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STRUCTURAL INVESTIGATIONS OF TITANIUM(IV) OXIDE POWDER DOPED WITH SULPHUR

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Abstract. Structural features of titanium(IV) oxide powder doped with sulphur (S-TiO_2) have been determined. Using scanned electronic microscopy, X-ray phase and diffraction analyses the oxide morphology has been studied. Surface composition of S-TiO_2 nanoparticles has been examined by X-ray photoelectron and IR-spectroscopy.

Keywords: titanium(IV) oxide, dopant, nanoparticle, sulphur.

1. Introduction

The interest of many researches to semiconductor nanoparticles is caused first of all by their particular thermodynamic, photo- and electrophysical, magnetic and photochemical properties, which sometimes sharply differ from the properties of the same compounds in macro- and microcrystal states [1-6]. Obviously, the transfer from micro- to nanocrystal state of semiconductors opens up new possibilities for their properties control not by means of chemical composition change but by changing nanoparticles size only.

Changing of properties together with crystal size affect the interaction between semiconductor crystal and light wave and its result – light absorption, dynamics of photogenerating charge carriers as well as their destruction processes, *i.e.* photochemical activity of the material.

Photochemical activity is a compound property to stimulate the proceeding of chemical processes under light. If we examine titanium(IV) oxide semiconductor (TO), the high photoactivity is characteristic of anatase modification of TiO_2 only. Therefore, the first-priority task is to synthesize nanosized titanium(IV) oxide with the structure of anatase, which high photochemical activity may be adjusted by obtaining TiO_2 with a certain defectiveness degree of its crystal structure. The increase of defectiveness of anatase structure may be ensured by modifiers ions [7-9]. As it was mentioned in [10, 11] and confirmed by our previous investigations [12-14] sulphur is of great interest among the modifiers. The change of crystal lattice parameters and the presence of sulphur ions in TO structure indicate the successful doping of TO by sulphur ions. The data concerning the optimal oxidation degree of sulphur ions (-2, +4, +6), which guarantees the highest photocatalytic properties of the product, are contradictory.

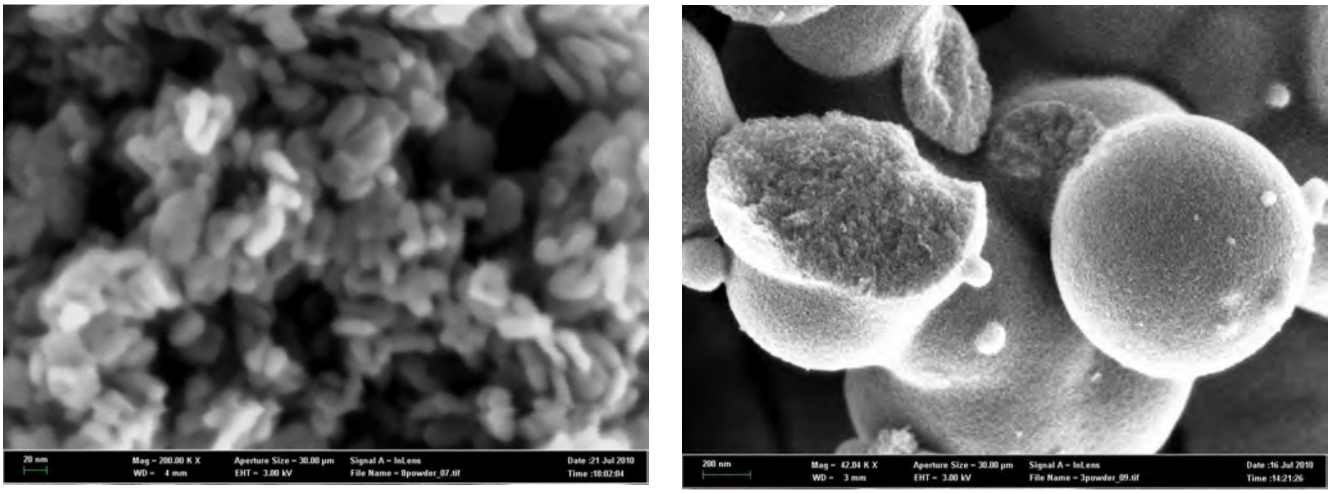
Ions dopants of other elements in TO structure form energetic levels in band gap and change the location of its valence band [15]. Due to the mentioned changes the photocatalyst edge of absorption may shift to the visible part of spectrum.

