

## Carbon modified TiO<sub>2</sub> photocatalysts for water purification

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Carbon can form different structures with TiO<sub>2</sub>: carbon-doped TiO<sub>2</sub>, carbon coated TiO<sub>2</sub> and composites of TiO<sub>2</sub> and carbon. The presence of carbon layer on the surface of TiO<sub>2</sub> as well as the presence of porous carbon in the composites with TiO<sub>2</sub> can increase the concentration of organic pollutants on the surface of TiO<sub>2</sub>, facilitating the contact of the reactive species with the organic molecules. Carbon-doped TiO<sub>2</sub> can extend the absorption of the light to the visible region by the narrowing of the band gap and makes the photocatalysts active under visible light irradiation. TiO<sub>2</sub> loaded carbon can also work as a photocatalyst, on which the molecules are adsorbed in the pores of carbon and then they undergo the photocatalytic decomposition with UV irradiation. Enhanced photocatalytic activity for the destruction of some organic compounds in water was noticed on the carbon coated TiO<sub>2</sub> and TiO<sub>2</sub> loaded activated carbon, mostly because of the adsorptive role of carbon. However, in carbon-doped TiO<sub>2</sub>, the role of carbon is somewhat different, the replacement of carbon atom with Ti or oxygen and formation of oxygen vacancies are responsible for extending its photocatalytic activity towards the visible range.

**Keywords:** TiO<sub>2</sub>/AC, carbon-doped TiO<sub>2</sub>, carbon-coated TiO<sub>2</sub>, photocatalysis.

### INTRODUCTION

Photocatalytic activity of TiO<sub>2</sub> depends on the rate of generation of free radicals (electrons and holes), which are formed when semiconductor is excited with the wavelength energy equals or higher than the energy of its band gap (UV or visible light), their reactivity and their recombination rate. The mechanism of the destruction of organic compounds can go indirectly owing to the attack of OH radicals, which are formed after the reaction of photogenerated holes with adsorbed water on the surface of the semiconductor or directly by the reaction of adsorbed organic molecules on the surface of semiconductor with holes or active centers (surface defects)<sup>1</sup>.

Modification of TiO<sub>2</sub> by carbon attracts great attention because of a few reasons, firstly because of a high adsorption ability of porous carbon, and secondly, because non metal anion doping can cause the narrowing of the band gap, the anodic shift of the quasi Fermi potential, and make the catalyst active under visible light<sup>2-5</sup>.

From the point of view of the adsorptive properties of carbon, preparation of composites between carbon (activated carbon, carbon microspheres, carbon fibres, carbon nanotubes) and TiO<sub>2</sub>, coating of TiO<sub>2</sub> with carbon layer and loading of TiO<sub>2</sub> on the activated carbon were performed<sup>6-14</sup>.

The mechanism of organic compounds decomposition on TiO<sub>2</sub> loaded activated carbon is going by with increasing the concentration of organic compounds on the catalyst surface and its efficient degradation during UV irradiation. TiO<sub>2</sub> loaded on the activated carbon (AC)<sup>13-22</sup>, carbon fibers<sup>23</sup>, carbon nanotubed<sup>12</sup> and exfoliated graphite<sup>24</sup> with efficient adsorption and decomposition of organic compounds such as phenol, 4-chlorophenol, Methyl Orange, Methylene Blue, iminoctadine triacetates, oils, dichloromethane, etc. were reported. The synergistic ef-

fect for the mixture of TiO<sub>2</sub> with activated carbon (AC), was observed by some researchers<sup>3, 6, 8, 25</sup>. The improvement of the photocatalytic properties of TiO<sub>2</sub>/AC composite was explained by the high adsorption of the impurities on the surface of activated carbon and their transfer to TiO<sub>2</sub> surface and depended on the mass ratio of TiO<sub>2</sub> to the activated carbon.

