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Visible light absorption of TiO_2 nanoparticles surface-modified with vitamin B_6: A comparative experimental and DFT study

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Abstract: Surface modification of titanium dioxide nanoparticles (TiO_2 NPs) with the biologically active molecule pyridoxine hydrochloride (vitamin B_6) was found to alter the optical properties. Microstructural characterization involving transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis revealed that the anatase TiO_2 NPs had a narrow size distribution with an average diameter of 45 Å. The absorption onset of the surface-modified TiO_2 samples was red-shifted by about 0.4 eV compared to the unmodified particles. The mode of binding between vitamin B_6 and the surface Ti atoms was investigated by Fourier transform infrared spectroscopy (FTIR). From the Benesi–Hildebrand plot, the stability constant of the surface complex was found to be of the order 10^2 M^{-1}. The experimental findings were supported by detailed quantum chemical calculations based on the density functional theory (DFT). Agreement was found between the experimentally measured absorption spectra of the TiO_2 NPs surface-modified with vitamin B_6 and the theoretically calculated electronic excitation spectra of the corresponding model system.

Keywords: anatase; pyridoxine hydrochloride; charge transfer complex; optical properties; quantum chemical calculations.

INTRODUCTION

Titanium dioxide is the photocatalytic material that has been the most extensively studied over the past years because it is inexpensive, nontoxic and stable.[1]

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However, the use of TiO_2 for photocatalytic applications driven by solar light is limited because TiO_2 has a wide band gap (E = 3.2 eV) and thus absorbs less than 5 % of the available photons of the solar spectrum. Therefore, there has been tremendous interest in recent years to improve the visible light absorption of TiO_2, including sensitization with organic dyes,[2] doping with nitrogen and other elements,[3–5] and use of plasmonic Au and Ag nanoparticles.[6–8] Another emerging approach in the design of visible-light responsive TiO_2 is based on the formation of a charge-transfer complex (CTC) between surface Ti atoms and bidentate benzene derivatives. This type of binding is considered to be exclusive for colloidal TiO_2 particles in the nanocrystalline domain due to the change of the coordination of Ti surface atoms from octahedral to square-pyramidal.[9,10] Hitherto, CTC formation, accompanied with a red-shift of the absorption onset of up to 1.3 eV, has been reported for TiO_2 nanoparticles (NPs) surface modified with either catecholate- or salicylate-type of ligands.[11–17] Recently, it was shown that the formation of Ti–O–C linkages between surface Ti atoms and aromatic mono-hydroxy compounds can occur.[18,19] To date, a limited number of studies concerning the photocatalytic production of H_2[20,21] and the photocatalytic degradation of organic dyes[22] over visible-light responsive TiO_2 have been reported, while, on the other hand, there is a lack of information about the possibility of using TiO_2 NPs for the selective detection of colorless biomolecules.[9,23]

On the theoretical side, quantum chemical calculations based on the density functional theory (DFT) have been extensively used to support experimental findings, and electronic structure of variety of inorganic/organic hybrids and the geometry of ligands coordinated to the surface of metal oxides, and the vibrational spectra of attached ligands have been calculated.[14–20,24–26]

This study is a continuation of on-going efforts to design visible-light responsive TiO_2 NPs taking advantage of the condensation reaction between surface hydroxyl groups (Ti–OH) and benzene derivatives. For the first time, the Ti–O–C linkage between biologically active molecule pyridoxine hydrochloride (vitamin B_6) and TiO_2 NPs was achieved. Microstructural characterization involving transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis revealed that TiO_2 colloids consisted of relatively uniform nanoparticles with an average size of about 45 Å and a low level of crystallinity. Special attention was paid to the optical properties of TiO_2 NPs. Absorption spectroscopy was used for optical characterization of surface-modified TiO_2 NPs surface-modified with vitamin B_6, as well as determination of composition and stability constant of surface complex. In addition, detailed quantum chemical calculations based on the density functional theory (DFT) were performed and the theoretically obtained UV–Vis spectra of a properly designed model cluster were compared with experimentally obtained spectroscopic data. Infrared spectroscopy was used in order to understand the coordination of vitamin B_6 to the surface Ti atoms.

EXPERIMENTAL

Chemicals

All used chemicals were of the highest purity available and were used without further purification (Alfa Aesar, JT Baker). Milli-Q deionized water (resistivity 18.2 MΩ cm) was applied as the solvent.

