Fe_3O_4NPs was achieved at 700 °C. Nevertheless, the photoactivities constants are significantly lower from their non-decorated counterparts, due to the shading effect of Fe_3O_4 NPs on the incident UV illumination.

Declaration of competing interest

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

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Appendix

Supporting Information.

SEM images, XRD patterns, N_2 adsorption-desorption isotherms, HRTEM-STEM-EDX elemental maps of TiO_2 ST-NT powders annealed at different temperatures, and dependency of the TiO_2 ST-NT powder weight on the photoactivity rate constants archived for TiO_2 ST-NT powders annealed at 600 °C.

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Figure captions

Fig. 1. Scheme of synthetic steps and materials involved in the preparation of TiO_2 ST-NT powders and TiO_2 ST-NT@Fe_3O_4NPs powders.

Fig. 2. SEM (scale bar: 100 nm) and TEM (scale bar: 50 nm) images of TiO_2 ST-NT powders annealed at a) 400 °C, b) 500 °C, c) 600 °C, and d) 700 °C. Insets show SAED patterns taken from the single tubes.

Fig. 3. XRD patterns of TiO_2 ST-NT powders annealed at 400, 500, 600, and 700 °C.

Fig. 4. SEM (scale bar: 100 nm) and HR-TEM (scale bar: 50 nm) images of TiO_2 ST-NT@Fe_3O_4NPs powders annealed at a) 400 °C, b) 500 °C, c) 600 °C, and d) 700 °C. Insets show FFT patterns obtained for the corresponding Fe_3O_2 NPs denoted in a white dash square.

Fig. 5. Photocatalytic decomposition rates of MB for a) TiO_2 ST-NT and b) TiO_2 ST-NT@Fe_3O_4 powders annealed at different temperatures.

Fig. 6. Effect of CH_3OH as a hole scavenger on the photocatalytic degradation of MB for TiO_2 ST-NT powders annealed at different temperatures: a) kinetics of MB degradation with CH_3OH, b) rates constants (k) for reactions with and without CH_3OH.

Tables

Table 1. Crystallite size calculated by Scherrer equation and, N_2 physisorption measurements of the specific surface area (S_{BET}) calculated by BET method, pore volume (V_p), and pore diameter (D_p) calculated by BJH method of TiO_2 ST-NT powders annealed at different temperatures.

				BJH
Sample	Crystallite size (Å)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)
TiO_2ST-NT 400°C	343	37	0.053	5
TiO_2ST-NT 500°C	435	30	0.051	8
TiO_2ST-NT 600°C	534	26	0.049	11
TiO_2ST-NT 700°C	817	18	0.028	-

Table 2. Photocatalytic rates constants (k) of MB degradation for TiO_2 ST-NT and TiO_2 ST-NT@Fe_3O_4NPs powders annealed at different temperatures under UV illumination (λ= 350 nm). The rate constants were calculated by linear fitting of the curves depicted in Fig. 5.

Annealing temperature (°C)	k (min^{-1}) TiO_2 ST-NT	k (min^{-1}) TiO_2 ST-NT@Fe_3O_4NPs
400	0.054	0.020
500	0.062	0.022
600	0.248	0.077
700	0.187	0.110

Table 3. Apparent quantum yield (Φ_{app}) calculated for the photocatalytic degradation of MB with TiO_2 ST-NT annealed at different temperatures.

Annealing temperature (°C)	Φ_{app} (%) TiO_2 ST-NT
400	17.4×10^{-3}
500	17.2×10^{-3}
600	3.26×10^{-3}
700	5.97×10^{-3}