

Methylene Blue decomposition under visible light irradiation in the presence of carbon-modified TiO₂ photocatalysts

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ABSTRACT

Carbon modified TiO₂ was used for Methylene Blue (MB) dye decomposition under artificial solar light irradiation. TiO₂/C photocatalysts were prepared by modification of commercial anatase TiO₂ (Z.Ch. POLICE Company, Poland) in different alcohols atmosphere at 120 °C for 4 h under elevated pressure. Thermogravimetric analyses shown that the amount of carbon present in TiO₂ depends on amount of carbon in used alcohols. Modification does not change the specific surface area of photocatalysts. Used low temperature and elevated pressure conducted to change the amorphous phase presented in pristine material to anatase structure and also conducted to increasing of crystalline size of anatase. The optimal amount of carbon needed to increasing the activity of photocatalyst under visible light irradiation amounted 0.02% of mass.

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1. Introduction

Titanium dioxide is well known as a semiconductor with high photocatalytic activity under UV light irradiation. It is also known that the different features of TiO₂ photocatalyst, such as specific surface area, particle and pore size, crystalline structure, phase composition have an important influence on its photoactivity [1–3]. Presently, the particular attention is being paid to activation of titania photocatalysts with the usage of visible light. It was found that doping of TiO₂ by ions of some metals or non-metallic elements causes to changes in titania structure and the modified photocatalysts were capable of absorbing the light in the visible region [4–12]. Recently, it has been reported that carbon doping of TiO₂ has the best photo-response compared to other ions. Also carbon presents in titanium dioxide particles is assumed to play as sensitizer in photocatalytic reaction [13]. Lettmann et al. [5] obtained photo stable carbon-modified TiO₂ photocatalyst by pyrolysis of titania alcoholic suspension. It was proved the increase of photocatalytic activity of new material under visible light irradiation was the effect of carbon presence in TiO₂ lattice. Orth-Gerber et al. [6] discovered that during the calcination at 400 °C of prepared N-doped TiO₂ by hydrolization of titanium tetrachloride with tetrabutylammonium hydroxide, in the structure of anatase material it was possible to observe carbon instead of nitrogen. That type of modification leads to obtaining TiO₂ photocatalysts also active under visible light.

Wong et al. [7] spoke on the issue of ion-assisted electron-beam evaporation application in the presence of CO₂ and CO to prepare TiO_xC_y thin films. The influence of beam current on the carbon content and crystallinity of the films was also studied. It was proved that more carbon content was incorporated when ion beam raised and CO₂ gas was utilized as the ion source. The photocatalytic activity of new materials was tested using Methylene Blue as an organic pollutant. The best results were obtained for TiO₂-C film with 1.25 at.% carbon dopant after annealing. Lin et al. [14] presented a simple method of uniform carbon-covered titania (CCT) photocatalysts via pyrolysis of sucrose highly dispersed on the surface of TiO₂ in flowing N₂. In this case was also confirmed that carbon covering of TiO₂ surface leads to increase the transformation temperature of anatase to rutile phase. CCT materials showed better photocatalytic activity in comparison with pure titania during Methylene Blue degradation under UV-Vis irradiation. Carbon deposition made the adsorption edge of titania shift to the visible region. Yun et al. [15] also presented similar preparation method and conclusions. Carbon-doped TiO₂ nanoparticles were prepared by sol-gel auto-combustion method and tested during the photodegradation of Methylene Blue under visible light [16]. Also in this case it has been proved that carbon doping of pure titania results in improving the photocatalytic activity. Matos et al. [17] also reported the higher photocatalytic activity of carbon-doped TiO₂ during the Methylene Blue decomposition under visible light. Three different lamps were used as a source of UV-Vis irradiation: Hg lamp, metal halide lamp and sodium lamp emitted pure visible light. Tested material was prepared by solvothermal synthesis and calcinations in air atmosphere at 550 °C for 5 h. It was found that

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pyrolysis and thus removal of carbon from the hybrid C–TiO₂ structure is responsible for a remarkable lost of adsorption sites in the sample. Presented results pointed out to a better photoactivity of TiO₂–C materials than commercial TiO₂–P25 by using lamps with photons in the visible region. The adsorption shift of 412 nm corresponds to the band gap energy (E_g) of 3.00 eV that was lower than the value of E_g measured for TiO₂–P25 (3.22 eV). Value of E_g indicates that the carbon-doped TiO₂ materials are photoactive under visible light irradiation that has also been proven by kinetic results.