Synthesis and characterization of surface-modified TiO_2 NPs by vitamin B_6

The colloid consisting of TiO_2 NPs was prepared by the dropwise addition of titanium(IV) chloride to cooled water, as described elsewhere.[27] Briefly, the pH of the solution was between 0 and 1, depending on the $TiCl_4$ concentration. Slow growth of the particles was achieved by using dialysis at 4 °C against water until the pH 3.5 was reached. The concentration of the TiO_2 colloids was determined from the concentration of the peroxide complex obtained after dissolving the colloid in concentrated H_2SO_4.[28]

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 LaB_6 instrument operated at 200 kV. TEM images were acquired with a Gatan Orius CCD camera at 2× binning. X-ray diffraction (XRD) powder patterns were recorded using a Rigaku SmartLab instrument under $CuK_{\alpha1,2}$ radiation. The intensity of diffraction was measured by continuous scanning at 2° min^{-1}. The data were collected at 0.02° intervals.

Surface modification of colloidal TiO_2 NPs was achieved by the addition of vitamin B_6 up to concentrations required to cover all surface sites ($[Ti_{surf}] = 12.5[TiO_2]/D$, where $[Ti_{surf}]$ is molar concentration of surface Ti sites, $[TiO_2]$ is the molar concentration of TiO_2, and D is the diameter of the particle in angstroms[29]). In order to avoid precipitation or “gelling” of the TiO_2 colloid due to enhanced particle–particle interaction upon surface modification that eliminates the surface charge, the pH of the stock colloidal solutions was adjusted in the range from 2 to 4.

For the determination of the binding constant, the absorption spectra of colloidal solutions with a fixed TiO_2 concentration and the increasing concentrations of vitamin B_6 were recorded at room temperature using Thermo Scientific Evolution 600 UV–Vis spectrophotometer. The continual variations method (Job’s method)[30] was applied for the spectrophotometric determination of the complex composition. The solutions were prepared by mixing equimolar solutions of Ti_{surf} and vitamin B_6 (0.025 M). The sum of the concentration of Ti_{surf} and modifier was constant (0.025 M), but their proportions were continuously varied: volumes of TiO_2 solution used varied from 1 to 9 mL and those of the modifier solutions from 9 to 1 mL with the total volume always being 10 mL.

Infrared spectroscopy measurements of free vitamin B_6 and that bound to the surface of TiO_2 NPs were performed using a Thermo Nicolet 6700 FTIR spectrometer at spectral resolution of 8 cm^{-1} in the region of 4000–400 cm^{-1} in the form of KBr pellets.

DFT calculations

DFT and TD-DFT calculations were performed to examine the electronic excitation spectra of TiO_2 NPs surface-modified with vitamin B_6. The model system used for calculations, $[Ti_8O_{14}(OH)_3]^+$ cluster, was derived from bulk anatase TiO_2.[18] The ground state geometry of the $[Ti_8O_{14}(OH)_3(B_6)]^+$ was optimized using the CAM-B3LYP (Coulomb-attenuating method) functional,[31,32] which takes into account a long-range correction in combination with the 6-31G(d,p) basis set.[33,34] The frequency calculations were realized at the same level of theory. To preserve the crystal structure of anatase, the titanium and oxygen atoms of the cluster were frozen during the optimization, while all atoms of the ligand molecules were allowed to relax. The electronic excitation spectra were also calculated at the same level of theory within the TD-DFT formalism.[35] The solvent effect of water on the absorption spectrum was included *via* the SMD solvation model.[36] All the calculations were performed using the Gaussian 09 suit of programs.[37] The convoluted UV–Vis spectrum was obtained using GaussSum[38] software.

RESULTS AND DISCUSSION

A representative TEM image at high magnification of the colloidal TiO_2 particles, prepared by the hydrolysis of titanium(IV) chloride, is presented in Fig. 1a. The TEM image indicated the presence of nearly spherical TiO_2 NPs with a low level of crystallinity and an average size of about 45 Å. Analysis of the selected area electron diffraction (SAED) pattern (inset to Fig. 1a) revealed that the observed diffraction ring corresponds to the (101) plane of the anatase crystal structure. A typical XRD pattern of the colloidal 45-Å TiO_2 NPs is shown in Fig. 1b. The characteristic peaks at 25.3, 37.8, 48.1, 53.9/55.1 and 62.1° correspond to 101, 004, 200, 105/211, and 204 reflections from TiO_2 with an anatase crystal structure (JCPDS 21-1272). It should be noticed that there is no indication of the presence of any other crystalline phase. The crystallite size, determined from diffraction peak broadening using the Scherrer equation, was found to be around 15 Å.