Coating of TiO<sub>2</sub> with a thin porous carbon layer significantly increased adsorption abilities of the photocatalyst and through that accelerated the decomposition of organic compounds, which were in a high quantity adsorbed on their surface. The enhanced photocatalytic activity of carbon-coated TiO<sub>2</sub> was obtained also due to the improvement of the crystallinity of the anatase particles, because carbon coating TiO<sub>2</sub> retarded the phase transformation from anatase to rutile, which usually occurs during heating TiO<sub>2</sub> at 700°C and through that improved the crystallinity of anatase phase in TiO<sub>2</sub>. Carbon coating TiO<sub>2</sub> reduced the amount of UV rays reaching the surface of the TiO<sub>2</sub> particles, therefore balance among different factors controlled by the carbon layer on the TiO<sub>2</sub> particles was required to get its high photocatalytic activity<sup>9-11</sup>.

Preparation of carbon-coating TiO<sub>2</sub> with obtaining the TiO<sub>2n-1</sub> phase, the reduced phase of TiO<sub>2</sub> produced very positive results in the activity of these photocatalysts towards visible range. Their crystal structure is understood by the introduction of oxygen vacancies into rutile framework in an ordered manner. Such prepared photocatalysts decomposed iminoctadine triacetate with higher efficiency than TiO<sub>2</sub> under visible light with the cut off UV rays<sup>26</sup>.

Formation of oxygen vacancies is important for the preparation of visible light active photocatalysts. It was reported that replacement of carbon atom with Ti or oxygen and formation of some oxygen vacancies could be responsible for the extension of the photocatalytic activity of carbon-doped TiO<sub>2</sub> to the visible range<sup>27</sup>. Choi et al.<sup>28</sup>

investigated carbon-doped TiO<sub>2</sub> and they claimed that substitution of C for O in the TiO<sub>2</sub> leads to a photocatalytic decomposition of Methylene Blue under visible light irradiation.

The other authors reported that carbon-doped TiO<sub>2</sub> had extended absorption of the light to the visible range and two absorption maxima could be observed in UV-Vis spectra, so the excitation of such prepared catalyst was possible with both, UV, and Vis light<sup>5, 29</sup>.

## PREPARATION METHODS

### Carbon-doped TiO<sub>2</sub>

Carbon-doped TiO<sub>2</sub> can be prepared, starting from different precursors. Kisch and coworkers<sup>29</sup> prepared carbon-doped TiO<sub>2</sub> photocatalyst from TiCl<sub>4</sub> and tetrabutylammonium hydroxide, Shen et al.<sup>30</sup> prepared C/TiO<sub>2</sub> photocatalyst through calcination of TiCl<sub>4</sub> in air at 350°C. Calcinations of TiO<sub>2</sub> with urea and thiourea<sup>31</sup> or oxidation of TiC at high temperatures<sup>28</sup>, were also reported. The other methods of the preparation of the C/TiO<sub>2</sub> photocatalyst were based on the heating of TiO<sub>2</sub> with the vapors of n-hexane<sup>32</sup> and ethanol<sup>33</sup> or by mixing of TiO<sub>2</sub> with liquid ethanol and heating under pressure<sup>34</sup>. Carbon-doped TiO<sub>2</sub> nanotube arrays were prepared by annealing TiO<sub>2</sub> nanotube arrays at high temperatures under the controlled CO gas flow<sup>35</sup>. Carbonate species-doped TiO<sub>2</sub> photocatalysts were prepared from urea and thiourea, mixed with anatase powder and calcination at 400 and 500°C<sup>36</sup>.

### Carbon-coated TiO<sub>2</sub>

Carbon-coated TiO<sub>2</sub> can be prepared by using either TiO<sub>2</sub> powder or TiO<sub>2</sub> precursor, mixed with carbon precursor such as poly(vinyl alcohol) (PVA), poly(ethylene terephthalate) (PET) or hydroxyl propyl cellulose (HPC) in different ratios, either in powder or aqueous solution and then heat-treated at different temperatures 700 – 1100°C in inert atmosphere, either in N<sub>2</sub> or Ar gas flow<sup>9-11</sup>. Impregnation of TiO<sub>2</sub> with saccharose and heating at 400 – 600°C was also reported<sup>37</sup>.

Carbon-coated Ti<sub>n</sub>O<sub>2n-1</sub> was prepared from the mixture of rutile-type TiO<sub>2</sub> with PVA, different mixing ratios as well as different temperatures of heat treatment, from 900 to 1100°C gave different n-values in Ti<sub>n</sub>O<sub>2n-1</sub><sup>26, 38</sup>.

