Morpho-stuctural and photocatalytic properties of TiO_2 -C composite materials

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Doctoral (Ph.D.) theses

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1. Introduction

Nowadays the most challenging task for the researchers is to develop efficient alternatives for the degradation of dangerous environmental pollutants. One of the most promising methods are the AOPs (advanced oxidation processes), which can be applied to degrade dangerous organic compounds by generating highly reactive radicals. The heterogeneous photocatalysis is one of the AOPs which is in the spotlight of current science. This process is based on semiconductor materials, called also as photocatalysts. When these materials absorb a photon equal or greater than its band-gap energy, then charge carriers are generated, which can yield highly oxidative radicals applicable in the degradation of hazardous chemicals.

In the last decades one of the widely investigated semiconductor material was titanium-dioxide [1], which was proven to be efficient for water and air purification and also to inactivate bacteria. Although, there are some major draw-backs of this material, including limited excitation by UV-A or irradiations with greater energy and the fast electron-hole recombination. The lifetime of the charge carriers can be prolonged by contacting TiO_2 with other semiconductors or conductor materials in order to transfer the electrons from the host nanocrystal [2] or create shape-tailored crystals with crystallographic planes favoring the spatial separation of the charge carriers. The **c**arbon **n**ano**t**ube (CNT), which is a remarkable material in this period may solve this problem. It may improve the photocatalytic' feature of the TiO_2 when used as composite (TiO_2-CNT) material. It can be combined with other carbon types e.g. active carbon, graphite and carbon aerogel as well [3].

By tuning the ratio of the active crystal facets might enhance the efficiency of the TiO_2 photocatalyst [4]. It is possible to control the shape of the crystal by capping agents, which adsorb specifically to given facets, thus stabilizing that crystallographic plane during the crystal growth process [5]. A promising shape-tailoring possibility is using HF as the capping agent [6].

Recently, another material with unique mechanical and electrical properties emerged with high stability: multiwall carbon nanotubes (MWCNT). Applying this material in composites: combined with TiO_2 offers a composite material (TiO_2-CNT) with enhanced photocatalytic efficiency, due to their synergetic effect, namely reducing the e^-/h^+ recombination rate. This suggests that it is possible to combine TiO_2 with other types of carbon e.g. active carbon, graphite and carbon aerogel, these are named to TiO_2-C hybrid materials [7].

The specific ratio of the different facets might promote the spatial separation of the charge carriers. In the case of TiO_2 the {001} facets can be oxidative (favoring the accumulation of holes), while the {100} and {101} planes can be reductive (accumulating electrons) [8-9].

2. Objectives of the present Ph. D. thesis

1., The synthesis of TiO_2-CNT composites by physical mixing (ultrasonication) considering the following aspects:

  a., the impact of the carbon nanotube content,
  b., the type and quality of the carbon nanotubes and TiO_2
  c., the effect of the ultrasonication conditions.

2., The investigation of TiO_2-CNT composites obtained via hydrothermal crystallization, using the CNTs as a crystallization promoter. The following research goals were followed:

  a., the impact of the hydrothermal treatment time on the morphology and photoactivity of TiO_2,
  b., the role of the HF as capping agent in the crystallization process, and
  c., the effect of the calcination on the TiO_2-CNT composites.

3., The morphological control of TiO_2 in case the hydrothermal crystallization using different non carbon shaping agents.

4., The impact of different carbon types (carbon aerogel, graphite, active carbon) on the morphology of TiO_2 crystals.

3. Methods and instrumentation

The composites were heat treated in a *Thermolyne 21100* tubular furnace (the total length was 38 cm, the interior diameter: 5.5 cm, the quartz tube: 64 cm, the inner diameter was 4 cm).

The X-ray diffraction (XRD) patterns were recorded on a „*Rigaku Miniflex II*” diffractometer in the $20° \leq 2\ \Theta° \leq 40°$ region ($\lambda_{Cu\ K\alpha}$ = 0.15406 nm, 30 kV, and 15 mA).

The diffuse reflectance spectra (DRS) of the samples were recorded with a *Jasco-V650* diode array spectrophotometer equipped with an *ILV-724* integration sphere. The band-gap values were estimated based on the Kubelka Munk theory [9].

Raman measurements were executed in a *Bruker Equinox 55 spectrometer* equipped with an *FRA 106 Raman* module, and *Nd-YAG* laser (1064 nm). The Raman spectra were recorded with a spectral resolution of 1 cm^{-1}.

Thermoanalytical measurements (TG-DTA) were carried out in a *SETARAM LABSYS 1600* instrument, the heating rate was 5 °C·min^{-1}. The applied reference material was MgO.

The morphological characteristics of the composites were investigated using *Hitachi S-4700 Type II* scanning electron microscope (25 kV). Part of the obtained materials' morphological features were studied using a *Phillips CM 10* type transmission electron microscope (TEM), operating at 100 kV and *FEI Technai G2 20 X-TWIN* instrument (200 kV). The HRTEM measurements were performed on a *JEM ARM 200F TEM* while acquiring electron diffraction patterns (300 kV).

To investigate the surface' characteristics of the catalysts we applied XPS, which was performed on a *Specs Phoibos 150 MCD* 9 spectroscope, with monochromatized Al Kα radiation ($h \cdot v$ = 1253.6 eV; 14 kV and 20 mA).

To evaluate the composites' photocatalytic performance we used a „fast activity evaluation", where the model pollutant (c_{phenol}=0.5 mM, $c_{rhodaminB}$= 0.01 mM) was degraded using $c_{composite}$= 1 g·L^{-1} and 3×LighTech 40 W fluorescent lamps ($\lambda_{max} \approx 365$ nm). The main photocatalytic investigations were carried out in a Pyrex glass reactor (T=25.0 ± 0.5 °C), where the applied fluorescent lamps were *Vilber-Lourmat T-6L UV-A"* type (6W, λ_{max} = 365 nm).

