Research Article

Photoluminescence Enhancement of Titanate Nanotubes by Insertion of Rare Earth Ions in Their Interlayer Spaces

Thalles M. F. Marques,1 Cleanio Luz-Lima,2 Marco Sacilloti,3 Kazunori Fujisawa,4 Nestor Perea-Lopez,4 Mauricio Terrones,4 Eder Nascimento Silva,5 Odair Pastor Ferreira,6 and Bartolomeu Cruz Viana1,2,4

1Pós-Graduação em Ciências dos Materiais, Universidade Federal do Piauí (UFPI), 64049-550 Teresina, PI, Brazil
2Departamento de Física, Universidade Federal do Piauí (UFPI), 64049-550, Teresina, PI, Brazil
3Departamento de Física, Universidade Federal de Pernambuco (UFPE), 50670-901 Recife, PE, Brazil
4Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA 16802, USA
5Departamento de Física, CCET, Universidade Federal do Maranhão, 65085-580 São Luís, MA, Brazil
6Laboratório de Materiais Funcionais Avançados (LaMFA), Departamento de Física, Universidade Federal do Ceará (UFC), 60440-554 Fortaleza, CE, Brazil

Correspondence should be addressed to Odair Pastor Ferreira; opferreira@gmail.com and Bartolomeu Cruz Viana; bartolomeu@ufpi.edu.br

Received 27 July 2016; Revised 14 December 2016; Accepted 26 December 2016; Published 25 January 2017

Copyright © 2017 Thalles M. F. Marques et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The optical properties of titanate nanotubes (TiNts) intercalated with rare earths (RE) ions were intensively investigated in this study. To prepare the nanomaterials, sodium titanate nanotubes (Na-TiNts) were submitted to ion exchange reactions with different rare earth elements (RE: Pr3+, Er3+, Nd3+, and Yb3+). To the best of our knowledge, it is the first time that these RE-TiNts were synthesized. All samples were characterized by Raman spectroscopy, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). Furthermore, the optical properties were examined using photoluminescence spectroscopy (PL) and UV-Vis-NIR absorption spectroscopy. The PL intensity (visible range) of the RE-TiNt samples showed a strong dependence when the temperature was decreased down to 20 K. This PL enhancement probably was promoted by electronic modifications in titanate layer band gap and/or interface charge transfers due to RE ions intercalation.

1. Introduction

Oxide based nanostructures exhibit some properties that differ from their bulk counterparts [1, 2]. In particular, alkali metal titanates, usually possessing a layered or tunnel-type structure, have been subject of extensive investigations due to their excellent ion exchange ability added to the exceptional photocatalytic activities [3–6]. Kasuga et al. [7] demonstrated the possibility of producing alkali metal titanate nanoparticles with tubular morphology through hydrothermal treatment of TiO2 in the high alkaline medium. Ever since, titanate nanotubes (TiNts) have attracted both scientific and technological interest due to its unique combination of morphology, size, and functionality [8]. Furthermore, TiNts have large surface area (~180 m2·g−1) and porosity that leads to a wide variety of applications involving their surfaces [9–11].

Optical properties of nanomaterials are widely investigated due to their potential applications in small devices [1–3, 8]. The optical properties of TiNts have been tuned in according to the desired application using different methods to dope and/or inserting ions into the structure of the nanotubes [3, 6, 7, 12, 13]. For example, Li and Zhong [14] have
inserted Sn$^{2+}$ and Pb$^{2+}$ in titanate nanotubes via ion exchange reaction and these nanomaterials were applied in photocatalysis using visible light for dye degradation. Haro-González et al. [15] have prepared Eu$^{3+}$ doped titania nanotubes via hydrothermal treatment of Eu$^{3+}$ doped TiO$_2$ nanopowders and they have studied the luminescent properties of these nanomaterials.