The improvement of photocatalytic activity of carbon-modified TiO₂ materials was also possible to observe while decomposition of Methylene Blue in the presence of carbon-modified TiO₂ nanotubes [18,19].

Although using of MB was very popular in the last year as a standard material, some authors proved that it should not be. Yan et al. [20] indicated that there are two significant problems in photocatalytic activity test. One is the inadequacy of MB as a probe molecule for semiconductor photocatalysis, since the photoinduced reaction by MB photoabsorption may mislead into believing that a given semiconductor material has visible-light photocatalytic activity. The other problem is the photoirradiation systems for activity tests.

Methylene Blue may be potential water contamination, therefore the main aim of this work it was development and evaluation of carbon-modified TiO₂ photocatalysts through using colour finding of this thiazine dye. These photocatalysts were prepared by modification of TiO₂ under elevated pressure in the atmosphere of different alcohols.

2. Materials and methods

2.1. Materials

The hydrated amorphous titanium dioxide was used as a precursor for modified catalysts preparation. TiO₂·xH₂O was supplied by Chemical Factory "Police" SA (Poland). Before modification pure TiO₂ was washing to obtained pH 7 in filtrate and then heated for 24 h at 105 °C. Different types of alcohols (methyl, ethyl, isopropyl, n-butyl, 2-butyl and tert-butyl alcohols) with high purity were used as a source of carbon (POCH Company, Poland). Aqueous solution of Methylene Blue C₁₆H₁₈N₃S (MB)–thiazine dye (λ_{max} = 664 nm, molar mass = 320 g/mol) with concentration of 5 mg/L was used as an organic compound.

2.2. Photocatalysts preparation technique

New group of carbon-modified TiO₂ photocatalysts has been prepared using modification under elevated pressure. The diagram of pressure autoclave BLH-800 (Berghof, Germany) was presented and described in details in another paper [21]. The amount of 4 g pristine TiO₂ and 5 mL of appropriate alcohol (1:1 mass ratio) were placed inside pressure reactor and heated up to programmed temperature (120 °C) for 4 h. After that time the reactor was cooled down to room temperature and prepared materials were dried at 105 °C for 24 h.

2.3. Photocatalytic activity tests

Photocatalytic activity tests were proceeded by adsorption measurements. Glass beaker with 0.2 g/L appropriate photocatalysts and 500 mL of MB solution was placed in darkroom and stirred for 1 h to secure the establishment of adsorption–desorption equilibrium. Then, 5 mL of the solution was taken and centrifuged. Concentration of residual compound was estimated using UV–Vis spectrophotometer (Jasco V-630, Japan).

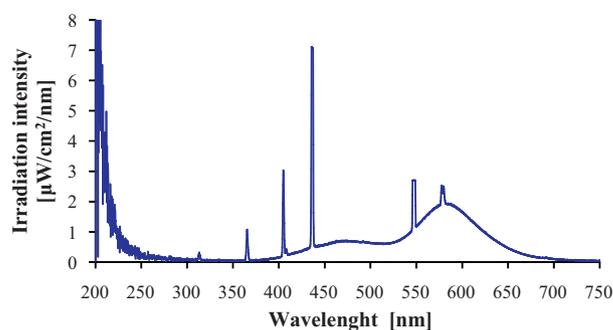


Fig. 1. Emission spectrum of artificial solar light (100W bulb, Philips).