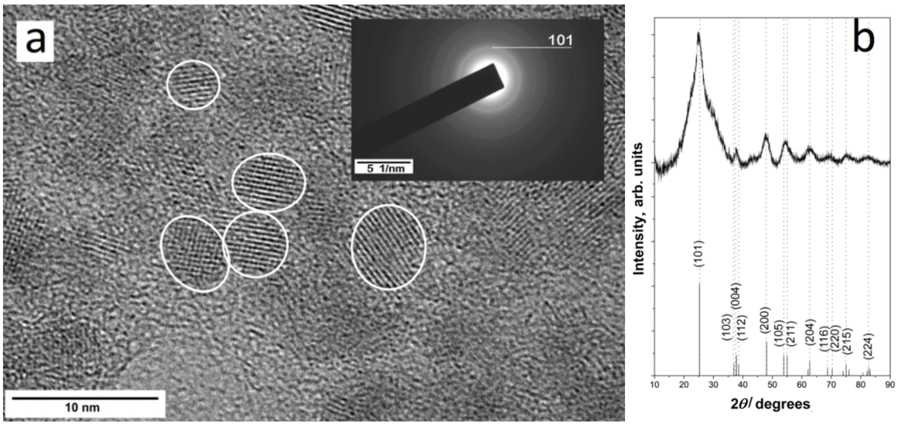

Fig. 1. a) Typical TEM image of colloidal TiO_2 particles; inset: corresponding SAED pattern and b) XRD pattern of dried TiO_2 colloid; the most pronounced reflections are indexed according to JCPDS card No. 21-1272 (anatase TiO_2).

In TiO_2 NPs with diameters smaller than 20 nm, the presence of undercoordinated surface Ti atoms significantly changes the properties of the nanoparticles compared to those of bulk material.[9,10] Surface modification of colloidal 45-Å TiO_2 NPs by vitamin B_6 induced a red shift in the absorption onset compared to unmodified ones (compare curves a and b in Fig. 2). The red-shift of the absorption threshold in the modified semiconductor nanoparticles is attributed to the excitation of localized electrons from the surface modifier into the conduction band continuum states of the semiconductor particle.[39] In this case, the observed red shift of about 0.4 eV is smaller compared to the literature data for 45-Å TiO_2 NPs surface-modified by bidentate benzene derivatives.[12–17] On the other hand, with exception of recent reports for phenol and its derivatives,[18,19] there is a lack of information concerning coordination of mono-hydroxy compounds to TiO_2. To the best of our knowledge, this is the first example of Ti–O–C linkage between surface Ti atoms and a colorless biomolecule, vitamin B_6.

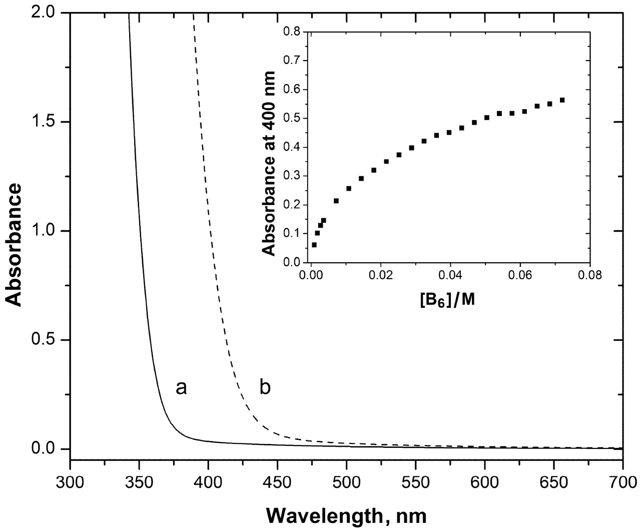

Fig. 2. Absorption spectra of: a) bare TiO_2 and b) TiO_2 NPs surface-modified by vitamin B_6. Inset: absorbance at 400 nm of CTC *vs*. modifier concentration (18.0 mM TiO_2, pH 2.5, data were recorded 24 h after surface modification).