Photoelectronic properties of titanate nanotubes have been investigated [16]. It has been suggested that the photoluminescence emission process is from the exciton states trapped in titanate octahedral ([TiO$_6$]$_n$) units. The excitonic properties of titanate nanomaterials depend on the particular environment of the interlayer space. Therefore, the position and oxidation states of the cations intercalated can modify the [TiO$_6$] octahedron promoting or not excited states inside of its band gap with lifetime sufficient to have photoluminescence (PL) [16]. Then, there is a critical role of the layer composition and structure on charge separation to luminescence (PL) [16]. Then, there is a critical role of the photogenerated charge carriers. The intercalated ions can modify and control these properties of the layered nanostructures [16–18].

Rare earths (RE) doping and/or intercalating nanomaterials are widely investigated due to their excellent luminescent characteristics arising from the transitions of electronic levels which have optical applications such as lasers, optical amplifiers, phosphors, and other optical devices [19]. The choice of host materials has a great importance in the design of the rare earth-based luminescent properties for efficient applications [8, 20, 21]. In this work, in order to obtain different photoluminescence (PL) properties in titanate nanotubes, they were used as a host. Na$^+$-intercalated titanate nanotubes (Na-TiNts) were prepared by hydrothermal method before being submitted to ion exchange reactions with different rare earth ions (Pr$^{3+}$, Er$^{3+}$, Nd$^{3+}$, and Yb$^{3+}$). To the best of our knowledge, it is the first time that these nanotubes (Pr-, Er-, Nd-, and Yb-TiNts) were prepared and their optical properties studied. Thus, this work proposes a very simple route to modify the optical properties of titanate nanotubes and obtain efficient PL emitters at room and low temperatures.

2. Experimental Procedures

All chemicals (reagent grade, Sigma-Aldrich, and Vetec) were used without further purification processes. Deionized water was used to prepare all solutions.

2.1. Titanate Nanotubes Preparation. Na-TiNts were prepared using commercial TiO$_2$ (anatase) powder (purity of 99.8%). Typically, 2.0 g of the TiO$_2$ was mixed in 60 mL of 10 mol L$^{-1}$ NaOH solution and then transferred into a Teflon-lined autoclave and heated at 150 $^\circ$C for 72 h [22].

2.2. Ion Exchange Reactions of the Titanate Nanotubes. The as-prepared Na-TiNts are suitable for rare earths ion exchange reactions without additional process of protonation. These reactions were carried out by suspending 100 mg of Na-TiNts in 100 mL of 0.05 mol L$^{-1}$ Pr(NO$_3$)$_3$·6H$_2$O, Nd(NO$_3$)$_3$·6H$_2$O, Er(NO$_3$)$_3$·5H$_2$O, and Yb(NO$_3$)$_3$·5H$_2$O (purity of 99.9%) aqueous solutions. After this, the suspension was left under magnetic stirring for 24 h at room temperature. The solid products were isolated by centrifugation at 3500 rpm. Then, the products were washed several times with deionized water aiming to remove residual soluble ions from the precursors. Finally, the samples were dried under vacuum conditions at room temperature during 6 h to obtain the RE intercalated titanate nanotubes (RE-TiNts).

2.3. Characterization. After the Na-TiNt and Re-TiNT preparations, the Raman spectroscopy experiments were performed using a Bruker Senterra spectrometer equipped with an Olympus BX5 microscope in all samples. A solid-state laser line at 532 nm was used for measuring the Raman spectra. Power density of laser was below 10$^7$ W/m$^2$ to avoid sample overheating. A spectral resolution of 3 cm$^{-1}$ was used and measurements were carried out using a backscattering geometry. X-ray powder diffraction (XRD) patterns were obtained using a Shimadzu XRD6000 diffractometer, using CuK$_\alpha$ ($\lambda = 1.5406$ Å) radiation operating at 30 mA and 40 kV. A scan rate of 1’ min$^{-1}$ was used. Transmission electron microscopy (TEM) images were obtained using a JEOL-JEM-2010F operating with 200 kV. The TEM samples were prepared by dropping aqueous suspension containing powder samples onto a holey carbon-coated copper grid and letting the water to evaporate at room temperature. The elemental analysis by energy dispersive X-ray spectroscopy (EDS) was performed using an Oxford X-ray detector attached to a Tescan FEG-Mira3 scanning electron microscope. The wavelength dependence of the optical diffuse reflectivity of the powder samples was measured using Perkin-Elmer Lambda 950 UV-Vis-NIR Spectrophotometer. Diffuse reflectance spectra were acquired using the Labsphere DRA-CA-30I accessory. Photo luminescence measurements were carried out upon excitation using an Ar$^+$ laser line at 488 nm on the powder pellet samples using a microscope with 50x objective lenses to focalize the laser beam. The emission signal was collected using the objective lenses and analyzed by a Renishaw inVia spectrometer equipped with an 1800 lines/mm grating and detected by a CCD. Low-temperature measurements were performed in a helium flux cryostat (Advanced Research Systems). A digital temperature controller (Lakeshore) with 0.1 K of stability was used for monitoring the temperature in the range of 20–300 K. The spectra were measured after an appropriate stabilization time for each thermal step.

