

Synthesis and Characterization of Anatase TiO₂ Nanofibers using Electrospinning Method

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الخلاصة

تم تحضير الليفات نانوية من أوكسيد التيتانيوم بتركيب أناتيس باستخدام تقنية الغزل الكهربائي. التركيب المورفولوجي والتركيب النانوي للليفات أوكسيد التيتانيوم تم فحصها من خلال حيود الاشعة السينية ، المجهر الذري الماسح ، والمجهر الالكتروني الماسح . تم حساب فجوة الطاقة وكذلك السلوك البصري باستخدام مطياف الاشعة فوق البنفسجية - المرئية، ومطياف التألقية الضيائية . لقد تم دراسة تأثير عامل الفولتية المسلطة في تقنية الغزل الكهربائي ، حيث وجد نقصان قطر الليف النانوي من (155-48) نانومتر بزيادة الفولتية المسلطة من (15-21) كيلوفولت.

Abstract

TiO₂ nanofibers with anatase structure were synthesized by an electrospinning method. Morphology and the nanostructure of the crystalline TiO₂ nanofibers were characterized by means of x-ray diffraction (XRD), atomic force microscope (AFM), field emission scanning electron microscopy (FESEM). The energy gap was estimated and optical behavior was studied using UV-Vis spectroscopy, and Photoluminescence spectroscopy (PL). The effect of applied voltage parameter on TiO₂ nanofibers was also studied. The results shows that the average diameter of the prepared nanofibers decreases from (155- 48) nm with increasing the applied voltage from (15 - 21 kV) respectively.

Keywords: TiO₂, nanofibers, Electrospinning.

Introduction

Nanostructured metal oxide materials have drawn considerable attention because of their potential applications in many fields such as electronics, Photonics, sensors and catalysis [1]. Nanosized ceramics with large surface area per unit volume can have enhanced electrical, physical, and chemical properties with respect to their bulk counterparts [2, 3].

Dimensionality is a crucial factor in determining the physical, chemical, electrical, and optical properties of nanomaterials. Thus, controlling the size and shape of nanomaterials is of great interest and challenge in the fields of nanoscience and nanotechnology [4-7]. One-dimensional (1D) nanostructured materials such as nanowires, nanorods, nanowhiskers, nanotubes and nanofibers have been intensively studied worldwide owing to their potential technological applications. [8–12].

Nanofibers belong to an exciting class of one dimensional nanomaterials and possess several special properties that makes them suitable for many value-added applications ranging from medical to consumer products and from industrial to high-tech applications, including energy storage, fuel cells, and information technology [4,13-15]. Another interesting aspect of using nanofibers is that it is feasible to modify not only their morphology and their (internal bulk) content but also their surface structure to carry various functionalities [16,17]. Furthermore, it is even feasible to control secondary structures of nanofibers in order to prepare nanofibers with core/sheath structures, nanofibers with hollow interiors and nanofibers with porous structures [18].

Among the transition metal oxides, TiO_2 has received considerable attention in the field of nanotechnology because of its unique properties and novel applications. TiO_2 exists in nature in three crystalline modifications: rutile, anatase, and brookite. It is noted that titania nanorods, and nanotubes have been synthesized using sol-gel and electrochemical methods with channels in anodic alumina membranes [19]. This process is composed of three steps, fabrication of templates, coating of the surfaces of templates with titania, and removal the templates. To curtail the multiple steps, an electrospinning technique was employed to synthesize fiber nanostructures due to the simplicity [20, 21].

Most recently, TiO_2 based nanofibers fabricated by electrospinning have been of great interest due to the wide potential applications of nanofibers [22]. Electrospinning is a simple and versatile method for generating ultra-thin fibers from a rich variety of materials that include polymers, composites and ceramics [23]. The following parameters and processing variables affect the electrospinning process: (i) system parameters such as molecular weight, molecular weight distribution and architecture (branched, linear, etc.) of the polymer, and polymer solution properties

(viscosity, conductivity, dielectric constant, and surface tension, charge carried by the spinning jet) and (ii) process parameters such as electric potential, flow rate and concentration, distance between the capillary and collection screen. (iii) ambient parameters such as temperature, humidity and air velocity in the chamber. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated [24,25].

