Self-organized and self-assembled TiO₂ nanosheets and nanobowls on TiO₂ nanocavities by electrochemical anodization and their properties

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Abstract

In this research work, we prepared for the first time TiO₂ nanosheets and nanobowls assembled on an arrangement of TiO₂ nanocavities, and studied their morphological, optical, and structural properties. The assembled nanostructures were synthesized by a fast two-step electrochemical anodization using fluorides and ethylene glycol. By Field Emission Scanning Electron Microscopy, we showed that these nanostructures have a morphology well organized and ordered with a homogeneous distribution. Also, other characteristics such as photoluminescence, reflectance spectra, band gap energy, and Raman spectra were studied and compared with the optical and structural properties of TiO₂ nanotubes. We found that the time of anodization is a key parameter to control the final shape of the individual elements in the nanostructure. Our results show that when nanobowls or nanosheets are self-assembled on nanocavities the morphological, optical, and structural properties change significantly in comparison to TiO₂ nanotubes. Furthermore, the emission was improved considerably and the band gap energy was modified to higher energy values. Likewise, the interference fringes are generated in the reflectance spectra by the length of the nanocavities and by the thickness of the nanobowls and the nanosheets. Finally, a reduction on the displaced the E₉(1) Raman mode was observed with decreasing of the length of the nanocavities.

1. Introduction

Due to their unusual physical, electrical and chemical properties and attractive applications in the field of the electrochemistry and electronics, nanosheets are being widely studied [1, 2]. Nanosheets are nanostructured materials that have a shape of sheet whose thickness is lesser than 100 nm and their length is by the order of a few micrometers [2, 3]. Commonly, nanosheets are synthesized either by exfoliation or hydrothermal and solvothermal processes [1–7] and they have been applied to Li-ion batteries and supercapacitors for improving the charge and discharge time, and in solar cells [1–8]. In 2019, Zhao et al investigated GeSe nanosheets, and demonstrated that these can be used in surface plasmon resonance sensor by depositing it by spin coating, improving the sensitivity of the sensor in the detection of heavy metals and chemical molecular identification [9]. However, all these fabrication processes are highly expensive and do not allow a precise control of the periodicity of the nanostructures [3–9].

In the same way, nanobowls are nanostructured materials that have a shape of bowl or cup whose outer diameter is about or smaller than 100 nanometers [10]. Because of their excellent physical, optical and chemical properties, nanobowls are used in the field of the nanophotonics and photoelectrochemistry, in applications such as sieves for selecting particles, as nanocontainers or as light trappings [11, 12]. Typically, nanobowls are synthesized by a colloidal crystal template, a facile solid state dewetting, microwave heating, atomic layer deposition or template-sol-gel processes [10–17]. Nonetheless, nanobowls are usually fabricated in larger
dimensions, closed to 500 nm of outer diameter, and having a high manufacturing cost [12–17]. Recently, Umh et al showed that TiO2 nanobowls can be used as photonic crystals. They reported that TiO2 nanostructures had two bands of reflection and can be modified with increasing of the cavity diameter of nanobowls by modifying the voltage of anodization [18].

Another technique widely employed in the synthesis of nanostructures is electrochemical anodization, since it improves the morphology of the material, creates highly defined geometrical structures and decreases the cost of synthesis [19]. This process commonly uses fluorides and ethylene glycol, and results in a periodic array for the creation and growth of self-ordered and self-organized TiO2 nanotubes (TiO2-nt) like a honeycomb [20]. The self-organization process, morphology, properties, and chemical composition of the nanomaterial can be controlled using the correct anodization parameters such as voltage, current and chemical reagents (water, fluorides, and ethylene glycol) [21–26]. For example, Bae et al fabricated a nanotemplate of Al2O3 nanotubes with Au nanosurfaces for refractometric sensing applications. The sensor was fabricated by electrochemical anodization and by sputtering. The authors demonstrated that the sensor changes its reflectance spectrum with the different refractive index of the target due to the nanotubes morphology and Au nanosurfaces [27].

For the above, in this work, we show for the first time a study about TiO2 nanosheets (TiO2-ns) and nanobowls (TiO2-nb) assembled on the top part of an ordered array of TiO2 nanocavities (TiO2-nc) by electrochemical anodization, which in turn were grown on a template of Ti nanobowls (Ti-nb). In order to demonstrate the quasi-periodicity of our materials, we show and analyze images of the morphology of the self-assembled structures by Field Emission Scanning Electron Microscopy (FESEM) of each of them and we study the effect of the morphology on their optical properties, such as photoluminescence (PL) and reflectance, and on their structural properties by Raman spectroscopy.

2. Experimental details

In order to prepare the self-assembled materials, a titanium rectangular foil (1.5 cm²) with a thickness of 100 μm was used as anode while a platinum electrode as counter electrode with an Inter-Electrode Spacing of 1 cm between them. Ti foils were firstly degreased by sonication process with trichloroethylene, acetone and deionized H2O, followed by a dry nitrogen blowing. For the fabrication of nanosheets and nanobowls assembled on nanocavities (TiO2-ns/TiO2-nc and TiO2-nb/TiO2-nc), a two-step electrochemical anodization was carried out using an organic electrolyte solution containing 0.255 wt% NH4F and 1 v/v% water in ethylene glycol at a constant voltage of 30 V, in both cases. In the first-step anodization (1 h), we grew a preliminary arrangement of TiO2-nt on the Ti foil, as shown in figure 1(a), right away we made a detachment process with a solution of phosphoric acid and hydrochloric acid to remove the first package of nanotubes and create a template of Ti-nb, that is, a network of bowls-shaped sites to promote a better nucleation (figure 1(b)). Finally, both self-ordered and self-assembled TiO2-ns and TiO2-nb on the top of TiO2-nc were gotten after the second-step anodization during 20 and 50 min, respectively, all of them at room temperature (figure 1(c)).