3. Results and Discussion

In Figure 1(a) the Raman spectra of intercalated TiNts are shown. Firstly, the peaks around 158 and 190 cm$^{-1}$ are assigned to lattice modes (Na$^+$-O-Ti). The peaks at 275, 448, 662, and 700 cm$^{-1}$ are assigned to Ti-O stretching in the edge-shared TiO$_6$ and the peaks at 906 cm$^{-1}$ represent the stretching vibration of the nonshared Ti-O bonds in distorted TiO$_6$ unit [6, 23, 24]. It was observed that the highest (906 cm$^{-1}$) and the two lowest (158 and 190 cm$^{-1}$) energy
modes have their wavenumbers and intensities extensively affected by the ion exchange with different RE ion species. Additionality, some of the medium energy modes (between 200 and 800 cm$^{-1}$) are also changed. The most affected mode is that related to Ti-O bonds whose oxygen atoms are not shared among the TiO$_6$ units (at the corner of the TiO$_6$ octahedral slab). Thus, the different RE ions inserted into the TiNts structure promote the reordering of the interlayer regions leading to these changes in Raman modes [25]. The changes can be explained as follows: the Na$^+$ ions were substituted by hydrated RE ions that may occupy different sites in the interlayer spaces. Due to this reordering the RE-O-Ti interlayer bond could deviate from a linear connection with the different intercalated ions and leads to shifting of the band at 906 cm$^{-1}$ toward lower frequencies [25]. This explanation is supported by observing the difference between the electronegativity as well as the covalent radii of the Na and RE atoms. In general, the more electronegative ion will attract more easily the oxygen atoms, stretching the Ti-O bonds. Also, another important aspect to be pointed out is the considerable changes of the bands below 200 cm$^{-1}$, which are related to the interlayer structure modifications. Thus, the coordination environments for Na$^+$ ion and other intercalated RE ions are different in the structural analysis, as also mentioned previously for other interlayer cations [23, 25].

To better understand the relationship between the crystalline structure and vibrational properties, X-ray diffraction experiments were performed because they provide information about the interlayer region and crystallinity of the layers. The X-ray diffraction data (Figure 1(b)) suggested that both structure and morphology of TiNts were preserved after the RE ions intercalation. The peaks around 10$^\circ$ ($2\theta$) in Na-TiNts, attributed to (200) plane which is related to interlayer distance [25, 26], were slightly shifted to lower $2\theta$ position when RE ions were intercalated indicating an increase of

---

**Figure 1:** (a) Raman spectra; (b) X-ray diffractograms; and (c) UV-Vis reflectance spectra of Na-TiNts and RE-TiNts samples. The dashed lines on (a) and (b) parts are only eyes guide to show the displacement of the bands at 158, 190, and 906 cm$^{-1}$ in Raman spectrum and (200) peak in diffractogram (peak related to interlayer spacing) of Na-TiNts after intercalation of RE ions, respectively.
The TiN spectrum shows four broad and intense bands at 1.67, 2.08 eV which indicates Pr ions absorption peak of Yb$^{3+}$ at 2.11 eV and three bands at 2.56, 2.63, and 2.78 eV. However, for Pr-TiN, it is possible to the absorption edge of the titanate nanotubes at around 3.0 eV. Furthermore, it is possible to observe changes in the interlayer distance (see Table S1 in Supplementary Material available online at https://doi.org/10.1155/2017/3809807). This increase of the interlayer distance is expected since the ionic radius of Na$^+$ is smaller than that of RE hydrated ions [25, 27, 28]. Furthermore, it is possible to observe changes in the absorption edge when RE ions were inserted into the TiN tubes [29, 30]. The Nd$^{3+}$ ions absorption peaks and high PL intensity were observed at 1.81 eV and 1.86 eV for Nd-TiN and Yb-TiN, respectively. The Nd-TiN spectrum shows a strong overlap of the peaks from the RE ions directly excited, like the emission energy of RE-TiN as compared to pristine sample. Pr$^3+$ and Er$^{3+}$ ions had the highest luminescence intensity, being the emission band centered around 1.89 eV.

