

Effect of the C and S additives on structural, optical and photocatalytic properties of TiO₂

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Nanoscale composite materials based on titanium dioxide, carbon [1] and sulphur were obtained. Analysis of SEM-images of the samples shows that they consist of roundish agglomerates about 1–3 microns in size. Investigation of the obtained powders by means of energy-dispersive spectroscopy based on energy-dispersive technique proves that these materials include the elements Ti, O, and S, no unexpected elements being detected. X-ray analysis revealed the phase of anatase in all the composites, a peak characteristic of rutile appearing at maximum amounts of sulphur in the powder. Size of crystallites in composite agglomerates lessens as compared with pure titanium dioxide (14 nm) and is equal to 6–9 nm, this is supported by studies using TEM. Interplanar distance equals to 0.351–0.351.

Analysis of nitrogen sorption–desorption isotherms for the synthesized samples showed the presence of a hysteresis loop which is the evidence for mesoporous structure of the powders. The isotherms correspond to type IV of IUPAC classification for mesoporous materials with H1 type of hysteresis loop. Predominance of pores up to 6 nm is characteristic of composite samples. Specific surface of composites increases in comparison with pure titanium dioxide more than 4 times. It was established, that increasing of sulphur amount in composites leads to increasing of specific surface area from 80 to 133 m²/g, a radius and pore volume decreasing.

Absorption spectra of nanocomposites showed a bathochromic shift as compared with the absorption band of pure TiO₂. It was found that modification of this semiconductor with carbon and sulphur leads to band gap narrowing of composites (from 3.39 for pure TiO₂ to 3.22 for composites), similar to dioxide titanium powder modified with carbon only [2].

Vibrational spectra of the powders contain bands around 3300 cm⁻¹ (surface-adsorbed H₂O), 2340 cm⁻¹ (carbon dioxide, physically adsorbed on the surface), 1630 cm⁻¹ (deformational bonds in adsorbed water), 910–1100 cm⁻¹ (Ti–O bonds) and around 500–900 cm⁻¹ (Ti–O–Ti stretching vibration).

Nanocomposite samples showed higher photocatalytic activity in the destruction of organic dye safranin T under UV irradiation compared to pure titanium dioxide. It may be connected with the participation of carbon in the inhibition of electron–hole recombination [3], prolongation of charges lifetime, increasing of efficiency of interfacial charge separation from TiO₂ to carbon, and formation of doping electronic states. The rate constants of photocatalytic reactions increase as the amount of adsorbed substrate increases. This fact points out that adsorbed molecules react first. So, these composites are the perspective materials for water purification from organic compounds.

1. Patent UA 109548. Trychlib V.A. Strelko V.V. A method for producing of micro-, mesoporous carbon adsorbents. 2016.
2. Bondarenko M.V., Khalyavka T.A., Camyshan S.V., Petrik I.S. Photocatalytic properties of titanium dioxide modified with carbon under UV and VIS irradiation // *Chemistry, Physics and Technology of Surface*. – 2016. – Vo. 7, № 4. – P. 432-438.
3. X.F. Lei, X.X. Xue, H. Yang, C. Chen, X. Li, J.X. Pei, M.C. Niu, Y.T. Yang, X.Y. Gao Visible light-responded C, N and S co-doped anatase TiO₂ for photocatalytic reduction of Cr(VI) // *Journal of Alloys and Compounds* 646 (2015) 541-549.