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Raman spectroscopy of the laser irradiated titanium dioxide

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Abstract. Evolution of anatase phase for the TiO₂ nanocrystals at their laser irradiation is researched by the method of combinational light dispersion. The observed changes of intensity, frequency and halfwidth of TiO₂ phonon lines are interpreted taking into account the effects of nonstoichiometry, superficial strains and phonon confinement. The found out parameter changes in the low frequency E_g mode show that laser irradiation results in substantial improvement of the structural ordering in the area of TiO₆ octahedrons bonds.

Keywords: Titanium dioxide, Intercalation, Anatase, Raman spectroscopy.

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1. Introduction

Nowadays titanium dioxide is used as electrode material for the lithium power sources [1-3]. The nanodispersed forms of TiO₂ are very important, as they give possibilities to carry out lithium intercalation in the “host”-material more effectively. However, even in the case of nanodispersed TiO₂ using the availability of their «guest» positions is supposed to be improved. Therefore, the various external influences are used for their activation, which allow to increase «guest» loading and, accordingly, to form the power sources with higher specific power characteristics.

2. Experimental

Laser radiation was used to activate “guest” positions in nanodispersed TiO₂ of the firm «Aldrich» (average size of particles < 25 nm, anatase phase); laser radiation was made in vacuum ($P = 10^{-5}$ Torr) by using Nd:YAG-laser that operates in the mode of the modulated Q-factor (wavelength is $\lambda = 1.06$ μm , pulse duration is $\tau = 10$ ns, frequency of these pulses is $f = 28$ Hz, energy in the pulse is $E = 0.02$ - 0.04 J, duration of irradiation is $t = 4.5$ - 5.5 min).

Main structural transformations during laser radiation with nanodispersed titanium dioxide lie in a change of elementary cell parameters (Table 1) (experimental error $\pm 0.0001 \dots 0.0005$ E) and Frenkel

defects formation. At the same time, existent point defects get sufficient energy for their migration inside the bulk. Laser radiation has the biggest influence on materials with availability of native point defects and considerable heterogeneities (including other phases, interfaces, etc). Co-ordination disturbance of titanium and oxygen atoms is probably related to the appearance of fields of thermoelastic strains in their surrounding as a result of laser beam thermal influence. Localization of thermal energy causes the change in lattice parameters, which at the same time influences on the sizes and charge state of energy favorable «guest» positions for the intercalated lithium ions. The average size of coherent-scattering regions for different modes of laser irradiation did not change for the methodic error.

X-ray researches were realized using the diffractometer STOE STADI P with the linear position-sensitive detector (PSD) accordingly to the scheme of the modified Gin'e geometry, in the Bregg-Brentano mode (CuK α_1 - radiation; $\lambda = 1.54060$ E; Iogann type Gebended monochromator [111]; scanning step is $0.015^\circ 2\theta$, scanning time in the step is 400 s).

Raman spectra of nanodispersed titanium dioxide researches were carried out using the triple spectrometer of T64000 Jobin-Yvon (1800/mm, settling ability ≈ 1 cm^{-1}) in geometry of reverse dispersion, using the line 488 nm of argon- krypton laser. With the purpose to eliminate local overheating of the samples, laser radiation power did not exceed 1 mW/cm^2 .

Table 1. Changes of tetragonal lattice parameters and the values of “guest” loading of TiO₂ as a result of laser irradiation.

№ sample	Energy in the impulse E, Joule	Irradiation time, min.	Lattice parameters, E		Li ⁺ “Guest” intercalation degree	Coherent-scattering region, E
			<i>a</i>	<i>c</i>		
1	0	0	3.7884	9.5086	1.87	95
2	0.02	4.5	3.7874	9.5057	1.43	95
3	0.02	5	3.7878	9.5039	2.65	93
4	0.02	5.5	3.7866	9.5027	1.78	93
5	0.03	4.5	3.7884	9.5034	2.07	95
6	0.03	5	3.7872	9.5054	2.32	94
7	0.03	5.5	3.7873	9.5050	2.12	95
8	0.04	4.5	3.7874	9.5042	2.11	94
9	0.04	5	3.7866	9.5016	1.47	94
10	0.04	5.5	3.7877	9.5033	3.50	95