For Pr-TiN, the absorption edge is at 2.08 eV and the broad band at 2.08 eV indicates Pb$^{3+}$ ions absorption peaks and that this ion was inserted into the TiN tubes [30]. The Nd-TiN spectrum shows four broad and intense bands at 1.67, 2.11, 2.34, and 2.42 eV attributed to Nd$^{3+}$ ions absorptions [31]. In the spectrum of Er-TiN bands can be seen at 1.89, 2.26, 2.37, 2.54, and 3.28 eV associated with trivalent erbium (Er$^{3+}$) absorption [32]. This indicates that the absorption bands due to the ions absorption are not visible because it is out of the spectral range studied here; the absorption peak of Yb$^{3+}$ ion is around 1.26 eV [21, 33]. On the other hand, it is possible to see the Yb-TiN spectrum slightly broad in the edges around 2.25 and 2.95 eV which could be associated with defects promoted in titanate electronic structure by ion exchanging [13]. The changes occurred in the TiN spectrum profile when RE ions were inserted, like a slightly flat absorption on visible range, and a shifting of the absorption edge band can be attributed to charge transfer between TiN tubes host and RE ions, promoting modifications into the electronic structure of the titanate layers [34–36].

All analyses aforesaid indicate that pristine nanotubes after ion exchange reactions were modified due to substitution of Na by RE ions. To evaluate these substitutions directly, the chemical compositions of RE-TiN samples were investigated by energy dispersive X-ray spectroscopy (EDS). The Na/Ti and RE/Ti atomic ratios are shown in Table I. The amount of Na$^+$ ions in pristine nanotubes is in agreement with the Na$_{x}$H$_{2}$Ti$_{3}$O$_{7}$·nH$_{2}$O (0 ≤ x ≤ 2) chemical formula [22]. After ion exchange reactions, the sodium content drastically decreased in nanotubes. On the other hand, it was possible to detect the RE ions, suggesting that ion exchange reactions were very efficient to substitute Na ions by RE. These findings were demonstrated by a very low Na/Ti atomic ratio in all RE ion exchanged samples and RE/Ti atomic ratio between 0.14 and 0.19. Also, the amount of oxygen and titanium in the samples was almost unchanged after the reactions. The RE-TiN interlayer distances measured by TEM images (0.72, 0.83, 0.86, and 0.87 nm for Pr-, Er-, Nd-, and Yb-TiN, respectively) are larger than Na-TiN one (0.70 nm). These findings were demonstrated by a very low Na/Ti atomic ratio in all RE ion exchanged samples and RE/Ti atomic ratio between 0.14 and 0.19. Also, the amount of oxygen and titanium in the samples was almost unchanged after the reactions. The chemical composition of the titanate nanotubes is in agreement with the Na$_{x}$H$_{2}$Ti$_{3}$O$_{7}$·nH$_{2}$O (0 ≤ x ≤ 2) chemical formula [22]. After ion exchange reactions, the sodium content drastically decreased in nanotubes. On the other hand, it was possible to detect the RE ions, suggesting that ion exchange reactions were very efficient to substitute Na ions by RE. These findings were demonstrated by a very low Na/Ti atomic ratio in all RE ion exchanged samples and RE/Ti atomic ratio between 0.14 and 0.19. Also, the amount of oxygen and titanium in the samples was almost unchanged after the reactions.
Figure 2: TEM (a) and HRTEM (b) images of RE-TiNts. The interlayer average distances of RE-TiNts samples were shown (white lines in HRTEM images).