Since hybrid semiconducting materials exhibit optical properties that are distinct from their constituents, not absorbing in the visible spectral region, Benesi–Hildebrand analysis for molecular complexes[40,41] could be employed for the determination of the stability constant. The stability constant, K_b, was determined from the absorbances (A) of a series of solutions (Fig. 2, inset) containing a fixed concentration of 45-Å TiO_2 NPs ($[TiO_2]$ = 18.0 mM, *i.e.*, $[Ti_{surf}]$ = 5.0 mM) and increasing concentrations of ligand ($[B_6]$, 0.9–72.0 mM). On plotting $1/A$ *vs*. $1/[B_6]$, a straight line was obtained, and from the ratio of the intercept ($1/K_bA_{max}$) and the slope ($1/A_{max}$), the K_b value was found to be 3.0×10^2 M^{-1}. The determined stability constant is an order of magnitude smaller compared to the reported values for 45-Å TiO_2 NPs surface-modified with catecholate- and salicylate-types of ligands.[12–17] For example, stability constant for CTC between 45-Å TiO_2 NPs and catechol was reported to be 2.5×10^3 M^{-1}.[12] A similar ratio between the adsorption constant values was observed upon adsorption of catechol and phenol onto Degussa P25 TiO_2 powder.[42] Significantly lower

Langmuir adsorption constant for phenol was reported than that of for catechol (0.0098 and 0.0585 mg L^{-1}, respectively).

The stoichiometric ratio between Ti_{surf} atoms and vitamin B_6 was examined by the Job's method of continuous variation[30] assuming that only one type of complex is present in solution. According to the Job's method, the stoichiometric ratio (n) was determined from the plot of the absorbance as a function of the mole fraction (x) of metal or ligand. The ratio $x_{max}/(1-x_{max})$, where x_{max} corresponds to the mole fraction in the absorbance maximum, equals the stoichiometric ratio (n). The stoichiometric ratio between Ti_{surf} and vitamin B_6 was obtained by plotting the absorbance of the complex *vs*. $x = [Ti_{surf}]/([Ti_{surf}]+[B_6])$. The Job's plot reached a maximum value at a mole fraction of $[Ti_{surf}]/([Ti_{surf}]+[B_6]) \approx 0.6$ (Fig. 3), indicating the molar ratio between Ti_{surf} atoms from 45-Å TiO_2 NPs and vitamin B_6 in the complex to be $[Ti_{surf}]:[B_6] = 1.5:1$.

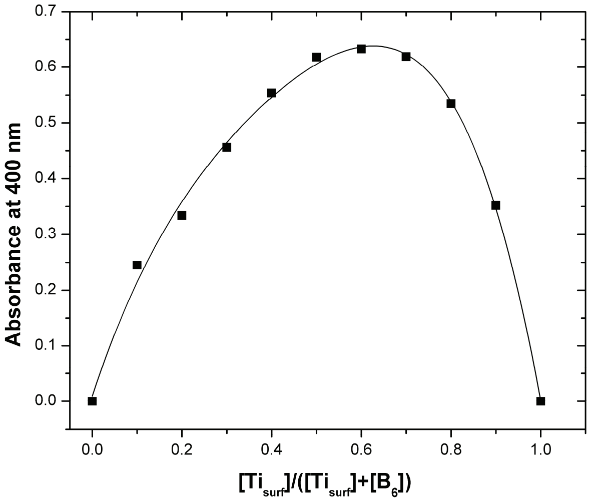

Fig. 3. Job's curve of equimolar solutions for vitamin B_6–Ti_{surf} complex; $[Ti_{surf}]+[B_6] = 0.025$ M.

