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IR SPECTRAL MANIFESTATION OF TIN IMPURITY SITES IN TITANIUM DIOXIDE

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It is known that titanium dioxide as photocatalyst has significant drawback - limited absorption spectrum in the ultraviolet region makes it impossible to use solar energy. To expands the absorption spectrum of TiO_2, the doping of impurities (metal, non-metal, etc.) were used. They affected the electronic structure and spectral characteristics of TiO_2. The aim of our work was to investigate the influence of tin impurities on spectral characteristics of titanium dioxide using experimental and theoretical methods. The TiO_2 powders modified by different amount of tin (Sn/TiO_2) were synthesized by sol-gel method. The samples were characterized by SEM, EDX, FT-IR and UV-VIS spectroscopy. It has been found that Sn/TiO_2 consists of fragmented agglomerates in the range of 5–10 μm. EDX spectroscopy proved that powders include Ti, O and Sn elements. Modification of titanium dioxide with tin led to band gap narrowing of samples, which explains by insertion of Sn atoms into crystal lattice of titanium dioxide, because Ti^{4+} and Sn^{4+} ions radii are close. The band gap values increased with increasing of tin content. The work also analyzes the vibrational spectra of Sn/TiO_2 both experimentally and theoretically. In order to interpret the results obtained, quantum chemical calculations on the spatial and electronic structures of cluster models of titanium dioxide (anatase) with inserted tin atoms using the density functional theory B3LYP method and the basis set 6-31G (d, p) were carried out and the corresponding FT-IR spectra have been simulated. By comparing the experimental and theoretical results, the influence has been analyzed of the number and arrangement of impurity tin atoms in clusters on the observed IR spectra of the samples. This makes it possible to forgive the most probable structural motives of titanium dioxide particles doped with tin atoms, as well as to establish the fact of the presence of tin atoms in the samples. Based on the comparison of the IR spectra of samples with different numbers of tin atoms, it is possible to quantify their composition.

Keywords: *infrared spectra, titanium oxide nanoparticles, tin impurities, quantum chemistry, cluster models*

INTRODUCTION

The goal problem of increasing the efficiency of photoactive materials, such as titanium dioxide, is the expansion of the spectral range of their sensitivity. One of the main ways to expand the spectral region of sensitivity of titanium dioxide and other photoactive solids to the long-wavelength region of the spectrum is considered to be due to their doping with another elements impurities [1–3]. It was shown [4] that the introduction of impurities of various nature, including metal ions, indeed leads to the appearance of stable absorption bands adjacent to the fundamental absorption edge of TiO_2 and extending up to the IR absorption range (up to 800–900 nm). In this case, the appearance of photoactivity of the doped samples is observed in the visible region of the spectrum with a red border at about 600–700 nm.

Earlier we examined the effect of carbon and sulfur on the electronic structure and spectral characteristics of titania nanoparticles both experimentally [5] and theoretically [6]. This paper is devoted to experimental and theoretical examination of the effect of tin additives in TiO_2 nanoparticles on their electron structure and IR spectra. The choice of tin as an admixture is conditioned by its capability to substitute titanium isomophously despite a considerable difference between their ionic radii.

EXPERIMENTAL

Preparation of TiO_2 samples modified with tin. The samples of titanium dioxide modified with tin were synthetized by sol–gel method [7]. The mixture of titanium (IV) tetrabutoxide (Aldrich), citric acid, castor oil and $SnCl_2$ calcinated at 500 °C for 2 h in the presence of air oxygen. Tin was added at various atomic percentages (1.69, 2.29 and 3.77 % at.). After cooling, the obtained powders were triturated until smooth. The samples were designated as $1Sn/TiO_2$, $2Sn/TiO_2$ and $3Sn/TiO_2$, respectively, as dependent on the tin atomic percentage.

Characterization of Sn/TiO_2 powders. To analyze sample composition (elemental analysis) and its morphology, a scanning electron microscope (SEM JSM 6490 LV, JEOL, Japan) with an integrated system for electron microprobe analysis INCA Energy based on energy-dispersive and wavelength-dispersive spectrometers (EDS + WDS, OXFORD, United Kingdom) with HKL Channel system (OXFORD) was used.

Room temperature FT-IR spectra were recorded with a Perkin Elmer Spectrum One spectrometer in the spectral region of 4000–400 cm^{-1} with spectral resolution of 4 cm^{-1}.

UV-vis diffuse reflection spectra (DRS) of powders were measured using a Perkin-Elmer Lambda Bio 35 spectrophotometer in the range between 200 and 1000 nm which allowed converting data of corresponding spectra using the Kubelka–Munk equation. The value of E_g was estimated using the method proposed by Wood and Tauc by the extrapolation of the linear part of the plot $(h\nu*\alpha(h\nu))^{1/n}$ versus hν toward energy axis at $\alpha(h\nu)=0$ (n = ½ for direct allowed transitions, $n = 2$ for indirect allowed transitions).