Figure 3: Room temperature PL spectra of RE-TiNts and Na-TiNts samples at (a) atmospheric pressure and (b) under vacuum (∼10⁻⁵ Pa). Some absorptions peaks due to RE ions inserted into the nanotubes can be seen.
to see an enhancement of the PL intensity (~2, ~5, ~14, ~24, and ~30 times more intense for Pr, Er, Na, Yb, and Nd, resp.) probably, due to water release promoted by the vacuum conditions, suggesting that the interlayer space of the nanotubes was reordered and energy of ion-layer bonds and electronic levels were modified. Now, Yb-TiNts show the highest luminescence intensity with a more defined emission peak centered at 2.05 eV. For Er- and Pr-TiNts, emission peaks at 2.05 eV and 1.95 eV were observed, respectively. The spectrum of Nd-TiNts showed a peak around 1.95 eV. On the other hand, under vacuum Na-TiNts showed a weak broad PL peak around 2.05 eV. Some extra absorption peaks were observed on the spectra of Yb-, Nd-, and Er-TiNts, as it was observed in the PL spectra at atmospheric pressure. Thus, the water release and reordering of the interlayer space allowed another enhancement of the electronic recombination (PL) promoted by the excitation through inserted levels and/or interface densities of state into the electronic structure of TiNts intercalated with RE [17,18,29].

Analyzing the PL of the RE-TiNts at atmospheric pressure (with structural water, Figure 3(a)), the intensity of PL peak could be related to the electronic effects promoted by the concentration of RE into the nanotube structures. The two most intense PL peaks are from Pr- and Er-TiNts, which have the highest concentration according to EDS quantifications (see Table 1). After the dehydration process, the electronic states promoted by vacancies compete with RE concentration changing the PL emission characteristics. Thus, it is very difficult to say, using that laser line (488 nm), which phenomena (electronic states inserted into the band gap of TiNts or interface energy states with charge transfer between RE and TiNts layers) can contribute the most to the PL emission efficiency. To understand better the PL mechanism, it is necessary to perform experiments with lower wavenumber laser lines to reach the energy of the band gap of pristine nanotubes.

The PL spectra at low temperatures were performed and they are shown in Figure 4. All of these PL peaks showed shifts with the decrease of temperature, and it may be due to some variations into the electronic structures. Furthermore, the intensity of PL peaks increase along with decreasing temperature which suggests that PL peaks could be related to shallow energy levels inserted by the ions and/or interface effects that are not thermally stable for electrons at that level [29]. In Na-TiNts spectrum (Figure 4(a)), the PL intensity increases almost linearly with the decrease of temperature and the peak position shifts to higher energies. The Nd-TiNts spectrum (Figure 4(b)) has shown the same behavior in the PL intensity and peak position, but there was stabilization at 45 K and the absorptions of Nd$^{3+}$ ions are more evident at low temperatures. For Pr-TiNts (Figure 4(c)), during the decrease of temperature, the PL peak position shifts toward higher energies and PL intensity increases. Below 220 K, an absorption peak appears around 2.08 eV that can be related to Pr$^{3+}$ direct absorption. For Er-TiNts (Figure 4(d)), the increase of intensity is almost linear as the temperature decreases and the peak position shows a shift to higher energy. Similar to Nd-TiNts, the Er$^{3+}$ absorptions (at 1.89, 2.11, 2.26, and 2.34 eV) are more evident at low temperatures. Yb-TiNts spectrum (Figure 4(e)) has shown the same shift to higher energy at low temperatures. However, there was a decrease of the intensity from 35 K to 9 K. This observation corroborates with an absorption plateau at UV-Vis measurements suggesting that Yb$^{3+}$ ions modify the electronic structure of titanate nanotubes. As the emission process comes from electronic structure of the titanate nanotube walls which were affected by the RE insertion, this emission might be absorbed by the lanthanide ion into the interlayer promoting the absorption peaks in the PL spectra. The result of PL enhancement during the increase of temperature from 9 K to 35 K for Yb-TiNts is probably due to thermal rectification of surface trap states or densities of states. A similar effect was observed for photoinduced PL efficiency enhancement of QDs during surface passivation [35, 41, 42]. At higher temperatures, the main part of nonradiative process that limits the quantum efficiency is the thermal escape, induced by multiple phonon absorption and promoting the PL quenching. At lower temperatures, the most of the excited electrons return to the shallow level via nonradiative transitions, which can lead to the PL enhancement [29].

