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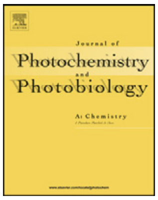

Methylene Blue decomposition under visible light irradiation in the presence of carbon-modified TiO_2 photocatalysts

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ABSTRACT

Carbon modified TiO_2 was used for Methylene Blue (MB) dye decomposition under artificial solar light irradiation. TiO_2/C photocatalysts were prepared by modification of commercial anatase TiO_2 (Z.Ch. POLICE Company, Poland) in different alcohols atmosphere at 120 °C for 4 h under elevated pressure. Termogravimetric analyses shown that the amount of carbon present in TiO_2 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 amounted of carbon needed to increasing the activity of photocatalyst under visible light irradiation amounted 0.02% of mass.

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 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 lattice. Orth-Gerber et al. [6] discovered that during the calcination at 400 °C of prepared N-doped TiO_2 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 TiO_2 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 CO_2 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 CO_2 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 TiO_2–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 TiO_2 in flowing N_2. In this case was also confirmed that carbon covering of TiO_2 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 TiO_2 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 TiO_2 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–TiO_2 structure is responsible for a remarkable lost of adsorption sites in the sample. Presented results pointed out to a better photoactivity of TiO_2–C materials than commercial TiO_2–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 TiO_2–P25 (3.22 eV). Value of E_g indicates that the carbon-doped TiO_2 materials are photoactive under visible light irradiation that has also been proven by kinetic results.

The improvement of photocatalytic activity of carbon-modified TiO_2 materials was also possible to observe while decomposition of Methylene Blue in the presence of carbon-modified TiO_2 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 inadequancy 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 TiO_2 photocatalysts through using colour finding of this thiazine dye. These photocatalysts were prepared by modification of TiO_2 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. $TiO_2 \cdot xH_2O$ was supplied by Chemical Factory "Police" SA (Poland). Before modification pure TiO_2 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 $C_{16}H_{18}N_3S$ (MB)–thiazine dye ($\lambda_{max} = 664$ 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 TiO_2 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 TiO_2 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).

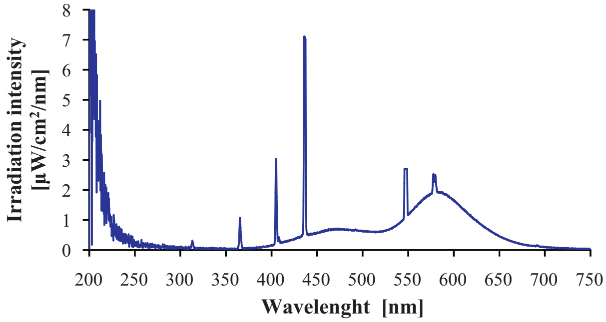

Fig. 1. Emission spectrum of artificial solar light (100 W bulb, Philips).

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/m^2 UV and 448 W/m^2 Vis) for 24 h. Tests on the appointment of photoactivity were conducted at pH 7 which was the natural pH value for the prepared TiO_2/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 ($BaSO_4$ 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 Kα radiation ($\lambda = 1.54056$ 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). N_2 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 TiO_2 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 TiO_2/C nanoparticles

Fig. 2 shows the XRD patterns of pure TiO_2 and carbon-modified TiO_2 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