An *Agilent 1100* HPLC equipped with a UV-Vis detector was used for the analytic measurement of phenol degradation. The filtered samples were injected manually to a *Licrospher RP-18* column.

UV-Vis spectroscopy was applied to follow the degradation of dyes. We used an *Agilent 8453* diode array spectrophotometer.

4. Thesis

T 1. Considering the nature of the TiO_2 and the carbon nanotube, the composite containing Aldrich anatase was found to be more efficient than the bare TiO_2 among the TiO_2-CNT composites produced by the ultrasonication method (UHI.). Furthermore, it was found that the single walled carbon nanotubes were more active composite components than the multi walled carbon nanotubes.

In the first step the influence of the different TiO_2 were investigated in TiO_2-carbon nanotube composites which were made by ultrasonication (UHI.). All of the composites were less efficient, than their base photocatalyst, except with the one based on AA. A possible reason could be, that the semiconductor crystals are large (d > 85 nm; a^S_{BET}=9.9 m^2·g^{-1}) with small specific surface area has a better contact with the FSWCNT (Figure 1.). (at*: Phys. Status Solidi B 248, No. 11 (2011) 2496–2499*)

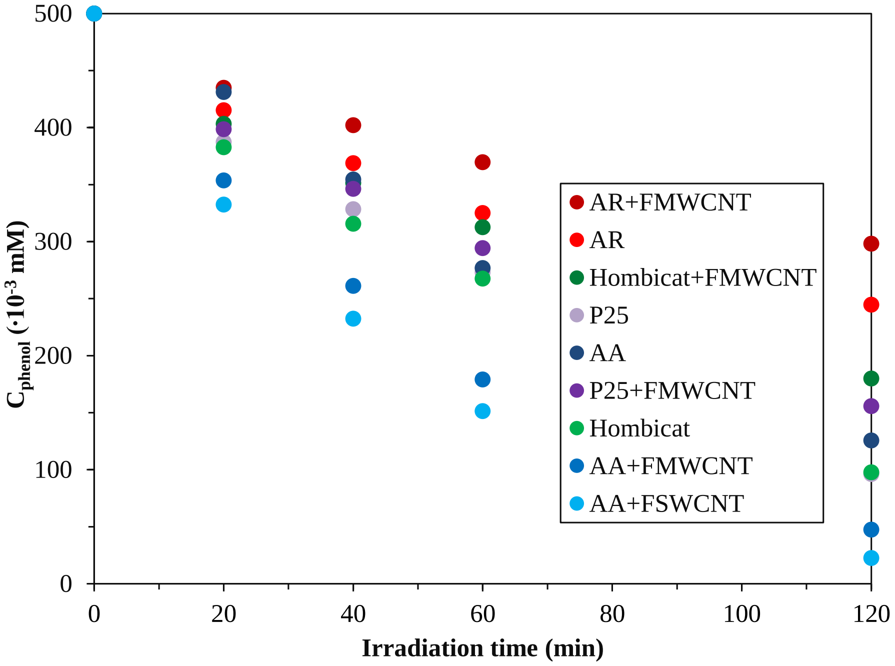

Figure 1. The photocatalytic efficiency of different TiO_2 -CNT composites in the UV light driven phenol degradation

T2. The 1% FSWCNT content was the optimum value to achieve high photocatalytic activity.

We studied the influence of the carbon nanotube content and the (commercial) TiO_2's type. Different TiO_2-CNT composites were obtained with different CNT content (0.1-10 %) and tested in the photodegradation of phenol. Based on the experimental results, the most efficient composite was the one obtained from Aldrich anatase and 1 % FMWCNT (Figure 2.). However, the application of the composites with 0.1 % CNT content is more economic, because the efficiency is similar to the performance of the nanocomposites with 1 % FSWCNT and the price of the single walled nanotube is more expensive. (1 g SWCNT ≈ 287 700 Ft, 2g MWCNT ≈ 30 600 Ft).

(at: *Phys. Status Solidi B 248, No. 11 (2011) 2496–2499*)

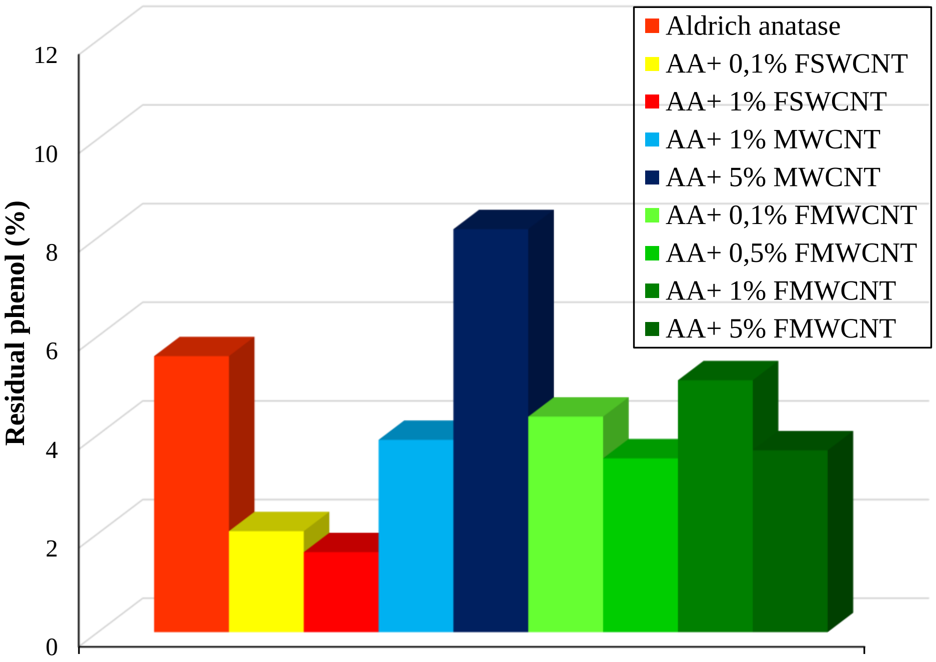

Figure 2. Photocatalytic efficiency carbon nanotube - AA composites during phenol degradation

T3. The duration of the hydrothermal crystallization has a major impact on the obtained crystals' morphology.