To understand the effect of the morphology of nanosheets and nanobowls on their morphological, optical, and structural properties, we fabricated: (1) TiO2 nanocavities without self-assembled nanostructures, for this, we grew nanocavities with the same procedure as the nanosheets (figure 1), but with a time of just 12 min in the second-step anodization, and (2) standard TiO2 nanotubes with same electrolyte solution, voltage, and anode-cathode spacing as in the synthesis of our nanosheets but with a three-step anodization process with an anodization times of 4 h, 20 h and 1 h for the first, second and third step, respectively, and with a detachment process after the first and second step of anodization to create and improve the template of Ti-nb [28–32]. Likewise, we also studied the effect of the morphology of self-assembled nanostructures on the crystalline structure of the anatase phase, thus, through thermal treatment at 400 °C for 2 h by a hot plate process, we converted the amorphous structure of our materials to the anatase crystalline phase.
After the synthesis, the superficial and transversal morphologies of the resulting nanomaterials were analyzed by FESEM (FEI SCIOS). PL spectra at room temperature using a fluorescence spectrometer (Fluoromax-3, Jobin Yvon) were calculated and studied. A specular reflectance spectrum was determined by a Semiconsoft MProbe UVVisSR thin film measurement System and Raman spectra were analyzed by Raman microscope model alpha 300 R, utilizing the green laser excitation (532 nm).

3. Results and discussion

The time of the second-step anodization is a key factor for the control of the final shape of the nanostructure. A time of 20 min gave as a result the formation of self-organized nanostructures in the form of sheets with a quasi-homogeneous distribution density. The upper part of figure 2 shows the superficial morphology of TiO$_2$-ns. The diameter and thickness of TiO$_2$-ns were about 80–90 nm and 37 nm, respectively, and a distance between one nanosheet and another of approximately 29 nm, however, these nanosheets were not completely flat because their edges were slightly clearer (figure 2(b)), in other words, they had a slightly concave shape. For this, we assume that a treatment time of less than 20 min in the second-step anodization could result in flatter nanosheets.

In the other hand, the time of 50 min in the second-step anodization turned out in self-organized nanostructures with a shape of bowls and a quasi-homogeneous distribution density. This nanostructure can be seen in figures 2(c) and (d). Apparently, the surface size of the nanobowls is smaller than that of the nanosheets (figure 2(b)) because we cannot see the depth in these 2D images. The diameter and thickness were about 76 nm and 74 nm, respectively; and the separation distance between nanobowls of around 30 nm. Likewise, our TiO$_2$-nb had shorter dimensions (thickness and diameter) than another published in literature [9–17].

Additionally, in figures 2(b) and (d), it can be seen the top of the nanocavities (TiO$_2$-nc) as some little black circles, like pores, between the spaces of the nanosheets and nanobowls. Both TiO$_2$-ns and TiO$_2$-nb were placed preferably among the nanocavities to achieve the most stable structure. In figure 2(b), the inner diameter of the TiO$_2$-nc was about 25 nm, while in figure 2(d) the TiO$_2$-nc are ellipse shaped with an inner major axis of 52 nm and an inner minor axis of 37 nm, approximately.

Figure 3(a) shows the successive arrangement of the synthesis of nanosheets assembled on nanocavities: firstly, the bottom of the image shows the template of Ti-nb on which, secondly, we made TiO$_2$-nc grow, whose length is about 330 nm and, finally, on the top these short nanotubes (nanocavities), we synthesized TiO$_2$-ns. The Ti-nb template showed a good homogeneous organization which helped to have a preferential growth and get a better organization of the short TiO$_2$-nt [22]. Hence, if short nanotubes get a good organization, nanosheets will be organized too. Additionally, an oxide layer between nanocavities and nanosheets is observed (see...
The oxide layer and amount of electrolyte inside the short nanotubes increase the TiO₂-ns distance. Consequently, the length of the short nanotubes was about 128 nm, considerably smaller than that of the effect of the anodization time on the length of short nanotubes such as the titanium foil area and inter-electrode space between the nanocavities. Also, the diameter size in the nanobowls because their standard deviation was lower than that of the nanosheets. Mean of 88 nm and a coefficient of variation of 82% respect to average. This means that we have more control over the diameter size in the nanobowls because their standard deviation was lower than that of the nanosheets.

Figure 3. FESEM image of the cross-section of (a) TiO₂-ns and (b) TiO₂-nb assembled on TiO₂-nc, synthesized by electrochemical anodization.

Figure 3(a)) and this layer is similar to ‘the entire surface layer’ reported by another study [29]. Figure 3(b) shows a FESEM image of TiO₂-nb assembled on TiO₂-nc. Due to the longer anodization time, 50 min, a dissolution process occurred which caused the nanosheets to get a concave shape in the form of bowls. We assume that the [TiF₆]²⁻ ions migrated to the top part of ‘the entire surface layer’, etching the inner part of the nanotubes and the nanobowls. According to Chong et al, ‘the entire surface layer’ decreases and ruptures as the anodization time and amount of electrolyte inside the short nanotubes increase [29]. The reduction in the length of the short nanotubes can also be caused by the increase in the pressure of the oxygen bubbles generated in the compact oxide layer (first stage of anodization) [29]. However, several variables must be considered to understand the effect of the anodization time on the length of short nanotubes such as the titanium foil area and inter-electrode distance. Consequently, the length of the short nanotubes was about 128 nm, considerably smaller than that of the TiO₂-ns (330 nm) and, conversely the inner diameter of nanocavities was longer with respect to the diameter of the short nanotubes in figure 3(a). The ratio between the superficial area of a nanosheet and the internal cross section area of a nanotube was around 11, while the same relationship for the TiO₂-nb was barely about three. From FESEM images, we can observe that new complex nanomaterials were synthesized. As a result of a fast two-step anodization process, a hybrid material was developed [33]. Namely, two types of nanostructures were assembled: nanosheets or nanobowls (two-dimension) on short nanotubes (one-dimensional). According to Povolotskaya et al, hybrid material can create new properties, so we expect that the properties of the self-assembled nanostructures improve.