Photocatalytic activity tests were carried out after adsorption measurements. Methylene Blue solution sample was irradiated by artificial solar light (100 W light bulb with radiation intensity of 0.2 W/m² UV and 448 W/m² Vis) for 24 h. Tests on the appointment of photoactivity were conducted at pH 7 which was the natural pH value for the prepared TiO₂/C powders. Emission spectrum of used light source in Fig. 1 is presented. The radiation intensity was measured using the radiation intensity meter LB 901 equipped with CM3 and PD204AB Cos sensors. The emission spectrum was measured by USB4000 (Ocean Optics, Netherlands) equipment. After irradiation time the concentration of MB was determined by UV–Vis spectrophotometer. The Total Organic Carbon (TOC) measurements were performed to check the mineralization rate of MB and MB co-products in solution. The TOC content was measured with Multi N/C 2000 analyzer (Analytik Jena, Germany).

2.4. Characteristic of photocatalysts

The photocatalysts were characterized by UV–Vis/DR using spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra (BaSO₄ was used as the reference). Both the spectra and band gap energy calculations (E_g) were performed using Jasco procedure described in our previous paper [22].

X-ray diffraction patterns were obtained by using with X'Pert PRO diffractometer with Cu K α radiation (λ = 1.54056 Å). Titania anatase over rutile ratio was calculated in a way described previously [23–25]. Diffuse reflectance FTIR/DRS spectra were recorded using FTIR spectrometer (Jasco, Japan) equipped with DR accessory of Harrick Company (USA). N₂ adsorption measurements at 77 K for calculation of N₂–BET SSA (the Brunauer–Emmet–Teller specific surface area) were performed using Quadrasorb SI (Quantachrome, United States) instrument. All samples were degassed in vacuum for 24 h at 80 °C prior to nitrogen adsorption–desorption measurements. The secondary particles size of tested carbon-modified TiO₂ nanoparticles was determined using Zetasizer Nano Series ZS (Malvern Instruments, United Kingdom), permitting measurements from 0.3 nm to 10 μm (Dynamic Light Scattering method). Carbon content in photocatalysts samples was measured by DTA–TG test performed on STA449 equipment (Netzsch Company, Germany) from room temperature to 1000 °C at a constant rate of 10 °C/min under air with a flow rate of 25 mL/min.

3. Results and discussion

3.1. Structure and morphology of TiO₂/C nanoparticles

Fig. 2 shows the XRD patterns of pure TiO₂ and carbon-modified TiO₂ nanomaterials. Physico-chemical properties of tested samples were presented in Table 1. Temperature of modification amounted only 120 °C but this modification was conducted under elevated

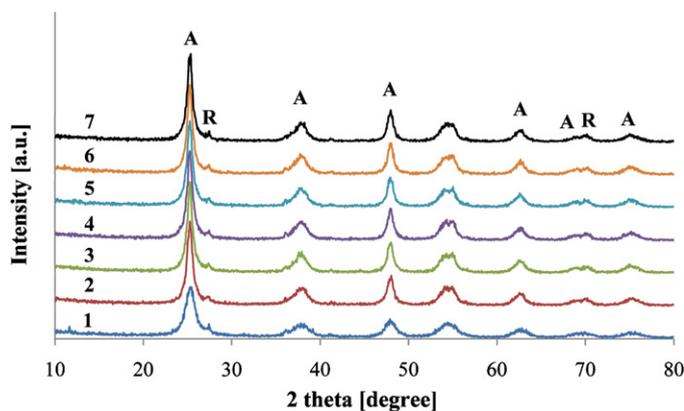


Fig. 2. XRD patterns of: (1) pure TiO₂; (2) TiO₂ modified by methanol; (3) TiO₂ modified by ethanol; (4) TiO₂ modified by isopropanol; (5) TiO₂ modified by n-butanol; (6) TiO₂ modified by 2-butanol; (7) TiO₂ modified by tert-butanol. A, anatase; R, rutile.

pressure and this condition was enough for transformation of amorphous phase to anatase structure, what is difficult to observe on the XRD pattern because of high content of anatase phase. Taking modification temperature under account transformation from anatase to rutile phase is impossible in 120 °C but as it can be seen in Table 1 the ratio of anatase to rutile changed as a result of modification. It proves the presence of amorphous phase in pure sample. The presence of amorphous phase cannot be excluded in TiO₂/C samples due to temperature conditions on which modification was carried out. "Police" S.A. Company confirmed the presence of amorphous phase in unmodified sample. It was also noted that anatase crystallite size increased (9 nm vs. 16 nm). Yun et al. [15] reported that carbon presence always influences the degree of crystallinity which has a bearing on the photocatalytic sites and hence the activity. Furthermore, the secondary particle size that should be considered as the size of agglomerates, decreased in all of cases. However, this change did not affect significantly the change of surface area. If we take into account the carbon content in the obtained samples, it is possible to observe that during TiO₂ modification using butyl alcohols the carbon content decreases with bond order of alcohols. It should be understood the more branched chain of alcohol the less carbon in the sample.

