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TiO_2 Nanoparticles with High Photocatalytic Activity Under Visible Light

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Abstract TiO_2 nanoparticles (C-TNT) with high visible light activity were obtained by carbonization of titania nanotubes (TNT) in an ethanol atmosphere under elevated pressure at 180 and 220 °C. New material was characterised by means of UV–Vis/DR, FTIR/DRS, TEM, and XRD. The photocatalytic activity was tested during monoazo dye decomposition under artificial solar light irradiation. Modified photocatalyst (220 °C, 4 h) had higher photocatalytic activity than both the pristine and commercial P25 catalysts.

Keywords Titania nanotubes · Dye decomposition · Elevated pressure

1 Introduction

Recently researchers have been trying to find new photocatalysts active not only under UV light irradiation but also under visible light. To reach this goal modifications of TiO_2 by doping of metals and non-metals have been extensively performed and reported [1–5]. Recently a new way of making active photocatalysts under visible light is carbon doping. Sakthivel and Kisch [6] obtained carbon modified titanium dioxide by hydrolyzed titanium tetrachloride with tetrabutylammonium hydroxide. At the subsequent calcination step they observed that owing to prolonged heating at 400 °C they managed to obtain an anatase material which contained carbon. Shen et al. [7] prepared vis-active carbon doped TiO_2 by mild oxidation of titanium carbide (TiC), and tested it for trichloroacetic acid photodegradation. Park et al. [8] reported the preparation of vertically grown carbon doped TiO_2 ($TiO_{2-x}C_x$) nanotubes arrays. These modified materials showed much higher photocurrent density and more efficient water splitting under visible light illumination (>420 nm) than pure TiO_2 nanotubes arrays. Choi et al. [9] prepared C-doped TiO_2 photocatalyst by high-temperature oxidation of TiC powders at 623–1073 K in air. C-doping into TiO_2 enhances photon-to-carrier conversion efficiency, which leads to an improvement of photocatalytic activity. Hamal and Klabunde [10] prepared new Ag(C,S)-TiO_2 nanoparticle photocatalysts by mixing titanium(IV) isopropoxide, ammonium thiocyanate or thiourea, ammonium water and $AgNO_3$ solution. The mixture was then calcinated at 500 °C for 2 h in air. The new nanoparticle photocatalysts degrade the gaseous acetaldehyde 10 and 3 times faster than P25-TiO_2 under visible and UV light, respectively. High visible light activity of nanoparticle photocatalysts is predominantly attributed to an improvement in anatase crystallinity, high surface area, low band gap and effect of precursor materials. Janus et al. [11–13] obtained vis-active photocatalysts by carbonisation of TiO_2 in organic precursor atmosphere under atmospheric and elevated pressure.

In this paper a novel method for carbon doping into TiO_2 nanotubes is presented.

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2 Experimental

Titania nanotubes (TNT) were prepared by the method of Kasuga et al. [14]. The modification was conducted under elevated pressure at 180 and 220 °C for 4 h in an ethanol atmosphere by the method of Janus and Morawski [15]. 4 g of TNT and 5 mL of ethanol were placed in a pressure reactor (BLH-800, BERGHOF, Germany). The reactor was closed and heated up to 180 and 220 °C for 1 h, after that the mixture was kept in this temperature for 4 h at the pressure 10 and 12 bar pressure, respectively. After heating the reactor was cooling slowly to the room temperature, then the catalyst was dried at 105 °C for 24 h.

The photocatalysts were characterized with UV–VIS/DR using spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra ($BaSO_4$ was used as a reference). Both, spectra and band gap energy calculation (E_G) were performed by Jasco procedure according to the equation:

$$E_G = \frac{h \cdot c}{\lambda}$$

where E_G is the band gap energy (eV), h the Planck's constant, c the light velocity (m/s) and λ is the wavelength (nm) [16].

Diffuse reflectance FTIR/DRS spectra were recorded by using FTIR spectrometer (Jasco, Japan) equipped with DR accessory of Harrick Company (USA).