To analyze the morphology over a short range, a comparison between the diameter size distribution of nanobowls and nanosheets assembled on short nanotubes is shown in figure 4. The images were taken at 45° with respect to the vertical of the nanobowls and nanosheets. Figure 4(a) shows the superficial morphology of nanobowls on nanocavities, the nanostructures are shaped like small bowls or cups organized in hexagonal controlled-packed, where each nanobowl is surrounded by several TiO₂-nb, i.e., nanobowls grew among the space between the nanocavities. Also, figure 4(b) shows a histogram where we did an analysis about the diameter of TiO₂-nb. The diameter with the highest frequency was 75 nm with a standard deviation of 19 nm, an arithmetic mean of 76 nm and coefficient variation of 24% respect to average.

Figure 4(c) shows the superficial morphology of nanosheets on nanocavities, we can observe that the nanosheets have a greater variation in diameter than the nanobowls. Figure 4(d) shows a frequency histogram of the diameter of TiO₂-ns. The highest frequency was 88 nm with a standard deviation of 72 nm, an arithmetic mean of 88 nm and a coefficient variation of 82% respect to average. This means that we have more control over the diameter size in the nanobowls because their standard deviation was lower than that of the nanosheets.

Figure 5(a) shows a micrograph of short TiO₂-nt before the growth of nanosheets. These nanocavities, also named ‘U-tubes’ are connected by ‘the entire surface layer’ on the top part of the nanostructures [29, 34]. The length of the nanocavities was about 135 nm, and the inner diameter of about 21 nm. The image of the cross-section is shown in figure 5(b), here, we can see the roughness in the top part of nanocavities due to the organic electrolyte. According to the chemical dissolution model, the first stage is the creation of the compact oxide layer, secondly, the dissolution process that creates initial pores on the surface of the oxide layer, however, because we formed the Ti-nb template by the detachment process of the nanotubes, the new nanotubes can be grown more efficiently and quickly in the third stage of anodization [35]. In the red box, we can see the internal shape of the nanocavities; this cross-section image was obtained after the Focus Ion Beam process (FIB).

Additionally, figure 5(c) shows the superficial morphology of standard nanotubes whose the inner diameter and length were about 93 nm and 2.5 μm, respectively. As we can see, the nanostructures are organized in a closed-packed of nanotubes due to three steps of anodization and two detachments, since a better template of Ti-nb improve the periodicity of the nanostructures [20].
Because the nanosheets and nanobowls were assembled on the nanocavities, a new morphology was obtained that changed significantly the reflectance spectra. Figure 6(a) shows the reflectance spectra for TiO$_2$-nb/TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc, TiO$_2$-nc and TiO$_2$-nt. The reflectivity of Ti foil was 34% in the violet band and it increases as the wavelength increases. Also, the larger nanotubes have a similar phenomenon, however, the reflectivity decreases to 18% in the violet band. Furthermore, a considerable reduction in reflectance is observed because the absorption edge for TiO$_2$-nt had a band gap energy of 3.0 eV and these results agree with other reports \cite{36, 37}.

**Figure 4.** FESEM image taken at 45° with respect to the vertical of (a) highly ordered TiO$_2$-nb, and (c) TiO$_2$-ns; with their frequency histogram of the diameter for (b) TiO$_2$-nb and (d) TiO$_2$-ns, respectively.

**Figure 5.** FESEM image of the superficial morphology of (a) the nanocavities and (c) the nanotubes, and imagen of cross-section of (b) the nanocavities and (d) the nanotubes.
For nanocavities, the reflectance spectrum changes considerably because of interference fringes (see figure 6(a)). In other words, two bands with a high reflection, the main peak at 565 nm and secondary at 395 nm. In this way, when the nanosheets were assembled on the top part of the nanocavities, their spectrum had two dips of reflectance at 430 nm and 680 nm. As the nanocavities, the spectra of nanosheets presented interference fringes with two maximum reflection peaks displaced to the near ultraviolet (522 nm and 380 nm). For the nanobowls assembled on nanocavities, three bands of high reflection are observed at 400 nm, 510 nm and 760 nm (figure 6(a)). This manipulating of the propagation of light in the different reflectance spectra is attributed to two variables: length of the nanocavities and self-assembled nanostructures. A similar phenomenon of the interference fringes in the reflectance spectrum was observed in multilayer films, Sta et al reported the optical properties of the TiO$_2$ thin films, when they increased the account layers of thin films, the number of the interference fringes increased and the band gap energy decreased [38]. In fact, TiO$_2$-nb/TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc, and TiO$_2$-nc can be used as a partial photonic crystal because they have a reflectance spectrum similar to other reports where structural color has been studied in birds, butterflies, turkeys, and mosquitos [39–41]. For instance, TiO$_2$-nc shows a reflectance spectrum similar to the study reported by Eliason et al where they demonstrated that the microstructures of birds wings were organized in a hexagonal packed of melanosomes and this created a partial photonic band gap on the visible spectrum [41].

