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A QUANTUM CHEMICAL STUDY ON THE EFFECT OF TITANIUM DIOXIDE MODIFICATION WITH NON-METALS ON ITS SPECTRAL CHARACTERISTICS

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The experimental results obtained in the study on the possibility of sensitizing titanium dioxide (polymorphic anatase phase) to the visible region of the spectrum by doping and co-doping with impurities of non-metals in order to create effective photocatalysts for the decomposition of organic compounds have been analyzed.

The presence of impurity atoms appears to result in a change in the electronic structure of the titanium dioxide matrix, in the appearance of "impurity bands" and in the narrowing of the energy gap of titanium dioxide. Such a modification is accompanied by an extension of the spectral range of sensitivity of photoactive solids to the long-wavelength region of the spectrum and, therefore, can be used to improve the catalytic properties of these materials.

Spectral manifestations of carbon impurities in titanium dioxide in the form of carbide and carbonate, as well as sulfur in the forms of sulfite, sulfide, and sulfate, have been studied by the density functional theory method. A $Ti_{14}H_{22}O_{39}$ cluster model was chosen for the titanium dioxide matrix. The calculations were carried out in the framework of the cluster approximation, using functional B3LYP and basis set 6-31G (d, p).

Comparison of the results of quantum chemical calculations with the available experimental data shows that the impurity sulfur and carbon atoms in titanium dioxide, which are in different coordination states and different oxidation states, appear in different spectral ranges. This circumstance makes it possible to elucidate the structure of the samples based on the experimental spectra.

A change in the coordination and oxidation states of impurity atoms leads to spectral shifts and splitting of peaks, which can reach 1.5 eV (XPS). The presence of admixtures of non-metals leads to a change in color (deepening in the case of sulfide or carbide) of the samples, appearing in the corresponding UV spectra.

Keywords: anatase, oxygen defect, carbon impurity, sulfur impurity, XPS spectra, UV/Vis spectra, quantum chemical density functional theory (DFT) method, cluster models

INTRODUCTION

Examination of nanoparticles, their ensembles (powders) and nanocomposites based on a number of wide-gap metal oxides has acquired particular relevance in recent years in connection with a number of properties of such objects that are interesting from a scientific and practical point of view. These are, in particular, their specific photoactivity, which appears as photostimulated formation and annealing of optically active defects (photostability and photosensitivity, photochromism) of oxide materials; photostimulated molecular transformations on the surface of dispersed solids, being a base of so-called heterogeneous photocatalysis, promising for converting solar energy into chemical one and for purifying water and air from pollutions, *etc.*; photoelectron-chemical conversion of solar energy [1].

Photostimulated (photocatalytic) reactions can, in most cases, be divided into two stages:

photoexcitation of a system (solid) and molecular (chemical) transformations on the surface. For a number of reasons, the most active in such processes are solids, in particular, metal oxides with a sufficiently large energy gap ($E_g > 3$ eV). For the most popular photocatalyst today – titanium dioxide ($E_g = 3.0$ and 3.2 eV for the anatase and rutile modifications, respectively), which has a number of unique properties (chemical stability, non-toxicity, low cost), only about 4–5 % of the solar radiation energy at the surface of the Earth is absorbed by this oxide in the range of the most effective fundamental absorption.

BACKGROUND

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 their doping with anionic or cationic impurities, *etc.*, co-doping, i.e. introduction of two or more impurities of the cationic, anionic or mixed type (N, C, S, B, P, *etc.*). It was shown [1] that the introduction of impurities of various natures, including metal ions, indeed leads to the appearance of stable absorption bands adjacent to the fundamental absorption edge of TiO₂ and extending up to the IR absorption range (up to 800–900 nm for a number of impurities as dependent on methods of their introduction). 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. It was also shown that, as a rule, upon co-doping, the activity of the samples is higher than upon the introduction of the corresponding impurities separately.