Photocatalytic activity of photocatalysts was tested during monoazo dye decomposition (Reactive Red $\lambda_{max} = 516$ nm) under artificial solar light irradiation (radiation intensity was about 354 W/m^2 Vis and 0.25 W/m^2 UV, light bulk, Philips, Fig. 1a). Radiation intensity of natural solar light is about 8 and 0.25 W/m^2, emission spectrum in Fig. 1b) is presented. Photochemical decolourisation of dye (Reactive Red–mon oazo dye) in the absence of TiO_2 doesn't occur.

Photocatalytic decomposition of azo dye was carried out in a batch type reactor, 0.1 g of photocatalyst was added to 500 mL of aqueous dye solution with concentration of 5 mg/L. The dyes' solution was mixed with a magnetic stirrer during the reaction. Firstly, the solution mixture was stirred for 15 min without irradiation in order to get the equilibrium of dye adsorption, and then the solution was irradiated for 5 h under artificial solar light irradiation. To determine the concentration of the dye, the reaction mixture was centrifuged and the solution was loaded in a UV–Vis spectrometer (Jasco, Japan). The dye concentration in the solution was calculated by means of a computer program based on the calibration curve.

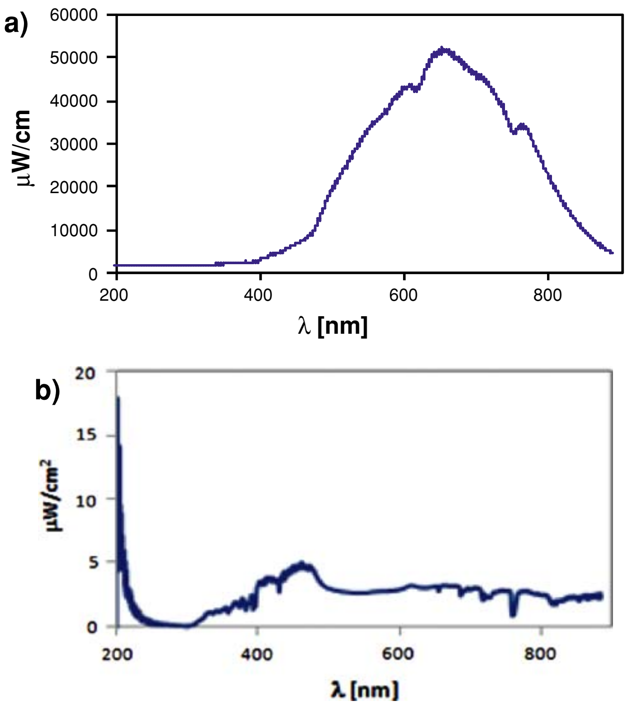

Fig. 1 Emission spectra of **a** light bulk (100 W, Philips) **b** solar light

3 Results and Discussion

The modification of TNT (nanotubes) at 180 and 220 °C for 4 h under elevated pressure (10 and 12 bar) resulted in changes in TNT structure—nanotubes turned into nanoparticles. In Fig. 2 TEM micrographs of modified and unmodified TNT are presented. After modification the obtained nanoparticles had about 15 nm in size. In Fig. 3 XRD diffraction pattern of photocatalysts are presented. Modification of TNT by carbon doping led to an appearance of a well crystallized anatase with a small amount of rutile (12%). Before modification anatase structure was also present. In Fig. 4 FTIR/DRS spectra of modified and unmodified nanotubes are shown. Some bands can be observed: at 3695 cm^{-1}, assigned to the stretching of a hydroxyl group that was chemisorbed on a surface defect site, 3300 cm^{-1}, assigned to hydroxyl for both dissociated water and molecularly adsorbed water which decreased with temperature treatment; and 1623 cm^{-1}, pertaining to H–O–H bending for a molecular water [17]. As it is possible to observe the modified TNT has new carbon bonds on TiO_2 surface in 1517–1419 and 3010–2860 cm^{-1} regions (methyl groups) and at 1440 cm^{-1} (CO groups), the intensity of the hydroxyl groups did not change after modification. The intensity of Ti–O bands (with max ca. 900 cm^{-1}) [18] insignificantly increased. The amount of carbon groups increased while the modification temperature was also increasing.

