Photocatalytic performance of thermally prepared TiO$_2$/C photocatalysts under artificial solar light

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A simple method of preparation of artificial solar light-active TiO$_2$ photocatalysts is presented. The new TiO$_2$/C samples were obtained by thermal treatment (150, 250, 350 and 450 °C) of industrial titanium dioxide (TiO$_2$-starting) in the presence of naphthalene vapours. The obtained nanomaterials were investigated by means of UV-vis/DR, Fourier transform infrared spectroscopy/diffuse reflectance infrared and X-ray powder diffraction methods. Brunauer–Emmett–Teller (BET) specific surface area and carbon content were also measured. The photocatalytic activity of the photocatalysts was investigated on the basis of phenol degradation under artificial solar light. TiO$_2$/C photocatalysts show higher photocatalytic activity in comparison with TiO$_2$-starting and commercial KRONOClean 7000 photocatalysts. It was noted that the highest decomposition and mineralisation degree of phenol and its degradation co-products were found for sample obtained at 450 °C and contained 0.19 wt.% of carbon. The carbon content, BET surface area and anatase crystallite size are the mean features, which strongly contribute the photocatalytic activity of new carbon-modified TiO$_2$ photocatalysts under artificial solar light. Modification of TiO$_2$ with naphthalene vapours is a promising method, especially taking the mineralisation of phenol and the co-products of its degradation into account.

1. Introduction: Photocatalytic process using TiO$_2$ as a photocatalyst is one of the most effective methods for degradation of organic contaminations such as: phenol [1–4], pesticides [5, 6], dyes [7–10], drugs [11] or bacteria and viruses [12, 13]. Photocatalysis is an economic method where pollutants are converted into simple chemicals such as carbon dioxide, water and non-toxic mineral acids [14, 15]. Currently, many scientists have been focusing on activation of TiO$_2$ under visible light. One solution is to improve efficiency of TiO$_2$ by modification of its surface. It was found that modification with carbon causes the changes in TiO$_2$ structure. Thus, carbon-modified photocatalysts exhibit activing under visible light [16–18]. It was also noted that TiO$_2$ modified with carbon is an effective photocatalyst for photocatalytic decomposition of phenol under visible light [19–23]. Morawski *et al*. [19] investigated the photodegratation of phenol under visible light in the presence of TiO$_2$ modified in the atmosphere of n-hexane. It was concluded that the presence of 0.85% of carbon in tested sample causes only a slight increase of photoactivity. However, the carbon modification of TiO$_2$ impacts on the turbidity of solution after sedimentation and increase the stability of modified TiO$_2$ under visible light. The photocatalyst containing 0.85 mass% of carbon had the smallest turbidity in comparison with unmodified TiO$_2$. Yu *et al*. [20] modified TiO$_2$ with nano-sized graphene (NGR) as a carbon precursor. The significant absorption of visible light for NGR-modified TiO$_2$ samples was possible to observe. It was concluded that photogenerated electrons could be transferred to surface sites due to the low interfacial charge-transfer resistance between TiO$_2$/C and contamination. The amount of hydroxyl radicals increases hence phenol decomposition is more effective. Visible light-active TiO$_2$/C was also obtained by Mani *et al*. [21]. In this case a citric and ascorbic acids were used as an effective carbon sources. It was noted that the sample modified with citric acid exhibits higher activity than sample modified with ascorbic acid in photocatalytic degradation of phenol and Cr(VI). The photocatalytic activity was attributed to the C doping rather than high surface area. It can be observed that simultaneous usage of phenol and chromium(VI) is an advantage over individual treatments due to selective trapping of ˙OH radicals by phenol, which can prevent the re-oxidation of Cr(III), thereby enhancing Cr(IV) reduction. The samples active under visible light were obtained also by Wojtoniszak *et al*. [22]. TiO$_2$ was modified with graphitic carbon via CVD method. Acetylene was used as a carbon feedstock. It was found that samples treated in CVD for a shorter time and higher temperature exhibit higher activity in visible range. The best photocatalytic activity showed material obtained at 500 °C in 10 s of deposition time. TOC removal rate increased from 4% for unmodified TiO$_2$ to 9% for mentioned sample. TiO$_2$ modified with active carbon (CM-n-TiO$_2$) was used by Shaban *et al*. [23]. It was found that active carbon modification cause narrowing the band-gap energy of obtained samples from 3.14 eV to 1.86 eV. It was observed that the photocatalytic activity of modified TiO$_2$ was higher in comparison with unmodified TiO$_2$. Total decomposition of phenol was achieved after 90 min for CM-n-TiO$_2$ when for unmodified TiO$_2$ it was c.a. 42%.