In this work, TiO₂ nanofibers was synthesized by electrospinning using polyvinylpyrrolidone (PVP) and Ti tetraisopropoxide as precursors, and the effects of the applied voltage as one of important processing parameters was then investigated on the crystal structure, morphology, and microscopy of electrospun TiO₂ nanofibers. The nanofibers were characterized by XRD, AFM, SEM, UV-Vis, and PL spectroscopy.

Experimental

The chemicals used in this study were high purity titanium tetraisopropoxide (TIP) (Ti [OCH (CH₃)₂]₄, 97% Sigma Aldrich,), polyvinylpyrrolidone (PVP, Sigma Aldrich Mw = 1,300,000), acetic acid (CH₃COOH, 99.7% Scharlau, Spain), ethanol (99% Scharlau, Spain).

In a typical procedure, 1 g of titanium tetraisopropoxide (TIP) was mixed with 2 ml of acetic acid and 2 ml of ethanol. The solution was rested for 10 min before being added into 5 ml of PVP solution in ethanol. The concentration of the PVP solution was kept 7 wt% and the resulting mixture was constantly stirred for 10 min. The spinning solution was immediately loaded into a plastic syringe with 21-gauge stainless steel needle was used as the nozzle. The emitting electrode from a Gamma High Voltage Research ES30P power supply capable of generating DC voltages up to 25 kV was attached to the needle. The grounding electrode from the same power supply was attached to a plate of aluminum with clean glass substrates fixed on it which was used as the collector plate and was placed 20 cm in front of the tip of the needle. Upon the application of a high voltage ranging between 15 and 21 kV across the needle and the collective plate, a fluid jet was ejected from the nozzle. The feed rate of the precursor solution was 1ml/h which can be controlled using a syringe pump (KDS 200). As the jet accelerated towards the collector, the solvent evaporated, leaving only ultra-thin fibers on the collector. The obtained fibers were left exposed to moisture for approximately 10 h to allow complete hydrolysis of TIP and consequently subjected to calcination at a high temperature of 500 °C for 3 h with heating rate of 5°C/min to remove residual PVP.

The x-ray diffraction (XRD) measurements, which were used to characterize the crystalline phase of the TiO₂ fiber, were carried out on an x-ray diffractometer (type miniflex II Rigaku, Japan) using (CuK α) radiation. The surface morphology was studied using atomic force microscopy (AFM). The samples were observed under a (Hitachi S-4160) field emission scanning electron microscope (FE-SEM) after being gold-coated. The optical absorption spectra of the TiO₂ film were recorded using UV–visible spectrophotometer (Shimadzu UV-1601). The photoluminescence (PL) spectra were recorded at room temperature (25 °C) using a PL spectrophotometer (Shimadzu) by exciting the samples at 260 nm.

Results and discussion

Figure (1) shows that the XRD patterns of the as-prepared samples calcined at 500°C for 3 hours in air atmosphere. The peaks shown in the XRD patterns correspond to the (101), (004), (112), (200), (105), (211), and (204) planes of TiO₂ tetragonal anatase phase. These patterns can be well indexed to tetragonal anatase (JCPDS no. 21- 1272). No peaks of brookite or rutile phase were detected, which indicate the high purity of the as-prepared samples. The crystallite size can be estimated using the Scherrer formula [26]:

$$D = k\lambda / \beta \cos \theta$$

Where D is the crystallite size in nanometers, k a constant (=0.9 assuming that the particles are spherical), λ is the wavelength of the X – ray radiation (CuK α =0.1541nm), β is the FWHM of the strongest peak, and θ is the diffraction angle. The crystallite sizes of the powders were calculated on the diffraction peaks of anatase (101) crystalline plane. According to these calculations, the crystallite sizes of the fibers were (24.62, 25.10, 25.32 nm), for the fibers prepared in (15, 18, 21 kV) respectively. These results revealed that the resultant fibers obtained in different applied voltages were all in the TiO₂ anatase phase, and with an increase of the applied voltage, crystallites size of the samples was getting larger. Also, it can be found that films prepared in high applied voltage show relative sharp peaks indicating the coalescence of crystalline anatase-phase TiO₂.

The surface morphology and roughness have been indicated in figure (2) using AFM images, the roughness average is (3.16, 7.45, 8.11 nm) for the

fibers prepared in (15, 18, 21 kV) respectively. The roughness average increased with the applied voltages, and this has great advantages in many applications of TiO₂ nanofibers such as sensing and photocatalyst.