### TiO<sub>2</sub> loaded carbon

TiO<sub>2</sub> loaded activated carbon can be prepared by sol-gel method from the mixture of titania precursor and either activated carbon or activated carbon precursor through hydrolysis and heat treatment<sup>16-18, 39</sup>. Loading of TiO<sub>2</sub> particles onto activated carbons or carbon spheres can be carried out by the hydrolysis of titanium oxysulfate TiOSO<sub>4</sub> under autogenous hydrothermal conditions<sup>14</sup>. The other methods of loading TiO<sub>2</sub> on activated carbon are as follows: Chemical Vapour Deposition (CVD), Direct Air-Hydrolysis (DAH), and High Temperature Impregnation (HTI), among those the CVD method gave the best bounding of TiO<sub>2</sub> with the carbon surface, anatase particles were placed in the pores of activated carbon<sup>21</sup>.

Coating carbon multiwalls nanotubes with TiO<sub>2</sub> was performed by two methods: sol gel from alkoxides and by

hydrothermal deposition of anatase-type TiO<sub>2</sub> in autoclave from TiOSO<sub>4</sub> precursor<sup>12</sup>.

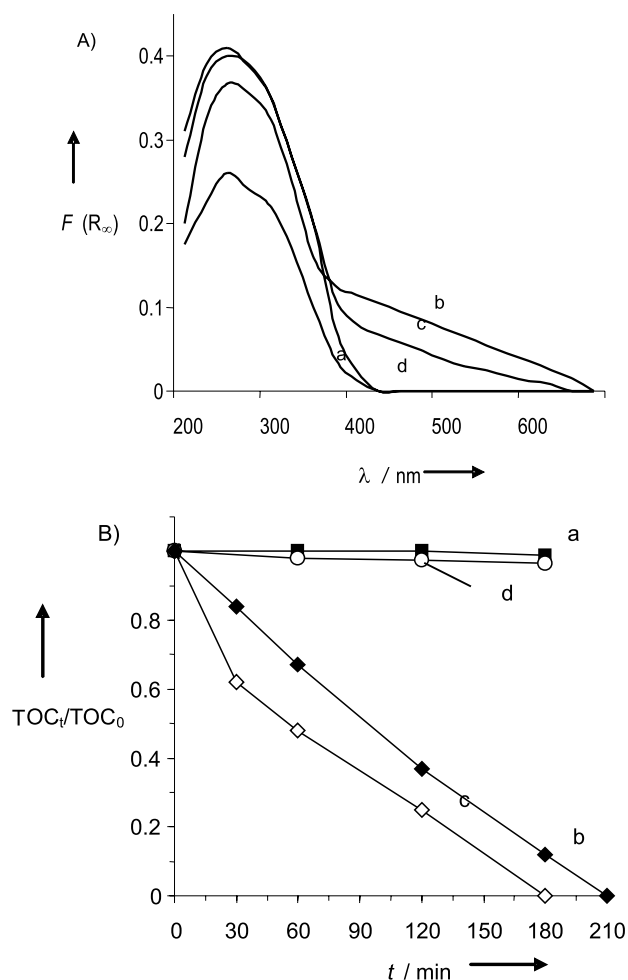
TiO<sub>2</sub>-loading onto carbon foam was carried out under hydrothermal conditions prepared through carbonization of polyimide, using the urethane foam template<sup>40</sup>. The preparation of TiO<sub>2</sub> loading on some floating materials such as wood chips<sup>41</sup> or exfoliated graphite<sup>24</sup> was also reported. TiO<sub>2</sub>-loaded carbon microspheres with the diameter of 25 nm were prepared from cellulose/TiO<sub>2</sub> microsphere composites, which were formed by a one-step phase separation, using cellulose xantate and sodium polyacrylate aqueous solutions dispersing TiO<sub>2</sub> powder (P-25)<sup>8</sup>.