On the other side, to determine the consequence of the assembly of TiO$_2$ nanostructures on the optical properties, the reflectance spectra were utilized to calculate the optical band gap energy of the indirect transitions by Kubelka-Munk function [42]. Figure 6(b) shows the band gap energy of all TiO$_2$ nanostructures. A notable variation of band gap width of these nanostructures is observed. The band gap energy for TiO$_2$-nt was 3.0 eV,
whereas, an increasing of band gap energy was shown for TiO$_2$-nb/TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc, and TiO$_2$-nc. The band gap for the TiO$_2$-ns/TiO$_2$-nc was higher (3.18 eV) than the nanotubes. In the case of nanocavities, the band gap was 3.25 eV, while that TiO$_2$-nb/TiO$_2$-nc had the highest band gap energy (3.28 eV). It is clear the band gap energy increases as an effect of the length of the nanotubes and the thickness of the nanobowls and nanosheets. Defect states such as oxygen vacancies can displace the band gap energy to high energy $^{[42-44]}$. For this reason, we carried out a PL study to validate how defect states can be modified the optical properties.

Figure 7(a) shows PL spectra of TiO$_2$-nb/TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc, and TiO$_2$-nt. In order to understand the effect of the self-assembled nanostructures (TiO$_2$-nb and TiO$_2$-ns) on the emission, we compared their PL intensity with the nanocavities and nanotubes. We can see that the nanobowls assembled on nanocavities had a greater intensity than the TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc and TiO$_2$-nt. In addition, TiO$_2$-nb/TiO$_2$-nc had approximately the same PL intensity than the nanosheets because the self-assembled nanostructures created more defect states than the nanotubes and nanocavities.

To identify the main mechanisms that generate the emission, we deconvolved the PL spectra for TiO$_2$-nb/TiO$_2$-nc, TiO$_2$-ns/TiO$_2$-nc, and TiO$_2$-nt and they are illustrated in figures 7(b)–(e), respectively, and shown in table 1. The first mechanism of emission is generated by self-trapped excitons (STE) at 415 nm band (peak 1 for all structures) $^{[45]}$. Other mechanisms are single-ionized oxygen vacancies (Vo$^+$) at...
Table 1. Defect states of different TiO₂ films.

| Nanostructures | TiO₂-nb/TiO₂-nc (nanobowls, 128 nm) | TiO₂-ns/TiO₂-nc (nanosheets, 330 nm) | TiO₂-nc (nanocavities, 135 nm) | TiO₂-nt (nanotubes, 2.5 μm) |
|----------------|-----------------------------------|-------------------------------------|-------------------------------|----------------------------|
|                | Height | Width | Area   | Height | Width | Area   | Height | Width | Area   | Height | Width | Area   |
| STE [50]       | 35.7 k | 54    | 2.3 M  | 28.8 k | 43    | 1.58 M | 15 k   | 80    | 1.51 M | 4.1 k  | 49    | 257 k  |
| Vo* [47, 48, 50–52] | 22.4 k | 76    | 2.1 M  | 27.1 k | 64    | 2.1 M  | 5.6 k  | 139   | 0.99 M | 3.9 k  | 73    | 367 k  |
| Vo** [48–50, 52]  | 9.8 k  | 158   | 1.9 M  | 7.7 k  | 133   | 1.4 M  | 0.6 k  | 79    | 6.6 k  | 1.5 k  | 180   | 349 k  |
| Stated of Ti³⁺ [53] | 3.4 k  | 106   | 463 k  | 2.3 k  | 102   | 308 k  | 1.3 k  | 103   | 171.7 k| 0.6 k  | 101   | 85 k   |
437 nm, 443 nm, 448 nm, (peak 2 for the four structures) and doubly-ionized oxygen vacancies (Vo*) at 471 nm, 495 nm, and 621 nm (peak 3) [46–51]. These nanomaterials had another emission band of 750 nm to 850 nm (peak 4) that is associated with excited states of Ti3+ [52]. Usually, the excited states are related to the rutile phase. In fact, TiO2-nb/TiO2-nc showed the highest emission in violet, blue, and green bands of the electromagnetic spectrum at 418 nm, 448 nm, and 498 nm, respectively, caused by STE and oxygen vacancies.

Particularly, the PL intensity of the TiO2-nb/TiO2-nc film by STE was 1.2 times larger than the TiO2-ns/TiO2-nc film (peak 1 in figures 7(b) and (c)), 2.3 times larger than the TiO2-nc film and 8.7 times larger than the TiO2-nt film. Similarly, the area by Vo* of the TiO2-nb/TiO2-nc film was 1.14 times larger than the TiO2-ns/TiO2-nc film, 3.8 times larger than the TiO2-nc film and 5.58 times larger than the TiO2-nt film (peak 2 and 3 in figures 7(b)–(e)). Besides, the PL intensity in the infra-red band of the TiO2-nb/TiO2-nc film was 1.4 times higher than TiO2-ns/TiO2-nc film, 2.6 times higher than the TiO2-nc film and 5.6 times higher than the TiO2-nt film (peak 4 in figures 7(b)–(e)). Figure 7(f) shows the area of the defect states of TiO2-nb/TiO2-nc, TiO2-ns/TiO2-nc, TiO2-nc and TiO2-nt. Here, TiO2-nb/TiO2-nc had the greatest area of Vo* than other structures. We can clearly see that a relationship is found between Vo* and the band gap energy (Eg), the band gap energy increases with increasing of Vo*. We assume that the increase in emissions is caused by the assembly of nanostructures and quasi-periodic arrangement of nanobowls and nanosheets, because we developed a hybrid nanostructure with a unique and complex morphology.

