

Carbon modified TiO₂ photocatalysts for water purification

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Carbon can form different structures with TiO₂: carbon-doped TiO₂, carbon coated TiO₂ and composites of TiO₂ and carbon. The presence of carbon layer on the surface of TiO₂ as well as the presence of porous carbon in the composites with TiO₂ can increase the concentration of organic pollutants on the surface of TiO₂, facilitating the contact of the reactive species with the organic molecules. Carbon-doped TiO₂ 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. TiO₂ 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 TiO₂ and TiO₂ loaded activated carbon, mostly because of the adsorptive role of carbon. However, in carbon-doped TiO₂, 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: TiO₂/AC, carbon-doped TiO₂, carbon-coated TiO₂, photocatalysis.

INTRODUCTION

Photocatalytic activity of TiO₂ 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)¹.

Modification of TiO₂ 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 light²⁻⁵.

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 TiO₂, coating of TiO₂ with carbon layer and loading of TiO₂ on the activated carbon were performed⁶⁻¹⁴.

The mechanism of organic compounds decomposition on TiO₂ loaded activated carbon is going by with increasing the concentration of organic compounds on the catalyst surface and its efficient degradation during UV irradiation. TiO₂ loaded on the activated carbon (AC)¹³⁻²², carbon fibers²³, carbon nanotubed¹² and exfoliated graphite²⁴ with efficient adsorption and decomposition of organic compounds such as phenol, 4-chlorophenol, Methyl Orange, Methylene Blue, iminooctadine triacetates, oils, dichloromethane, etc. were reported. The synergistic ef-

fect for the mixture of TiO₂ with activated carbon (AC), was observed by some researchers^{3, 6, 8, 25}. The improvement of the photocatalytic properties of TiO₂/AC composite was explained by the high adsorption of the impurities on the surface of activated carbon and their transfer to TiO₂ surface and depended on the mass ratio of TiO₂ to the activated carbon.

Coating of TiO₂ 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 TiO₂ was obtained also due to the improvement of the crystallinity of the anatase particles, because carbon coating TiO₂ retarded the phase transformation from anatase to rutile, which usually occurs during heating TiO₂ at 700°C and through that improved the crystallinity of anatase phase in TiO₂. Carbon coating TiO₂ reduced the amount of UV rays reaching the surface of the TiO₂ particles, therefore balance among different factors controlled by the carbon layer on the TiO₂ particles was required to get its high photocatalytic activity⁹⁻¹¹.

Preparation of carbon-coating TiO₂ with obtaining the TiO_{2n-1} phase, the reduced phase of TiO₂ 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 iminooctadine triacetate with higher efficiency than TiO₂ under visible light with the cut off UV rays²⁶.

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 TiO₂ to the visible range²⁷. Choi et al.²⁸

investigated carbon-doped TiO₂ and they claimed that substitution of C for O in the TiO₂ leads to a photocatalytic decomposition of Methylene Blue under visible light irradiation.

The other authors reported that carbon-doped TiO₂ 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^{5, 29}.

PREPARATION METHODS

Carbon-doped TiO₂

Carbon-doped TiO₂ can be prepared, starting from different precursors. Kisch and coworkers²⁹ prepared carbon-doped TiO₂ photocatalyst from TiCl₄ and tetrabutylammonium hydroxide, Shen et al.³⁰ prepared C/TiO₂ photocatalyst through calcination of TiCl₄ in air at 350°C. Calcinations of TiO₂ with urea and thiourea³¹ or oxidation of TiC at high temperatures²⁸, were also reported. The other methods of the preparation of the C/TiO₂ photocatalyst were based on the heating of TiO₂ with the vapors of n-hexane³² and ethanol³³ or by mixing of TiO₂ with liquid ethanol and heating under pressure³⁴. Carbon-doped TiO₂ nanotube arrays were prepared by annealing TiO₂ nanotube arrays at high temperatures under the controlled CO gas flow³⁵. Carbonate species-doped TiO₂ photocatalysts were prepared from urea and thiourea, mixed with anatase powder and calcination at 400 and 500°C³⁶.

