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OPTICAL AND STRUCTURAL PROPERTIES OF TiO_2 NANOFIBERS PREPARED BY THE ELECTROSPINNING METHOD

The presented paper is devoted to investigation of structural and optical properties of titania nanofibers. The investigated samples were prepared by the electrospinning method from polymeric solutions, containing TiO_2 precursor, followed by a calcination procedure to obtain highly crystalline, pure inorganic nanofiber materials. The structural properties have been investigated by Scanning electron microscopy (SEM, FEI Nova) and X-ray diffractometry (XRD, Rigaku Ultima). The phase identification of the samples showed the anatase phase of TiO_2. Linear dimensions of nanofibers were calculated. Optical properties were studied with use of UV—VIS spectrophotometer Shimadzu UV-1700 and photoluminescence (PL) setup (excitation with $\lambda = 355$ nm) in the range 350—1100 nm and 370—900 nm, correspondingly. The absorption edge of the samples was in the range of 395—410 nm. The PL maximums appeared at the range of 420—510 nm and 550—710 nm. The mechanisms of luminescence were discussed.

INTRODUCTION

TiO_2 is well known material for optical, catalytic and sensing applications. It has polymorphic nature and three different phases: rutile, anatase and brukite. The development of various deposition techniques allows synthesis of novel titanium dioxide structures with dimensions on the nanometer scale. The decrease of the dimensions below certain levels may lead to the formation of quantum-size effects such as the absorbance edge shift and the room temperature photoluminescence peaks appearance [1].

In the recent decades the attention of scientists was attracted to fabricate metal oxide nanofibers with 2—300 nm cross-section and 0,001—1 mm in length. In these nanostructures the depletion layer width is bigger or in the same range as nanofiber diameter. It results in the relevant influence of surface state on optical and electrical properties of such nanostructures [1]. There have been developed a great number of technological routs to fabricate TiO_2 nanostructures: hydrothermal method [2], magnetron sputtering [3], thermal evaporation method and so on. The mentioned technological routs allow to obtaining TiO_2 nanostructures with different shapes: nanoparticles, nanorods and nanotubes.

In the last decade, electrospinning deposition is to be prospective for nanofibers fabrication. It is based on interaction between charged jet of polymeric solution with electrostatic field. The jet is narrowed by electrostatic effects to the cylindrical shape and hardened because of solvent evaporation. The precipitated nanofibers are 20—200 mkm in length and with diameter of 50—500 nm [5—8].

In the presented paper the structural and optical properties of titania nanofibers, fabricated by electrospinning method, are reported. The influence of Li doping on these properties was investigated. The peculiarities of optical properties have been discussed.

EXPERIMENTAL

Electrospinning deposition setup is shown in fig. 1. Ethanol solution of Titanium (IV) isopropoxide (TTIP) with initial concentration 1 mol/l was mixed with polyvinyl alcohol in ratio 1:20. Lithium doping was provided by addition of the corresponding alkaline dopant ($LiNO_3$) in ethanol. The solutions were supplied by capillary to the rotating template, preheated to 150 °C. High voltage was applied between capillary and template. The voltage value and distance between capillary and template were kept constant for all depositions 5 kV and 1 cm, correspondently. After fabrication, as-deposited nanofibers were collected and calcinated in air atmosphere at 600 °C for 2 hours.

Structural properties of annealed samples have been investigated by Scanning electron microscopy (SEM) and X-ray diffractometry (XRD).

XRD tests were measured by Rigaku Ultima XRD-setup (CuK_α, $\lambda = 0{,}154$ nm) in the range of 2θ angle 20—80°. Scanning electron microscopy FEI Nova has been used to obtain surface images of the investigated nanofibers.

Optical properties were studied with use of UV—VIS spectrophotometer Shimadzu UV-1700 in the range 350—1100 nm. Photoluminescence (PL) spectra were measured by setup, presented in fig. 2. The luminescence was stimulated