Models and methods of calculations. Parent cluster of $Ti_{14}H_{22}O_{39}$ was used as a working model. From one to three tin atoms substituted Ti ones so forming tin-containing clusters.

The calculations of vibrational spectra of the cluster models were carried out within harmonical approximation using the density functional theory B3LYP method and the basis set 6-31G (d, p), using the PC GAMESS software package (FireFly version 8.2.0 by A. Granovsky) [8].

RESULTS AND DISCUSSION

The Sn/TiO_2 samples are fragmented agglomerates (Fig. 1). Examination of these powders by means of energy-dispersive spectroscopy based on energy-dispersive technique proves that materials include the elements Ti, O, and Sn (Fig. 1).

Table 1 shows the atomic percentage and atomic ratio in the Sn/TiO_2 samples. The tin content increases in the range of samples $1Sn/TiO_2$, $2Sn/TiO_2$ and $3Sn/TiO_2$.

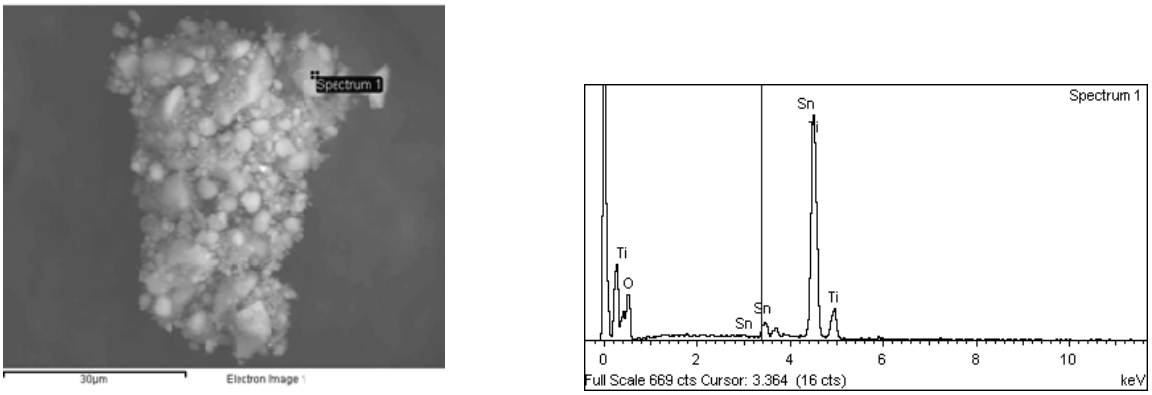

Fig 1. SEM images and energy-dispersive spectrometry (EDS) spectrum of $2Sn/TiO_2$

Table 1. The atomic percentage and ratio of the elements of the Sn/TiO_2 samples obtained by EDS technique

Samples	atomic percentage , %			atomic ratio , %		
	Ti	O	Sn	Ti	O	Sn
$1Sn/TiO_2$	31.64	66.67	1.69	1.0	2.11	0.05
$2Sn/TiO_2$	31.03	66.68	2.29	1.0	2.15	0.07
$3Sn/TiO_2$	29.58	66.65	3.77	1.0	2.25	0.13