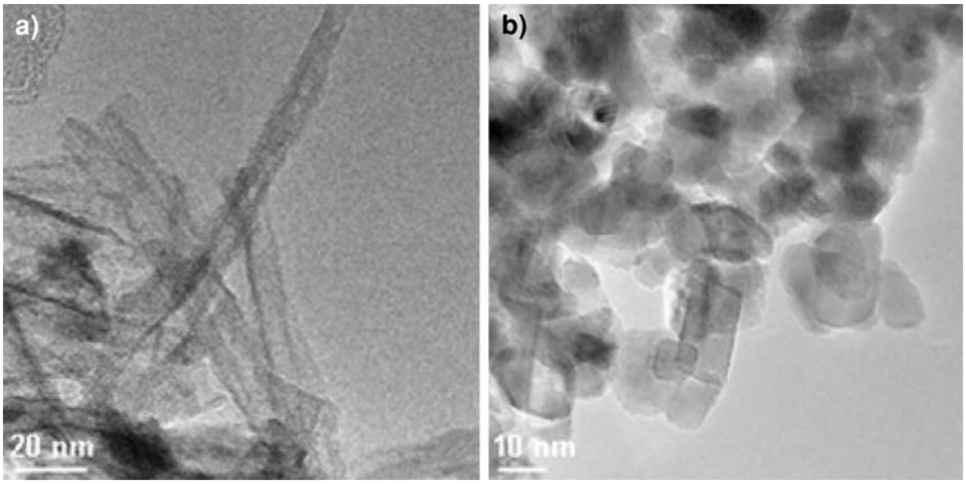

Fig. 2 TEM images of **a** pure TNT and **b** carbon modified TNT (220 °C, 4 h)

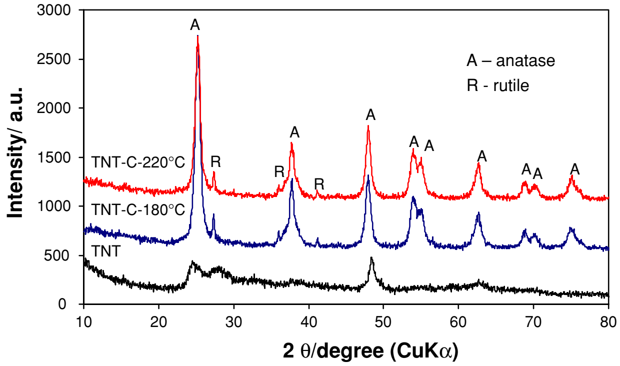

Fig. 3 XRD spectra of pure TNT and carbon modified TNT at 180 (TNT-C-180 °C) and 220 °C (TNT-C-220 °C)