Carbon-coated TiO₂

Carbon-coated TiO₂ can be prepared by using either TiO₂ powder or TiO₂ 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 N₂ or Ar gas flow⁹⁻¹¹. Impregnation of TiO₂ with saccharose and heating at 400 – 600°C was also reported³⁷.

Carbon-coated Ti_nO_{2n-1} was prepared from the mixture of rutile-type TiO₂ with PVA, different mixing ratios as well as different temperatures of heat treatment, from 900 to 1100°C gave different n-values in Ti_nO_{2n-1}^{26, 38}.

TiO₂ loaded carbon

TiO₂ 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^{16-18, 39}. Loading of TiO₂ particles onto activated carbons or carbon spheres can be carried out by the hydrolysis of titanium oxysulfate TiOSO₄ under autogenous hydrothermal conditions¹⁴. The other methods of loading TiO₂ 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 TiO₂ with the carbon surface, anatase particles were placed in the pores of activated carbon²¹.

Coating carbon multiwalls nanotubes with TiO₂ was performed by two methods: sol gel from alkoxides and by

hydrothermal deposition of anatase-type TiO₂ in autoclave from TiOSO₄ precursor¹².

TiO₂-loading onto carbon foam was carried out under hydrothermal conditions prepared through carbonization of polyimide, using the urethane foam template⁴⁰. The preparation of TiO₂ loading on some floating materials such as wood chips⁴¹ or exfoliated graphite²⁴ was also reported. TiO₂-loaded carbon microspheres with the diameter of 25 nm were prepared from cellulose/TiO₂ microsphere composites, which were formed by a one-step phase separation, using cellulose xantate and sodium polyacrylate aqueous solutions dispersing TiO₂ powder (P-25)⁸.

PHOTOCATALYTIC ACTIVITY

Visible light activity of carbon-doped TiO₂

Sakthivel et al.²⁹ prepared C/TiO₂ photocatalyst from TiCl₄ and tetrabutylammonium hydroxide, which showed decomposition of 4-chlorophenol under visible artificial light irradiation with the higher rate than undoped TiO₂. The diffuse reflectance spectra and the mineralisation of 4-chlorophenol with visible artificial light are presented in Fig.1²⁹.

In the case of carbon-doped TiO₂ samples two absorption maxima in the range of UV and Vis were observed

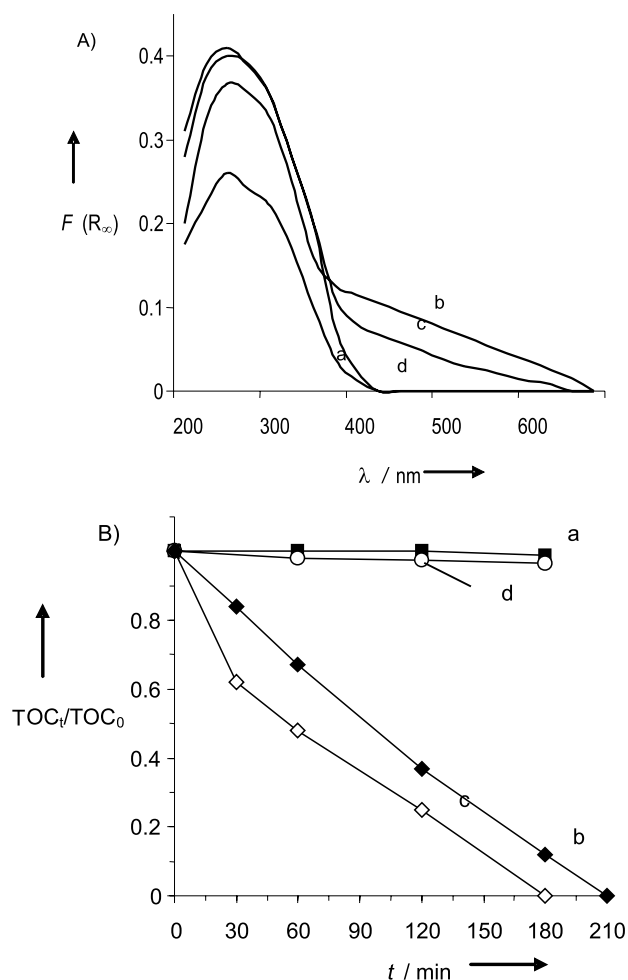


Figure 1. A) Diffuse reflectance spectra of modified and pure TiO₂, B) mineralisation of 4-chlorophenol with artificial visible light ($\lambda = 455$ nm); a) TiO₂, b) TiO₂ - 2.98%C, c) TiO₂ - 0.42%C, d) TiO₂ - 0.03%C

