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Co-doping of titanium dioxide for photocatalysis

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The dispersed, photocatalytic, and optical properties of TiO₂ nanoparticles doped with sulfur and tin have been studied. The dependence of the TiO₂ band gap on the content of dopants has been determined. It is shown that the simultaneous doping of titanium dioxide with tin and sulfur increases the photocatalytic activity of the material compared to that of undoped material, and the band gap decreases to 2.98 eV, which is 0.13 eV less than in the case of doping with tin alone.

Keywords: titanium dioxide nanoparticles, structural and optical properties, co-doping.

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Titanium dioxide (TiO₂) is widely used in developing gas sensors, photoelectrodes, solar elements, photocatalysts for reactions of decomposing a wide range of organic and inorganic substances (phenols, pesticides, toxins, etc.) [1–3]. For photocatalysis, most demanded are large-surface-area TiO₂-based materials in the form of nanopowders and nanoporous structures. This is first of all connected with an increase in the area of the photocatalyst surface just where chemical reactions proceed. The role of the surface is also associated with changes in the electronic subsystem of the material [4–6]. Generally, nanostructured materials possess specific thermal, electrical, optical and magnetic properties [7–10].

One of the main problems in improving efficiency of such photoactive materials as titanium dioxide is the necessity of extending the spectral range of their sensitivity without degrading other parameters. The titanium dioxide spectral range can be extended by doping with metal and nonmetal atoms. It is known that activity of co-doped samples is higher than in case appropriate dopants are introduced separately [11]. The increase in activity of the doped titanium dioxide samples in the visible electromagnetic spectrum range is explained by formation of extra energy levels inside the semiconductor band gap, which are associated with doping elements and internal defects (oxygen vacancies, interstitial titanium ions); this results in an apparent narrowing of the band gap [12,13]. Doping of the titanium dioxide can promote occurrence of photocatalytic reactions due to enhancement of separation of photogenerated electrons and holes. However, doping with metal ions can also promote enhancement of the charge-carriers recombination and reduction of the total photocatalytic efficiency [14,15]. Being added to the TiO₂ photocatalyst, tin cations make narrower the band gap and improve the charge-carriers separation; introduction of sulfur anions additionally shifts upward the valence band edge and enhances the photocatalytic activity in the visible

range of the radiation spectrum. This work is devoted to studying the effect of doping the nanostructured titanium dioxide with tin and sulfur simultaneously. In the experiments, commercially available titanium dioxide nanopowder Degussa P25 with the particle size below 50 nm was used. Doping with tin and sulfur was performed by mechanically mixing titanium dioxide with tin sulfate (SnSO₄) at the Sn concentrations of 1, 2, 3, 4, 5 at.%. When the doping metal content is higher, its particles essentially cover the surface and thus reduce the photocatalyst efficiency. The resulting mixture was annealed at 400°C in electric furnace SNOL 8.2/1100 for 18 h. The obtained sample was rinsed in distilled water, centrifuged, and dried in an oven at 105°C for 2 h.

Photocatalytic activity of the doped TiO₂ was investigated using a model organic pollutant, namely, methylene blue (MB). In our work, a conventional batch reactor equipped with a source of visible-range radiation (lamp Philips TL-D 18W/54-765 with a light filter for 400–746 nm) was used. The MB concentration in the solution was determined by the photometric method using spectrophotometer Shimadzu UV-2600. The photocatalyst was pre-dispersed for 10 min in the MB solution of interest by using an ultrasonic bath. At the first stage, sorption equilibrium was established (by keeping in a dark box for 30 min); then the radiation source was switched on in order to perform the photocatalysis, and the MB concentration was detected every 30 min.

Morphology and size of the sample nanoparticles were determined using scanning electron microscope Mira-3 Tescan. Microphotographs of the initial powder P25 and doped titanium dioxide are presented in Fig. 1; one can clearly see that the particle size is below 50 nm in all the samples.