2. Experimental

As a result of experimental investigations we obtained TO nanopowder doped with sulphur (S-TiO_2) by solid-phase and sol-gel synthesis methods. Each method has its peculiarities and advantages. The aim of the present work is the investigation and comparison of S-TiO_2 powder structure obtained by different methods.

Solid-phase synthesis of TO doped with sulphur consists in burning of preliminary prepared paste mixture of metatitanium acid and thiourea. Accordingly to sol-gel method necessary components are mixed till sol forming. Then the obtained sol is evaporated under stirring to its paste state, dried at 393 K for 24 h and burned. The burning stage, which is the same for both methods, consists of two phases: heating with the rate of 8.5 K/min and isothermal treatment at 723 K for 1 h. The synthesis last stage is sharp cooling of the samples in air.

Fig. 1 presents SEM-images of S-TiO_2 powders obtained by solid-phase (S-TiO_2-s) and sol-gel (S-TiO_2-sg) methods. One can see that the powder obtained by solid-phase synthesis consists of parallelepiped nanoparticles, whose linear sizes vary from 10 to 40 nm. The particle of sol-gel powders are smaller in size (~10 nm) but they assemble into regular spherical agglomerates with a diameter about 1 μm.



a b

Fig. 1. SEM-image of S-TiO_2 powders obtained by solid-phase (a) and sol-gel (b) methods

Table 1

Results of X-ray analysis for TiO_2-s, S-TiO_2-s and S-TiO_2-sg powders

Sample	Crystals average diameter, nm		Defectiveness degree, % $<e> = <\Delta d>/d$	Parameters of crystal lattice			
	by Sherrer	by Williamson-Hall		*a*, Å	*c*, Å	*c*/*a*	*V*, Å
TiO_2-s	16	29	0.401	3.7862	9.505	2.5105	136.25
TiO_2 [16]				3.789	9.495		
S-TiO_2-s	21	35	0.334	3.7855	9.527	2.5167	136.52
S-TiO_2-sg	19	25	0.136	3.7833	9.513	2.5145	136.17
S-TiO_2 [16])				3.793	9.503		

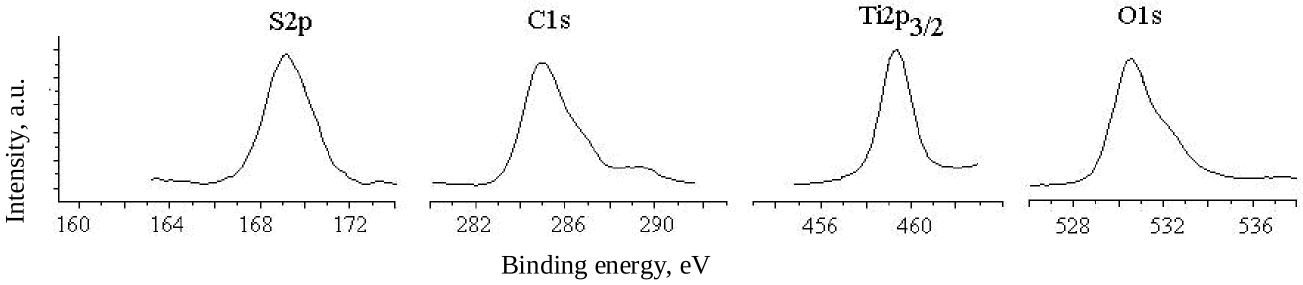


Fig. 2. Normalized X-ray photoelectron spectra of S2p, C1s, $Ti2p_{3/2}$, and O1s for S-TiO_2