We aimed different crystallization times (1, 5 and 24 h) in order to study the crystallization process. After 1 hour, monodisperse plate-like crystals were formed. The edges of the crystals were undeveloped (no clear facet boundaries were formed), only the {001} facets were clearly observable. The crystallographic plane boundaries appeared after 5 h of hydrothermal treatment, meaning that the other facets (e.g. {101}) were formed as well. However, the nanoplates were incomplete. In the case of 24 hours of hydrothermal treatment, whole plates, with well-defined morphology were obtained, but the size of the crystals varied within a broad range (100 nm - 1.5 µm Figure 3.), moreover some twin crystals were also observed. In all the cases the XRD patterns indicated anatase as the only crystal phase (at: *Nanoscale 7 (2015) 5776-5786*).

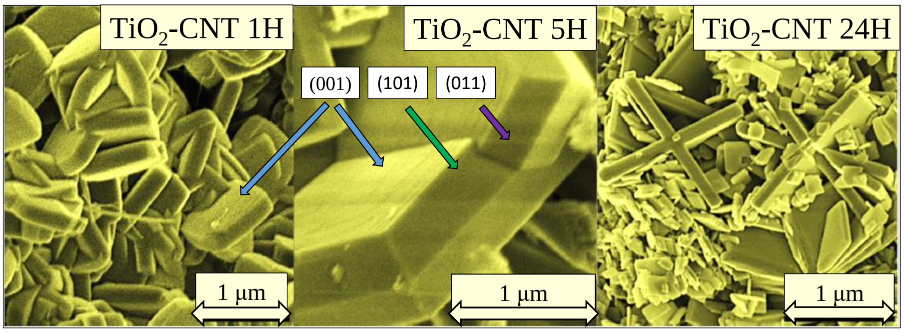

Figure 3. SEM micrographs of the TiO_2 obtained at different crystallization times in the presence of carbon nanotubes

T.4. During the calcination process a repeated recrystallization occurs, causing an increase in the concentration of Ti^{3+} and concomitantly, with it, the photocatalytic efficiency towards phenol degradation.

As calcination was applied to the hydrothermally treated materials the appearance of an interesting secondary structural feature was noticed, the presence of holes (TiO_2-CNT 1H-C and 5H-C). These entities did not appear in the sample hydrothermally treated for 24 h + calcination (TiO_2-CNT 24H-C) at the first sight (SEM), but after acquiring TEM micrographs, they were detected also within these crystals.

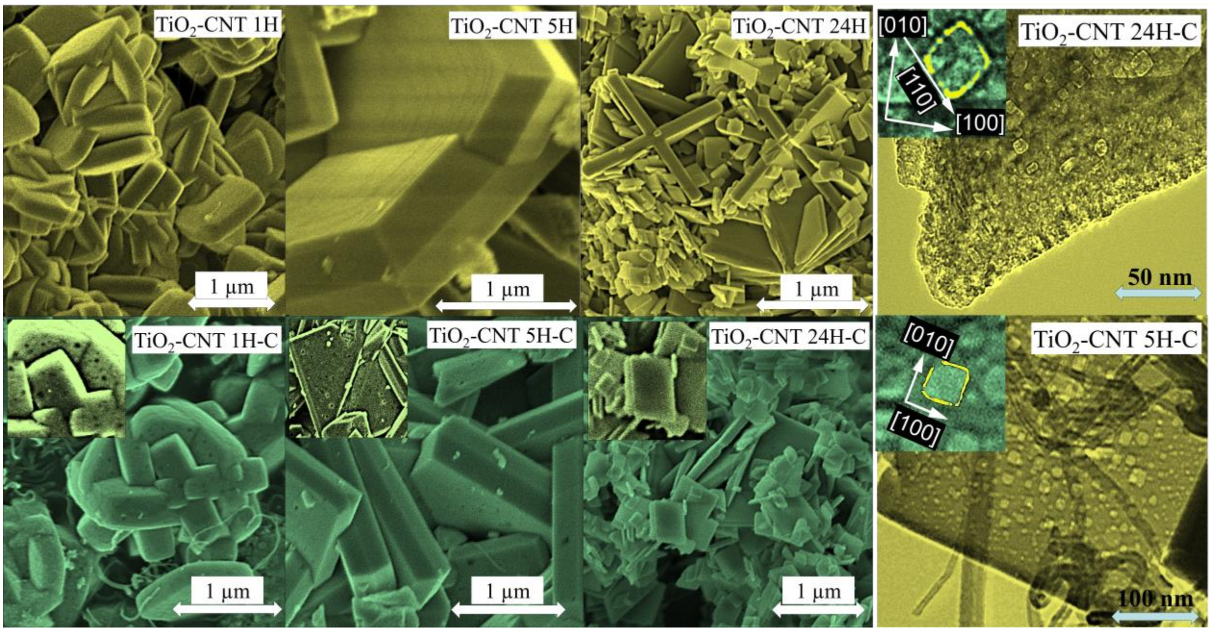

Figure 4. The effect of the calcination on the hydrothermally treated TiO_2 photocatalysts - SEM micrographs

In case of TiO_2-CNT 1H-C and 5H-C samples the edges of the holes were parallel with the crystallographic planes {010} and {100} (Figure 4.), while in the case of TiO_2-CNT 24H-C they suffered a 90° rotation and became parallel {110} plane. The main reason behind of this phenomenon could be the already mentioned stabilization process during the crystallization inside the TiO_2 particles.

Ti2p 3/2 spectra of the non-heat treated samples (TiO_2-CNT 1H, TiO_2-CNT 5H and TiO_2-CNT 24H) was examined. A relatively small amount (0.35 at. %) of Ti^{3+} was detected within these materials, and did not change with the increase of the hydrothermal treatment duration.