The main aim of this work was to obtain visible light-active titanium dioxide modified with carbon. The relation between carbon content and the new materials' photocatalytic activity has been studied. The photocatalysts were prepared by thermal treatment of the industrial titanium dioxide in the glass ampule placed inside the horizontal furnace in the presence of naphthalene vapours. Using naphthalene as a carbon precursor for obtained visible active samples is the novelty of this study. The photocatalytic activity of obtained samples was measured during phenol decomposition under artificial solar light. In this Letter the mineralisation degree was also measured.

2. Experimental

2.1. Materials and reagents: Titanium dioxide from sulphate technology supplied by Chemical Plant Grupa Azoty Zakłady Chemiczne 'POLICE' S.A., (Poland) was used as an output material. Commercial TiO$_2$ KRONOClean 7000 (Kronos International, Inc. Germany) was used as reference carbon-modified titania photocatalyst.

Naphthalene (purity 99%, Avantor Performance Materials Poland S.A.) was used as a carbon source. Phenol (purity ≥99%, Avantor Performance Materials Poland S.A.) was used as a model organic contaminant. All the chemicals were used as received without further purification. High purity water for the photocatalytic experiments and sample analysis was produced by a Millipore Elix Advantage water purification system.

2.2. Preparation of TiO₂/C photocatalysts: Carbon-modified TiO₂ (TiO₂/C) photocatalysts were obtained by thermal modification of TiO₂-starting. The amount of 5 g of TiO₂-starting and 0.1 g of naphthalene were placed inside the glass ampule (total volume 70 ml) in the central part of horizontal furnace (Nabertherm, Germany). In order to displace the air, the centre of the ampule was flashed three times with argon (99.5%, Messer, Poland). The end of the ampule was tightly plugged with stopper in order to avoid the leakage of naphthalene vapours into indoor area. Then the samples were calcined for 4 h at 150, 250, 350 and 450 °C (samples assigned as: TiO₂/C-150, TiO₂/C-250, TiO₂/C-350 and TiO₂/C-450). Next, the ampule with appropriate sample was allowed to self-cool down to 25 °C. Subsequently, the samples were dried at 105 °C for 24 h in vacuum drier to remove the organic carbon residues from the surface of TiO₂/C photocatalysts. This is a very simple route to remove naphthalene particles. Indeed, the unbounded but adsorbed naphthalene molecules on the surface of TiO₂ could be a potential pollutant. Moreover to prove that no carbon was rinsed from the surface of modified TiO₂ additional experiment was conducted. The TiO₂/C photocatalysts were added to ultrapure water (containing no organic or inorganic carbon). Than the total organic carbon was measured using the carbon analyser (TOC Multi N/C 2000, Analytik Jena, Germany)

2.3. Characterisation of TiO₂/C photocatalysts: The surface properties of tested nanomaterials were examined by means of FT-IR 4200 spectrophotometer (Jasco, Japan) equipped with a diffuse reflectance accessory (Harrick, USA). The crystalline structure of the photocatalysts was characterised using X-ray powder diffraction (XRD) analysis (Philips X'Pert X-ray diffractometer) using Cu Kα radiation ($\lambda = 1.54056$ Å). The mean size of anatase crystallites diameter D (nm) was calculated using Scherrer's equation [24]. The specific surface area (S_{BET}) of obtained photocatalysts was determined on the basis of N₂ adsorption-desorption at 77 K using a Quadrasorb SI analyser (Quantachrome, USA). Prior to analysis, each sample was degassed at 105 °C for 12 h under high vacuum. The values of S_{BET} were calculated using multi-point analysis of adsorption isotherms applying Brunauer–Emmett–Teller method. Total carbon content in tested samples was determined by means of Multi N/C 2000 analyser (Analytik Jena, Germany) equipped with module for the analysis of solid samples HT 1300.