In summary, the optical properties of the nanotubes are modified by the change of morphology. These nanomaterials can be used to gas sensors, multiplicators, and LEDs. For example, the high amount of oxygen vacancies is related to the increasing of the reactivity in a gas sensor and this, in turn, can enhance the sensor response of the device [53, 54].

The physical origin of the luminescence of our TiO2 nanostructures can be explained by the mechanism of emission that is shown in figure 8. For nanotubes of larger length (figure 8(a)), the emission in violet, cyan, and infra-red bands are created by a PL process.

The mechanism starts with the excitation of electrons, when the excitation energy is greater than the band gap energy (3.00 eV). So, the electrons are transferred from the valence band to the conduction band, and after by a relaxation process, an energy decay of the electrons is realized. Consequently, the electrons are trapped and

Figure 8. Schematic diagram of the emission physical mechanism of (a) TiO2-nt (2.5 μm), (b) TiO2-nc (135 nm), (c) TiO2-ns/TiO2-nc (330 nm), and (d) TiO2-nb/TiO2-nc (128 nm).
recombined by the STE and this recombination generates the emission of a photon. Then, the electrons are trapped and recombined by Vo* and Vo**, and finally, by the states of Ti3+. The energy levels of STE, both types of oxygen vacancies, and Ti3+ defects are 0.18 eV, 0.35 eV, 0.36 eV, and 1.69 eV, below the conduction band minimum. Figures 8(b)–(d) show the physical mechanism of emission for TiO2-nc, TiO2-ns/TiO2-nc, TiO2-nb/TiO2-nc, respectively. Similar color emissions of nanotubes and nanobowls assembled on nanocavities are observed, however, an increase in the energy levels below the conduction band minimum is detected because the STE, Vo*, Vo**, and Ti3+ defects are localized at 0.42 eV, 0.62 eV, 0.9 eV, and 1.86 eV, correspondingly. In the case of nanosheets assembled on nanocavities, violet, blue and infrared bands are observed whose energy levels are 0.27 eV, 0.46 eV, 0.67 eV, and 1.73 eV, correspondingly. For nanocavities, a red band of emission is observed at 1.33 eV below the conduction band minimum.

In order to study the effect of the morphology on the vibration modes and phases of nanomaterial, Raman spectra were calculated for all TiO2 nanomaterials after the synthesis and thermal treatment, see figures 9(a) and (b), respectively, in the region of $-20 \text{ cm}^{-1}$ to $1800 \text{ cm}^{-1}$. In figure 9(a) we can observe that the nanotubes with length in the order of micrometers had the highest intensity at $161 \text{ cm}^{-1}$, this band is related to the Raman active mode of symmetries of $E_g(1)$ which corresponds to the anatase phase [55]. Usually, the amorphous nanotubes do not present the $E_g(1)$ mode. However, the anatase phase is observed in these spectra because the nanotubes are organized in a closed-packed array. In another study, the crystallinity of the amorphous nanotubes can be increased only by a water vapor treatment [56]. It is clear that the intensity of the anatase phase increases with increasing of the thickness of the TiO2 film. Other Raman scattering bands were located at $391 \text{ cm}^{-1}$ ($B_{1g}$ mode), $509 \text{ cm}^{-1}$ ($A_{1g} + B_{1g}$ mode), and $638 \text{ cm}^{-1}$ ($E_g$ mode) [56]. Besides, the Raman modes of ethylene glycol from $1000 \text{ cm}^{-1}$ to $1400 \text{ cm}^{-1}$ were observed [56]. At $1593 \text{ cm}^{-1}$, the graphite mode that corresponds to a monolayer of graphene was noticed and it is caused by ethylene glycol [56, 57]. Furthermore, the self-assembled nanostructures films had a lower $E_g(1)$ mode intensity, and higher intensity in the amorphous phase that corresponding to Ti–O phase ($215 \text{ cm}^{-1}$, 425 cm$^{-1}$), and Ti–O stretching ($610-635 \text{ cm}^{-1}$) than the nanotubes [56]. Another important vibration mode is $7 \text{ cm}^{-1}$ (see inner graph in figure 9(a)), these bands are produced only in nanocavities and self-assembled nanostructures. The highest intensity at $7 \text{ cm}^{-1}$ was TiO2-nb/TiO2-nc,
secondly, TiO$_2$-ns/TiO$_2$-nc, and thirdly, TiO$_2$-nc. From these spectra, we can observe that vibrations at low frequency decrease with increasing of the length of the nanocavities and thickness of the two-dimension structures. The origin of the vibrations at 7 cm$^{-1}$ is associated with the confinement of acoustic phonons, this can give information about size, form, and concentration of the nanomaterials [58–60].

On the other hand, significant changes in the Raman spectra after thermal treatment were observed (see figure 9(b)). The main band of these spectra corresponds to symmetries of E$_{g1}$ at 154 cm$^{-1}$. The intensity of the E$_{g1}$ mode for the self-assembled nanostructures and nanocavities after annealing was more defined than the Raman spectra after synthesis. The bands at 391 cm$^{-1}$, 509 cm$^{-1}$ and 638 cm$^{-1}$ were higher and more defined than the bands in the samples without annealing. Also, as an effect of the thermal treatment, the vibrations in the range of 1000 cm$^{-1}$ to 1600 cm$^{-1}$ were not observed in these spectra [61]. Besides, the peak related to graphene disappeared. In summary, the intensities of the anatase modes increase for all nanostructures with the length of the nanotubes.