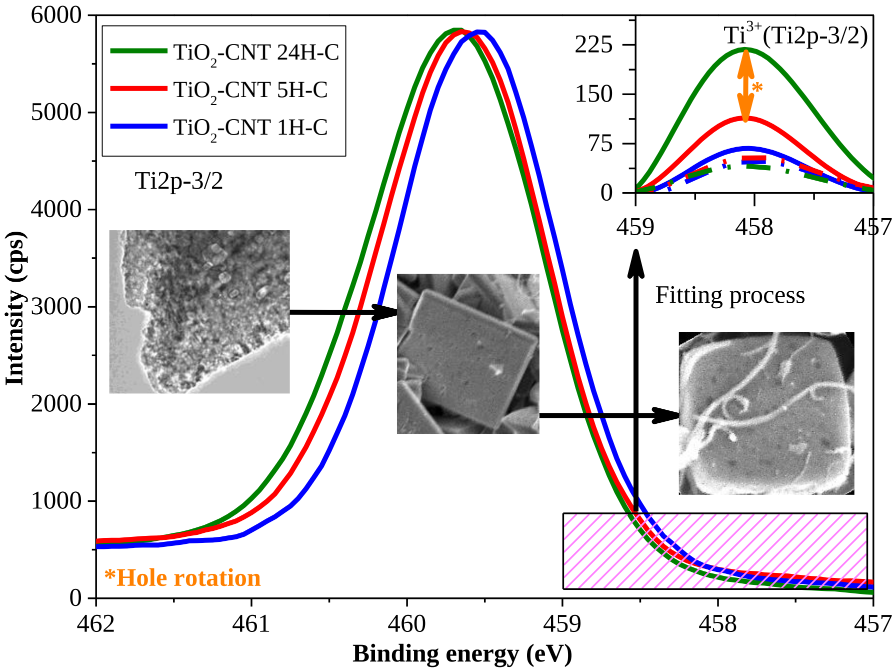

Figure 5. Ti 2p3/2 spectra of the heat-treated photocatalysts

When the calcined materials (“C”-series) spectra was investigated, it was noticed that, with the increase of the hydrothermal treatment time an increase of the Ti^{3+} amount was detected. As the holes performed the rotation (Figure. 5, sample TiO_2-CNT 24H-C), the concentration of Ti^{3+} was nearly threefold, achieving 1.1 at % value.

Because the Ti^{3+} concentration does not increase with the hydrothermal treatment time in the case of the non-calcined sampled, points out that the Ti^{3+} drastic increase, as obtained for the calcined samples, can most probably assigned to the presence/rotation of the holes.

The mechanism involves three steps (I.-III.) illustrated in Figure. 6.

Each of these steps involves a recrystallization process, which means, that new edges/corners were generated raising the possibility for the appearance of crystal defects, evidenced (via XPS) by the presence of increased Ti^{3+} concentration.

This is important, because on the TiO_2' surface the Ti^{3+} centers can sometimes react with the O_2 in the aqueous system, and produce reactive radicals, which can enhance considerably the photocatalytic activity [10].

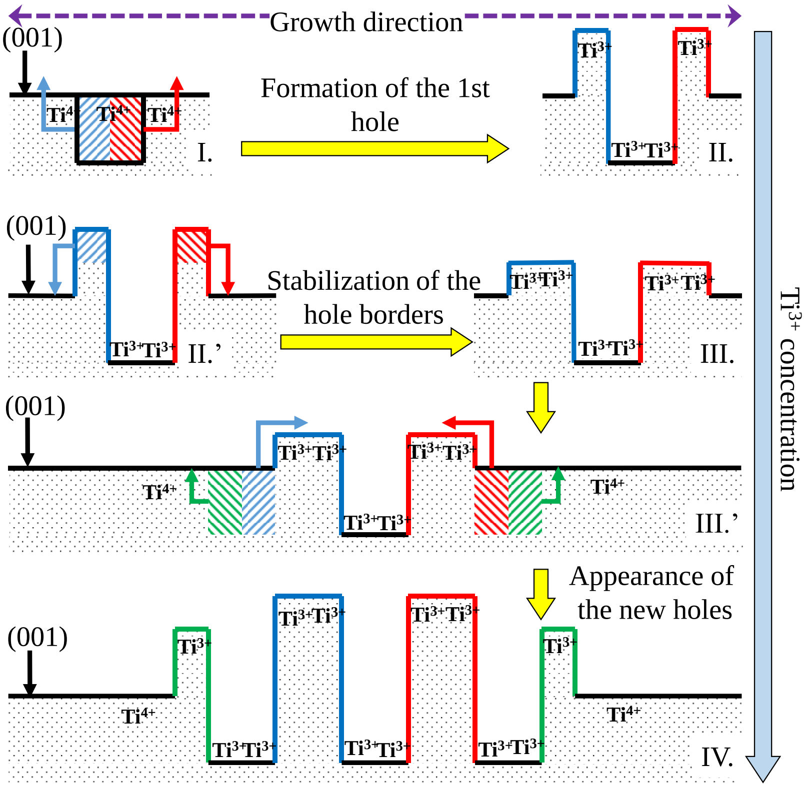

Figure 6. The schematic representation of the proposed hole-formation mechanism

One difference in the structure between the two samples is the orientation of the holes, which indicates that if an activity difference is observed, then this morphological feature should be the reason behind it. Along with the appearance of the holes, the quantity of Ti^{3+} would increase, while the sample with the rotated holes the quantity of Ti^{3+} was threefold. This important difference was should be visible also in the shown photocatalytic efficiency values [10].