2.4. Photocatalytic experiments: The photocatalytic activity of new materials was evaluated by the decomposition of phenol solution under artificial solar light. The irradiation of the solution was operated using halogen lamp with a power of 60 W (Philips) with the radiation intensity of about 0.3 W/m² UV and 720 W/m² Vis. The radiation intensity was measured using the radiation intensity meter LB 901 with CM3 and PD204AB Cos sensors. In Fig. 1 the emission spectrum of used light source is presented. Emission spectra was measured by means of meter of radiation intensity of UV and Vis distribution USB4000 (Ocean Optics, Netherlands).

The experiments were conducted in glass beaker containing 500 ml of phenol solution with the initial concentration of 10 mg/l and 0.1 g of appropriate photocatalyst. First, the mixture was magnetically stirred for about 30 min in the dark to ensure the establishment of the adsorption–desorption equilibrium between TiO₂-based photocatalysts surface and phenol molecules. Then the solution of
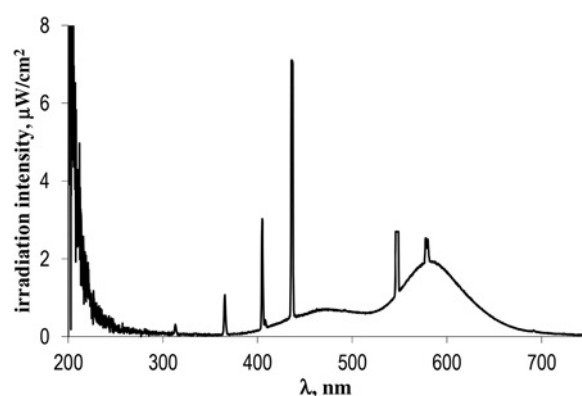
Fig. 1 *Emission spectrum of artificial solar light source (0.3 W/m² UV and 720 W/m² Vis)*

phenol was irradiated under artificial solar light for 24 h. The concentration of phenol in the solution after the photocatalytic process was determined by means of the V-630 UV-vis spectrometer (Jasco, Japan). Decomposition degree of phenol was calculated as

$$R = \frac{C_0 - C_e}{C_0} \cdot 100\% \qquad (1)$$

where:

C_0 – initial concentration of phenol measured after dark adsorption [mg/l],

C_e – concentration of phenol after irradiation time [mg/l].

Prior to all measurements of phenol concentration, the solution was filtered by membrane filter with 0.45 μm pore diameter. The mineralisation degree of phenol and its co-products was calculated on the basis of total organic carbon concentration measurements using TOC Multi N/C 2000 analyser (Analytik Jena, Germany).

3. Results and discussion
3.1. Fourier transform infrared spectroscopy/diffuse reflectance infrared (FTIR/DRS) analysis: The FTIR/DRS spectra of TiO₂-starting, carbon-modified photocatalysts and reference material are presented in Fig. 2. It can be observed that all of tested materials show a very broad band in the range of 3700–2600 cm⁻¹ characteristic for the O-H stretching mode of interacting hydroxyl groups and the symmetric and asymmetric O-H stretching modes of molecular water coordinated for Ti⁴⁺ ions [25]. The weak band at 3680 cm⁻¹ possible to observe in TiO₂/C samples was assigned to stretching mode of different types of free hydroxyl groups [26]. The narrow band at 1620–1610 cm⁻¹ was attributed to the molecular water bending mode [27]. It was noted that the increase of the calcination temperature to 450 °C leads to the insignificant decrease of bands intensity in the wavelength range 3700–2600 cm⁻¹. This fact can be explained by the releasing of water molecules from the surface of the photocatalysts during calcination. All samples have also strong bands at 970–930 cm⁻¹ ascribed to the self-absorption of titania [28]. The characteristic peaks assigned the naphthalene groups are possible to observe only for TiO₂/C photocatalysts modified at 350 and 450 °C. The bands observed at 1512 cm⁻¹ can be assigned to a C=C stretching vibrations mode. The C-C skeletal vibrations can be observed at about 1410 cm⁻¹ [29–31]. It does not mean that there was no carbon in two other materials, what was proved by carbon content measurements (listed in Table 1). The typical thermal decomposition of naphthalene is
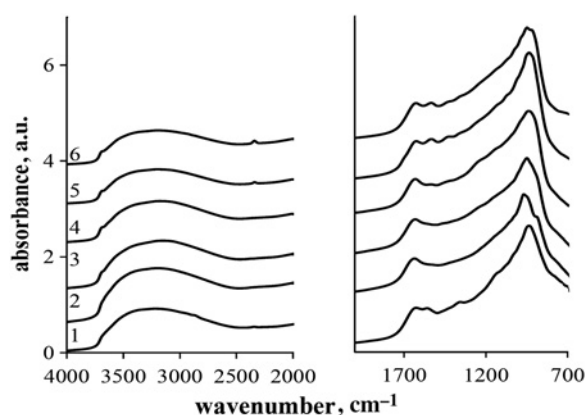
Fig. 2 *FTIR/DRS spectra of: 1-KRONOClean 7000, 2-TiO₂-starting, 3-TiO₂/C-150, 4- TiO₂/C-250, 5- TiO₂/C-350, 6- TiO₂/C-450*