## PHOTOCATALYTIC ACTIVITY

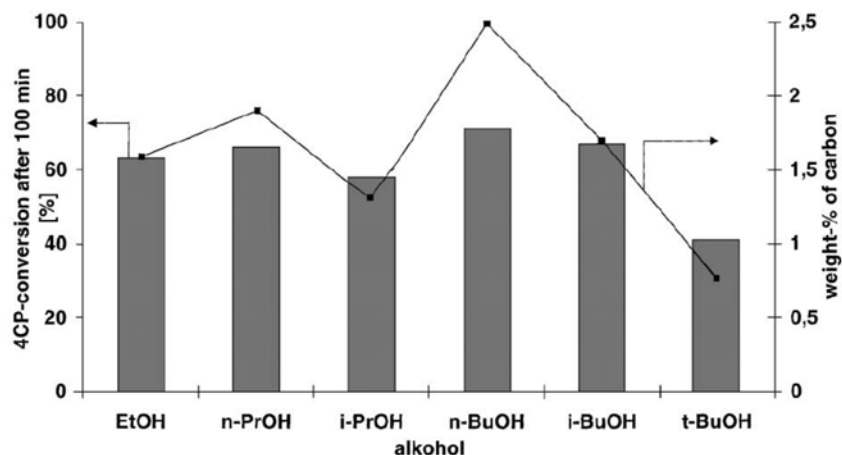
### Visible light activity of carbon-doped TiO<sub>2</sub>

Sakthivel et al.<sup>29</sup> prepared C/TiO<sub>2</sub> photocatalyst from TiCl<sub>4</sub> and tetrabutylammonium hydroxide, which showed decomposition of 4-chlorophenol under visible artificial light irradiation with the higher rate than undoped TiO<sub>2</sub>. The diffuse reflectance spectra and the mineralisation of 4-chlorophenol with visible artificial light are presented in Fig.1<sup>29</sup>.

In the case of carbon-doped TiO<sub>2</sub> samples two absorption maxima in the range of UV and Vis were observed



**Figure 1.** A) Diffuse reflectance spectra of modified and pure TiO<sub>2</sub>, B) mineralisation of 4-chlorophenol with artificial visible light ( $l = 455 \text{ nm}$ ); a) TiO<sub>2</sub>, b) TiO<sub>2</sub> - 2.98%C, c) TiO<sub>2</sub> - 0.42%C, d) TiO<sub>2</sub> - 0.03%C



**Figure 2.** Conversion of 4-chlorophenol after 100 min of irradiation versus carbon content in carbon-doped TiO<sub>2</sub> prepared from TiO<sub>2</sub> Hombikat heat treated in suspensions with various alcohols

on the recorded UV-Vis spectra (Fig. 1A), showing that these photocatalysts could be excited with the wavelengths in the visible region. The higher content of carbon resulted in higher absorption of visible light and consequently the mineralisation of 4-chlorophenol under visible light proceeded faster on the carbon-doped TiO<sub>2</sub>. The other explanation for the activity of carbon-doped TiO<sub>2</sub> under visible light irradiation was the observed narrowing of the maximum band gap in carbon-doped samples (0.14 eV in the sample contained around 3 wt % of carbon) and the anodic shift of a flat-band potential, related to the presence of carbon, similar as the noted for the nitrogen-doped TiO<sub>2</sub> active under visible light.

Lettmann et al.<sup>5</sup> reported that the highly condensed coke-like species can act as a photosensitiser. They coated TiO<sub>2</sub> (Hombikat) with carbonaceous species by impregnation and decomposition with various alcohols, and they observed the activity of these photocatalysts under visible light irradiation for the decomposition of 4-chlorophenol, which was higher for the samples having higher content of carbon. The results are presented in Fig. 2<sup>5</sup>.