4. Conclusions

In summary, we have reported the synthesis of titanate nanotubes intercalated with rare earths (RE) ions (RE: Pr$^{3+}$, Er$^{3+}$, Nd$^{3+}$, and Yb$^{3+}$). The morphology, structure, and optical properties of these novel titanate nanotubes were studied. The RE-TiNts samples have shown a higher PL emission than pristine Na-TiNts. The intensity and energy of the PL peaks are dependent on the temperature. The luminescence mechanism was briefly discussed and it was proposed that possible origin of the PL broad peaks would be due to the electronic levels inserted into the TiNts band gap and/or interface electronic densities introduced by the RE intercalations. Based on the results showed here, these novel nanomaterials could be used in applications involving optical devices like lasers, sensors, and phosphors.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors gratefully acknowledge financial support from the Brazilian funding agencies CNPq and FAPEPI and also acknowledge support from CAPES-PROCAD 2013 Grant 183995.
Figure 4: Temperature-dependent PL spectra: (a) Na-TiNts; (b) Nd-TiNts; (c) Pr-TiNts; (d) Er-TiNts; and (e) Yb-TiNts.
References

[1] D. V. Bavykin and F. C. Walsh, “Elongated titanate nanostructures and their applications,” European Journal of Inorganic Chemistry, vol. 2009, no. 8, pp. 977–997, 2009.

[2] A. Fujishima, K. Hashimoto, and T. Watanabe, TiO$_2$ Photocatalysis: Fundamentals and Applications, BKC, 1999.

[3] X. Chen and S. S. Mao, “Titanium dioxide nanomaterials: Synthesis, properties, modifications and applications,” Chemical Reviews, vol. 107, no. 7, pp. 2891–2959, 2007.

[4] V. Ildayev, Z.-Y. Yuan, T. Tabakov, and B.-L. Su, “Titanium oxide nanotubes as supports of nano-sized gold catalysts for low temperature water-gas shift reaction,” Applied Catalysis A: General, vol. 281, no. 1-2, pp. 149–155, 2005.

[5] R. Tenne, “Inorganic nanotubes and fullerene-like nanoparticles,” Nature Nanotechnology, vol. 1, no. 2, pp. 103–111, 2006.

[6] B. C. Viana, O. P. Ferreira, A. G. Souza Filho et al., “Decorating titane nanotubes with CeO$_2$ nanoparticles,” Journal of Physical Chemistry C, vol. 113, no. 47, pp. 20234–20239, 2009.

[7] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, “Formation of titanium oxide nanotube,” Langmuir, vol. 14, no. 12, pp. 3160–3163, 1998.

[8] M. Pedroni, F. Piccinelli, S. Polizzi, M. Bettinelli, and P. Haro-González, “Upconversion Ho-Yb doped titane nanotubes,” Materials Letters, vol. 80, pp. 81–83, 2012.

[9] N. M. dos Santos, J. M. Rocha, J. M. Matos et al., “Metal cations intercalated titane nanotubes as catalysts for ãβ unsaturated esters production,” Applied Catalysis A: General, vol. 454, pp. 74–80, 2013.

[10] D. V. Bavykin, J. M. Friedrich, and F. C. Walsh, “Protonated titanates and TiO$_2$ nanostructured materials: synthesis, properties, and applications,” Advanced Materials, vol. 18, no. 21, pp. 2807–2824, 2006.

[11] R. Camposeco, S. Castillo, I. Mejia et al., “Active TiO$_2$ nanotubes for CO oxidation at low temperature,” Catalysis Communications, vol. 17, pp. 81–88, 2012.