In the first approach the hydrothermal treatment time's effect was investigated. As the hydrothermal treatment time prolongs the photocatalytic activity of the materials was nearly unchanged (Figure 7.). However, with the appearance of the crystallographic holes, each of the studied catalysts' activity increased significantly (from $5.81 \cdot 10^{-4}$ to $9.27 \cdot 10^{-4}$ $mM \cdot min^{-1} \cdot m^{-2}$ and from $6.16 \cdot 10^{-4}$ to $13.66 \cdot 10^{-4}$ $mM \cdot min^{-1} \cdot m^{-2}$) as it is shown in Table 1. Furthermore, these activity values were far superior compared to the commercially available P25, namely a near 30-fold activity increase was achieved. Additionally, if the samples NP-24H-C and NP-5H-C were compared then the first one was with 32 % more active (Table 1.) towards UV light driven photocatalytic phenol degradation.

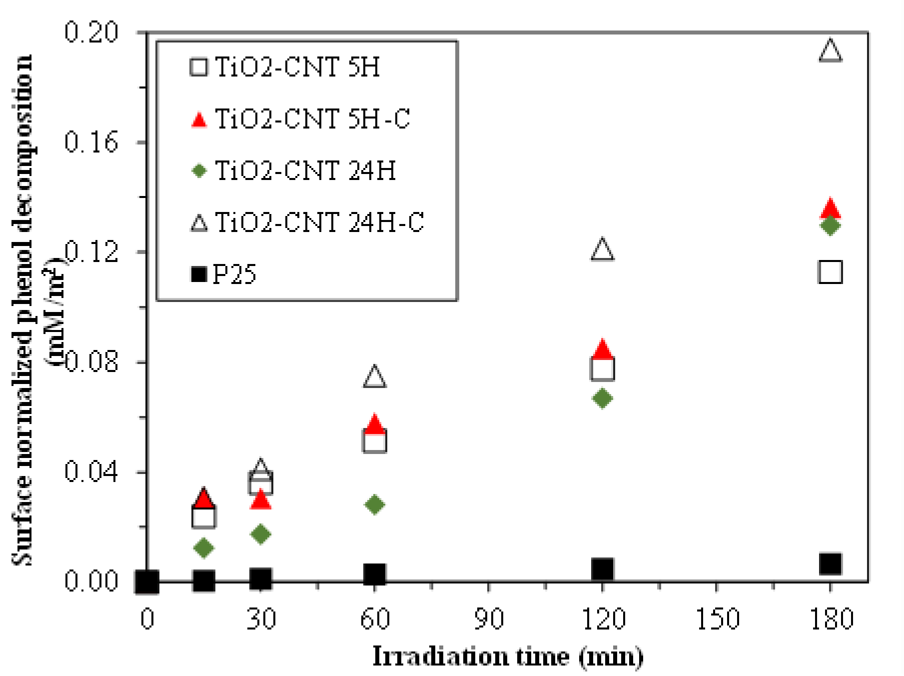

Figure 7. The surface normalized photocatalytic activity of the obtained composites for the degradation of phenol

Consequently all morphological features influenced the trend of the photocatalytic activity within the investigated samples, meaning that both the dominance of {001} Miller indexed facets, and the presence of the holes play a major role by influencing the Ti^{3+} content (at: *Nanoscale 7 (2015) 5776-5786*).

Table 1. Comparation of the TiO_2-CNT 1H, 5H, 24H samples and their calcinated version

Sample	Holes	C (wt. %)	Surface normalized photocatalytic activity $(mM\cdot min^{-1}\cdot m^{-2})\cdot 10^{-4}$	Surface area $(m^2\cdot g^{-1})$ calculated*
P25	-	0	0.41	49.10
TiO_2-CNT 1H	-	>50	-	-
TiO_2-CNT 5H	-	2	5.81	0.57*
TiO_2-CNT 24H	-	2	6.16	0.49*
TiO_2-CNT 1H-C	Yes	>50	-	-
TiO_2-CNT 5H-C	Yes	2	9.27	0.52*
TiO_2-CNT24H-C	Yes	2	13.66	0.45*

T5. In case of individual shape-tailored crystals, the catalytic surface was efficient but small, while in case of hierarchical TiO_2 nanostructures the catalytic surface was large but inefficient.

Due to the comparison of the TiO_2 agglomerates (Microegg-ME) and the individual TiO_2 crystals[1] (Microplates-MP) we calcined the agglomerates at different temperatures (500, 650, 800 and 1000 °C) to achieve higher crystallinity grade which can result in higher photocatalytic activity. We observed from the XRD patterns that all samples were anatase which remained stable up to 800 °C.

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[1] The single crystal definition is: which there is long-range order, without dislocation and no grain boundaries, so it is completely uniform, accordingly don't participate in chemical reactions. Therefore in this work my samples have been named as individual/ discrete crystal, but actually I don't compare one piece with the agglomerates.