3. Results and discussion

TiO₂ with the anatase structure belongs to the spatial group of D_{4h}^{19} symmetry. In this structure, the titanium ions are surrounded by six ions of oxygen that are located in vertexes of the partly distorted octahedron, at the same time three ions of metal that co-ordinate each of anions lie in the vertexes of semi-perfect triangle. Accordingly to the theoretical group analysis for tetragonal anatase structure, optical phonon modes active in the process of Raman scattering for G-points of Brillouin center zone ($\vec{q}=0$) can be presented by six nonreducible representations: $G = 3E_g + 2B_{1g} + A_{1g}$. As a result, it is possible to observe in the experimental Raman spectrum $3E_g$ nonpolar modes with frequency positions 143, 197 and 639 cm⁻¹ [4] (see, Fig. 1 as $E_g(1)$, $E_g(2)$ and $E_g(3)$, accordingly), $2B_{1g}$ nonpolar modes at ~ 399 and ~ 519 cm⁻¹ and A_{1g} mode at ~ 513 cm⁻¹. Phonon B_{1g} modes nearly ~ 513 and ~ 519 cm⁻¹ are well spectrally separated only at low temperatures [5].

The narrow and very intense phonon band at 143 cm⁻¹ $E_g(1)$ corresponds to oscillation of bridges between the octahedrons of TiO₆. Oscillations at 143, 197 cm⁻¹ ($E_g(1)$, $E_g(2)$ modes) and 393 cm⁻¹ (B_{1g} mode) are mainly O-Ti-O bending. The high-frequency bands at 639 cm⁻¹ ($E_g(3)$ mode) and at 514 cm⁻¹ (A_{1g} mode) are Ti-O strain oscillation (valency).

In our case for the unirradiated anatase, nc-TiO₂ samples frequency position of $E_g(1)$ phonon band is 145 cm⁻¹, which is higher as compared to the bulk TiO₂ (143 cm⁻¹). This effect can be conditioned by decreasing of crystal size [6], increasing of superficial strains [7], nonstoichiometry of chemical composition and by surface oxidization of particles [8], change of the lattice parameter [9]. The size of TiO₂ nanocrystals (found from the analysis of the low-frequency $E_g(1)$ of phonon mode) is about 12 nm [6]. In addition, broadening and shifting frequency (143 cm⁻¹) of $E_g(1)$ mode in the paper [8] is

connected to the «stoichiometry defects» in oxygen sublattice: at disturbance of the stoichiometry ratio O/Ti from 2.0 down to 1.89 there were broadening and high-frequency shift of $E_g(1)$ mode more than by 10 cm⁻¹ [10].

The authors also studied the effect of laser irradiation with the energy influence in the TiO₂ transparence area on its phonon spectra, which is not studied enough up to date. From Fig. 1, we can see that with increasing the nanocrystalline (nc) TiO₂ laser irradiation dose up to 0.04 J, the growth of integral intensity takes place for all phonon bands. The band intensity of $E_g(1)$ mode increases almost 10-fold (Fig. 2) and B_{1g} and $E_g(2)$ mode – by ~1.7 times. This effect of dominant intensity increase for $E_g(1)$ mode can be conditioned by improvement of structural order in TiO₂ inside the areas that connect TiO₆ octahedrons. It should be mentioned that with increase of the irradiated dose the frequency of $E_g(1)$ of phonon mode decreases from ~145.0 down to ~143/5 cm⁻¹ with its practically stable halfwidth ($\Delta \approx 8.0...8.2$ cm⁻¹) (Fig. 3). This effect of changing parameters for other phonon bands of nc-TiO₂ with the increase of irradiation dose is considerably lower. For example, for B_{1g} mode $\Delta\omega \approx 397.8-396.8$ cm⁻¹ and $\Delta \sim 21.0-21.6$ cm⁻¹, and for $E_g(3)$ mode $\Delta\omega \approx 640.5 - 639.8$ cm⁻¹, $\Delta \sim 22.0-22.5$ cm⁻¹. One of the main reason of substantial broadening B_{1g} and $E_g(3)$ phonon modes in Raman spectra is the presence of defects in small crystallites [11], which shows their high sensitivity to the defects as compared to the intensity of 143 cm⁻¹ $E_g(1)$ mode [12].

It should be noted that the small shift of frequency and change in the halfwidth of phonon lines E_g and B_{1g} in Raman spectra are not necessary conditioned by the change of TiO₂ nanoareas. In each case, the change of Raman phonon spectra can have its own peculiarities, which is determined by nonstoichiometry of elemental and phase composition as well as by dispersion of dimensions. Important factors that influence on the

frequency position of phonon lines in TiO₂ nanocrystals can be vacancies in the oxygen sublattice, internal microstrains, conditions at the particle surface, type and concentration of different active superficial centers, related to the adsorbed oxygen and hydroxyl molecular complexes, etc. For example, one of the reason of internal microstrain changes can be nc-TiO₂ surface oxidation due to oxygen that appears when reducing the coordinate-unsaturated cations Ti⁴⁺ under irradiation by visible light with the wavelength 600 up to 800 nm [8].