Fig. 3 *XRD patterns of: 1-KRONOClean 7000, 2-TiO₂-starting, 3-TiO₂/C-150, 4-TiO₂/C-250, 5-TiO₂/C-350, 6-TiO₂/C-450*

possible to observe at higher temperature. Thereby, lower carbon content in photocatalyst calcined at higher temperature was due to this decomposition. The studies show that materials prepared at lower temperature (150 and 250 °C) contain more carbon, although carbon bands at 1512 and 1410 cm⁻¹ are less intensive. The reason is a thermal decomposition of naphthalene of higher temperature. The characteristic groups of naphthalene decomposition are observed. On the TiO₂ surface a lot of O-H groups are present, so that is highly likely that the group of naphthalene bond with O-H groups. In the case of commercial carbon-modified TiO₂ two additional broad bands at 1580 and 1420 cm⁻¹ assigned to the asymmetric and symmetric stretching vibrations of an arylcarboxylate group [32] are observed. The band at 1330 cm⁻¹ attributed to the C-O stretching vibrations can be also observed for KRONOClean 7000 sample. It was confirmed that the material contains 0.96 wt% of carbon (Table 1).

3.2. X-Ray diffraction and S_{BET} ANALYSIS: Fig. 3 provides the X-ray diffraction patterns of TiO₂-starting, carbon-modified TiO₂ photocatalysts and reference titania powder. The phase composition and crystallite size of studied photocatalysts are listed in Table 1. The TiO₂-starting showed a poorly crystalised anatase phase with an insignificant amount of rutile (up to 5%). Modification at low temperature (100–450 °C) could not cause a phase transformation from anatase to rutile. Theoretically, anatase transforms to rutile at temperature exceeding ∼600 °C [33]. A reflection of rutile in TiO₂-starting could be observed due to the addition of rutile nuclei during the production process (sulphate technology). Thus, the presence of rutile in obtained samples is not due to conversion of anatase to rutile. A small increase of the amount of anatase phase content is due to decrease of amorphous phase during the calcinations. It can be observed that the intensity
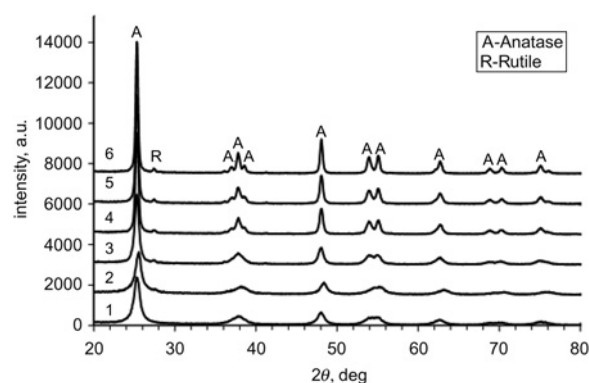
of all peaks for the carbon-modified TiO₂ increases with the increase of the modification temperature. The crystallite size of anatase and rutile increases from 14 to 38 nm and from 15 to 41 nm, respectively. The increase in the crystallinity are accompanied to the decrease in the surface area (312 m²/g for TiO₂-starting and 121, 69, 47, 35 m²/g for TiO₂/C photocatalysts calcined at 150, 250, 350, 450 °C, respectively). Higher calcination temperature results sintering of crystallites, caused their growth and thus contributes to the reduction of the BET specific surface area. It can be also seen that modification at higher temperature results in the decrease of carbon content (from 0.44 to 0.19 wt.%) in tested samples. N₂ adsorption/desorption isotherms measured for the prepared samples were shown in Fig. 4. In each case, the adsorption-desorption isotherms can be attributed to type II though a small hysteresis loop can be observed. The obtained isotherms indicate the mesoporous nature of the materials. While for TiO₂-starting the adsorption-desorption isotherms was identified as typical type IV with H2 type hysteresis loops [34].