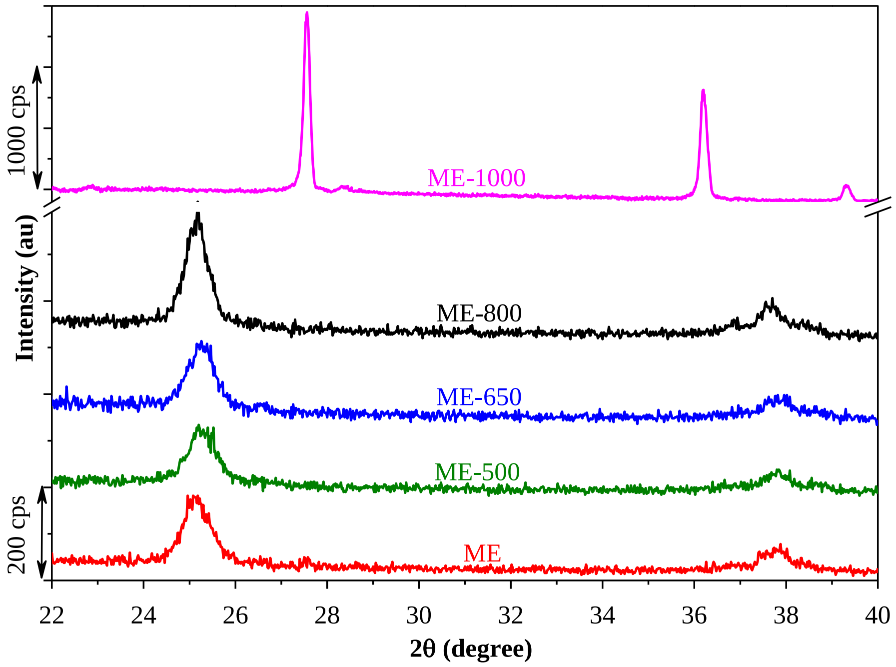

Figure 8. XRD patterns of the microegg - ME series

Increasing the calcination temperature resulted in the crystallite size increase, until the anatase rutile transformation occurred. Based only on the XRD patterns (Figure 8.) no clear signs have been detected which indicated that these nanocrystals are shape tailored or they are part of a secondary geometry. To enlighten this aspect SEM and TEM micrographs were evaluated and on Figure 9. pointing out the formation of egg-like agglomerates.

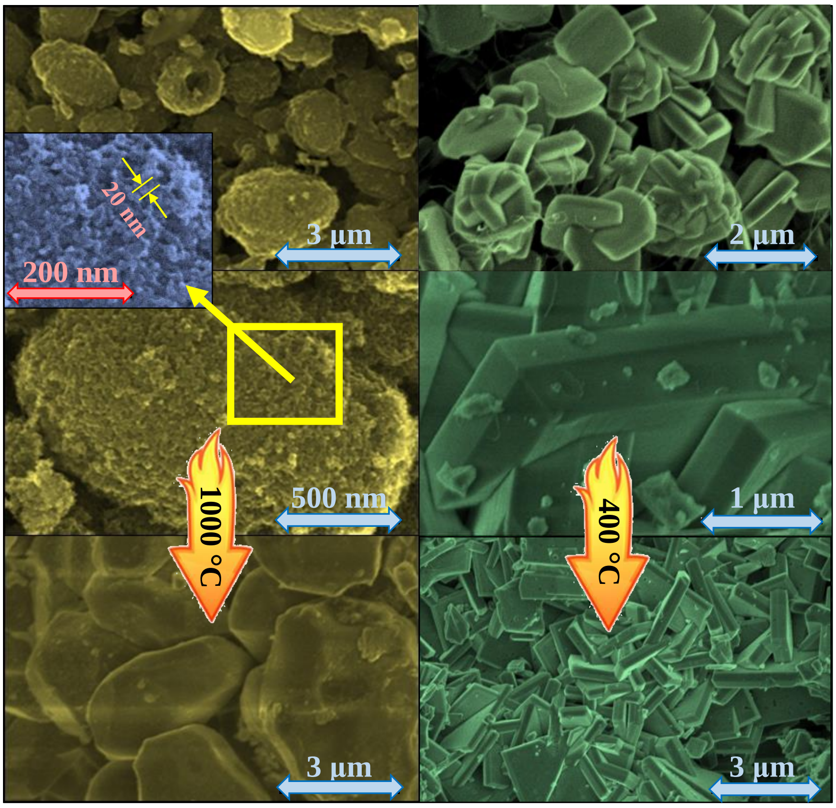

Figure 9. SEM micrographs of the hydrothermally obtained and calcined ME (yellow) and MP (green) photocatalyst series

Two approaches were considered in catalytic/photocatalytic processes: the classical one, using weight normalized kinetic parameters (e.g. reaction rates), or surface normalized kinetic approaches (e.g. surface normalized reaction rates). For the industry, the weight normalized parameter is more convenient (because easier to measure it) although, the efficiency of the catalysts depends on the chemical reactions on the surface. Although, catalytically, the surface normalized degradation is more important, because in each case the catalytic processes are surface quality/size dependent phenomena. Accordingly, the phenol degradation rates were normalized on the surface and surface efficiency degradation curves were also plotted.

The TiO_2 microeggs' and the individual crystals photocatalytic activity also was investigated for phenol degradation, under UV light irradiation using Aeroxide P25 (Evonik Industries) TiO_2 as the reference photocatalyst. With the increase of the calcination temperature a photocatalytic activity enhancement was observed. The phenol degradation yield in the case of ME series was 39.4 % (samples of ME series) up to 61.2 % (sample ME-800) (Figure 10.). The ME-1000 sample was inactive due to the large particle size and the complete absence of the anatase phase.