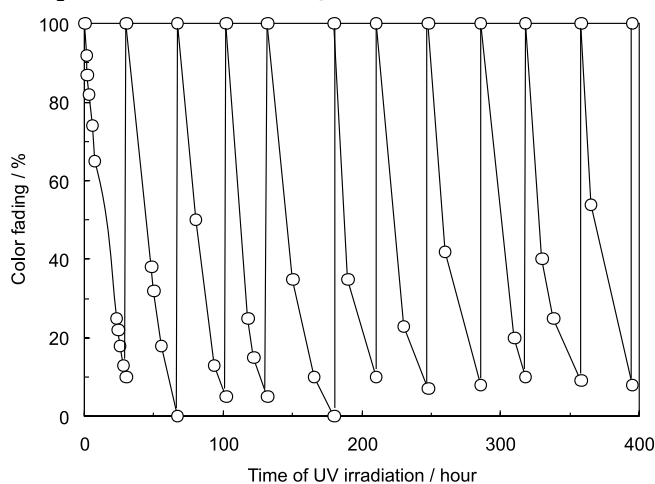
The explanation of visible light activity of such prepared carbon-doped TiO<sub>2</sub> was that coke-like species could act as a photosensitiser without the participation of TiO<sub>2</sub> (then decomposition was going by the formed after excitation singlet oxygen or superoxide radicals O<sub>2</sub><sup>•-</sup>) or these carbon species could inject an electron into the conduction band of TiO<sub>2</sub>, which reacted with adsorbed oxygen and formed reactive O<sub>2</sub><sup>•-</sup>.

Choi et al.<sup>28</sup> reported visible light activity of carbon-doped TiO<sub>2</sub> for Methylene Blue decomposition, shifting of the optical absorption edge to the lower energy in carbon-doped TiO<sub>2</sub> was noticed. They claimed that C atoms doped onto O sites and formation of impurity states in the band gap could contribute to the red shift.

Efficient solar water splitting has been observed by Park et al.<sup>35</sup> on carbon-doped TiO<sub>2</sub> nanotube arrays. The synthesized TiO<sub>2-x</sub>C<sub>x</sub> nanotube arrays showed much higher photocurrent densities and more efficient water splitting under visible-light illumination (> 420 nm) than pure TiO<sub>2</sub> nanotube arrays.

### TiO<sub>2</sub>-coated carbon – adsorption and decomposition under UV irradiation

Carbon coating TiO<sub>2</sub> showed high adsorption of Methylene Blue and its fast decomposition under UV irradiation<sup>9-11</sup>. Crystallinity of anatase particles was improved in the prepared carbon-coated TiO<sub>2</sub> and transformation of anatase to the not active rutile was suppressed, but also the amount of UV radiation reaching the surface of the TiO<sub>2</sub> particles was reduced. The highest rate constant for Methylene Blue decomposition was obtained on the sample prepared at 850°C with a carbon content of about 3.5 wt%, in which the transition from anatase to rutile was suppressed and carbon layer was thin enough to transmit UV rays<sup>11</sup>. In Fig. 3 there is shown cycling decomposition of Methylene Blue on carbon-coated TiO<sub>2</sub> prepared from powders of TiO<sub>2</sub> and PVA at 900°C with ratio of TiO<sub>2</sub>/PVA = 50/50 in weight<sup>9</sup>.



**Figure 3.** Color fading of MB solution under UV irradiation in the presence of carbon-coated TiO<sub>2</sub> sample (10 wt % of carbon) with cycling to use fresh MB solution, concentration of MB = 2.94·10<sup>-5</sup> M

Stable amount of MB decomposition in the following cycles confirms obtaining good relations between the adsorptivity of carbon with the photocatalytic activity of TiO<sub>2</sub> particles excited with UV rays.

### TiO<sub>2</sub> loaded carbon

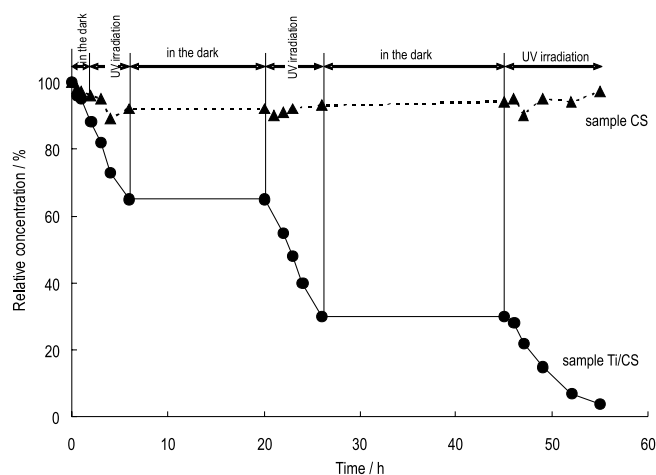
The synergistic effect between the activated carbon and TiO<sub>2</sub> was observed, which depended on the ratio of the