[12] X. Ding, X. G. Xu, Q. Chen, and L.-M. Peng, “Preparation and characterization of Fe-incorporated titane nanotubes,” Nanotechnology, vol. 17, no. 21, pp. 5423–5427, 2006.

[13] X. Sun and Y. Li, “Synthesis and characterization of ion-exchangeable titane nanotubes,” Chemistry—A European Journal, vol. 9, no. 10, pp. 2229–2238, 2003.

[14] X. Li and Y. Zhong, “Ion-exchangeable titane nanotubes with visible light responsive photocatalytic activities for dyes degradation,” Journal of Nanoscience and Nanotechnology, vol. 14, no. 9, pp. 7151–7156, 2014.

[15] P. Haro-González, M. Pedroni, F. Piccinelli et al., “Synthesis, characterization and optical spectroscopy of Eu$_3^+$ doped titane nanotubes,” Journal of Luminescence, vol. 131, no. 2, pp. 2473–2477, 2011.

[16] A. Riss, T. Berger, H. Grothe, J. Bernardi, O. Diwald, and E. Knözinger, “Chemical control of photoexcited states in titane nanostructures,” Nano Letters, vol. 7, no. 2, pp. 433–438, 2007.

[17] A. Riss, M. J. Elser, J. Bernardi, and O. Diwald, “Stability and photoelectronic properties of layered titane nanostructures,” Journal of the American Chemical Society, vol. 131, no. 17, pp. 6198–6206, 2009.

[18] A. Vittadini, M. Schirmer, M.-M. Walz et al., “Defects in oxygen-depleted titane nanostructures,” Langmuir, vol. 28, no. 20, pp. 7851–7858, 2012.

[19] Z. Tang, L. Zhou, L. Yang, and F. Wang, “A study on the structure transformation and luminescence of Eu(titane) titane nanotubes synthesized at various hydrothermal temperatures,” Journal of Alloys and Compounds, vol. 481, no. 1-2, pp. 704–709, 2009.

[20] B. Chi, E. S. Victorio, and T. Jin, “Synthesis of Eu-doped photoluminescent titane nanotubes via a two-step hydrothermal treatment,” Nanotechnology, vol. 17, no. 9, pp. 2234–2241, 2006.

[21] X. Huang, S. Han, W. Huang, and X. Liu, “Enhancing solar cell efficiency: the search for luminescent materials as spectral converters,” Chemical Society Reviews, vol. 42, no. 1, pp. 173–201, 2013.

[22] O. P. Ferreira, A. G. Souza, J. Mendes, and O. L. Alves, “Unveiling the structure and composition of titanium oxide nanotubes through ion exchange chemical reactions and thermal decomposition processes,” Journal of the Brazilian Chemical Society, vol. 17, no. 2, pp. 393–402, 2006.

[23] H. Liu, D. Yang, E. R. Wacławik et al., “A Raman spectroscopic study on the active site of sodium cations in the structure of Na$_2$Ti$_2$O$_7$ during the adsorption of Sr$_{2}^{2+}$ and Ba$_{2}^{2+}$ cations,” Journal of Raman Spectroscopy, vol. 41, no. 12, pp. 1792–1796, 2010.

[24] Y. Su, M. L. Balmer, and B. C. Bunker, “Raman spectroscopic studies of silicotitanates,” Journal of Physical Chemistry B, vol. 104, no. 34, pp. 8160–8169, 2000.

[25] B. C. Viana, O. P. Ferreira, A. G. Filho, A. A. Hidalgo, J. M. Filho, and O. L. Alves, “Alkali metal intercalated titane nanotubes: a vibrational spectroscopy study,” Vibrational Spectroscopy, vol. 55, no. 2, pp. 183–187, 2011.

[26] Q. Chen, G. H. Du, S. Zhang, and L.-M. Peng, “The structure of trititanate nanotubes,” Acta Crystallographica, Section B: Structural Science, vol. 58, no. 4, pp. 587–593, 2002.

[27] R. D. Shannon and C. T. Previtt, “Effective ionic radii in oxides and fluorides,” Acta Crystallographica Section B, vol. 25, no. 5, pp. 925–946, 1969.