For low frequencies, the peaks at 7 cm$^{-1}$ increase with decreasing of the intensity of the E$_{g1}$ mode in the self-assembled nanostructures and nanocavities. In addition, the peaks of the films after the thermal treatment were lower in intensity than the peaks of TiO$_2$ nanomaterials after the synthesis. However, the intensity of nanocavities was higher than the same material without annealed because it had lower amount of defect states and did not have nanobowls and nanosheets. Also, in this spectrum the nanotubes did not show vibration modes.

Figures 9(c) and (d) show the correlation between the defect states and the crystallinity of the TiO$_2$ films. A notable displacement of the E$_{g1}$ peak corresponding to the anatase phase is noticed because typically the E$_{g1}$ mode has been observed at 146 cm$^{-1}$ (see figure 9(c)). This displacement is related to the existence of oxygen vacancies in the amorphous structure [62]. From PL characterization, it can be noted that the nanotubes had the least amount of self-trapped excitons and oxygen vacancies than the other nanostructures. Therefore, the oxygen vacancies are not the only cause of distortion. Other origins could be the confinement of acoustic phonons and the different grain size according to the study carried out by Amoresi et al [62]. Additionally, a relationship between the final thickness of the TiO$_2$ film and wavenumber of the E$_{g1}$ mode is observed. In other words, a greater thickness of the TiO$_2$ film increases the displacement of E$_{g1}$, on the contrary, a thinner thickness approaches the value of E$_{g1}$. After the thermal treatment, the displacement is lower than that of the TiO$_2$ films after anodization because the thermal treatment passivates the surface of the material and reduces the defects that distort the lattice of the anatase phase (figure 9(d)).

4. Conclusions

We investigated for the first time TiO$_2$ nanosheets and nanobowls assembled on a TiO$_2$ nanocavities array. To grow and assemble the nanostructures, a rapid two-step electrochemical anodization process was developed. We demonstrated by FESEM that these nanostructures have a morphology well organized and were self-ordered among several short TiO$_2$-nt to achieve the most stable nanostructure. The time of the second anodization is a key parameter in the shape of the nanostructure: a shorter time, resulted in nanosheets while a longer time in nanobowls. Interestingly, the PL study showed that self-assembled nanostructures enhance emission eight times more than nanotubes. Also, the reflectance characterization showed that nanotubes with length in the order of nanometers increase the number of interference fringes. In addition, nanocavities, self-assembled nanobowls and nanosheets notably changed the reflectance spectra because they create a color interference fringe and partial optical band gap, being similar to other reports that utilized multilayer films or photonic crystals in nature. Moreover, as a consequence of the length of the nanotubes and thickness of the self-assembled nanostructures, the band gap is displaced to high energy values. Likewise, the Raman spectra showed an improvement in the crystallinity of the anatase phase with the increase in the length of the nanotubes, and the self-assembled nanostructures and nanocavities had a vibration mode at low frequencies that can be associated with the phonon acoustic confinement. To conclude, we developed several morphologies of the TiO$_2$ films by modifying parameters in the synthesis. As a consequence of this, the emission was enhanced, the reflectance spectrum was changed, band gap energy was increased and the intensity of the Raman spectra was modified. These nanostructures could apply to gas sensors, optical sensors, LEDs, and materials for plasmon effects. In the immediate future, we will study the mechanism of the formation of these nanobowls and nanosheets assembled on nanocavities.

