

Yaroslav Vakhula, Khrystyna Besaha and Iryna Lutsyuk

SURFACE MODIFICATION OF TITANIUM(IV) OXIDE SOL-GEL POWDERS BY SULFUR

*Lviv Polytechnic National University
12, S. Bandery str., 79013 Lviv, Ukraine*

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Abstract. The synthesis of titanium(IV) oxide nanoparticles modified by sulfur with the help of sol-gel method has been described. The structure of surface layers has been investigated using X-ray diffraction analysis, a scanning electron microscopy, IR-spectroscopy and X-ray photoelectron spectroscopy. The possible mechanism of powders surface modification by sulfur has been shown, as well as the dependence of specific surface on sulfur content.

Keywords: sol-gel powders, S-TiO₂, surface modification.

1. Introduction

During last decades physico-chemical processes occurring over solid body surface and their mechanisms are studied very intensively. Such processes play a great role during the production of elements for microelectronics and computer engineering, sorbents, catalysts, polymers fillers, *etc.* It is connected with the fact that the majority of the processes and phenomena which are the main in heterogeneous photocatalysis and adsorption take place over solid body surface or near-surface layers.

Lately the titanium oxide powders with the surface modified by inorganic and organic substances [1-3] have been used more often. The TiO₂ modification by sulfur gives the possibility to use the obtained composite as the high-effective photocatalyst [4, 5]. A lot of papers deal with the problems of titanium(IV) oxide obtaining, investigations of its structure, properties and photocatalytic activity. However, insufficient attention was paid to the peculiarities of modified product surface structure. Moreover, the difference between structures of modified surface and depth layers was not studied.

The aim of this work is the investigation of modifier's (sulfur) effect on the formation of S-TiO₂ powders surface structure, as well as their properties.

2. Experimental

2.1. Investigation Methods

X-ray diffraction analysis (XRD) of the powder was carried out using DRON-4 X-ray diffractometer. The conditions were as following: radiation Cu K α ; range of 2 θ angles was from 9 to 65°; $U = 34$ kV; $I = 14$ mA.

The investigation of surface structure was carried out by means of X-ray photoelectron spectroscopy (XPS) using XSAM-800 Kratos spectrometer. The sample surface structure was determined using the photoelectron lines area ratio taking into account their sensitivity factors. The thickness of analyzed layer was ≈ 5 nm. IR-spectra were recorded by the spectrophotometer "Specord M-80" within a range of 3700–300 cm⁻¹ using KBr and KRS-5 plates. Electron-microscopic investigations were carried out using ZEISS EVO 40XVP electron microscope with the system of X-ray microanalysis INCA Energy. X-ray emission analysis (XRE) was used for determination of qualitative and quantitative composition of the powders. The value of synthesized powders specific surface was measured using Brunauer-Emmet-Teller method by means of nitrogen low-temperature adsorption. XL-4 chromatograph was used to calculate the volume of adsorbed gases.

2.2. Powders Synthesis

The sol-gel synthesis of nanocrystalline titanium(IV) oxide powders modified by sulfur was carried out. Titanium tetrabutylate, thiourea, butanol and water were the initial compounds. 35.8 ml of tetrabutoxytitanium were hydrolyzed in 89.2 ml of butanol and 5.8 ml of water. Thiourea was dissolved in 15 ml of water. The obtained solutions were intensively mixed till milky sol was formed. The obtained sol was evaporated in the autoclave ($T = 373$ K, $t = 24$ h), dried ($T = 393$ K, $t = 12$ h) and burned out ($T = 773$ K, $t = 1$ h).

3. Results and Discussion

3.1. Composition and Structure of Powder Surface

In accordance with the developed procedure described in [6, 7] the white powders of S-TiO₂ were obtained. The results of XRD analysis show (Fig. 1) that powders structure is represented by one crystal phase – anatase ($d/n = 0.148; 0.166; 0.170; 0.189; 0.233; 0.237; 0.243; 0.253$ nm).

The obtained sol-gel powders consist of rounded dispersed particles with the diameter of 1 μm with the developed character of their surface (Fig. 2). These particles, in their turn, are combination of nanoparticles with the diameter of 10–20 nm in the whole volume.