The nature of the doping and co-doping effects is still unclear. In most works, it is believed that the introduction of impurities leads to a “narrowing” of the band gap due to the appearance of states near the edges of the conduction or valence band [1]. In particular, the appearance of absorption in the 400–550 nm range upon anionic doping of titanium dioxide with nitrogen is most often explained by the formation of a “subband” of filled nitrogen states (*N2p*) located above the states of the valence band (*O2p*) of TiO₂, which is in qualitative agreement with the results of quantum chemical calculations.

Impurities of non-metals can be in various coordination states and different oxidation states. This can appear in different positions of the corresponding peaks in the XPS and UV spectra. For example, carbon in oxides can form carbonate or carbide structures, which appear in the XPS spectra in the range of about 282–295 eV [2, 3]. Similarly, sulfur in oxides can form sulfate groups, which corresponds to a peak of 170 eV [4, 5]. The presence of impurities of non-metals can change the position of the titanium and oxygen peaks, but this shift is small.

In this work, we examined the manifestation of impurity carbon and sulfur atoms in titanium dioxide (anatase) in XPS and electronic spectra. The position of the corresponding peaks found by quantum chemical calculations is compared

with available experimental data, which makes it possible to identify spectrally various impurity groups in the TiO₂ structure.

EXPERIMENTAL

In this work, carbon impurities in titanium dioxide in the form of carbide and carbonate, as well as sulfur ones in the forms of sulfite, sulfide, and sulfate are examined. The Ti₁₄H₂₂O₃₉ cluster, studied in detail in our previous work [6], was chosen as a model for the titanium dioxide matrix.

The calculations were carried out in the framework of the cluster 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) [7–10].

RESULTS AND DISCUSSION

In order to simulate the effect of atomics C and S incorporation and isomorphic substitution of O atoms, anatase nanoparticles were represented as a set of clusters. The (001) face of a defect-free anatase surface was modeled by a cluster of the gross formula Ti₁₄H₂₂O₃₉ [11]. Different oxidation states of non-metal atoms were taken into account, so there can be carbide and carbonate, sulfide and sulfate structures incorporated into the bulk of titania nanoparticles (Fig. 1).

Impurity sulfur atoms in the structure of the TiO₂ cluster. According to the experimental data [2], sulfur in the structure of titanium dioxide appears in the XPS spectra near 169 eV. We considered cluster models of TiO₂ containing sulfur atoms in different oxidation states: one and two sulfide type sulfur atoms, sulfite and sulfate groups in the anatase structure. According to the results of calculations, the peaks *S2s* at 215 eV and *S2p* at 160 eV correspond to sulfide type sulfur atoms. The transition from one to two sulfur atoms in the cluster leads to a certain complication of the spectrum: the *S2s* peak splits into two components (214.8 and 215.2 eV, Fig. 2). According to the calculation data, the presence of a sulfite group corresponds to the presence of peaks in the spectra in the regions of 223 eV (*S2s*) and 167 eV (*S2p*). The presence of a sulfate group leads to similar shifts.

The presence of sulfur atoms in the anatase structure leads to the splitting of the titanium and

oxygen peaks in the XPS spectra (Fig. 2) in comparison with the cluster model of pure anatase [6].

In the presence of impurity sulfur atoms in TiO_2 samples, their color deepens. Based on the results of calculations of the UV spectra of the models considered, for example, for a cluster with an impurity sulfur atom of the sulfide type, the absorption spectrum contains 4 bands in the visible and near UV regions, of which the longest wavelength ($\lambda_{\text{max}} = 358 \text{ nm}$) is 78 % due to the transition of electrons from the highest occupied to the lowest unoccupied molecular orbital. A noticeable contribution (from 19 to 31 %) to this absorption band is also made by transitions from three occupied orbitals lying

below the HOMO to three vacant orbitals lying above the LUMO. The transition to a cluster with two sulfide type sulfur atoms leads to the presence of intense absorption bands with $\lambda_{\text{max}} = 360$ and 392 nm . Note that the sulfite and sulfate groups in the anatase structure are characterized by intense absorption in the near ultraviolet region – about $\lambda_{\text{max}} = 270\text{--}290 \text{ nm}$, while in the visible region the absorption is very weak. This may be due to the absence of direct contact between titanium and sulfur atoms, since they are separated by oxygen atoms.