The content of elements in the samples was determined energy dispersive X-ray fluorescence spectroscopy (Shimadzu EDX-8000). For this purpose, the powders were pressed into pellets whose spectra were

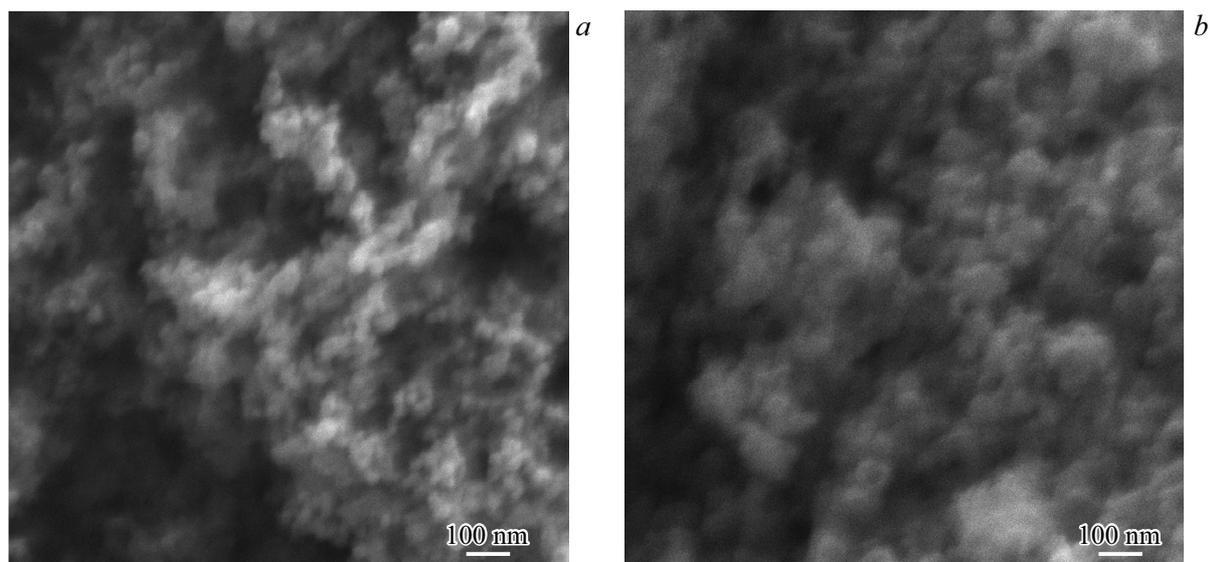


Figure 1. Microphotographs of titanium dioxide: *a* — commercial P25, *b* —commercial P25 doped with tin and sulfur (5 at.% of Sn).

Mass percentages of elements in the samples (in wt.%)

Element	TiO ₂ samples with different dopant contents				
	1 at.% of Sn	2 at.% of Sn	3 at.% of Sn	4 at.% of Sn	5 at.% of Sn
Ti	49.93	51.18	51.30	53.89	53.36
O	45.07	42.12	39.70	35.33	33.64
Sn	4.63	6.26	8.49	10.19	12.32
S	0.37	0.44	0.51	0.59	0.68