[28] Y. Matsumoto, U. Unal, Y. Kimura, S. Ohashi, and K. Izawa, “Synthesis and photoluminescent properties of titane layered oxides intercalated with lanthanide cations by electrostatic self-assembly methods,” Journal of Physical Chemistry B, vol. 109, no. 26, pp. 12748–12754, 2005.

[29] S. Luo, J. Fan, W. Liu et al., “Synthesis and low-temperature photoluminescence properties of SnO$_2$ nanowires and nanobelts,” Nanotechnology, vol. 17, no. 6, pp. 1695–1699, 2006.

[30] X. Li, B. Yang, J. Zhang, L. Hu, and L. Zhang, “Energy transfer between Er$^{3+}$ and Pr$^{3+}$ for 2.7 µm fiber laser material,” Fibers, vol. 2, no. 1, pp. 24–33, 2014.

[31] A. I. Gavrilov, N. A. Belich, S. V. Shuvaev, D. O. Gil, B. R. Churagulov, and E. A. Gudilin, “Synthesis of perovskite sodium neodymium titane and study of their photocatalytic properties,” Doklady Chemistry, vol. 454, no. 1, pp. 9–12, 2014.

[32] M. A. Menezes-Nava, O. Barbosa-García, J. L. Maldonado et al., “Yb$^{3+}$ quenching effects in co-doped polycrystalline BaTiO$_3$: Er$^{3+}$, Yb$^{3+}$,” Optical Materials, vol. 31, no. 2, pp. 252–260, 2008.

[33] M. K. Mahata, K. Kumar, and V. K. Rai, “Structural and optical properties of Er$_3^+$/Yb$_3^+$ doped barium titane phosphor prepared by co-precipitation method,” Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy, vol. 124, pp. 285–291, 2014.

[34] S. Okamoto and H. Yamamoto, “Luminescent properties of praseodymium-doped alkaline-earth titaneates,” Journal of Luminescence, vol. 102-103, pp. 386–389, 2003.
[35] H. Zhu, N. Song, and T. Lian, “Wave function engineering for ultrafast charge separation and slow charge recombination in type II core/shell quantum dots,” *Journal of the American Chemical Society*, vol. 133, no. 22, pp. 8762–8771, 2011.

[36] P. Dorenbos, “Systematic behaviour in trivalent lanthanide charge transfer energies,” *Journal of Physics Condensed Matter*, vol. 15, no. 49, pp. 8417–8434, 2003.

[37] Y. Suzuki and S. Yoshikawa, “Synthesis and thermal analyses of TiO$_2$-derived nanotubes prepared by the hydrothermal method,” *Journal of Materials Research*, vol. 19, no. 4, pp. 982–985, 2004.

[38] M. Sacilotti, D. Chaumont, C. B. Mota et al., “Interface recombination & emission applied to explain photosynthetic mechanisms for $(e^-, h^+)$ Charges' separation,” *World Journal of Nano Science and Engineering*, vol. 2, pp. 58–87, 2012.

[39] S. Kumar, M. Jones, S. S. Lo, and G. D. Scholes, “Nanorod heterostructures showing photoinduced charge separation,” *Small*, vol. 3, no. 9, pp. 1633–1639, 2007.

[40] V. M. Longo, M. das Graça Sampaio Costa, A. Zirpole Simões et al., “On the photoluminescence behavior of samarium-doped strontium titanate nanostructures under UV light. A structural and electronic understanding,” *Physical Chemistry Chemical Physics*, vol. 12, no. 27, pp. 7566–7579, 2010.

[41] L. An, J. Yi, C. Liu, W. An, and Y. Zhang, “Room and Low temperature photoluminescence properties of CdSe quantum dots synthesized rapidly in aqueous approach,” in *Proceedings of the International Conference on Electronics and Optoelectronics (ICEOE '11)*, pp. 195–198, Liaoning, China, July 2011.

[42] G. Morello, M. De Giorgi, S. Kudera, L. Manna, R. Cingolani, and M. Anni, “Temperature and size dependence of nonradiative relaxation and exciton-phonon coupling in colloidal CdTe quantum dots,” *Journal of Physical Chemistry C*, vol. 111, no. 16, pp. 5846–5849, 2007.