The spatial structure of cluster models and XPS spectra of impurity carbon atoms in TiO_2 samples are shown in Figs. 3 and 4.

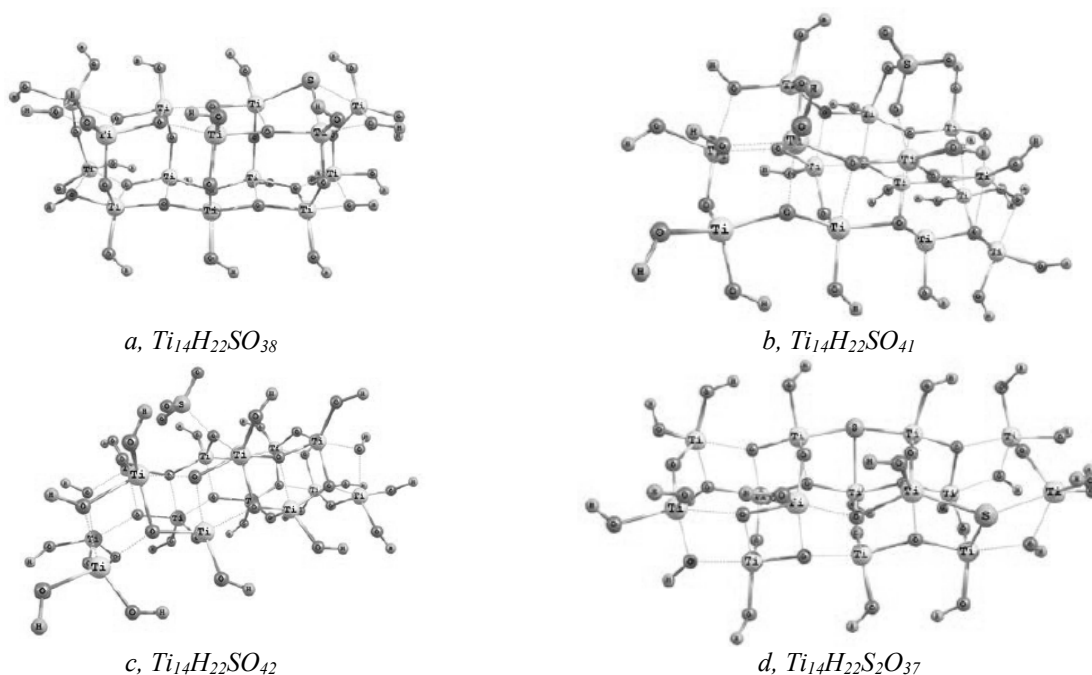


Fig. 1. Spatial geometry of the anatase models for incorporated one (a, b, c) and two (d) S atoms

Five peaks of $O1s$ can be observed in the XPS spectrum calculated for the $\text{Ti}_{14}\text{H}_{22}\text{O}_{39}$ cluster model (about 521 eV). Each peak can be assigned to a specific type of O atoms.

Impurity carbon atoms in the structure of the TiO_2 cluster. According to the experimental data [2], carbon in the structure of titanium dioxide appears in the XPS spectra in the range 282–290 eV. We have considered cluster models of TiO_2 containing carbon atoms in different

oxidation states: one and two carbide carbon atoms, as well as a carbonate group in the anatase structure. According to the calculation results, the $C1s$ peaks in the region of 278.1 eV correspond to the carbide type carbon atoms. The transition from one to two carbon atoms in a cluster leads to some complication of the spectrum: the $C1s$ peak splits into two components (277.6 and 278.6 eV, Fig. 3). According to the calculation data, the presence

of a carbonate group corresponds to the peaks in the spectra in the range of 270–271 eV (*C1s*). The presence of carbon atoms, similar to the sulfur atom in the anatase structure, leads to the

splitting of the titanium and oxygen peaks in the XPS spectra (Fig. 4) in comparison with the cluster model for pure anatase [6].

