Properties of TiO_2 mechanochemically modified with carbon and sulfur

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Introduction

It is known, that photocatalytic application of pure TiO_2 has inherent limitation due to its wide band gap in the near-UV spectrum rendering its inactivity under visible light [1-3]. The aim of our work is obtaining the nanocomposites based of TiO_2 doping with carbon (C/TiO_2), with sulfur (S/TiO_2) and co-doping with carbon and sulfur simultaneously ($C/S/TiO_2$) by mechanochemical technique and investigation its physico-chemical and photocatalytic properties. As source of carbon for modification we used activated carbon, sulfur source was thiourea.

Methods

Mechanochemical treatment, X-ray powder diffraction (XRD), scanning electron microscopy with an integrated system for electron microprobe analysis (SEM, EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), Infrared (IR) and Ultraviolet–visible spectroscopy (UV-VIS) spectroscopy.

Results

Analysis of SEM-images of the synthesized samples shows that they consist of fragmented agglomerates in the range of 1–21 μm (Fig. 1). Modification in all cases leads to decrease in particles size. It confirmed by the X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) study. During doping and co-doping of titanium dioxide with carbon and sulfur using mechanochemical treatment the formation of new phases does not occur.

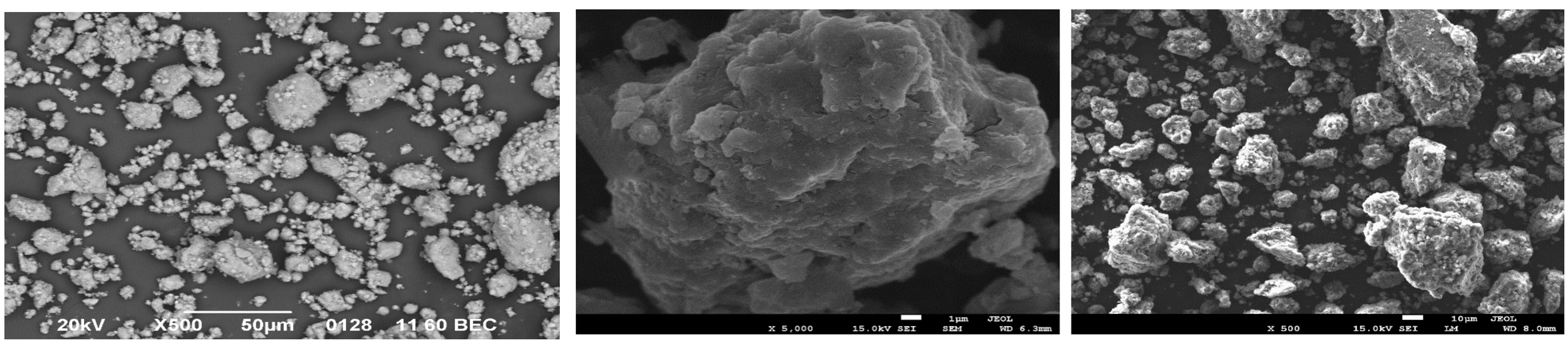

Fig 1. SEM images of C/TiO_2, S/TiO_2, $C/S/TiO_2$

All composites show the presence of a hysteresis loop which is the evidence for mesoporous structure of the powders (Fig. 2). The isotherms correspond to type IV of IUPAC classification for mesoporous materials with H1 type for C/TiO_2 and H2 type for S/TiO_2, and $C/S/TiO_2$ of hysteresis loop. The modification of TiO_2 by carbon and sulfur leads to increase of specific surface area (of about 3.3 times for S/TiO_2 and about 4.7 times for $C/S/TiO_2$), average pore volume and decrease of radius pore volume compared with TiO_2 (Table 1). It was identified C=O bonds on the surface of C/TiO_2, S/TiO_2 and $C/S/TiO_2$ samples and S^{2-} and $-NH_2$ on the surface of S/TiO_2 and $C/S/TiO_2$ powders. Absorption spectra of nanocomposites showed a bathochromic shift as compared with the absorption band of pure TiO_2.

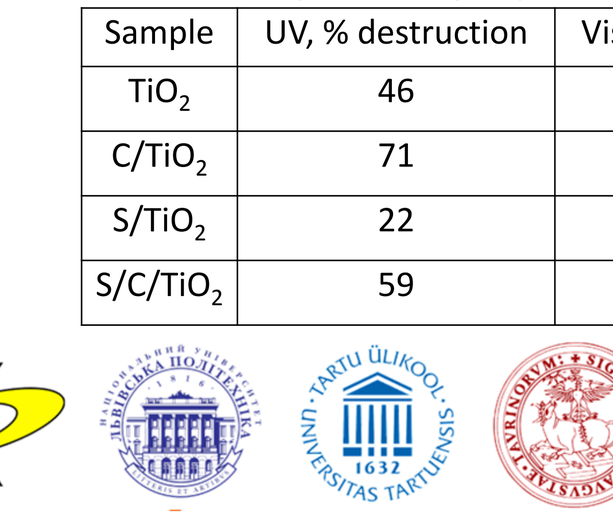

Fig 2. Isotherms of nitrogen sorption–desorption of the samples

Table 1. Textural characteristics of the samples.

Sample	S_{sp}, m^2/g	V_{tot}, cm^3/g	R, nm
TiO_2	29	0,15	12,8
C/TiO_2	28	0,16	11,1
S/TiO_2	34	0,15	13,9
$S/C/TiO_2$	31	0,16	13,2

Adsorption and photocatalytic activity at UV irradiation of nanocomposite samples increase compare with pure titanium dioxide which is associated with a decrease in particle size, increase in specific surface area. It was found that samples of titanium dioxide modified with carbon and sulfur show photocatalytic activity under visible irradiation in the destruction reaction of Safranin T, which is explained by their sensitization to visible light by the adsorbed dye (Table 2).

Table 2. Photocatalytic activity of powders in the destruction Safranin T

Sample	UV, % destruction	Visible, % destruction
TiO_2	46	–
C/TiO_2	71	29
S/TiO_2	22	18
$S/C/TiO_2$	59	40

Conclusion

- The mesoporous samples of TiO_2 doped with sulfur, carbon and carbon and sulfur simultaneously were obtained by mechanochemical treatment.
- The samples consist fragmented agglomerates in the range of 1–21 μm in size, their crystallite sizes vary from 29 to 25 nm.
- The isotherms correspond to type IV of IUPAC classification for mesoporous materials with H1 type for C/TiO_2 and H2 type for S/TiO_2, and $C/S/TiO_2$ of hysteresis loop.
- The powders C/TiO_2 include the elements Ti, O, C; S/TiO2 - Ti, O, S, N and C/S/TiO2 - Ti, O, C, S and N.
- It was identified C=O bonds on the surface of C/TiO2, S/TiO2 and C/S/TiO2 samples and S^{2-} and $-NH_2$ on the surface of S/TiO2 and C/S/TiO2 powders.
- The modified samples showed higher photocatalytic activity in the destruction of organic dye Safranin T under UV and visible irradiation compared to pure TiO2.

References

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