In order to obtain deeper insight into the optical properties of the inorganic/ /organic hybrid, the electronic excitation spectra of the $B_6/[Ti_8O_{14}(OH)_3]^+$ cluster was calculated using the TD-DFT method. The constructed model of the $[Ti_8O_{14}(OH)_3(B_6)]^+$ surface complex was based on the dehydration reaction between the two hydroxyl groups, the first, originating from vitamin B_6, and the second one, from the surface of the oxide. The calculated electronic excitation spectrum of the $[Ti_8O_{14}(OH)_3(B_6)]^+$ cluster is shown in Fig. 4, while the data associated with the first three lowest excitations are collected in Table S-I of the Supplementary material to this paper. The optimized structure of the model cluster is presented as the inset to Fig. 4, while the spatial distributions of the

HOMO and LUMO for the $[Ti_8O_{14}(OH)_3(B_6)]^+$ cluster are shown in Fig. S-1 of the Supplementary material. There is agreement between the experimentally measured absorption spectrum of the TiO_2 surface-modified with vitamin B_6 colloid and the theoretically calculated electronic excitation spectrum of the $[Ti_8O_{14}(OH)_3(B_6)]^+$ cluster (compare Figs. 2 and 4). It should be emphasized that the existing model system, ligand – $[Ti_8O_{14}(OH)_3]^+$ cluster,[18] was upgraded by including effect of the solvent on the absorption spectrum.[36] In addition, the optimized structure of $[Ti_8O_{14}(OH)_3(B_6)]^+$ cluster (see inset to Fig. 4) indicates that molecules of vitamin B_6 are not perpendicularly attached to the surface of the TiO_2 NPs. The optimal angle for the proposed Ti–O–C linkage/bridge was found to be 129°. Steric hindrance, induced by the tilted position of the attached vitamin B_6 molecules to the TiO_2 surface, might be the explanation for the non-equimolar composition of the surface of the complex.

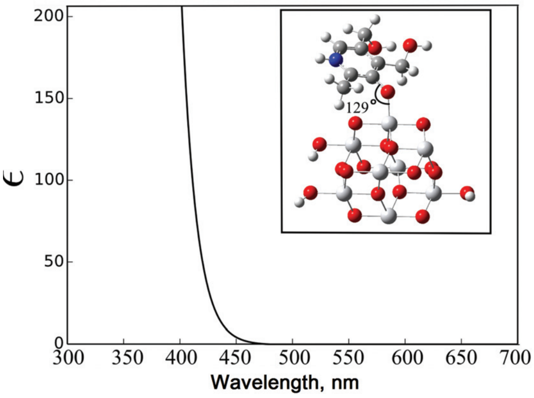

Fig. 4. The electronic excitation spectrum of $[Ti_8O_{14}(OH)_3(B_6)]^+$ clusters calculated by convolution with a full width at the half maximum of 5000 cm^{-1}. DFT-optimized structures for the $[Ti_8O_{14}(OH)_3(B_6)]^+$ clusters (gray: carbon, white: hydrogen, red: oxygen, large white: titanium, blue: nitrogen).

Although the optimized structure of the $[Ti_8O_{14}(OH)_3(B_6)]^+$ cluster indicates that attachment of vitamin B_6 molecules to the surface of TiO_2 NPs occurs over one attachment point (phenolate-type of linkage), infrared measurements were performed in order to clarify the mode of binding of the organic moiety to the surface of the oxide. Since the infrared spectrum of TiO_2 has a characteristic broad-band in 3700–2000 cm^{-1} spectral region, as well as bands at about 1620 and 500 cm^{-1},[43] it is possible to compare the FTIR spectra of the surface-modified TiO_2 powders with free ligand. The FTIR spectra of vitamin B_6, free and bound to the surface of colloidal TiO_2 NPs are presented in the fingerprint region from 1600 to 1240 cm^{-1} (see Fig. 5, curves a and b, respectively).

The FTIR spectrum of free vitamin B_6 is in agreement with literature data.[44,45] Briefly, the band at 1545 cm^{-1} belongs to the stretching vibrations protonated pyridine ring, while the bands around 1455 and 1390 cm^{-1} originate from the bending vibrations of C–H bonds from methylene and methyl groups, respectively. The bands at 1482 and 1415 cm^{-1} correspond to aromatic ring stretching vibrations. A characteristic band that belongs to the stretching vibrations of C–O bond of the phenolic group appears at 1280 cm^{-1}, while the band at 1329 cm^{-1} corresponds to the bending vibrations of the phenolic –OH group.[46]