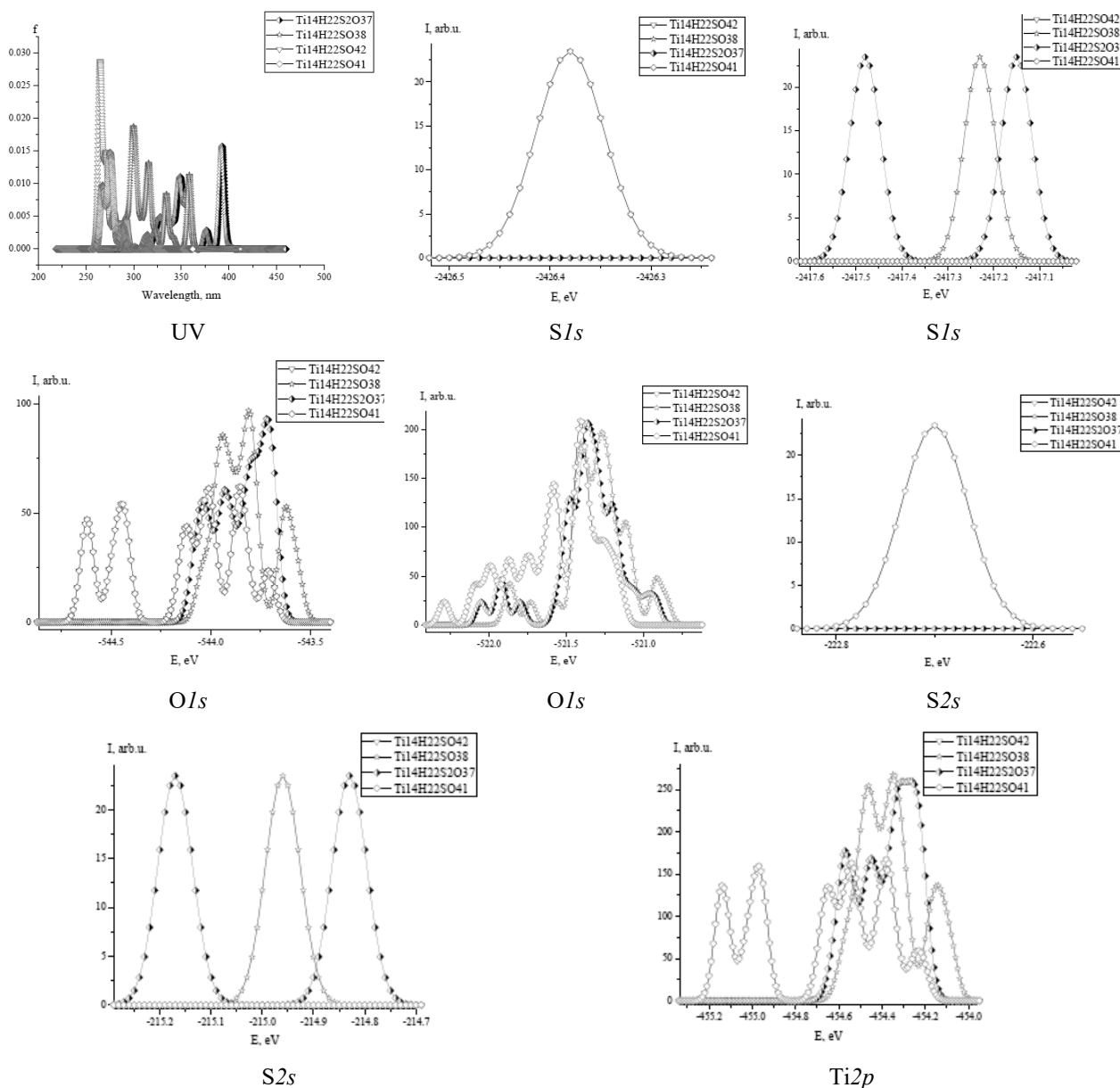


Fig. 2. UV and XPS spectra of the anatase models for incorporated one and two S atoms