To confirm the nanoparticle sizes of powders and to establish the peculiarities of their structure X-ray diffraction analysis (XRD) was used. The values of unit cells of TiO_2-s, S-TiO_2-s and S-TiO_2-sg powders are represented in Table 1, corrected by Ritweld full-profile method and compared with the literature data. Moreover, crystals size determined by Scherrer formula (D_{Sh}) and Williamson-Hall method ($D_{W\text{-}H}$) as well as average values of microstress $<e> = <\Delta d>/d$ are also represented there.

Comparing the results for TiO_2-s and S-TiO_2-s powders one can see that crystal sizes and lattice parameters increase due to the doping. It indicates a certain degree of anatase lattice filling by sulphur. The same increase of lattice parameters was observed by X. Tang and D. Li [16] who synthesized S-TiO_2 nanotubes. The samples of S-TiO_2-s and S-TiO_2-sg also differ by lattice parameters, which confirm the data of microscopic analysis.

The investigation of surface composition was carried out by means of X-ray photoelectron spectroscopy (XPS) using XSAM-800 Kratos spectrometer. The sample surface composition was determined using photoelectron lines area ratio taking into account their sensitivity factors. The thickness of analyzed layer was ~5 nm. Standard X-ray photoelectron spectra of S2p, C1s, $Ti2p_{3/2}$, and O1s core levels are represented in Fig. 2 for the S-TiO_2 powder in general. Atomic concentrations of every element (carbon, oxygen, titanium, and sulphur) in S-TiO_2-s and S-TiO_2-sg powders are 32.0, 53.5, 12.8, 1.7 and 35.0, 45.5, 16.1, 3.4 % respectively. Due to the data of XPS, in accordance with which titanium atoms content in S-TiO_2-s is lower than that in S-TiO_2-sg, the results of XRD become comprehensible. XRD shows that the sample obtained by solid-phase method has more defective structure.

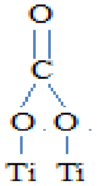
In accordance with XPS data, carbon is in the form of carbonic compounds (binding energy E_b = 285.0 eV) and compounds with the bonds of C–O type (shoulder in the region of 287 eV and peak near 289 eV) adsorbed on the particles surface. Oxygen is a part of oxides (E_b = 530.6 eV) and adsorbates (shoulder at 532 eV). Binding energy of titanium and sulphur core levels (459.0 ± 0.3 and 169.0 ± 0.3 eV, respectively) for S-TiO_2 powders are in agreement with the literature data for compounds of TiO_2 and $MeSO_4$ type, respectively.. Sulphur is in the form of S^{6+} ions only.

To determine S-TiO_2 structural peculiarities and structural composition of its individual fragments IR-spectroscopy was used for the obtained samples of S-TiO_2-s and S-TiO_2-sg. IR-spectra were recorded by spectrophotometer "Specord M-80" within the range of 3700–300 cm^{-1} using KBr and KRS-5 plates. It should be noted that vibration bands in the spectra (3727, 3665, 1670, 1620, 1562, 1358, 1270, 1220, 1170, 1105, 1060-1050, 1020, 995, 980, 950, 850, 770, 730, 641, 610, 571, 462 cm^{-1}) are identical for both samples.

In accordance with [17] anatase vibration spectrum is in the form of absorption bands in the region of 1000–700 cm^{-1}. ***Pro tanto***, bands with the maxima at 730, 770, 850 and 950 cm^{-1} refer to anatase vibrations. The absence of clear bands in the region of 1180–1060 cm^{-1} with the maxima at 1060, 1130 and 1180 cm^{-1} indicates the absence of oxygen molecular form adsorbed on titanium surface [18]. The weak vibrations in the region of 3725–3670 cm^{-1} explain the presence of small amount of hydroxyl groups on TiO_2 surface [19].