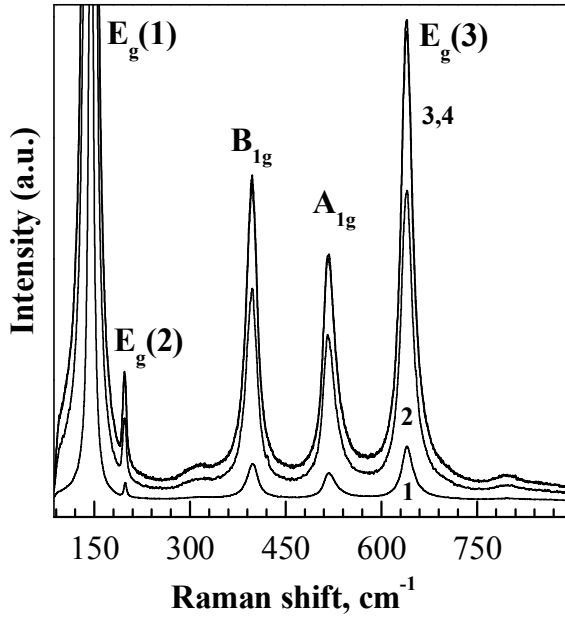


Fig. 1. Raman spectra of nc-TiO₂ : initial (curve 1) and irradiated by laser irradiation with the dose of 0.02, 0.03, 0.04 J (curves 2, 3, 4, accordingly). T = 300 K; λ_{exc} = 488.0 nm.

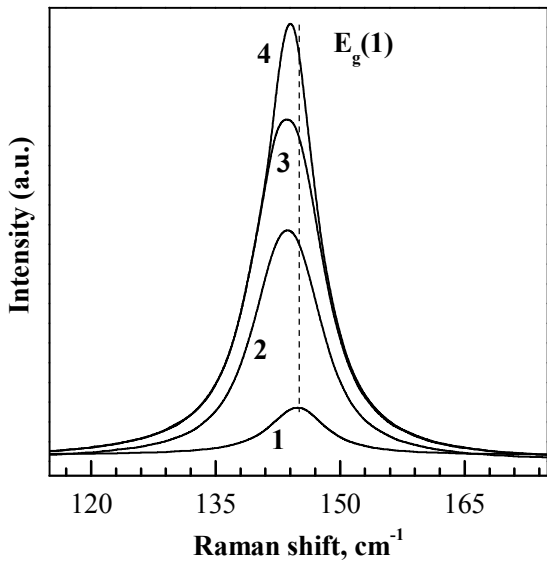


Fig. 2. E_g(1) mode of nc-TiO₂ at 144 cm⁻¹: spectra of initial (curve 1) and irradiated by laser irradiation with the dose 0.02, 0.03, 0.04 J (curves 2, 3, 4, accordingly). T = 300 K. λ_{exc} = 488.0 nm.

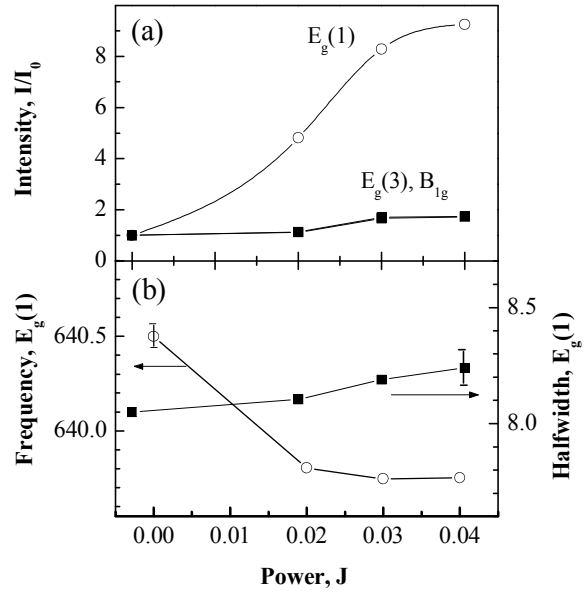


Fig. 3. Relative intensity change E_g(1), E_g(3), B_{1g} of phonon mode (a), frequency and halfwidth of E_g(1) mode vs laser irradiation power (b). T = 300 K. λ_{exc} = 488.0 nm.