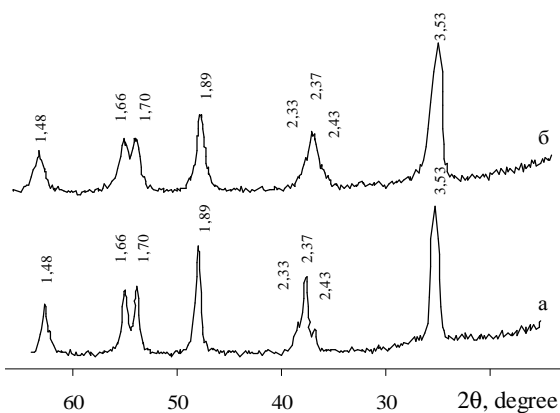


Fig. 1. X-ray photographs of the powders burned out at 773 K: TiO₂ (a) and S-TiO₂ (b)

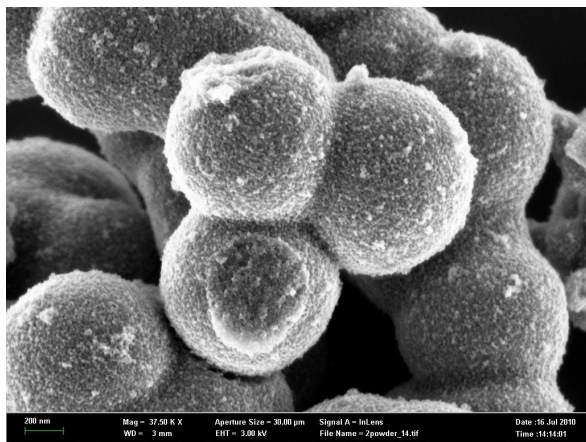


Fig. 2. Microphotograph of S-TiO₂ powders

The quantitative and qualitative composition of the synthesized powder surface layer was determined by X-ray photoelectron spectroscopy (XPS) and volumetric phase – by X-ray emission analysis (XRE). S-TiO₂

contains the following elements with the corresponding oxidation degree: Ti(IV), S(VI), C(II) and O(II). Namely, carbon is in the form of carbonic compounds and compounds with C–O bonds adsorbed over particles surface. Oxygen is a part of oxides and adsorbates. The values of the binding energy of titanium and sulfur correspond to the table data for the compounds of TiO₂ and MeSO₄ type, relatively. Sulfur has the oxidation number only +6.

In accordance with XPS and XRE the composition of powders surface particles differ from the composition of their volumetric phase. For example, the ratio Ti/S over the surface is 5.95, and the same ratio in the volume is 79.95. Such data allow to assert that TiO₂ modification takes place in the surface layers.

Today there is no common opinion concerning the modifier's effect on the powders specific surface. Some authors [8, 9] show the decrease of specific surface due to the modification, some of them [10, 11] assert the opposite opinion. We established that the dependence of specific surface value upon the sulfur content is complicated and variable (Fig. 3). The sample with 0.4 wt % of sulfur has the maximum value.

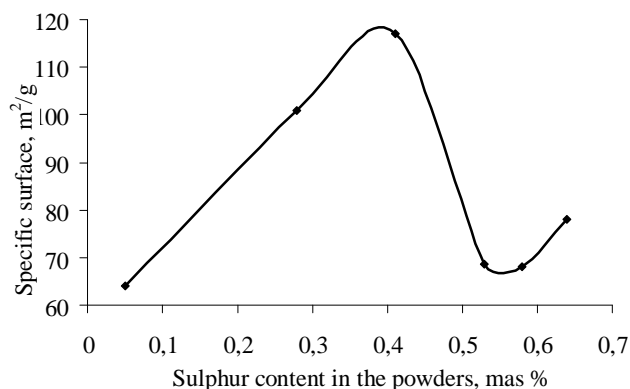


Fig. 3. Dependence of S-TiO₂ specific surface upon sulfur content

3.2. IR-Spectroscopy

The structural peculiarities of the synthesized powders surface were studied using IR-spectroscopy. IR-spectra of pure and modified by sulfur TiO₂ nanocrystalline powders are represented in Fig. 3. The comparison of absorption bands frequency show the similarity of spectra. There are six main absorption bands in the areas of 3700–3500, 2350–2000, 1650–1000, 1470–1180, 1180–1030 and 750–400 cm⁻¹ corresponding to the stretching vibrations of OH bonds, bidentant carbonate group, adsorbed CO, SO₂ group bonds (for modified sample), O–O bonds and Ti–O and Ti–O–Ti bonds, respectively.