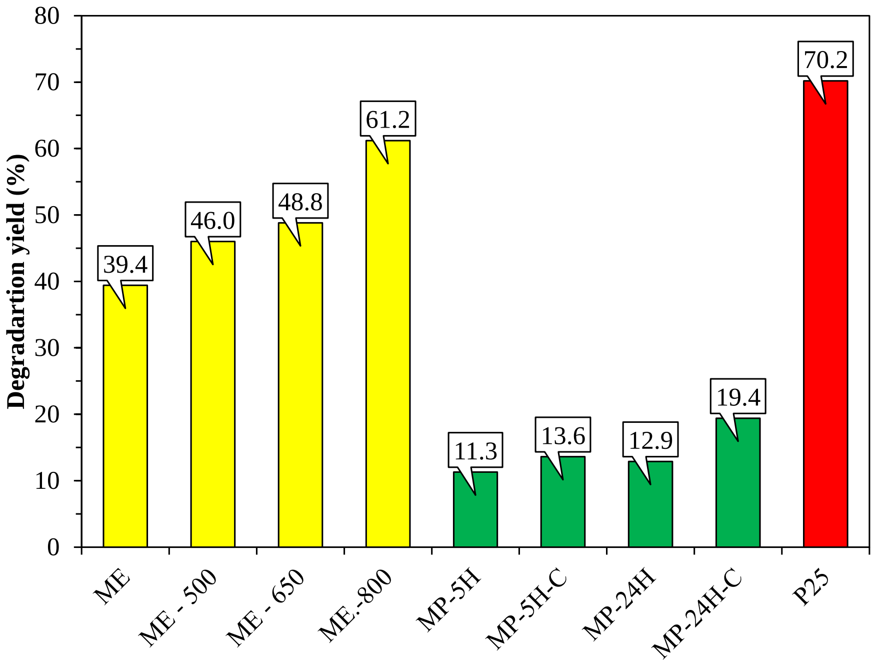

Figure 10. The comparison of the different degradation yields

Although the differences between the two degradation rates are significant, the efficiency of the sample ME-800 and P25 were comparable (in degradation yield terms). Subsequently, the surface normalized degradation intensity of phenol was determined using the procedure and a reversed order of activity was established within the ME series. The surface normalized degradation rates were remarkably low, varying between $0.18 \cdot 10^{-4}$ (sample ME) and $0.37 \cdot 10^{-4}$ $mM \cdot m^{-2} \cdot min$-1. These were much smaller values than the one calculated for P25: $1.42 \cdot 10^{-4}$ $mMm^{-2} \cdot min^{-1}$.

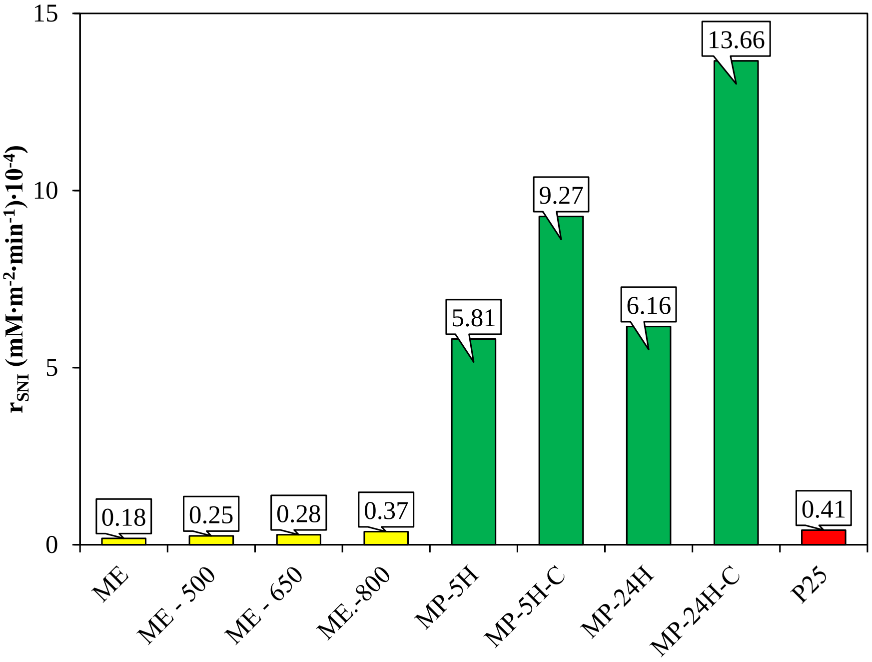

Figure 11. Normalized photocatalytic efficiencies of the studied sample series

At the single crystal case the main method in the increase of the crystallinity grade was the increase of the hydrothermal treatment time and a supplementary calcination at 400 °C. It was observed that with the hydrothermal treatment time increase, and after the calcination, all samples' activity was significantly enhanced (from 5.81 to 9.27 mM·min^{-1}·m^{-2} and from 6.16 to 13.66 mM·min^{-1}·m^{-2}). It should be noted that MP photocatalysts surface area values are very small, thus after the surface normalization, the photocatalytic activities were much higher (13.66·10^{-4} mM·min^{-1}·m^{-2}) than the one shown by P25 (0.41·10^{-4} mM·min^{-1}·m^{-2}) (Figure 11.) (at: *Ceramics International 42 (2016) 3077–3087*).

T6. The different carbon types act as crystallization promoters and influences in different way the shape, morphology and photocatalytic properties of the TiO_2 particles

I studied the TiO_2 crystal genesis in the presence of different carbon types: **A**ctive **c**arbon, **Gr**aphite, **C**arbon **ae**rogel and **C**arbon **fiber**s. The obtained TiO_2 were investigated by transmission and scanning electron microscopy, which showed that the particles possessed different crystal shape. Similarly, to the case of CNT in most of the cases anatase was obtained (Figure 12.).

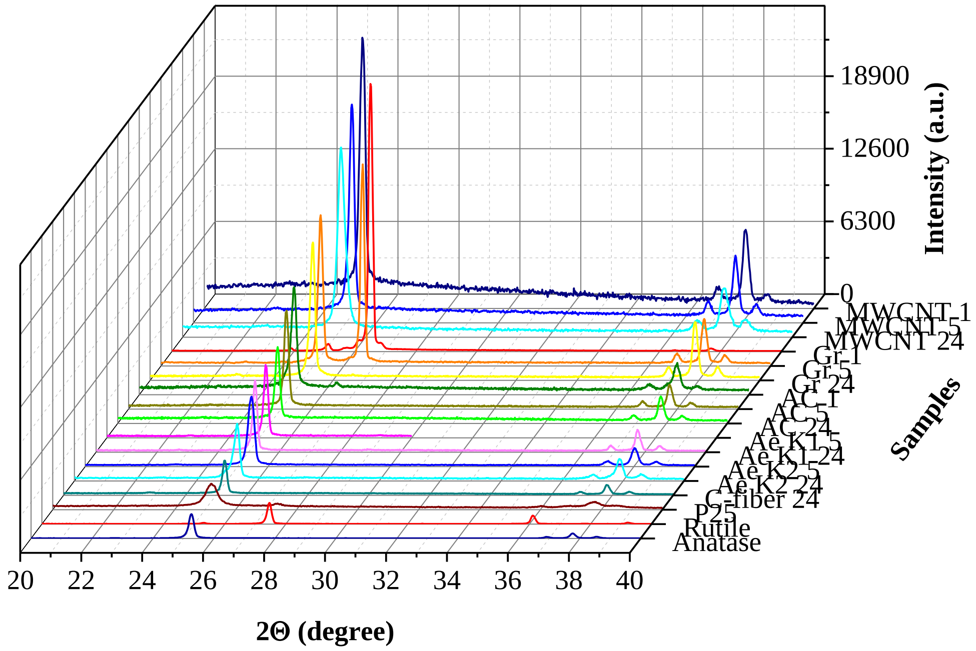

Figure 12. XRD patterns of Aldrich anatase, Aldrich rutile, P25 and the TiO_2-C samples obtained in the presence of different carbons