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References
[1] Zhong D, Jiang Q, Huang B, Zhang W H and Li C 2015 Synthesis and characterization of anatase TiO2 nanosheet arrays on FTO substrate J. Energy Chem. 24 626–31
[2] Li M, Chen Y, Li W, Li X, Tian H, Wei X, Ren Z and Han G 2017 Ultrathin anatase TiO2 nanosheets for high-performance photocatalytic hydrogen production nano Lett. 17 1604115
[3] Leng M, Chen Y and Yue J M 2014 Synthesis of TiO2 nanosheets via an exfoliation route assisted by a surfactant Nano Lett. 6 8531
[4] Bai X, Gao K, Huang X, Qin C, Zhang Y and Han X 2018 Electrochemical sensing characteristics of 3D TiO2 nanostructures with different crystal structures and morphologies J. Electrochem. Soc. 165 D663
[5] Wu G, Chen J, Guo Y, Li X, Luo B, Chu L, Han Y, Jiang B, Xu L and Li M 2017 Freestanding sodium-ion batteries electrode using graphene foam coaxially integrated with TiO2 nanosheets J. Electrochem. Soc. 164 A3060
[6] Gao C, Wei T, Zhang Y, Song X, Huan Y, Liu H, Zhao M, Yu J and Chen X 2019 A photoresponsive rutile TiO2 heterojunction with enhanced electron–hole separation for high-performance hydrogen evolution Adv. Mater. Commun. 31 (8) 1806596
[7] Chen J S and Lou X W 2009 Anatase TiO2 nanosheet: an ideal host structure for fast and efficient lithium insertion/extraction Electrochem. Commun. 11 2332
[8] Pazhamalai P, Krishnamoorthy K, Mariappan V K and Kim S J 2019 Blue TiO2 nanosheets as a high-performance electrode material for supercapacitors J. Colloid Interface Sci. 536 62
[9] Zhao Y, Gan S, Wu L, Zhu J, Xiang Y and Dai X 2019 GeSe nanosheets modified surface plasmon resonance sensors for enhancing sensitivity Nanophotonics AOP 9 (2) 327–36
[10] Fan X et al 2017 Assembly of gold nanoparticles into aluminum nanobowl array Sci. Rep. 7 2322
[11] Wang X D, Graugnard E, King J S, Lin Wang Z and Summers C J 2004 Large-scale fabrication of ordered nanobowl arrays Nano Lett. 4 2223
[12] Yang L, Kou P, He N, Dai H and He S 2017 Anomalous light trapping enhancement in a two-dimensional gold nanobowl array with an amorphous silicon coating Opt. Express 25 14115
[13] Chen T H, Tsai T Y, Hsieh K C, Chang S C, Tai N H and Chen H L. 2008 Two-dimensional metallic nanobowl array transferred onto thermomorphic substrates by microwave heating of carbon nanotubes Nanotechnology 19 465303
[14] Zhang M, Xia L, Deng Q, Shi L, Cao A, Pang H and Hu S 2015 Nanobowl array fabrication via conglutination process based on Thiol–Ene polymer IEEE Photon. J. 7 74
[15] Zhu L, Gao R, Zhao X, Zhang J, Zhang X, Yang I, Zhang Y, Chen L and Wang Y 2019 Site-selective growth of Ag nanoparticles controlled by localized surface plasmon resonance of nanobowl arrays Nano Lett. 11 6576
[16] Yoon S W, Park H K, Oh J H and Do Y R 2014 Full extraction of 2D photonic crystal assisted Y,Al2O3:Ce ceramic plate phosphor for highly efficient white LEDs IEEE Photon. J. 6 1
[17] Wang W, Dong J, Ye X, Li Y, Ma Y and Qi L 2016 Heterostructured TiO2–nanorod@nanobowl arrays for efficient photoelectrochemical water splitting Small 12 1469
[18] Umh H N, Yu S, Kim Y H, Lee SY and Yi J 2016 Tuning the structural color of a 2D photonic crystal using a bowl-like nanostucture ACS Appl. Mater. Interfaces 8 15802–8
[19] Shen S, Chen J, Wang M, Sheng X, Chen X, Feng X and Mao S S 2018 Titanium dioxide nanostructures for photoelectrochemical applications Prog. Mater. Sci. 98 299
[20] Lee K, Mazzare A and Schmuki P 2014 One-dimensional titanium nanofilms: nanotubes Chem. Rev. 114 9385
[21] Cummings F R, Roux I J L, Mathe M K and Knoesen D 2010 Structure induced optical properties of anodized TiO2 nanotubes Mater. Chem. Phys. 124 234–42
[22] Zhang M et al 2016 Fabrication of well-aligned TiO2 nanotube arrays with outstanding light-induced hydrophilicity performance J. Electrochem. Soc. 163 E372
[23] Konodo T, Nagao S, Yanagishita T and Masuda H 2016 Formation of porous anodic TiO2 with square nanoholes by pretexturing process J. Electrochem. Soc. 163 E206
[24] Boda M A, Ikram M and Rubab S 2019 Dynamics of photo-induced charge carriers in anodized titania nanotube array Mater. Res. Express Accepted 6 10
[25] Boda M A 2019 Efficient and cost effective multi-podal TiO2 nanotube array on replacing conventional platinum counter electrode by graphite foil Chem. Pap. 73 937–42
[26] Boda M A and Shah M A 2018 Fabrication of ZnFe2O4/TiO2 nanotube array composite to harness the augmented photocurrent density under visible light Appl. Phys. A 124 55
[27] Bae K, Lee J, Kang G, Do-Sik Y, Lee C W and Kim K 2015 Refractometric and colorimetric index sensing by a plasmon-coupled hybrid AAO nanotemplate RSC Adv. 5 103052
[28] Arenas-Hernandez A 2016 Síntesis y caracterización de nanotubos de Dióxido de Titanio MSc Thesis National Institute for Astrophysics, Optics and Electronics
[29] Chong B, Yu D L, Gao M Q, Fan H W, Yang C Y, Ma W H, Zhang S Y and Zhu X F 2015 Formation mechanism of gaps and ribs around anodic TiO2 nanotubes and method to avoid formation of ribs J. Electrochem. Soc. 162 H244–50
[30] Zhang G, Huang H, Zhang Y, Chan H L W and Zhou L 2007 Highly ordered nanoporous TiO2 and its photocatalytic properties Electrochem. Commun. 9 2854–8
[31] Shin Y and Lee S 2008 Self-organized regular arrays of anodic TiO2 nanotubes Nano Lett. 8 3171–7
[32] Sapha H, Sanwarli T, Palaseh E, Hromadko L, Zareb R, Skoda D, Urbansk M, Ng S, Prikril J and Macak J M 2017 Ideally hexagonally ordered TiO2 nanotube arrays Chem. Pap. 6 480