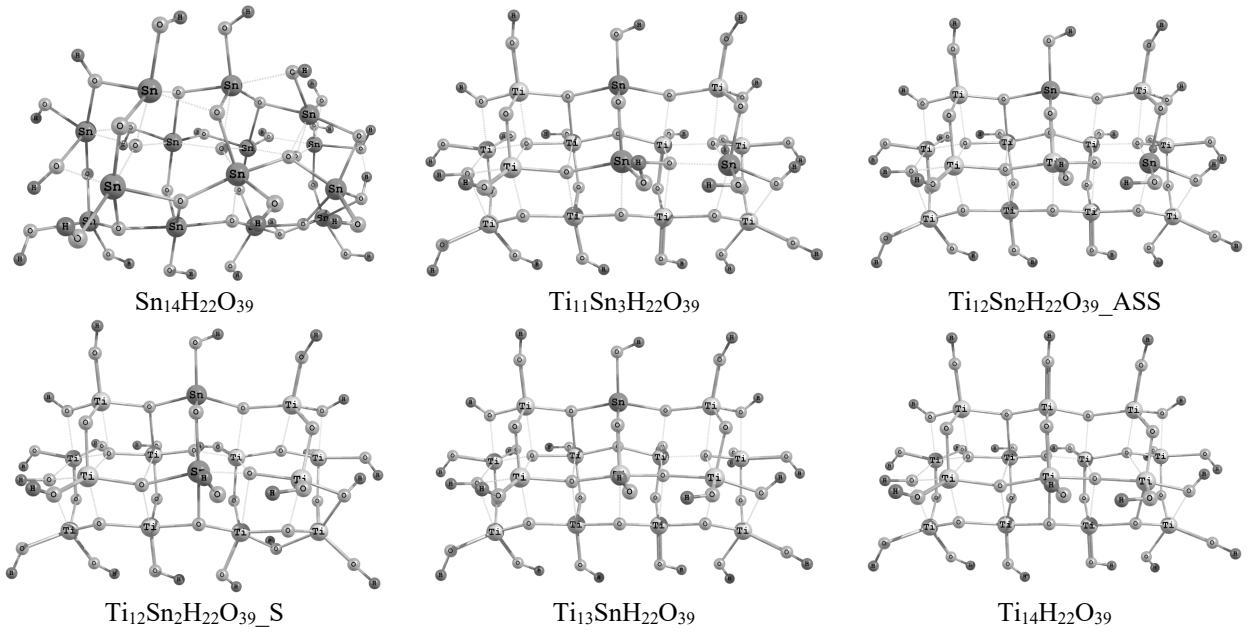

Fig. 2. Spatial geometry of the anatase model with various number of Sn atoms

Equilibrium spatial structures of the anatase-like model clusters $Sn_{14}H_{22}O_{39}$, and $Ti_{14}H_{22}O_{39}$ as well as of the clusters including 1, 2, or 3 impurity tin atoms are shown in the Fig. 2.

The results shown in Table 2 demonstrate the multidirectional nature of the change in the band gap as dependent on the number and location of impurity tin atoms in the structure of the considered cluster models. The asymmetric arrangement of tin atoms in the structure of titanium dioxide leads to decreasing of the band gap. A further increase in the number of incorporated tin atoms in titanium dioxide leads to the band gap closer to the value corresponding to the cluster model for pure SnO_2 (4.26 eV).

In the case of the Sn/TiO_2 samples the modification of titanium dioxide with tin leads to band gap narrowing of composites (Table 3).

Table 2. Band gap of the cluster models for Sn-doped TiO_2

Cluster models	Band gap, eV
$Ti_{14}H_{22}O_{39}$	4.98
$Ti_{13}SnH_{22}O_{39}$	5.23
$Ti_{12}Sn_2H_{22}O_{39}$_S	5.48
$Ti_{12}Sn_2H_{22}O_{39}$_ASS	4.86
$Ti_{11}Sn_3H_{22}O_{39}$	4.76
$Sn_{14}H_{22}O_{39}$	4.26

Table 3. Band gap of the Sn/TiO_2 samples

Sample	Band gap, eV
TiO_2	3.48
$1Sn/TiO_2$	3.32
$2Sn/TiO_2$	3.35
$3Sn/TiO_2$	3.41

This is explained by insertion of Sn atoms into crystal lattice of titanium dioxide, because Ti^{4+} ion radius (53 nm) is close to tin ion radius (69 nm) [9]. In the range from $1Sn/TiO_2$ to $3Sn/TiO_2$ with increasing of tin content, the band gap values also increased.

The functional groups of the Sn/TiO_2 samples were characterized by FTIR transmittance spectroscopy and the corresponding spectra are shown in Fig. 3. Related experimental and theoretical frequencies are compared in Table 4.

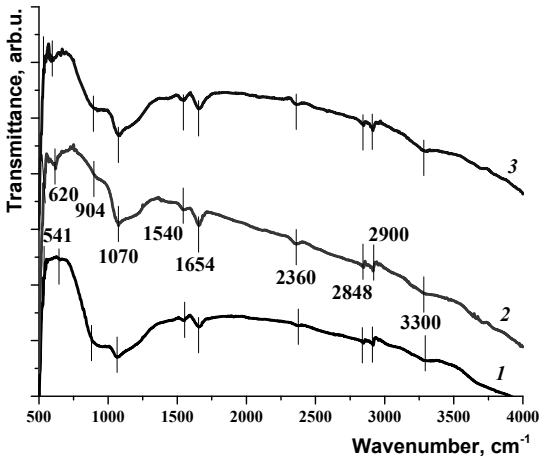

Fig. 3. Experimental FTIR spectra of the Sn/TiO_2 samples: *1* – $1Sn/TiO_2$, *2* – $2Sn/TiO_2$, *3* – $3Sn/TiO_2$