The DRS spectra of the TiO_2-C samples is shown in Figure 13. It is important to emphasize that the photocatalysts were able to absorb visible light, but this not necessarily means that they are capable to utilize these photons [11]. All of the TiO_2-C samples were grey, the samples obtained after 1 hour of hydrothermal treatment were dark grey, nearly black, while the 5, 24 hours samples were light grey, due to the higher amount of titania deposited on the used carbon surface.

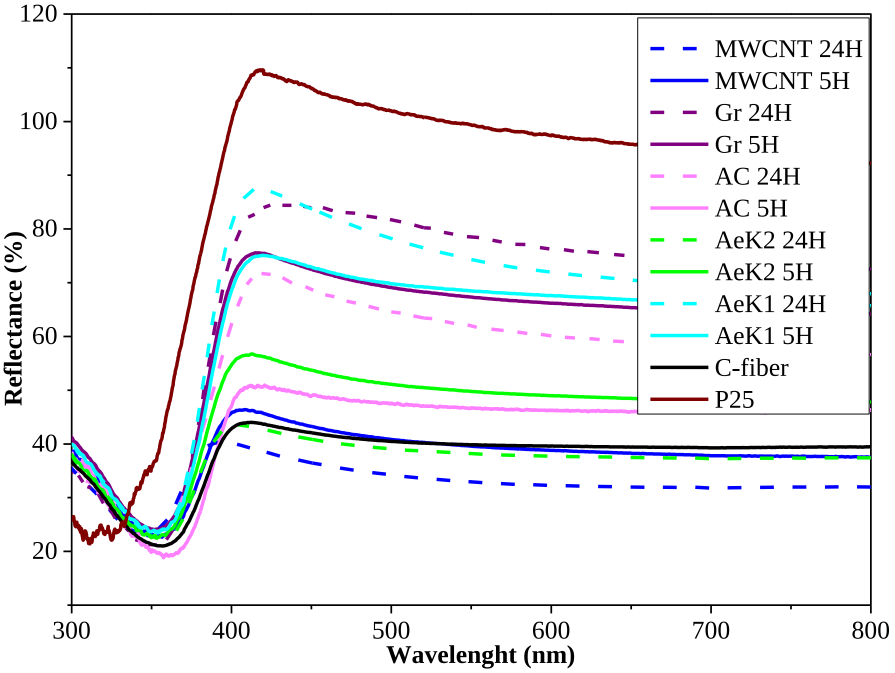

Figure 13. DRS spectra of the different TiO_2 -C samples

The TiO_2-C composites were not efficient in the photocatalytic degradation of phenol (except for the ones obtained in the presence of MWCNT). Therefore, we applied these composites in the degradation of rhodamine B, a model pollutant which was proven to be degradable by shape-tailored titania [12]. This pollutant was degradable by the investigated composite materials, although the P25's photocatalytic performance was slightly better (Figure 14.).

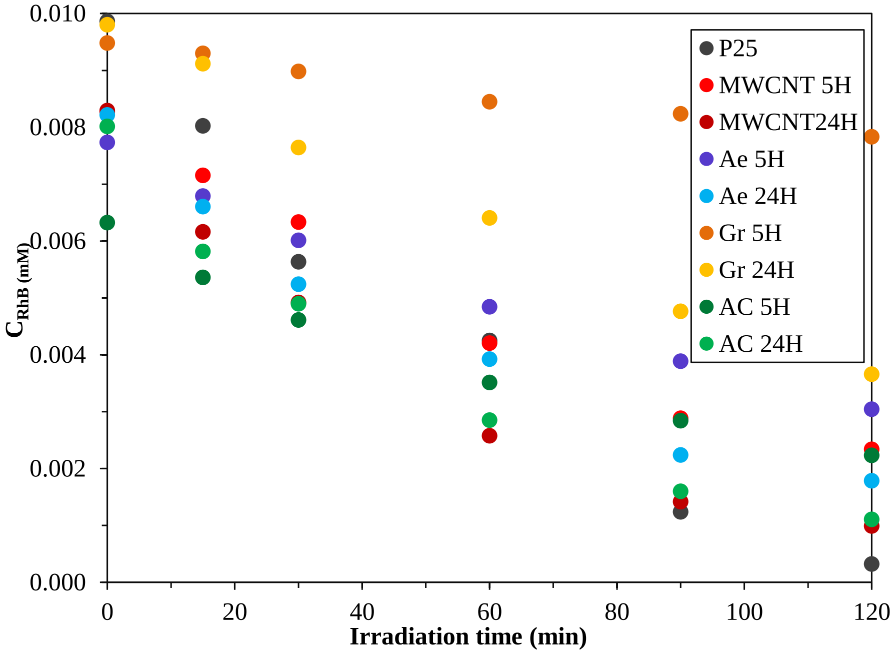

Figure 14. Degradation of Rhodamin B under UV by different TiO_2-C composites

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Scientific activity

Hungarian Scientific Database (MTMT) identifier: 10032931

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(Vizek szerves szennyezőinek eltávolítása nagyhatékonyságú oxidációs módszerekkel), InnoGeo Kft. Szeged, 2010. ISBN 978-963-06-9621-0

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Participation at conferences

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