3.3. Photocatalytic activity: The photocatalytic activity of the TiO₂-starting and new carbon-modified titania samples in comparison with KRONOClean 7000 was tested during decomposition of phenol. In Fig. 4 the decomposition and mineralisation degrees of phenol solution are presented. The mineralisation rate was calculated due to the fact that co-products formed during the incomplete decomposition of phenol molecules are often more toxic than the main pollutant. It can be seen that the photoactivity increases with the increase of the modification temperature. Moreover, photocatalysts modified at 250, 350 and 450 °C show higher photoactivity than the TiO₂-starting and KRONOClean 7000 photocatalysts. Lower photocatalytic activity in the case of the sample modified at 150 °C was due to the high

Table 1 Physicochemical properties of studied photocatalysts

Sample	Anatase content, %	Anatase crystallite size, nm	Rutile crystallite size, nm	S_{BET}, m²/g	$V^a_{total\ 0.99}$, cm³/g	$V^b_{micro\ DR}$, cm³/g	V^c_{meso}, cm³/g	Carbon content, wt.%
KRONOClean 7000	100	11	0	242	0.33	0.09	0.24	0.96
TiO₂-starting	95	14	15	312	0.27	0.11	0.16	0.0
TiO₂/C-150 °C	98	16	24	121	0.33	0.045	0.29	0.44
TiO₂/C-250 °C	98	26	30	69	0.30	0.024	0.28	0.40
TiO₂/C-350 °C	98	29	29	47	0.29	0.020	0.27	0.37
TiO₂/C-450 °C	98	38	41	35	0.25	0.015	0.24	0.19

[a]Total pore volume determined by the signal point nitrogen adsorption isotherms at relative pressures p/p_0 =0.99
[b]Micropore volume estimated using the method DR (Dubinin–Radushkevich)
[c]Mesopore volume was determined from the difference Vtotal 0.99 and Vmicro D
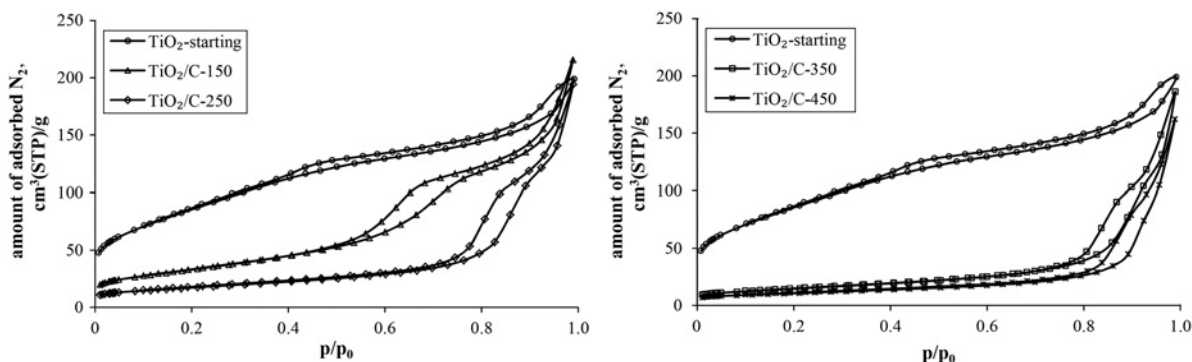
Fig. 4 *N₂ adsorption/desorption (at 77 K) isotherms*