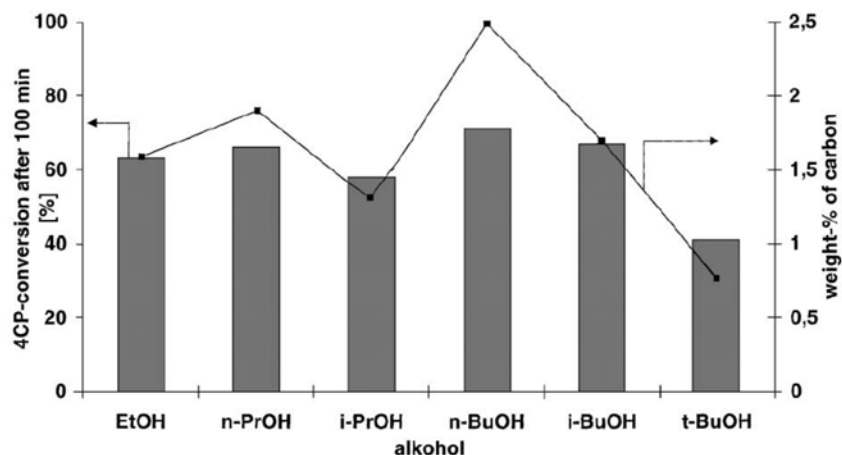


Figure 2. Conversion of 4-chlorophenol after 100 min of irradiation versus carbon content in carbon-doped TiO₂ prepared from TiO₂ Hombikat heat treated in suspensions with various alcohols

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 TiO₂. The other explanation for the activity of carbon-doped TiO₂ 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 TiO₂ active under visible light.

Lettmann et al.⁵ reported that the highly condensed coke-like species can act as a photosensitiser. They coated TiO₂ (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. 2⁵.

The explanation of visible light activity of such prepared carbon-doped TiO₂ was that coke-like species could act as a photosensitiser without the participation of TiO₂ (then decomposition was going by the formed after excitation singlet oxygen or superoxide radicals O₂^{•-}) or these carbon species could inject an electron into the conduction band of TiO₂, which reacted with adsorbed oxygen and formed reactive O₂^{•-}.

Choi et al.²⁸ reported visible light activity of carbon-doped TiO₂ for Methylene Blue decomposition, shifting of the optical absorption edge to the lower energy in carbon-doped TiO₂ 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.³⁵ on carbon-doped TiO₂ nanotube arrays. The synthesized TiO_{2-x}C_x nanotube arrays showed much higher photocurrent densities and more efficient water splitting under visible-light illumination (> 420 nm) than pure TiO₂ nanotube arrays.

TiO₂-coated carbon – adsorption and decomposition under UV irradiation

Carbon coating TiO₂ showed high adsorption of Methylene Blue and its fast decomposition under UV irradiation⁹⁻¹¹. Crystallinity of anatase particles was improved in the prepared carbon-coated TiO₂ and transformation of anatase to the not active rutile was suppressed, but also the amount of UV radiation reaching the surface of the TiO₂ 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 rays¹¹. In Fig. 3 there is shown cycling decomposition of Methylene Blue on carbon-coated TiO₂ prepared from powders of TiO₂ and PVA at 900°C with ratio of TiO₂/PVA = 50/50 in weight⁹.