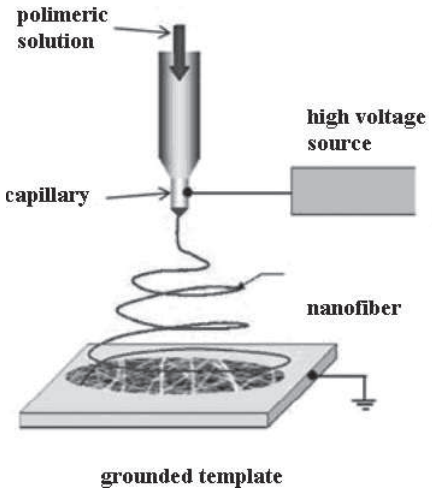

Fig. 1. Electrospining deposition setup

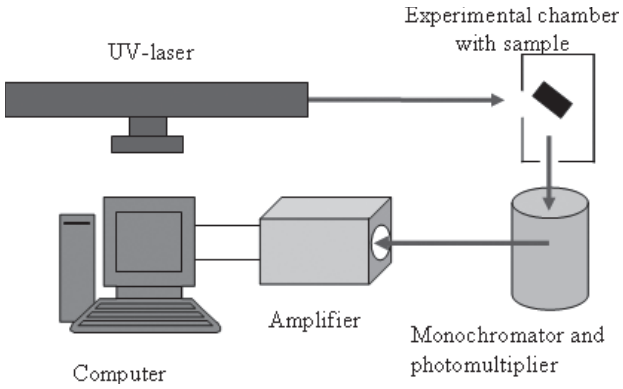

Fig. 2. Photoluminescence setup

by UV laser LCS-DTL-374QT with excitation wavelength $\lambda = 355$ nm. The emission spectra were amplified and recorded in the wavelength range 370—900 nm.

RESULTS AND DISCUSSION

XRD spectrum of the obtained powder is plotted in fig. 3. The one can see XRD peaks at following 2θ values: 25,96°; 38,56°; 55,06°; 62,12°; 70,28° и 76,02°. The obtained peaks correspond to TiO_2 anatase phase with (hkl) indices (101), (004), (211), (204), (220) and (215) [9—11].

Surface morphology of TiO_2 nanopowder, obtained by SEM is shown in fig. 4. The SEM image reveals a geometry of the obtained nanostructures. The one can claim that the fabricated TiO_2 nanopowder was formed by nanofibers with 295 ± 70 nm in diameter and 20 mkm in length.

Absorbance spectrum of TiO_2 nanopowder $\alpha(h\nu)$ is presented in fig. 5. The absorption edge lies in the region of photon energies 3,1—3,3 eV. It is known that titanium dioxide is semiconductor with indirect band gap. So, absorbance spectrum of TiO_2 nanofibers was plotted in specific scale $(\alpha h\nu)^{1/2}$ vs $h\nu$ (fig. 6). Band gap was estimated from the linear plot at the absorption edge region as intersection with ($h\nu$) axis. As one can see, the E_g value is about 2,5 eV. This value is much lower than for anatase single crystal bad gap value ($E_g = 2{,}8$ eV) [11]. The effect of decreasing of particles size to nano dimensions is expected to bring to blue