Also, we researched the influence of the process of electrochemical intercalation in TiO₂ on its phonon spectra at different stages of x intercalation. The nonpolar mode with the frequency positions 144, 168 and 774 cm⁻¹ (E_g(1), E_g(2) and E_g(3), accordingly), 2B_{1g} nonpolar mode at ~444 cm⁻¹ and A_{1g} mode at ~604 cm⁻¹ are observed in the experimental Raman spectrum (Fig. 4).

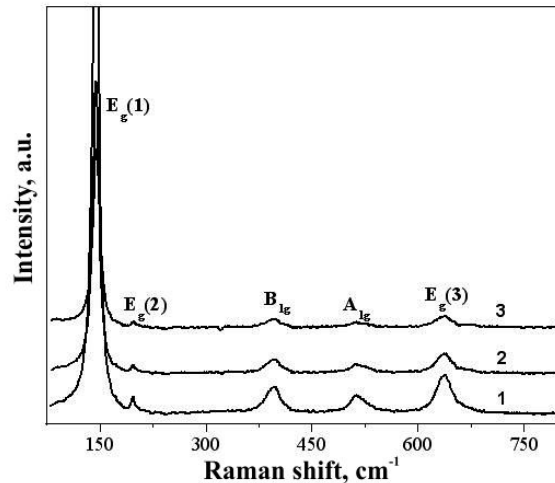


Fig. 4. Raman spectra of nc-TiO₂ intercalated by lithium at x = 0.05 (curve 1), x = 0.10 (curve 2) and x = 0.15 (curve 3). T = 300 K, λ = 488.0 nm.

Accordingly to Fig. 4, at the increase of intercalation degree x for nc-TiO₂ to up to 0.15 the decreasing of all phonon bands integral intensities takes

place. The intensity of the band for $E_g(1)$ mode decreases almost by 3.5 times (Fig. 5), and B_{1g} , $E_g(2)$ modes by ~ 2 times. This effect of dominant decrease in the $E_g(1)$ mode intensity can be conditioned by TiO_2 deformation in the TiO_6 coordination octahedron bonding structure areas during lithium intercalation [13], the degree of which grows gradually. In our case (Fig. 5), for the intercalated samples of anatase nc- TiO_2 with $x = 0.15$ the frequency position of the phonon band $E_g(1)$ mode is 145 cm^{-1} , which is some higher as compared to the samples intercalated to $x = 0.05$ (144 cm^{-1}). This effect can be conditioned by the lattice parameter changes as a result of lithium diffusion [14] and increase of superficial strains. It is important to note that the change of $E_g(1)$ phonon lines halfwidth in the Raman spectrum with the change of the intercalated lithium amount can be determined by the phase composition nonstoichiometry of intercalated titanium, which proves the uneven filling the vacant positions by lithium atoms in the bulk of anatase nanocrystal particles.

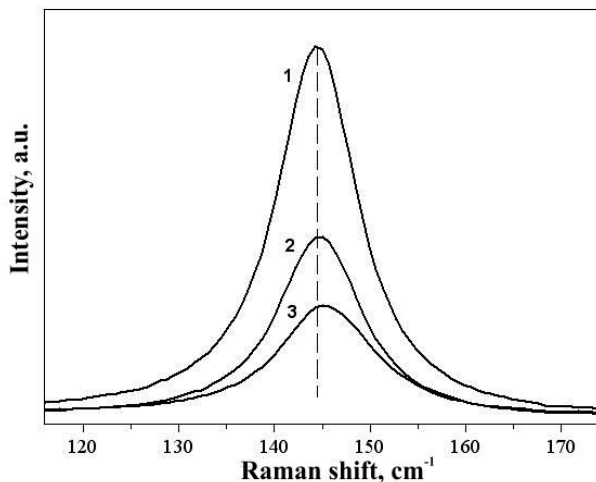


Fig. 5. $E_g(1)$ mode 144 cm^{-1} of nc- TiO_2 intercalated by lithium at $x = 0.05$ (curve 1), $x = 0.10$ (curve 2) and $x = 0.15$ (curve 3). $T = 300 \text{ K}$. $\lambda = 488.0 \text{ nm}$.

4. Conclusions

Considerable growth of the $E_g(1)$ mode intensity can be conditioned by the laser irradiated TiO_2 structural arrangement improvement, and reason of considerable broadening of B_{1g} and $E_g(3)$ phonon modes in the Raman spectrum is the small crystals defects. Decreasing the $E_g(1)$ mode intensity with increasing the lithium intercalation degree is conditioned by the intercalation caused structural deformation in TiO_2 nanocrystals, which proves insertion of the lithium atoms and their diffusion in the host-material structure.

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