The presence of impurity carbon atoms in TiO_2 samples leads to a deepening of their color. Based on the results of calculations of UV spectra of the models considered, for example, for a cluster with an impurity carbon atom of the carbide type, the absorption spectrum contains 3 bands in the visible and near UV regions, of

which the longest wavelength ($\lambda_{\text{max}} = 513 \text{ nm}$) is for 68 % due to the transition of electrons from the highest occupied to the lowest unoccupied molecular orbital. The transition to a cluster with two carbon atoms of a carbide nature (one of them is three-coordinated, the other is five-coordinated) leads to three intense absorption

bands – with $\lambda_{\max} = 474, 549, \text{ and } 675 \text{ nm}$. The carbonate group in the anatase structure is characterized by intense absorption in the near ultraviolet region – about $\lambda_{\max} = 268\text{--}296 \text{ nm}$,

while absorption in the visible region is very weak. This may be due to the absence of direct contact between titanium and carbon atoms, since they are separated by oxygen atoms.

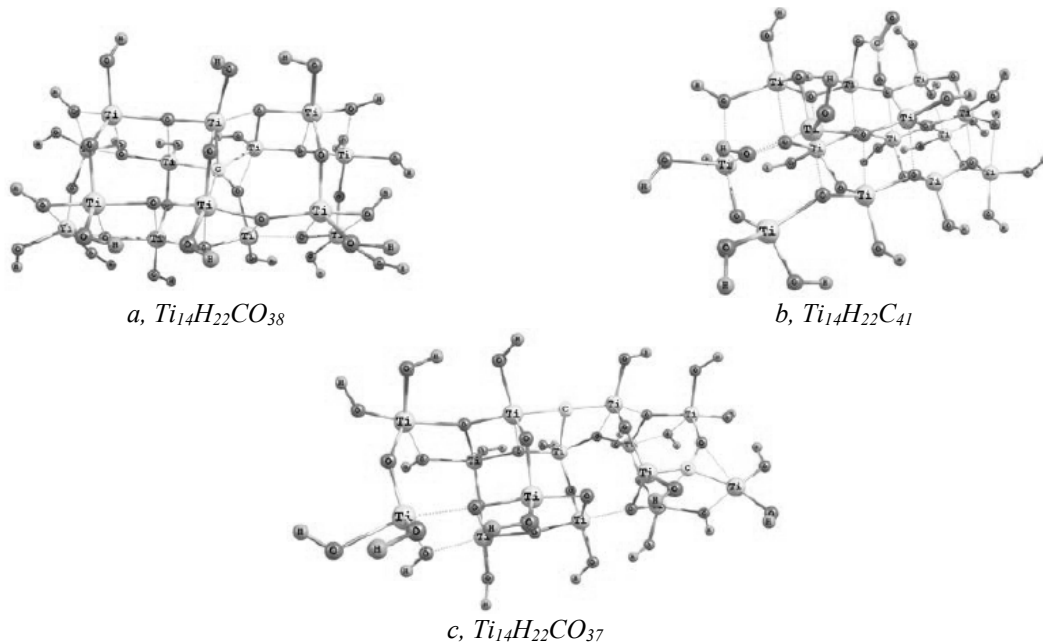


Fig. 3. Spatial geometry of the anatase models for incorporated one (a, b) and two (c) C atoms