concentration of carbon on the photocatalyst surface. The presence of too high carbon content in the sample can inhibit the interaction of surface Ti and C. The high carbon deposits and thereby the weaker interaction of Ti and C, the lower photocatalytic activity. In Fig. 4 the influence of the carbon content on phenol decomposition and mineralisation is also presented. The less carbon content the higher decomposition and mineralisation degrees. The similar results was previously observed by Janus *et al.* [26]. It was noted that the photocatalytic activity under UV irradiation increases with the decrease carbon content. In this case the highest photocatalytic activity was observed for the TiO₂/C-450 with 0.19 wt.% of carbon. It is highly likely that the photocatalytic performance of tested carbon-modified samples depends also on the type of carbon present on the surface of TiO₂/C photocatalysts, as well as the number of active sites. Titanium vacancies located at or near the surface are identified as the active sites for pollutant molecules adsorption leading to the formation of an active complexes and resulting in effective photodegradation of water contaminants [35]. It is possible that the lower photoactivity of the prepared TiO₂/C materials heat treated at lower temperatures is a consequence of active sites blocking by the naphthalene molecules. It should be noted that the commercial KRONOClean 7000 photocatalyst with the highest carbon content shows lower photocatalytic activity than all carbon-modified TiO₂ samples. Although, it is also well known that the efficiency of titania-based photocatalysts depends on specific surface area and crystallite size. The highest activity was estimated for sample modified at 450 °C with 38 nm of anatase crystallite. It is widely adopted that the optimal particle size of anatase crystallite for the best photoactivity is c.a.10 nm [36]. However, Almquist and Biswas [37] showed that photoactivity increase with particle size and the optimal effective particle size is in the range from 25 to 40 nm. They explained

this phenomena due to the significant effects of particle size at which light is absorbed and the photogenerated charge-carrier dynamics within the particle in this size range. It may also note that the photoactivity increases with decreasing BET specific surface area. In many cases a large surface area is the important factor determining the photocatalytic activity due to a large amount of adsorbed organic molecules promotes the reaction rate [38–40]. However, materials with high BET specific surface area are sometimes associated with large amounts of crystalline defects, which favour the recombination of electrons-holes. Unfortunately, fast recombination of photogenerated electrons and holes causes a poor photoactivity [41, 42]. It is speculated that the presence of carbon in obtained samples and also the optimal carbon content are necessary for preparation of the new photoactive materials. The very important things are also optimal crystallite size and BET specific surface area. It is also believed that the type of carbon in TiO₂/C photocatalysts has the important impact on photocatalytic activity (Fig. 5).

4. Conclusions: In this Letter a new promising method of modification of titanium dioxide by carbon deposition from naphthalene vapour was presented. A group of carbon-modified photocatalysts was obtained by thermal treatment of an crude titanium dioxide (TiO₂-starting) in the atmosphere of naphthalene. Photodecomposition and mineralisation of phenol and its co-products were studied under artificial solar light. The photocatalytic activity test shows that the less carbon content and the highest anatase crystallites the higher photoactivity of TiO₂/C materials. It was found that the highest decomposition and mineralisation degrees of phenol and its co-products were observed for sample obtained at 450 °C (mainly anatase phase 38 nm and with relative low S_{BET}) and containing 0.19 wt.% of carbon. Finally, the photocatalytic activity of new samples (TiO₂/C-350 and TiO₂/C-450) was higher in comparison with commercial TiO₂ KRONOClean 7000 [43].

Fig. 5 *Decomposition and mineralisation degrees of phenol and influence of the content of carbon*

6   References

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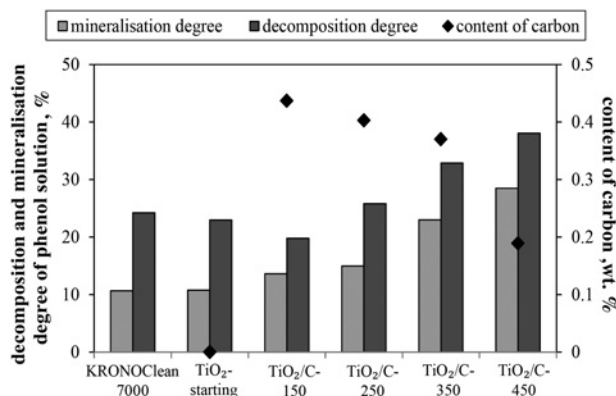
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