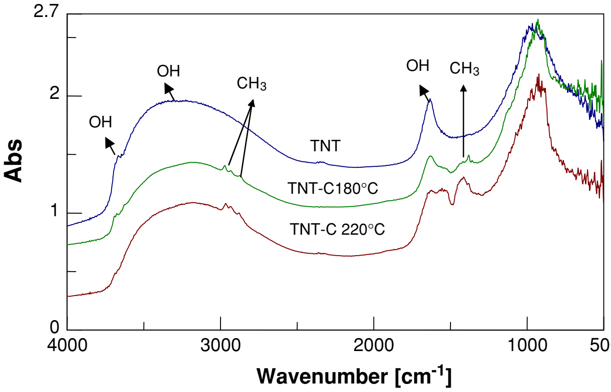

Fig. 4 FTIR/DRS spectra of carbon modified and unmodified TNT

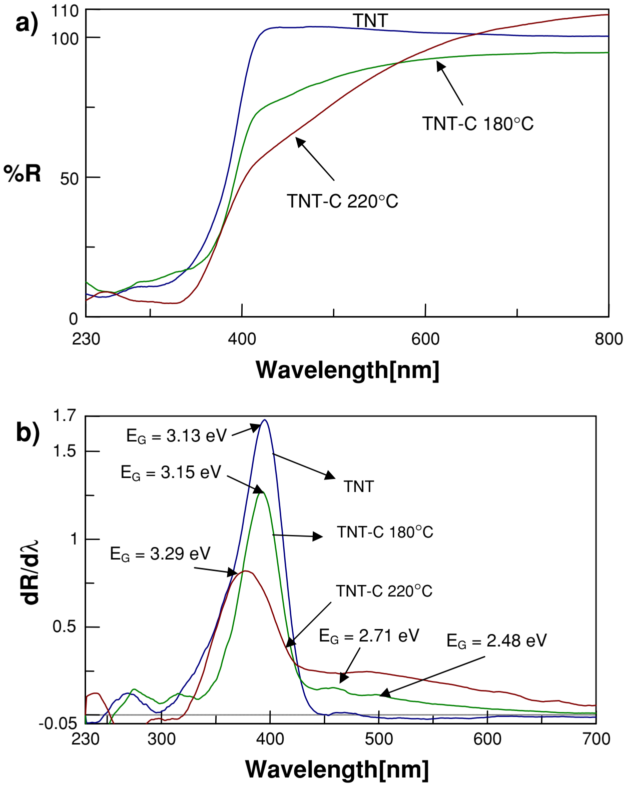

Fig. 5 **a** UV–Vis/DR spectra and **b** first derivative of UV–Vis/DR spectra of carbon modified and unmodified TNT

In Fig. 5a the UV–Vis/DR spectra are presented. Modification conducted to shift the spectrum into the visible region. On the UV–Vis/DR spectra of carbon doped TNT a new peak in the visible region appeared, which can correspond to their photocatalytic activity under visible light irradiation (band gap energy $E_G = 2.71$ eV; $E_G = 2.48$ eV (Fig. 5b). The photocatalytic activities of modified and unmodified TNT were tested during mono azo dye decomposition. In Fig. 5 the percentage of dye decomposition after 5 h of artificial solar light irradiation is presented. Pure TNT decomposed only 16.1% of the dye but carbon modified TNT at 220 °C decomposed the dye completely after 5 h of irradiation. For comparison purposes, commercial TiO_2 (P25, Degussa, Germany, mixture of 25% anatase and 75% rutile) decomposed the mono azo dye completely after 5.5 h of irradiation. Photocatalysts prepared only by thermal treatment had not higher photocatalytic activity, dye decomposition amounted 15.1% for titania nanotubes modified at 180 °C and 14.6% for titania nanotubes modified at 220 °C.

4 Conclusion

Carbon modification of TNT under elevated pressure leads to changes in the structure of the material and transformation of TiO_2 from nanotubes to nanoparticles with the size of about 15 nm. The obtained carbon doped materials revealed much higher photocatalytic activity than pure TNT under artificial solar light irradiation. TNT modified at 220 °C decomposed 100% of the dyes after 5 h of irradiation while commercial P25 decomposed the dye after 5.5 h of irradiation Fig. 6.

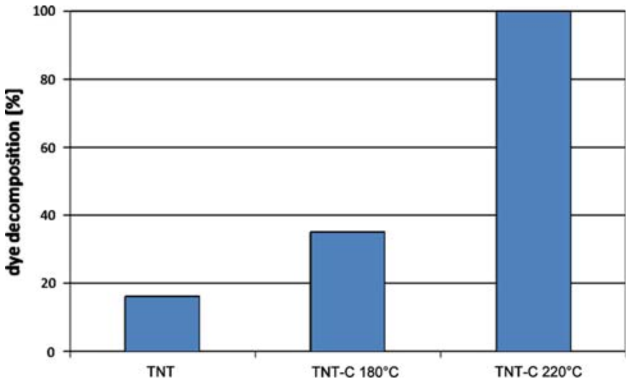

Fig. 6 Percentage of dye decomposition after 5 h of artificial solar light irradiation. Dye concentration = 5 mg/L, amount of photocatalyst = 0.2 g/L

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