activated carbon to TiO<sub>2</sub> but also, on the kind of precursors used. 4-chlorophenol was efficiently decomposed on the suspended mixture of activated carbon, without losing this beneficial synergistic effect, even when it was applied in a pilot plant, working with the total volume solution of 247 L and sunlight<sup>2</sup>. In some cases a synergistic effect was not observed, as it was reported for the decomposition of 2,4-dichlorophenoxyacetic acid<sup>3</sup>, or dichloromethane<sup>13</sup>, where the suspended mixture of TiO<sub>2</sub> and activated carbon showed lower photoactivity than the TiO<sub>2</sub>-loaded activated carbon.

Efficient adsorption and decomposition of organic compounds such as phenol, 4-chlorophenol, Methyl Orange, Methylene Blue, iminoctadine triacetates, oils, dichloromethane, were performed on TiO<sub>2</sub> loaded on different carbon structures such as activated carbon, carbon fibers, carbon nanotubes, exfoliated graphite, etc.<sup>12-18, 39-41</sup>.

However, in some cases the highest adsorptivity but not the highest rate constant for the decomposition of organic compounds was achieved. To have the enough enhancement of photocatalytic activity of TiO<sub>2</sub>, an appropriate adsorptivity was required on the support of TiO<sub>2</sub> photocatalyst, too low and too high adsorptivity for the pollutant generated less enhancement in photoactivity. It was reported that mounting of TiO<sub>2</sub> particles on AC can block entrance to the pores of AC, decreasing the adsorption capacity of AC<sup>17</sup>. Therefore, the balance between adsorption and decomposition has to be established for the degradation of pollutants on the TiO<sub>2</sub> loaded carbon photocatalysts in periodical cycles, with preserving their abilities for both, adsorption, and decomposition under UV light.

The mechanism of adsorption and decomposition of Methylene Blue on TiO<sub>2</sub> loaded carbon spheres prepared by hydrolysis of TiOSO<sub>4</sub> under hydrothermal conditions is presented in Fig. 4<sup>14</sup>.



**Figure 4.** Changes in relative concentration of MB in the solution in which pristine carbon spheres (CS) and anatase loaded one (Ti/CS) were dispersed<sup>14</sup>

Saturation with Methylene Blue adsorption on carbon spheres (CS) can be observed, and no change in Methylene Blue concentration with UV irradiation, whereas on the anatase loaded carbon spheres (Ti/CS) Methylene Blue could be adsorbed in the dark and decomposed with UV irradiation in the cycles.

## CONCLUSIONS

Carbon can modify TiO<sub>2</sub> particles in a different way, giving some benefits for its photocatalytic activity. Coating of TiO<sub>2</sub> particles with porous carbon, mixing with activated carbon or loaded on the adsorptive carbon can improve their ability for adsorption of pollutants and through that destruction of organic compounds under UV irradiation. On the other hand, doping of carbon to TiO<sub>2</sub> can extend their photoactivity towards visible range because of the replacement of carbon atom with oxygen or Ti and formation of some vacancies, and also there is observed red shift of the optical absorption edge and formation of some impurities state in the band gap. The nature of carbon, its structure, quantity and bounding with TiO<sub>2</sub> are important parameters, which characterize the photocatalytic properties of TiO<sub>2</sub>. Combination of carbon with TiO<sub>2</sub> gave possibilities to obtain new photocatalysts, especially the developing of visible light active photocatalysts is very perspective for a future use. Carbon doping to TiO<sub>2</sub> allowed a profound understanding of the hybridization of adsorption with the photocatalytic activity of photocatalysts. Formation of reduced phase of TiO<sub>2</sub>, Ti<sub>n</sub>O<sub>2n-1</sub> in carbon-coated TiO<sub>2</sub> provided new information about the visible light activity of this photocatalyst.

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