Table. 4. Interpretation of the IR spectra of Sn-doped TiO_2 samples

EXPERIMENTAL		CALCULATION	
ν, cm^{-1}	**Assignment**	**ν, cm^{-1}**	**Assignment**
	$Sn_{14}H_{22}O_{39}$		
-		520	stretching SnOH, bending SnOSn
-		747–1409	bending SnOH
-		2429	stretching OH Sn_2OH
-		3300–3868	stretching OH SnOH
	$Ti_{13}SnH_{22}O_{39}$		
-		513–527	bending OSnO
541	bending vibration Ti-O-Ti	547	bending vibration Ti-O-Ti
620	bending vibration Sn-O-Sn	620	stretching Sn-O, stretching Ti-O, bending Ti-OH
-		728, 734	stretching SnO
-		742–753	bending OSnO
904, 1070		897–909	bending SnOH
1654	bending vibrations in adsorbed water	-	-
2360	carbon dioxide physically sorbed on the surface	-	-
3300	Stretching vibrations υ(OH)	-	-

The bands near 541 cm^{-1} correspond to the Ti-O-Ti bending vibration, near 620 cm^{-1} – to the Sn-O-Sn one, 920 and 1070 cm^{-1} – to the Sn-OH stretching vibrations [10, 11].

The spectral behavior of some probable adsorbates was not considered in our model calculations. Thus, the absorption band observed experimentally at 1630 cm^{-1} refers to deformational vibrations in adsorbed water, at 2340 cm^{-1} – to the carbon dioxide physically sorbed on the surface [12, 13], at 3300 cm^{-1} – to the υ(OH) stretching vibrations and adsorbed water molecules coordinated on the samples surface.

With an increase in the number of tin atoms in the model, the picture becomes more complicated due to an increase in the number of different types of interactions.

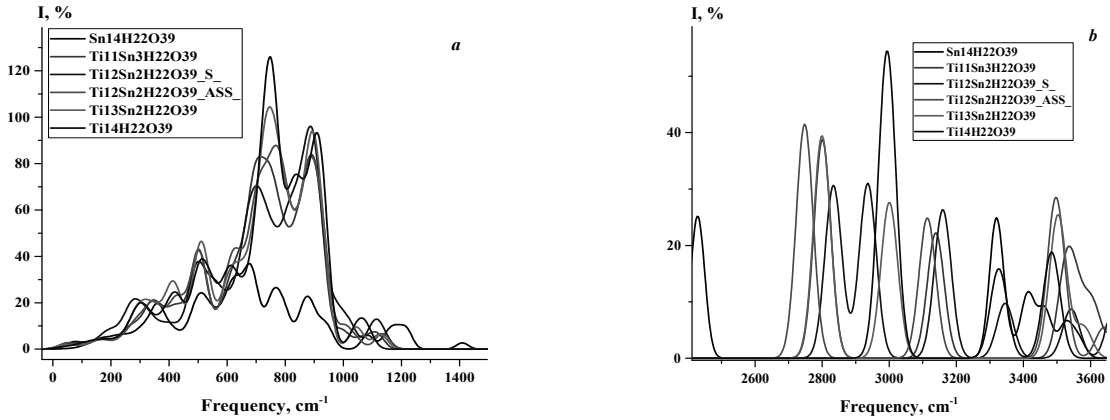

Fig. 4. IR-spectrum of the anatase model with various number of Sn atoms: bending (*a*) and stretching (*b*)

CONCLUSIONS

A combined experimental study on the vibrational spectra of titanium dioxide samples modified with various additives of tin dioxide and synthesized by the sol-gel method, along with quantum chemical calculations on the spatial and electronic structures of cluster models of titanium dioxide (anatase) with embedded tin atoms, and simulation of the corresponding IR spectra, has been carried out. The results obtained give an opportunity to elucidate the nature of the spectra observed and to interpret those spectra. By comparing the experimental data and theoretical results, the effect was studied of the number and arrangement of impurity tin atoms on the observed FT-IR spectra of the samples. This makes it possible to predict the most probable structural motifs of TiO_2 particles formed by tin admixtures.

ІЧ спектральний прояв домішкових центрів олова у діоксиді титану

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У роботі проаналізовано коливальні спектри зразків діоксиду титану, синтезованих золь-гель методом і модифікованих різною кількістю діоксиду олова. З метою інтерпретації одержаних результатів виконано квантовохімічні розрахунки рівноважної просторової будови та електронної структури кластерних моделей діоксиду титану (анатаз) із вбудованими атомами олова методом теорії функціоналу електронної густини B3LYP з базисним набором 6-31G (d, p) та змодельовано відповідні ІЧ спектри. Порівнянням дослідних та теоретичних результатів проаналізовано вплив кількості та локалізації домішкових атомів олова в кластерах на експериментальні ІЧ спектри зразків. Це дає можливість перебачити найбільш імовірні структурні мотиви частинок діоксиду титану, допованих атомами олова, а також встановити

факт наявності атомів олова в досліджених зразках. Виходячи з порівняння між собою ІЧ-спектрів зразків з різною кількістю атомів олова, можна зробити кількісну оцінку їхнього складу.

***Ключові слова**: інфрачервоні спектри, наночастинки оксиду титану, домішки олова, квантова хімія, кластерні моделі*

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