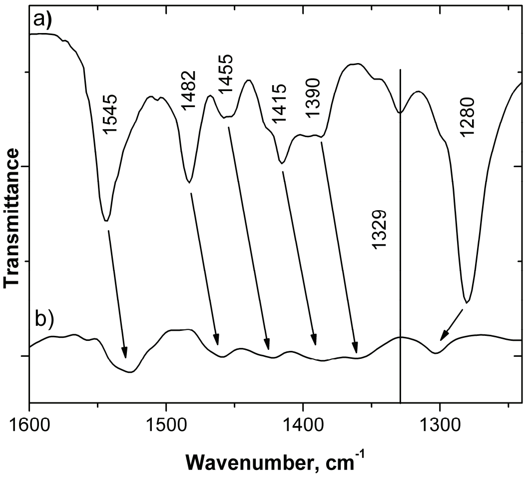

Fig. 5. FTIR spectra of vitamin B_6: a) free and b) adsorbed on 45-Å TiO_2 NPs.

Although the resolution and signals are both low, the FTIR spectrum of vitamin B_6 bound onto TiO_2 NPs (curve b in Fig. 5) has all characteristic bands present in the spectrum of free vitamin B_6, with the exception of the band at 1329 cm^{-1} that belongs to bending vibration of the phenolic –OH group. In addition, the band originating from the C–O stretching vibrations of the phenolic group is shifted to higher frequency (1305 cm^{-1}) and its intensity was decreased compared to results obtained for free vitamin B_6 much more than the intensities of the other bands. These results indicate that vitamin B_6 binds to the surface Ti atoms through a phenolate linkage, *i.e.*, in the same way as predicted in the model used for the DFT calculations (see inset to Fig. 4). The proposed structure is in agreement with literature data concerning surface complexes between phenol, as well as its derivatives (4-chlorophenol), and various commercial TiO_2 powders.[18,47,48]

CONCLUSIONS

The ability of vitamin B_6 to form surface complex with 45-Å TiO_2 NPs was tested. Binding of the modifier molecules to undercoordinated surface Ti atoms (defect sites) induced a 0.4 eV shift in the absorption to the visible spectral region. The stability constant of the CTC was found to be 3.0×10^2 M^{-1}. FTIR measurements revealed that vitamin B_6 is bound to the surface Ti atoms through phenolate linkages. The obtained experimental results were supported by detailed DFT calculations, and agreement between the experimental data and the theoretical predictions was found. The presented results indicate that tunable optical property of hybrids is not exclusively a consequence of the formation of binuclear (bridging) complexes between salicylate- and catecholate-type of ligands and surface Ti atoms and can be achieved through a single Ti–O–C linkage. It is obvious that the increased number of ligand molecules capable of forming hybrids with wide band gap oxides provides the possibility to extend this type of research from entirely fundamental to more applicable.

SUPPLEMENTARY MATERIAL

Parameters of electronic excitations calculated for $[Ti_8O_{14}(OH)_3(B_6)]^+$ clusters and spatial distributions of molecular orbitals are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

АПСОРПЦИЈА НАНОЧЕСТИЦА TiO_2 ПОВРШИНСКИ МОДИФИКОВАНИХ ВИТАМИНОМ B_6 У ВИДЉИВОМ ДЕЛУ СПЕКТРА: УПОРЕДНА ЕКСПЕРИМЕНТАЛНА И DFT СТУДИЈА

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Површинска модификација наночестица титан-диоксида (TiO_2) биолошки активним молекулима пиридоксин-хидрохлорида (витамин B_6) доводи до промене њихових оптичких својства. Микроструктурна карактеризација синтетисаних наночестица TiO_2 која обухвата трансмисиону електронску микроскопију (TEM) и дифракцију рендгенских зрака (XRD) показала је да наночестице анатаза имају уску дистрибуцију величина са средњим пречником од 45 Å. Праг апсорпције површински модификованих наночестица TiO_2 је за 0,4 eV померен ка већим таласним дужинама у односу на спектар немодификованих честица. Коришћењем FTIR спектроскопије утврђен је начин везивања витамина B_6 за површинске атоме титана. Константа стабилности површинског комплекса је одређена на основу Бенеси–Хилдебрандове (Benesi–Hildebrand) анализе и износи $3{,}0\times10^2$ M^{-1}. Експериментални резултати су поткрепљени детаљним квантно-хемијским прорачунима заснованим на теорији функционала густине (DFT). Утврђен је висок ниво сагласности између апсорпционог спектра наночестица TiO_2 и теоријски добијеног електронског ексцитационог спектра одговарајућег модела.

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