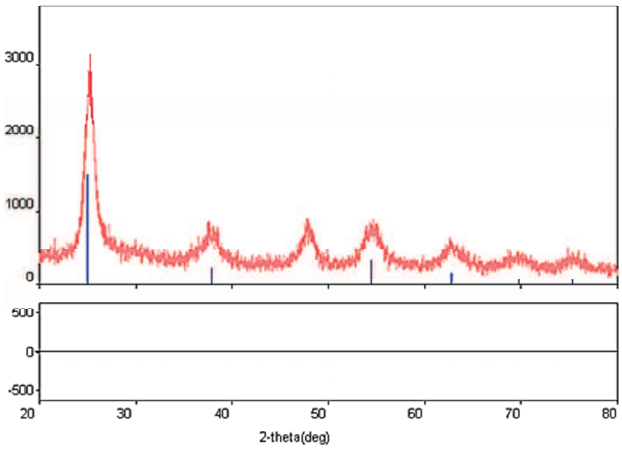

Fig. 3. XRD spectrum of TiO_2 nanopowder

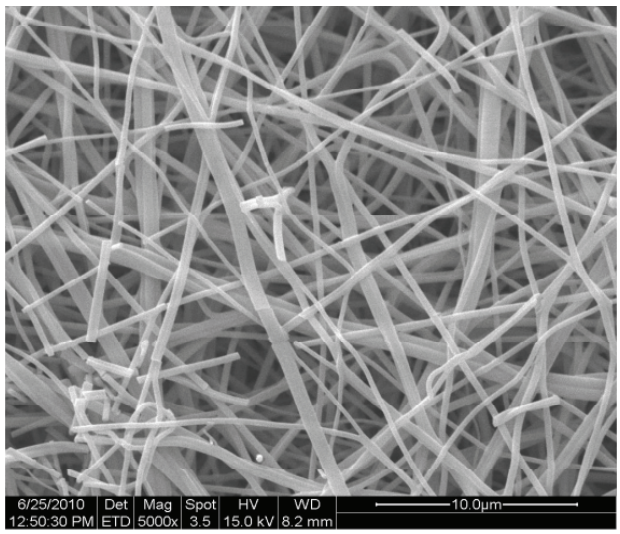

Fig. 4. SEM image of TiO_2 nanopowder

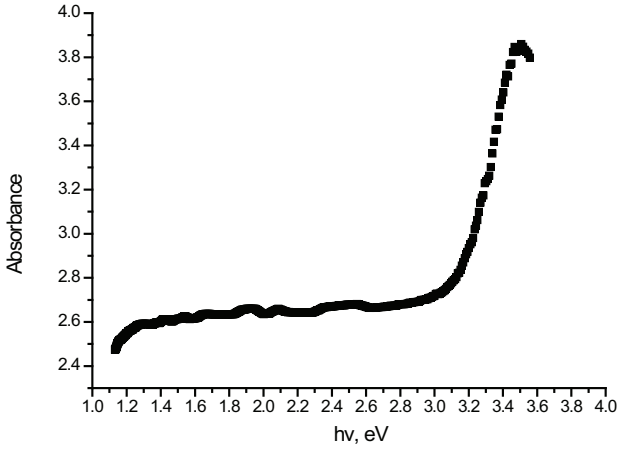

Fig. 5. Absorption spectrum of TiO_2 nanopowder

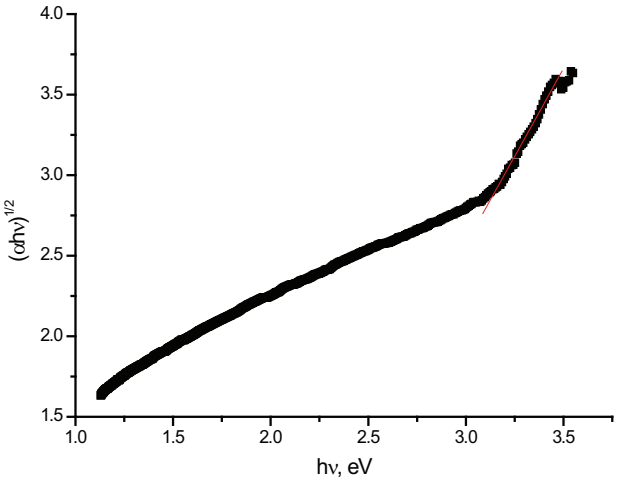

Fig. 6. Graphical evaluation of band gap value

shift of band gap [11]. The physical properties of the nanopowder drastically depend on the its density, which is characterized by a parameter called compaction [12]. It may happen that, because of the shapes of nanofibers the compaction of nanopowder is low and it includes the material and intergranular gaps, filled in with air. In this case Eg value will differ from the real number and represent only average value of material + void system [12].

The phenomenon can be explained by another mechanism. The random compaction of nanofibers on the plane can cause the high scattering coefficient, what can support red shift of band gap value [11].

PL spectrum of TiO_2 nanofibers is plotted in fig. 7. It can be seen that PL curve had a kind of complexity. By means of Origin Pro 7.0 software, the PL spectrum was split onto separate peaks. The PL peaks, located at 423, 481, 508, 555, 601, 632 and 702 nm have been found. The full explanation of photoluminescence in TiO_2 has not been done yet. The peaks at 423 and 481 nm are connected with excitons, located in TiO_6 octahedron. It is supposed that peaks at 508 and 555 nm are formed by oxygen vacancies and peaks, appeared at 601, 632 and 702 nm

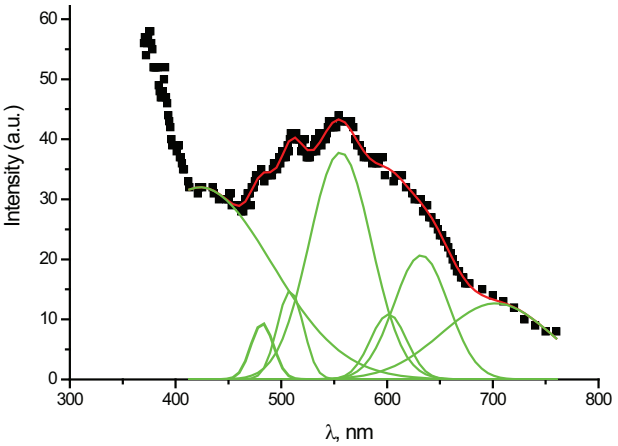

Fig. 7. PL spectrum of TiO_2 nanofibers, measured at room temperatures

relate to structural defects on the surface of nanofibers. In [11, 13, 14] it was discussed that Ti^{3+} surface states are responsible for emission peaks at 600—632 nm and peaks at higher wavelengths correspond to structural defects.