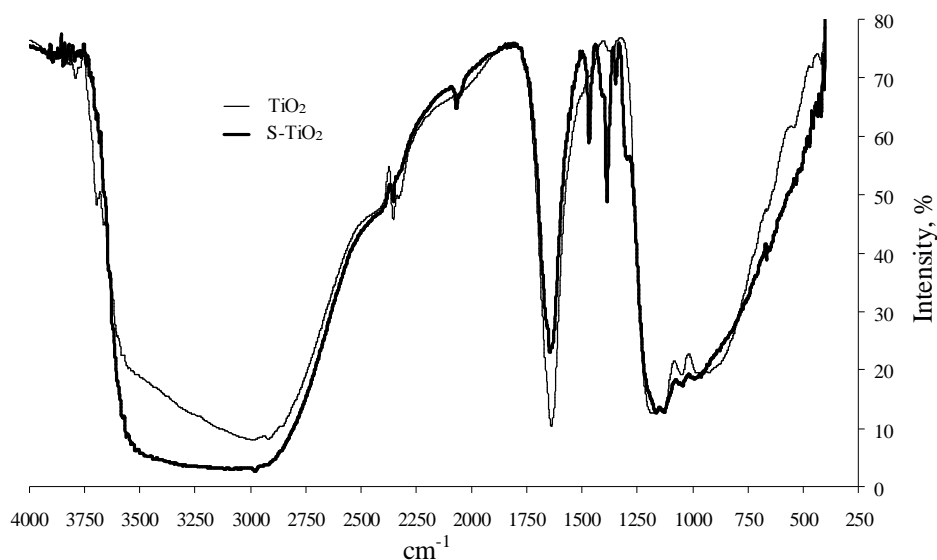


Fig. 4. IR-spectra of synthesized powders

One can see from Fig. 4 that stretching vibrations of OH bonds in the area of $3700\text{--}3500\text{ cm}^{-1}$ are non-intensive for both samples. The reason is the small amount of OH groups due to the high temperatures of samples burning [12].

The absorption bands in the area of $2350\text{--}2000$ and $1650\text{--}1500\text{ cm}^{-1}$ correspond to the absorption of adsorbed carbon oxide [13]. The absorption bands in the area of $1700\text{--}1000\text{ cm}^{-1}$ are typical of stretching vibrations in the surface carbonate-carboxyl compounds. The vibrations at $1560\text{--}1630$ and $1350\text{--}1420\text{ cm}^{-1}$ allow to refer the formed group to bidentant carbonate [13-15].

The absorption bands with low intensity in the area of $2200\text{--}2000\text{ cm}^{-1}$ show the small amount of adsorbed carbon(II) oxide.

The presence of vibrations with maxima at 1467 , 1386 , 1344 , 1286 , 1157 and 1123 cm^{-1} in the modified samples allows to refer them to the stretching vibrations of SO_2 bonds, and formed group – to the sulphates [15].

The absorption bands in the area of $1180\text{--}1060\text{ cm}^{-1}$ with maxima at 1172 , 1123 and 1036 cm^{-1} (TiO_2) and 1157 , 1123 and 1036 cm^{-1} (S-TiO_2) correspond to the stretching vibrations of O-O bonds coordinated with the data from Ref. [13].

The disappearance of absorption bands ($750\text{--}550\text{ cm}^{-1}$) typical for Ti-O bonds is caused by high-temperature treating resulting in the cation-oxygen bond opening [2]. The vibrations with low intensity in this area are also explained by the fact that non-polar vibrations of TiO_2 crystalline lattice are active in coordination scattering spectra and non-active in IR-spectra. Only polar vibrations become apparent in IR-spectra.

3.3. Scheme of S-TiO₂ Powder Modification

Sulfur-containing particles segregate to the surface of anatase crystals with the diameter of 20 nm. The formed globules, in their turn, form the nanostructured spheres presented in Fig. 2. The mentioned mechanism of S-TiO₂ formation explains the extremal character of the specific surface dependence on sulfur content. The specific surface increases till the moment when sulfur-containing particles form the compact layer over the surface of anatase crystals. The further increase of specific surface is explained by the filling of the second sulfur-containing layer but the value is less than previous maximum due to the increase in diameter of formed nanostructured sphere.

4. Conclusions

We established that modification by sulfur takes place only in the limits of surface layers of synthesized powders crystals by the thickness of 5–10 nm. The considerable difference between atomic content of titanium and sulfur over powder particles (5.95) and in their volume (79.95) confirms this fact. The results of XRD and IR-spectroscopy confirm that surface sulfur-containing structures, which are formed, belong to sulphates; carbon-containing structures – to carbonates and adsorbates; oxygen – to oxides and adsorbates.

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**ПОВЕРХНЕВЕ МОДИФІКУВАННЯ СІРКОЮ
ЗОЛЬ-ГЕЛЬ ПОРОШКІВ ТИТАНУ(IV) ОКСИДУ**

Анотація. Золь-гель методом синтезовано нанопорошки титану(IV) оксиду модифіковані сіркою. Структуру поверхневих шарів досліджено за допомогою рентгено-дифракційного аналізу, скануючої електронної мікроскопії, ІЧ-спектроскопії та рентгенівської фотоелектронної спектроскопії. Показаний можливий механізм модифікації поверхні, а також встановлено залежність питомої поверхні від вмісту сірки.

Ключові слова: золь-гель порошки, S-TiO₂, модифікування поверхні.