3.2. UV-Vis diffuse reflectance spectra

In Fig. 3 the UV-Vis/DR spectra of pristine TiO₂ and carbon-modified TiO₂ photocatalysts are presented. In general, modification of pure titania by carbon does not lead to significant changes in the energy band gap (3.36 eV for pure TiO₂ to 3.33 eV for titania powder modified by n-butyl alcohol). In addition, there was no clear shift of the absorption spectrum toward visible region. However, it is worth mentioning that the change in the character of absorption spectra were induced colour change after the modification process. As it can be observed in Fig. 3, the most reduced spectra

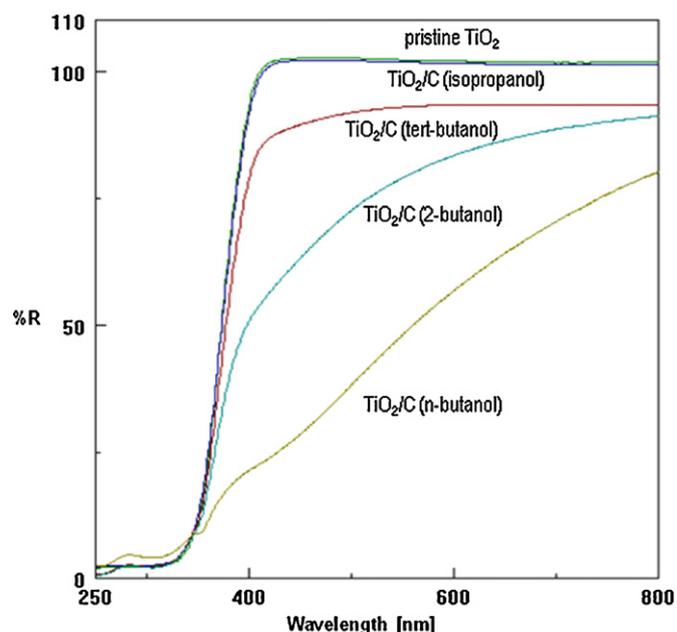


Fig. 3. UV-Vis diffuse reflectance spectra obtained for pure TiO₂ and TiO₂/C nanoparticles.

were obtained for the powder which contained the higher amount of carbon (0.9% mass) and had the darkest colour. In is possible to say that the character of UV-Vis/DR spectrum were dependent on the carbon content in the samples. In case of materials modified by methanol, ethanol and isopropanol colour of powders does not change in comparison to starting TiO₂. On this basis, it was possible to believe that these materials contain much less carbon than photocatalysts modified by butyl alcohols what was confirmed by thermogravimetric determination of carbon content.

3.3. Fourier transformation infrared diffuse reflectance analysis

In order to make the surface characteristics of obtained TiO₂ powders the FTIR measurements were performed. As it can be seen in Fig. 4 for a pristine TiO₂ and a sample modified by isopropyl alcohol (but also methyl and ethyl alcohol) did not confirm the carbon presence of the surface of prepared nanomaterials. Thermogravimetric analyses shown that the amount of carbon in the photocatalysts is very low and this is the reason that it is impossible to see carbon groups on FTIR/DRS spectra. A FTIR spectra of photocatalyst modified by isopropanol and n-butanol have been taken as an examples. It is possible to observe the intensity decrease of the bands associated with -OH vibrations (3300–3500 cm⁻¹) assigned to the dissociated and molecularly adsorbed water and -OH groups at 1630–1640 cm⁻¹ assigned for molecular water. The surface character of tested TiO₂ samples was changed from hydrophilic to hydrophobic by reduction the hydroxyl groups and appearance the -CH₃ groups (3100–2800 cm⁻¹) [29,30].