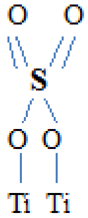
When a ligand of relatively high symmetry coordinates with a metal, its symmetry decreases. It is the basis for numerous determinations if anion, ***e.g.*** SO_4^{2-} or CO_3^{2-} coordinates with metal as monodental, chelate bidental or bridge bidental ligand.

The absorption bands in the region of 1700–1000 cm^{-1} are typical of bonds vibrations in surface carbonate-carboxyl compounds. The literature sources give a variety of carbonates differing by the structure, whose complex symmetry descends in the following row: carboxylate, non-coordinated carbonate, monodental, and bidental carbonates [20-22]. The clear vibration bands in the region of 1670–1620, 1270–1220, 1020–980 cm^{-1} allow to refer the obtained complexes to bidental ones:

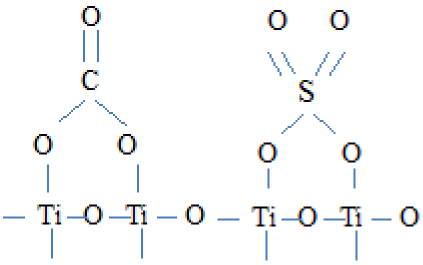


K. Nakamoto [22] observed the irreversible form of carbon oxide adsorption at the temperatures higher than 523 K for TiO_2. It is characterized by the adsorption bands at 1560 and 1360 cm^{-1} determined by CO^{2-} groups. These bands are also connected with irreversible adsorption of carbon oxide. The adsorption bands in the region of 2200–2000 cm^{-1} characterize the irreversible adsorption and are determined by vibrations of CO bonds in the complexes that are destroyed already at 423 K. Only such form of adsorption is observed during the interaction between carbon oxide and TiO_2 surface at 293 K.

The free sulphate-ion belongs to the point group of the highest symmetry. Among four fundamental vibrations in IR-spectrum only ν_3 and ν_4 are active. If the symmetry falls during the complex formation, the splitting of degenerate vibrations takes place. The vibrations which are active only in the spectrum of Raman scattering become active in IR-spectrum too [17]. In such a case both bands ν_1 (995 cm^{-1}) and ν_2 (462 cm^{-1}) of medium intensity are observed. The bands ν_3 (1060–1050, 1170, 1105 cm^{-1}) and ν_4 (641, 610, 571 cm^{-1}) split into three components. Obviously in such a complex the SO_4^{2-} is a bridge bidental group:



Thus, general results of X-ray structural analysis, X-ray photoelectron spectroscopy and IR spectroscopy allow us to present structural composition of synthesized S-TiO_2 as the following:



4. Conclusions

Changing the synthesis method we influence only sizes and forms of S-TiO_2 particles. The structural composition of the powder remains the same. We assume that sulphur doping takes place only within the limits of surface layers of titanium-oxygen skeleton, consequently the degree of sulphur doping will be limited. Insufficiently positive moment to our mind is simultaneous addition of sulphur and carbon to two titanium atoms resulting in the cross-linking of titanium-oxygen skeleton. Therefore we may expect the decrease of the samples specific surface with the increase of doping degree. However, we do not forecast the decrease of photocatalytic properties of S-TiO_2 powder due to the mentioned peculiarities.

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СТРУКТУРНІ ДОСЛІДЖЕННЯ ПОРОШКУ ТИТАНУ (IV) ОКСИДУ, ДОПОВАНОГО СІРКОЮ

Анотація. *Встановлено структурні особливості порошку титану (IV) оксиду, допованого сіркою (S-TiO_2). За допомогою скануючої електронної мікроскопії, рентгенофазового та рентгеноструктурного аналізів досліджено його морфологію, а за допомогою рентгенофотоелектронної та інфрачервоної спектроскопії вивчено поверхневий склад наночастинок S-TiO_2.*

Ключові слова: *титану(IV) оксид, додаток, наночастинка, сірка.*