

C- and N-Doped TiO₂: Visible Light Photocatalysis and EPR Investigation

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One of the principal problems for practical application of TiO₂ in photoelectrochemistry and photocatalysis is the enlarging of its light-absorption area to the wavelengths of the visible light. TiO₂ particles surface and volume doped with transition metal ions [1] or nonmetallic elements such as carbon, nitrogen and sulfur [2, 3], photocatalyzed complete visible light mineralization of various pollutants in water and air (Fig.1). Experimental and theoretical results indicated that these dopants generate localized energy levels (surface states) just above the valence band from which visible light excitation becomes feasible [2, 3]. Due to these intra-bandgap states the C- and N-doped titania exhibits a weak light absorption starting at about 550-700 nm. C-doped materials contained 0.4 – 4.0 % carbon in the form of elemental carbon and also carbonate, as was indicated by X-ray photoelectron spectra (XPS) [4]. To characterize these C- and N-doped materials in more detail and to obtain information on the nature of the carbon and nitrogen dopants in such systems, we investigated them by EPR method, which allows detection and characterization of paramagnetic defects, which may be of significant importance for understanding the mechanism of photocatalytic processes [5].

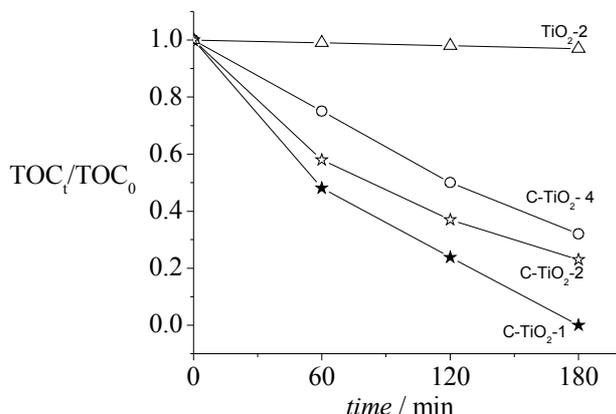


Fig. 1. The visible light $\lambda \geq 455$ nm activity of various TiO₂ based photocatalysts in 4-chlorophenol mineralization process at room temperature. C-TiO₂-1 and C-TiO₂-4 are the bulk-modified materials, while C-TiO₂-2 and C-TiO₂-3 are the surface modified samples. TOC₀ = 16 mg/L. [4-CPh]₀ = 2.5 · 10⁻⁴ mol/L; Similar behaviour has been observed also for N-doped TiO₂.

The bulk modified material C-TiO₂-1 is the most active one, although the difference to the surface modified sample C-TiO₂-2 is less than to the other bulk modified C-TiO₂-4. TiO₂-1 was self prepared through hydrolysis of TiCl₄, whereas TiO₂-2 and TiO₂-3 were commercial products from KerrMcGee Pigments GmbH and Kronos. Bulk modified materials C-TiO₂-1 and C-TiO₂-4 contain 0.42 and 1.48 wt % carbon. The surface modified C-TiO₂-2 contains 1.05 wt % carbon. N-doped TiO₂ samples contained 0.08-0.13 wt % of nitrogen. EPR spectra were detected by a standard X-band Bruker EPR spectrometer. Illumination of the powders was carried out in quartz tubes, air was pumped off at 5 · 10⁻⁶ Torr (30 min), then tubes were filled with He gas and sealed. The samples were illuminated *in situ* at 77 or 5 K with a 100 W tungsten halogen lamp in the spectral range of 400-1000 nm and with a 250 W high-pressure mercury lamp in the case of monochromatic irradiation at 578 and 365 nm.

In the paper we will report the experimental results on visible light photocatalysis in the presence of C-doped and N-doped TiO₂, changes in the EPR spectra of surface- and volume-doped samples both in dark and under illumination at different wavelengths. Kinetics of the

processes, the nature of defects, their dynamics under illumination and possible mechanisms will be discussed, as well as a correlation between the content of paramagnetic C- and N-centered species, and visible light photocatalytic activity of the samples.

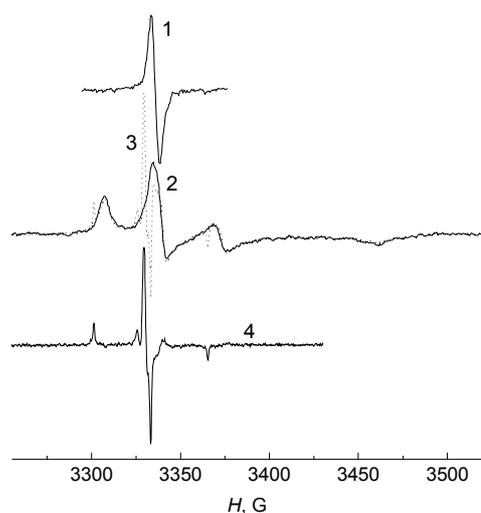


Fig. 2. EPR- spectra of the surface C-doped sample after 20 min illumination ($\lambda = 578$ nm) at 77 K (1); of N-doped samples before (2) and after 15 min illumination ($\lambda \geq 400$ nm) at 5 K (3). 4 is a spectrum obtained by subtraction of (2) from (3). (2) are NO^\bullet radicals, (4) are NO_2^{2-} radicals.

C- and N-doped TiO_2 samples have noticeably higher photocatalytic activity in gas- phase and liquid-phase photo-oxidation of different toxic organics under illumination by visible light than pure TiO_2 catalysts because of changing the photo-absorption properties. The visible light action can be connected with the

presence of CO_2^- -radicals, as well as with carbon defects (dangling bonds) on the surface of TiO_2 particles. Additional energy levels of both interstitial carbon atoms or surface defects (carbon particles) should be located in the band gap of TiO_2 , as it was shown for titania doped with metal nanoparticles of Cu, Pd, Pt and Ag [6], when doping of TiO_2 led to formation of electronic surface states in semiconductor band gap. Such additional levels created by dopants can absorb visible light, increasing photosensitivity of the C- and N-doped TiO_2 and their photocatalytic activity.

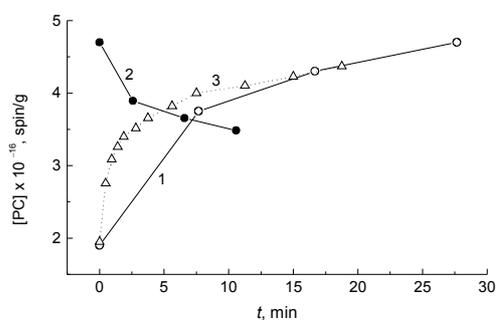


Fig. 3. Content of paramagnetic centers under illumination: at 578 nm (1), 365 nm (3) and the signal decay in the dark (2) for the C- TiO_2 -2 sample at 77 K.

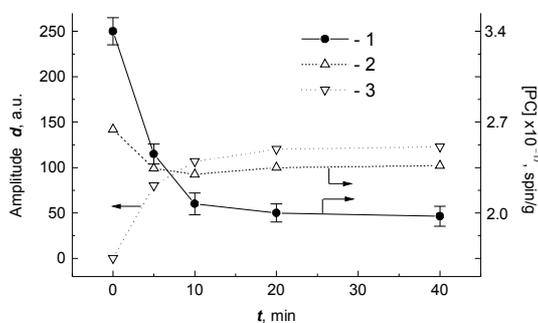


Fig. 4. Content of NO^\bullet centers (1, 2) under illumination with 578 nm (1) and 365 nm (2). 3 – the amplitude of the central line d of NO_2^{2-} centers.

T = 77 K.

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