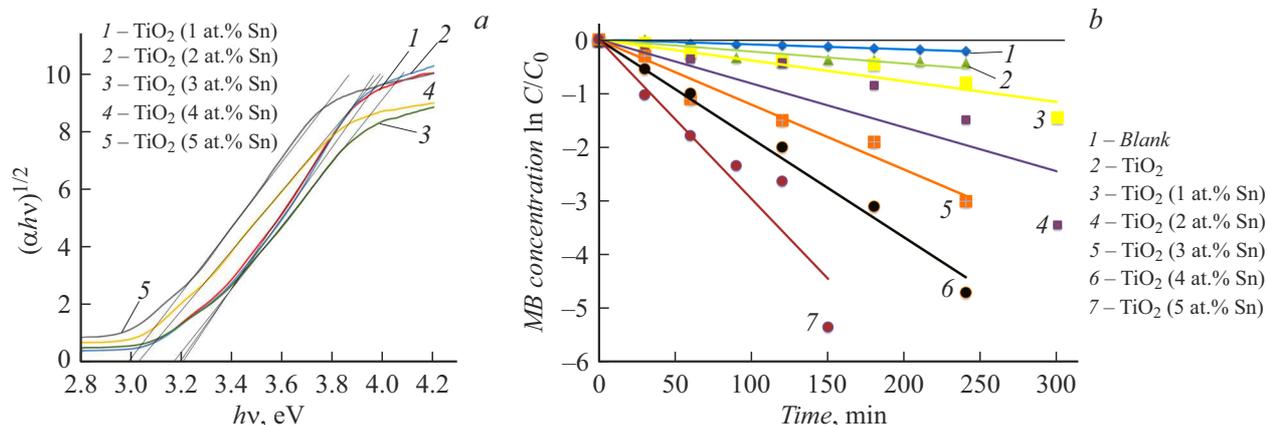


Figure 2. Diffuse-reflection spectra in the Tauc coordinates (*a*) and kinetics of methylene blue (MB) photocatalytic decomposition under the action of lamp Philips TL-D 18W/54-765 with a light filter for 400–746 nm (*b*).

measured in vacuum. The Table presents the results of determining the sample compositions.

The diffuse-reflection spectra of the photocatalytically active materials were measured using integrating sphere ISR-2600Plus. To find the band gap width of the samples, the obtained spectra were reconstructed via the Kubelka-Munk formula [16] in the Tauc coordinates [17]. Extrapolation

of the straight segments of the $(\alpha h\nu)^{1/2} = f(h\nu)$ plots to the intersection with the x-axis was used to determine the band gap (Fig. 2, *a*); here α is the absorption coefficient of the material.

The band gap of the undoped material was found to be 3.31 eV. That of the samples containing tin in the amounts of 1, 2, 3, 4 and 5 at.% was 3.2, 3.19, 3.16, 3.02 and 2.98 eV,

respectively. Sulfur not only additionally narrows the TiO₂ band gap, but also plays the role of a trapping center for photogenerated electrons and, in addition, improves the material photocatalytic characteristics via inhibiting recombination of photogenerated electrons and holes. Among the studied samples, the best photocatalytic activity in MB decomposition was exhibited by the sample with the tin content of 5 at.%.

For the comparison of photocatalytic properties and co-doping efficiency, data for pure titanium dioxide P25, titanium dioxide doped with tin and sulfur with different dopant concentrations, and a reference sample (MB solution free of the photocatalyst — *Blank*) are presented in the MB decomposition plot (Fig. 2, *b*). As the acquired data shows, sample P25 sorbs MB on the surface, but further irradiation with visible light causes practically no variations in the MB concentration. In the sample doped with 5 at.% of tin, the time of MB decomposition appeared to be 3 h, which is indeed a good result. For instance, paper [18] showed that, in the case of photocatalyst co-doped with copper and nitrogen (2Cu–3N–TiO₂), the MB concentration was by this moment 18% of the initial one, while that for sample P25 was 66%. An additionally prepared photocatalyst sample doped with 6 at.% of tin demonstrated decomposition of 91% of MB in 5 h. Calculated values of the effective reaction rate constant for P25, 2Cu–3N–TiO₂, TiO₂ (5 at.% of Sn) were (0.2, 1.4, 2.5) · 10^{−2} min^{−1}, respectively.

Thus, it has been shown that mechanical doping does not result in significant variations in the particle size of the titanium dioxide powder. It has been established that doping with Sn and S decreases the titanium dioxide band gap, and its maximum available variation by 0.3 eV (down to 2.98 eV) takes place at the Sn content of 5 at.%. When only tin is used as a dopant, a band gap decrease to 3.11 eV is available [19]. Data of the energy dispersive analysis (see the Table) demonstrates changes in the samples' stoichiometry; the sample with the Sn content of 5 at.% exhibits excess cations, which may be caused by formation of oxygen vacancies enhancing the material photocatalytic activity. Among the studied samples, the highest photocatalytic activity in the organic pollutant decomposition in the visible light range was exhibited by the titanium dioxide samples with the mean particle size of 50 nm, which were doped with both sulfur and tin (5 at.% of Sn).

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Conflict of interests

The authors declare that they have no conflict of interests.

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