The PL peaks at room temperature at UV region verify quantum-size effects appeared in the studied titania nanofibers. However, red shift of the peaks in comparison with lower dimensional TiO_2 nanostructures suggests to tailor the diameter of the nanotubes to lower values [13,14]. The PL peaks at 500—700 demonstrates the defect presence at the surface of nanofibers. At this stage it is quite difficult to explain the nature of these defects and additional measurements will be performed in future works.

CONCLUSION

TiO_2 nanofibers were successfully fabricated by electrospinning rout. The obtained samples had pure anatase edge phase of titania and linear dimensions 295 ± 70 nm in diameter and 20 mkm in length. Absorption of the samples lies in the region of photon energies 3,1—3,3 eV. Scattering and compaction effects in nanofibers make it difficult to estimate band gap value with standard calculations. Room temperature photoluminescence of the samples was measured. PL peaks at UV region correspond to excitons in TiO_2 lattice and Vis-IR peaks are related with structural defects.

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OPTICAL AND STRUCTURAL PROPERTIES OF TIO_2 NANOFIBERS PREPARED BY THE ELECTROSPINNING METHOD

Abstract

The presented paper is devoted to investigation of structural and optical properties of titania nanofibers and the influence of Li doping on these properties. The investigated samples were prepared by the electrospinning method from polymeric solutions, containing TiO_2 precursor, followed by a calcination procedure to obtain highly crystalline, pure inorganic nanofiber materials. The structural properties have been investigated by Scanning electron microscopy (SEM, FEI Nova) and X-ray diffractometry (XRD, Rigaku Ultima). The phase identification of the samples showed the anatase phase of TiO_2. Linear dimensions of nanofibers were calculated. Optical properties were studied with use of UV—VIS spectrophotometer Shimadzu UV-1700 and photoluminescence (PL) setup (excitation with $\lambda = 355$ nm) in the range 350—1100 nm and 370—900 nm, correspondingly. The absorption edge of the samples was in the range of 395—410 nm. The PL maximums appeared at the range of 420—510 nm and 550—710 nm for both samples. The mechanisms of luminescence were discussed.

Key words: optical properties, nanofibers, electrospining.

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ОПТИЧЕСКИЕ И СТРУКТУРНЫЕ СВОЙСТВА НАНОВОЛОКОН TiO_2 ПОЛУЧЕННЫХ МЕТОДОМ ЭЛЕКТРОСПИНИНГА

Резюме

Представленная работа посвящена исследованию структурных и оптических свойств нановолокон TiO_2 и влиянию легирования Li на эти свойства. Исследованные образцы были приготовлены методом электроспинига из полимерных растворов, содержащих прекурсор TiO2, и далее отжигались для формирования кристаллической структуры. Структурные свойства были исследованы с помощью сканирующей электронной микроскопии и рентгеновской дифракции. Рентгеноструктурный анализ показал, что данные нановолокна принадлежат фазе анатаза. Линейные размеры нановолокон были рассчитаны. Оптические свойства были изучены с использованием спектрофотометра Shimadzu UV-1700 и установки для исследования фотолюминесценции (длина волны возбуждения $\lambda = 355$ нм) в диапазоне 350—1100 нм и 370—900 нм соответственно. Край поглощения образцов приходится на диапазон 395—410 нм. Пики фотолюминесценции возникают в диапазоне 420—510 нм и 550—710 нм для обоих образцов. Механизм люминесценции обсуждается в данной статье.

Ключевые слова: оптические свойства, нановолокна, электроспининг.

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ОПТИЧНІ ТА СТРУКТУРНІ ВЛАСТИВОСТІ НАНОВОЛОКОН TIO2, ОТРИМАНИХ МЕТОДОМ ЕЛЕКТРОСПІНІНГУ

Резюме

Представлена робота присвячена дослідженню структурних та оптичних властивостей нановолокон TiO_2 та впливу легування Li на ці властивості. Досліджені зразки були приготовлені методом електроспінінгу з полімерних розчинів, що містять прекурсор TiO_2, та відпалених для формування кристалічної структури. Структурні властивості були досліджені за допомогою скануючої електронної мікроскопії та рентгенівської дифракції. Рентгеноструктурний аналіз показав, що дані нановолокна належать фазі анатаза. Лінійні розміри нановолокон були розраховані. Оптичні властивості були досліджені з використанням спектрофотометра Shimadzu UV-1700 та приладу для дослідження фотолюмінесценції (довжина хвилі збудження $\lambda = 355$ нм) у діапазоні 350—1100 нм і 370—900 нм відповідно. Край поглинання зразків припадає на діапазон 395—410 нм. Піки фотолюмінесценції виникають у діапазоні 420—510 нм і 550—710 нм для обох зразків. Механізм люмінесценції обговорюється у даній статті.

Ключові слова: оптичні властивості, нановолокна, електроспінінг.