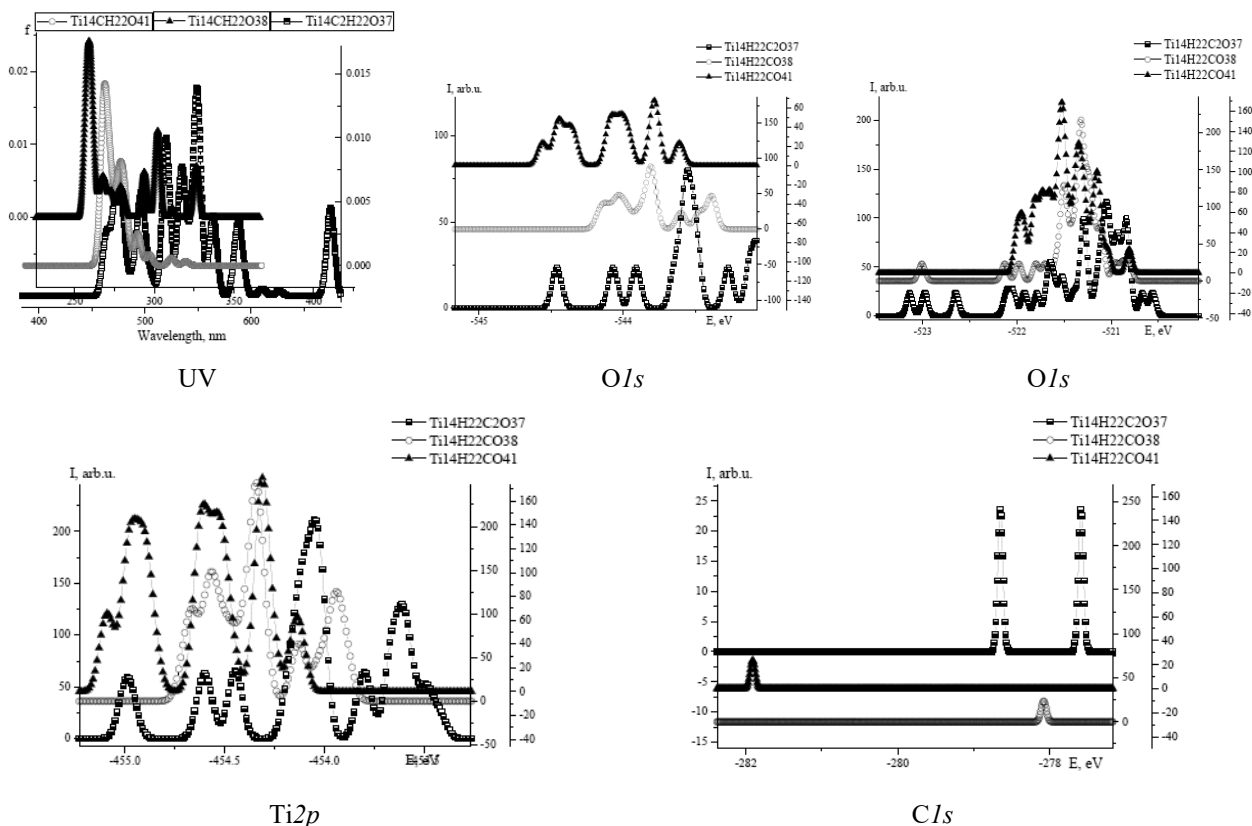


Fig. 4. UV and XPS spectra of the anatase models for incorporated one and two C atoms

CONCLUSIONS

Comparison of the results of quantum-chemical calculations with the available experimental data shows that impurity sulfur and carbon atoms in titanium dioxide, which are in various coordination states and different oxidation states, appear in different spectral ranges. This circumstance makes it possible to

elucidate the structure of the samples based on the experimental spectra.

A change in the coordination and oxidation state of impurity atoms leads to spectral shifts and splitting of peaks, which can reach 1.5 eV (XPS).

The presence of impurities of non-metals leads to a change (deepening in the case of sulfide or carbide) color of the samples, which appears in the corresponding UV spectra.