Table 1
Physico-chemical properties of starting and carbon-modified TiO₂.

Sample	Specific surface area S _{BET} [m ² /g]	Crystallite size of anatase PPS [nm]	Secondary particle size SPS [nm]	Carbon content [% mass]
Pristine TiO ₂	222	9	248	0.00
TiO ₂ /C (methanol)	213	16	230	0.07
TiO ₂ /C (ethanol)	247	16	213	0.08
TiO ₂ /C (isopropanol)	227	15	198	0.02
TiO ₂ /C (n-butanol)	200	16	223	0.90
TiO ₂ /C (2-butanol)	210	16	220	0.50
TiO ₂ /C (tert-butanol)	238	16	214	0.27

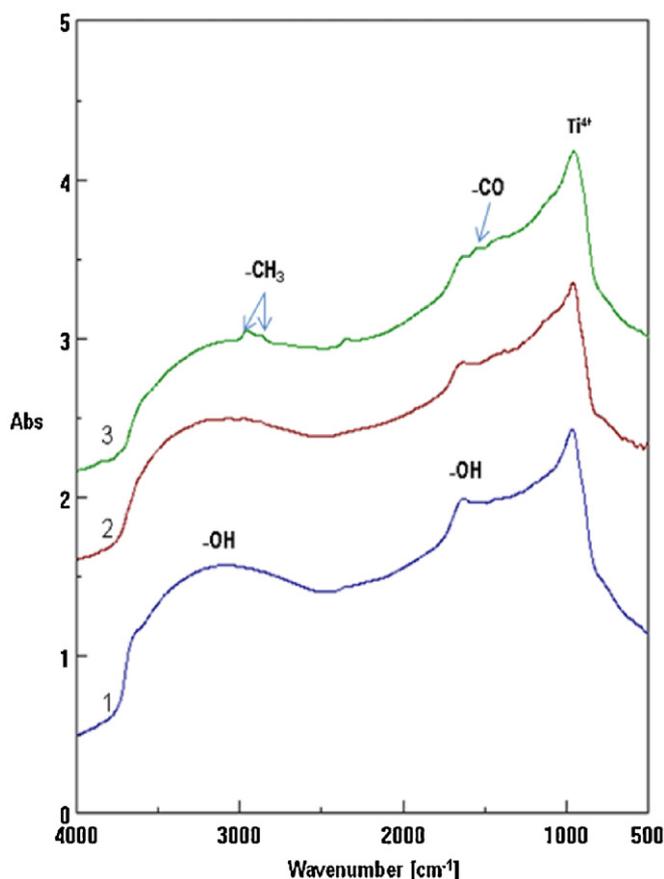


Fig. 4. FTIR spectra of illustrative TiO_2 nanoparticles: (1) pure TiO_2 ; (2) TiO_2/C (isopropanol); (3) TiO_2/C (n-butanol).

3.4. Adsorption of Methylene Blue

In many papers there was postulated that modification of titania by carbon improves the adsorption capacity of tested materials [22,26–28] and that comprises the crucial step of the photocatalysis. Adsorption properties of TiO_2/C powders are shown in Fig. 5 in relation to their photocatalytic activity. It was found that most of adsorption occurred within 60 min. After 24 h exposure it was possible to observe no dye adsorbed on the surface of powders obtained by modification of pure titania by methyl, ethyl and isopropyl alcohols and very light blue colour of the surface of materials modified by butyl alcohols. In both cases the solution colour was still bluish. It means MB adsorbed on the surface of photocatalyst was degraded