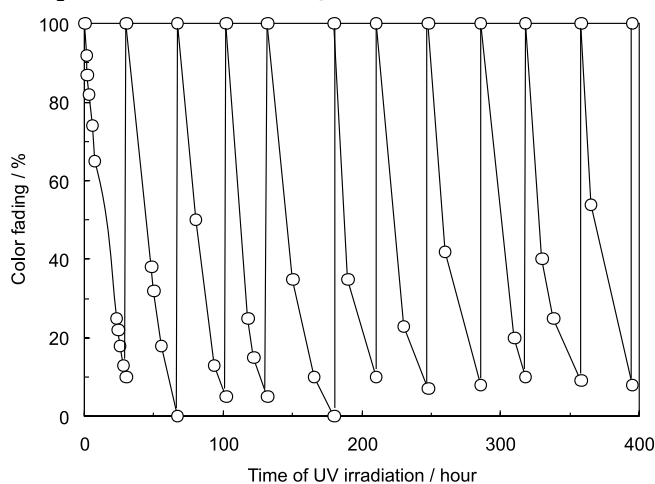


Figure 3. Color fading of MB solution under UV irradiation in the presence of carbon-coated TiO₂ sample (10 wt % of carbon) with cycling to use fresh MB solution, concentration of MB = 2.94·10⁻⁵ M

Stable amount of MB decomposition in the following cycles confirms obtaining good relations between the adsorptivity of carbon with the photocatalytic activity of TiO₂ particles excited with UV rays.

TiO₂ loaded carbon

The synergistic effect between the activated carbon and TiO₂ was observed, which depended on the ratio of the

activated carbon to TiO₂ 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 sunlight². In some cases a synergistic effect was not observed, as it was reported for the decomposition of 2,4-dichlorophenoxyacetic acid³, or dichloromethane¹³, where the suspended mixture of TiO₂ and activated carbon showed lower photoactivity than the TiO₂-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 TiO₂ loaded on different carbon structures such as activated carbon, carbon fibers, carbon nanotubes, exfoliated graphite, etc.^{12-18, 39-41}.

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 TiO₂, an appropriate adsorptivity was required on the support of TiO₂ photocatalyst, too low and too high adsorptivity for the pollutant generated less enhancement in photoactivity. It was reported that mounting of TiO₂ particles on AC can block entrance to the pores of AC, decreasing the adsorption capacity of AC¹⁷. Therefore, the balance between adsorption and decomposition has to be established for the degradation of pollutants on the TiO₂ 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 TiO₂ loaded carbon spheres prepared by hydrolysis of TiOSO₄ under hydrothermal conditions is presented in Fig. 4¹⁴.

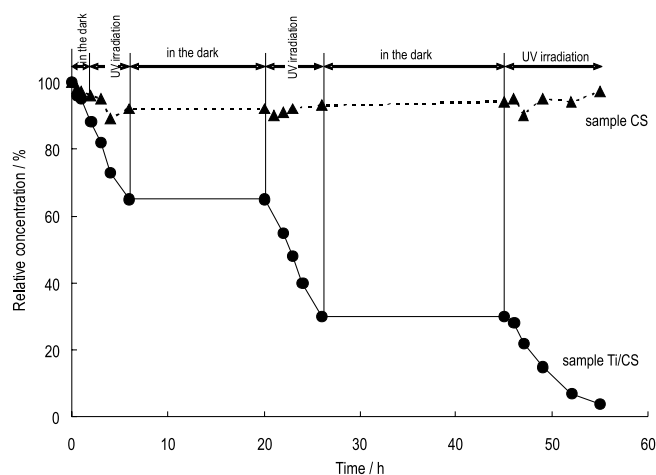


Figure 4. Changes in relative concentration of MB in the solution in which pristine carbon spheres (CS) and anatase loaded one (Ti/CS) were dispersed¹⁴

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 TiO₂ particles in a different way, giving some benefits for its photocatalytic activity. Coating of TiO₂ 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 TiO₂ 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 TiO₂ are important parameters, which characterize the photocatalytic properties of TiO₂. Combination of carbon with TiO₂ gave possibilities to obtain new photocatalysts, especially the developing of visible light active photocatalysts is very perspective for a future use. Carbon doping to TiO₂ allowed a profound understanding of the hybridization of adsorption with the photocatalytic activity of photocatalysts. Formation of reduced phase of TiO₂, Ti_nO_{2n-1} in carbon-coated TiO₂ provided new information about the visible light activity of this photocatalyst.

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