[33] Povolotskaya A V, Povolotskiy A V and Manshina A A 2013 Hybrid nanostructures: synthesis, morphology and functional properties Russ. Chem. Rev. 84 579–600
[34] Yoo J E and Schmuki P 2019 Critical factors in the anodic formation of extremely ordered titania nanocavities J. Electrochem. Soc. 166 C3389–98
[35] Zhong X M, Yu D L, Zhang S Y, Chen X, Song Y, Li D D and Zhuo Xu F 2013 Fabrication and formation mechanism of triple-layered TiO2 nanotubes J. Electrochem. Soc. 160 E125–9
Hoseinzadeh T, Ghorannevis Z, Ghoranneviss M, Salem M K and Sari A H 2017 Synthesis of different TiO2 nanostructures and their physical properties Chin. Phys. Lett. 34 116
Lin J, Liu X, Zhu S and Chen X 2015 TiO2 nanotube structures for the enhancement of photon utilization in sensitized solar cells Nanotechnol. Rev. 3 209–38
Sta I, Jlassi M, Hajji M, Boujmil M F, Jerbi R, Kandyla M, Kompitas M and Ezzouaia H 2014 Structural and optical properties of TiO2 thin films prepared by spin coating J. Solgel Sci. Technol. 72 421
Zhao Y, Xie Z, Gu H, Zhu C and Gu Z 2012 Bio-inspired variable structural color materials Chem. Soc. Rev. 41 3297–317
Elason C M, Bitton P P and Shawkey M D 2013 How hollow melanosomes affect iridescent colour production in birds Proc. R. Soc. B 280 20131505
Stavenga D G 2014 Thin film and multilayer optics cause structural colors of many insects and birds Mater. Today: Proc 1S 109–21
Choudhury B, Dey M and Choudhury A 2013 Defect generation, transition, and band gap reduction in Cu-doped TiO2 nanoparticles, Choudhury et al Int. Nano Lett. 3 25
Zhao H, Pan F and Li Y 2017 A review on the effects of TiO2 surface point defects on CO2 photoreduction with H2O J. Materiomics 3 17
Al-Hashem M, Akbar S and Morris P 2019 Role of oxygen vacancies in nanostructured metal-oxide gas sensors: a review Sens. Actuators B Chem. 301 126855
Zhang H, Zhou M, Fu Q, Lei B, Lin W, Guo H, Wu M and Lei Y 2014 Observation of defect state in highly ordered titanium dioxide nanotube arrays Nanotechnology 25 275603
Kernazhitsky L, Shymonavka V, Gavrillok T, Naumov V, Fedorenko I, Kshnyakin V, Burtsve A and Baran J 2019 Effect of Cr-doping on luminescence of nanocrystalline anatase TiO2 powders Ucr. J. Phys. 61 482
Guillen G G, Shaji S, Palma M I M, Avellaneda D, Castillo G A, Roy T K D, Gutierrez D I G and Krishnan B 2017 Effects of ablation energy and post-irradiation on the structure and properties of titanium dioxide nanomaterials Appl. Surf. Sci. 405 183–94
Li X, Gao C, Wang J, Lu B, Chen W, Song J, Zhang S, Zhang Z, Pan X and Xie E 2012 TiO2 films with rich bulk oxygen vacancies prepared by electrophotinising for dye-sensitized solar cells J. Power Sources 214 244–50
Zhang L, Yu W, Han C, Guo J, Zhang Q, Xie H, Shao Q, Sun Z and Guo Z 2017 Large scaled synthesis of heterostructured electrosprun TiO2/SnO2 nanofilbers with an enhanced photocatalytic activity J. Electrochem. Soc. 164 11651–6
Tripathi A K, Singh M K, Mathpa M C, Mishra S K and Agarwal A 2013 Study of structural transformation in TiO2 nanoparticles and its optical properties J. Alloys Compd. 549 114–20
Ganeshraja A S, Rajkumar K, Zhu K, Li X, Thirumurugan S, Xu W, Zhang J, Yang M, Anbalagan K and Wang J 2016 Facile synthesis of iron oxide coupled and doped titania nanocomposites: tuning of physicochemical and photocatalytic properties RSC Adv. 6 72791–802
Pandiyan R, Bartali R, Micheli V, Gottardi G, Lucia I, Ristic D, Goget G A, Ferrari M and Laidani N 2011 Influence of Nd3+ doping on the structural and near-IR photoluminescence properties of nanostructured TiO2 films Energy Procedia 10 167–71
Mercado C, Seeley Z, Bandypadhyay A, Bose S and McHale J I 2011 Photoluminescence of dense nanocrystalline titanium dioxide thin films: effect of doping and thickness and relation to gas sensing ACS Appl. Mater. Interfaces 3 2281
Lu H F, Li F, Liu G, Chen Z G, Wang D W, Fang H T, Lu G Q, Jiang Z H and Cheng H M 2008 Amorphous TiO2 nanotube arrays for low-temperature oxygen sensors Nanotechnology 19 405504
Díaz-Real J A, Dubed-Bandomo G C, Galindo-de-la-Rosa J, Arriaga L G, Ledesma-García J and Alonso-Vante N 2013 Study of the anodization time on the photocatalytic activity of TiO2 nanotubes Beilstein J. Nanotechnol. 9 2628–43
Lamberti A, Chiodoni A, Shahzad N, Bianco S, Quaglio M and Pirri C F 2014 Ultrafast room-temperature crystallization of TiO2 nanotubes exploiting water-vapor treatment Sci. Rep. 5 7808
Malard I M, Pimenta M A, Dresselhaus G and Dresselhaus M S 2009 Raman spectroscopy in graphene Phys. Rep. 473 51–87
Ovyuk N N 2010 Studying the initial stage of nucleation with low-frequency Raman scattering EPL 91 26001
Pighini C, Aymes D, Millot N and Saviot L 2007 Low-frequency Raman characterization of size-controlled anatase TiO2 nanopowders prepared by continuous hydrothermal syntheses J. Nanoparticle Res. 9 309–15
Cacciato G, Bayle M, Pugliara A, Bonafos C, Zimbone M, Privitera V, Grimaldi M G and Carles R 2015 Enhancing carrier generation in TiO2 by a synergistic effect between plasmon resonance in Ag nanoparticles and optical interference Nanoscale 7 13468–76
Likodimos V, Stergiopoulos T, Falaras P, Kunze J and Schmuki P 2008 Phase composition, size, orientation, and antenna effects of self-assembled anodized titania nanotube arrays: a polarized micro-raman investigation J. Phys. Chem. C 112 12687–96
Amoresi R A C, Teodoro V, Teixeira G F, Li M S, Simões A Z, Perazolli L A, Longo L and Zaghe M A 2018 Electrosteric colloidal stabilization for obtaining nTiO2/nTiO2 heterojunction: microstructural evolution in the interface and photonics J. Eur. Ceram. Soc. 38 1621–31