Квантовохімічне дослідження впливу модифікації діоксиду титану неметалами на його спектральні характеристики

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Проаналізовано експериментальні результати, отримані при вивченні можливості сенсibilізації діоксиду титану (поліморфної фази анатазу) до видимої області спектра шляхом допущення та ко-допущення домішками неметалів з метою створення ефективних фотокаталізаторів для розкладання органічних сполук.

Присутність домішкових атомів призводить до зміни електронної структури матриці діоксиду титану, появи «домішкових зон» і звуження енергетичної щільності діоксиду титану. Таке модифікування супроводжується розширенням спектральної області чутливості фотоактивних твердих тіл у довгохвильову область спектра і тому може бути використано для поліпшення каталітичних властивостей цих матеріалів.

Методом теорії функціонала електронної густини досліджено спектральні прояви домішок вуглецю в діоксиді титану у формі карбїду та карбонату, а також сірки в формах сульфїту, сульфїду і сульфату. Як моделі матриці діоксиду титану обрано кластер складу $Ti_{14}H_{22}O_{39}$. Розрахунки проводились в рамках кластерного наближення. з використанням функціоналу B3LYP та базисного набору 6-31G (d, p). Порівняння результатів квантовохімічних розрахунків з наявними експериментальними даними свідчить, що домішкові атоми сірки і вуглецю в діоксиді титану, що знаходяться в різному координаційному стані і різних ступенях окиснення, проявляються в різних діапазонах спектрів. Ця обставина дає можливість встановити структуру зразків, виходячи з експериментальних спектрів.

Зміна координації і ступеня окиснення домішкових атомів призводить до спектральних зсувів і розщепленню піків, які можуть досягати 1.5 eV (XPS). Присутність домішок неметалів призводить до зміни (поглиблення в разі сульфїду або карбїду) забарвлення зразків, що проявляється у відповідних УФ спектрах.

Ключові слова: анатаз, кисневий дефект, домішка вуглецю, домішка сірки, РФЕС спектри, квантовохімічний метод теорії функціонала електронної густини, кластерні моделі

Квантовохимическое исследование влияния модификации диоксида титана неметаллами на его спектральные характеристики

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Проанализированы экспериментальные результаты, полученные при изучении возможности сенсбилизации диоксида титана (полиморфной фазы анатаза) к видимой области спектра путем допирования и со-допирования примесями неметаллов с целью создания эффективных фотокатализаторов для разложения органических соединений.

Присутствие примесных атомов приводит к изменению электронной структуры матрицы диоксида титана, появлению «примесных зон» и сужению энергетической щели диоксида титана. Такое модифицирование сопровождается расширением спектральной области чувствительности фотоактивных твердых тел в длинноволновую область спектра и поэтому может быть использовано для улучшения каталитических свойств этих материалов.

Методом теории функционала плотности исследованы спектральные проявления примесей углерода в диоксиде титана в форме карбида и карбоната, а также серы в формах сульфита, сульфида и сульфата. В качестве модели матрицы диоксида титана выбран кластер состава $Ti_{14}H_{22}O_{39}$. Расчеты проводились в рамках кластерного приближения с использованием функционала B3LYP и базисного набора 6-31G (d, p).

Сравнение результатов квантовохимических расчета с имеющимися экспериментальными данными показывает, что примесные атомы серы и углерода в диоксиде титана, находящиеся в различном координационном состоянии и различных степенях окисления, проявляются в разных диапазонах спектров. Это обстоятельство дает возможность установить структуру образцов, исходя из экспериментальных спектров.

Изменение координации и степени окисления примесных атомов приводит к спектральным сдвигам и расщеплению пиков, которые могут достигать 1.5 эВ (XPS). Присутствие примесей неметаллов приводит к изменению (углублению в случае сульфида или карбида) окраски образцов, что проявляется в соответствующих УФ спектрах.

Ключевые слова: анатаз, кислородный дефект, примесь углерода, примесь серы, РФЭС спектры, квантовохимический метод теории функционала электронной плотности, кластерные модели

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