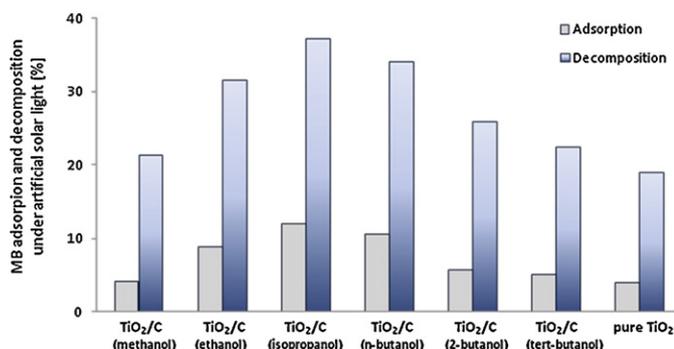


Fig. 5. Comparison of adsorption and decomposition rate of Methylene Blue in the presence of pure and carbon-modified TiO_2 powders.

and the concentration of MB in solution decreased (fades of solution colour). It can be noticed that after modification of pure TiO_2 by carbon adsorption capacity of new materials increased. It should be mentioned that this increasing was negligible in case of use of methyl, 2-butyl and tert-butyl alcohol. In contrast, the use of primary alcohol from the group of butyl alcohols resulted almost threefold increase of the adsorption. The increase in the adsorption abilities in this case is not due to change of surface area but appearance of hydrophobic group CH_3 on the surface in the case of modification by butyl alcohols. MB is a dye with hydrophilic character. The more hydrophobic groups on the surface of tested powders the higher adsorption of MB molecules on the surface. It was proved that the more complicated structure of butyl alcohol the less content of carbon in the sample and the less amount of CH_3 groups on the surface of TiO_2/C nanopowders. The unique adsorptive property of prepared nanomaterials should be related to their special surface properties resulted from the uniform carbon deposition.

3.5. Photodegradation of Methylene Blue under UV-Vis irradiation

Photodegradation of Methylene Blue (MB) in the presence of carbon-modified TiO_2 nanocatalysts was tested under artificial solar light. After 24 h exposure blue colour of MB solution was still possible to observe but the intensity of colour was lower. It may mean that the concentration of MB in solution decreased but it was not only solution decolorization but also photodegradation. This research was supported by TOC measurements. For pure TiO_2 mineralization rate was 12.0% and for carbon-modified powders it was 17.9% (TiO_2/C -methanol), 27.8% (TiO_2/C -ethanol), 32.6% (TiO_2/C -isopropanol), 30.4% (TiO_2/C -n-butanol), 21.7% (TiO_2/C -2-butanol), 19.1% (TiO_2/C -tert-butanol). As mentioned above, the results of the MB distribution are shown in Fig. 5. The degradation rate was determined based on the equation:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of MB after dark adsorption [mg/l] and C_e is the concentration of MB after 24 h of UV-Vis irradiation [mg/l].

As it can be seen the highest degree of MB decomposition was obtained when TiO_2/C modified by isopropanol was used as a source of carbon. The photocatalytic activity was correlated with the adsorption abilities of tested materials what was considered in each case. Degree of MB decomposition under artificial light with reference to starting TiO_2 powder increased almost twice. It is reasonable to speculate that in the case of tested materials significantly effect for photocatalytic decomposition of MB should be attributed not only to carbon content but also to adsorption properties. It is also worth mentioning that during the modification of pure TiO_2 by butyl alcohols it was possible to observe the declining decomposition rate of MB together with bond order of used alcohols and carbon content in tested samples. It was noticed that carbon content is strictly connected with the bond order of used alcohols. The carbon content in tested samples increases due to use straight chain alcohols (methanol, ethanol, n-butanol).

4. Conclusion

Photodegradation of Methylene Blue in the presence of carbon-modified TiO_2 nanoparticles under artificial solar light was studied. TiO_2/C powders were obtained under elevated pressure at 120°C for 4 h. Several types of alcohols with different bond order were used as a source of carbon. The most active photocatalyst toward MB degradation was found to be TiO_2/C modified by isopropanol because of the highest adsorption rate prior degradation. The

increase in the adsorption abilities was not due to change of surface area. Nevertheless, that improvement of photocatalytic activity of new nanomaterials cannot be attributed only to the adsorption effect. Activation effect of carbon should be also taken into account what was proved in the case of photocatalysts modified by butyl alcohols. The photocatalytic activity of those materials depends on both carbon content and adsorption capacity. The usage of branched chain alcohols caused the modification of smaller amount of carbon in photocatalysts samples.

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