TiO₂ nanofibers were investigated by FESEM analyses. Figure (3) represents FESEM images of pre-calcined as-spun fibers and titania fibers after calcination at 500 °C for 3h .The diameters of TiO₂ nanofibers ranging from (48-155 nm).The average diameters of pre-calcined as-spun fibers are (172, 264, 205 nm) , and in the calcined TiO₂ nanofibers are (145,101,82 nm) prepared in (15, 18, 21 kV) respectively. Figure (3d) illustrates homogenous distribution of TiO₂ nanofibers mats, and the fiber length reach many centimeters, therefore the aspect ratio is too high.

Figure (4a) shows the variation of the transmittance with the applied voltage, both the transmittance and the direct band gap increases from (3.35-3.45 eV) with increases the applied voltage from (15-21 kV) respectively as shown in figure (4b) .This large value of band gap is usually observed when we are dealing with fine particles in the nanoscale therefore this blue shift of the band gap was taken place because of the quantum confinement effect. We are very close to a quantum confinement region [27, 28].

The PL excitation spectra were evaluated in figure (5). For all samples, the PL excitation spectra have many peaks: (355,363,470 nm) which are corresponding to (3.49, 3.42, and 2.64 eV) respectively. Hence, this band corresponds to the photo absorption near the band energy (NBE) edge of the conduction band [29]. It has been demonstrated that the occurrence of emission peak in the visible region (470 nm) is due to the presence of defect levels below the conduction band. The native defects in wide gap semiconductors are expected to introduce deep levels inside the band gap [30]. The broad luminescence spectrum in the visible region is attributed to the electronic transition mediated by the defect levels, such as oxygen vacancies in the band gap [30]. The stronger the PL intensity, the larger the content of oxygen vacancies and defects, and this occurred with decreases the applied voltages [31].

Conclusions

Nanofibers of TiO_2 have been successfully fabricated using an electrospinning method. This method is simple and repeatable. TiO_2 nanofibers (diameter of ~48–155 nm) could be obtained and confirmed by XRD and the crystalline phase in the form of pure anatase structure. The applied voltage is an important parameter in the electrospinning method, and the effect of this parameter was studied on roughness, diameters, energy gap, and emission spectrum of TiO_2 nanofibers.

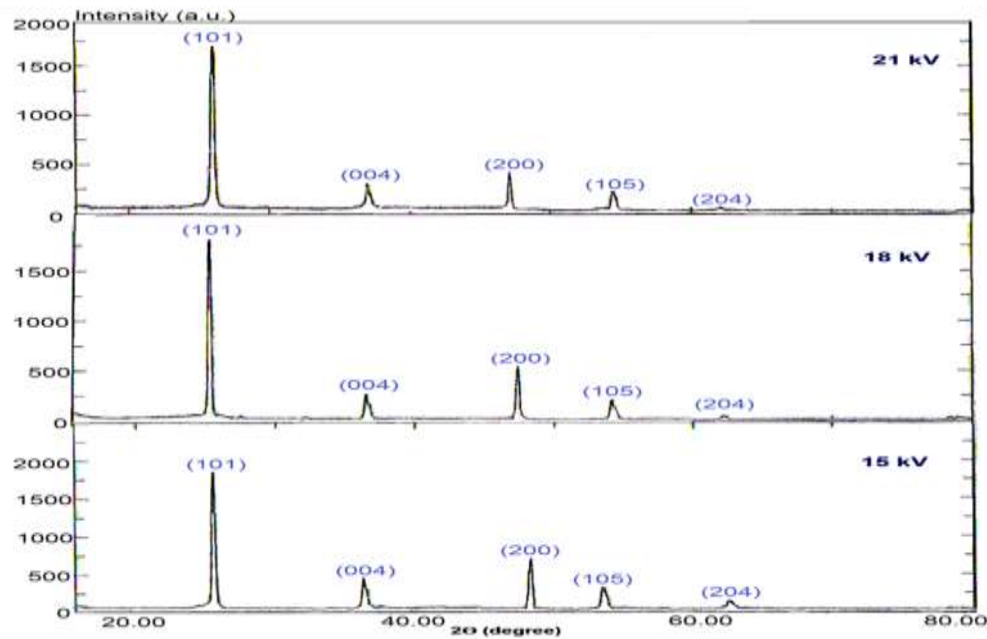


Figure (1): XRD spectra of TiO_2 nanofibers for different applied voltages.

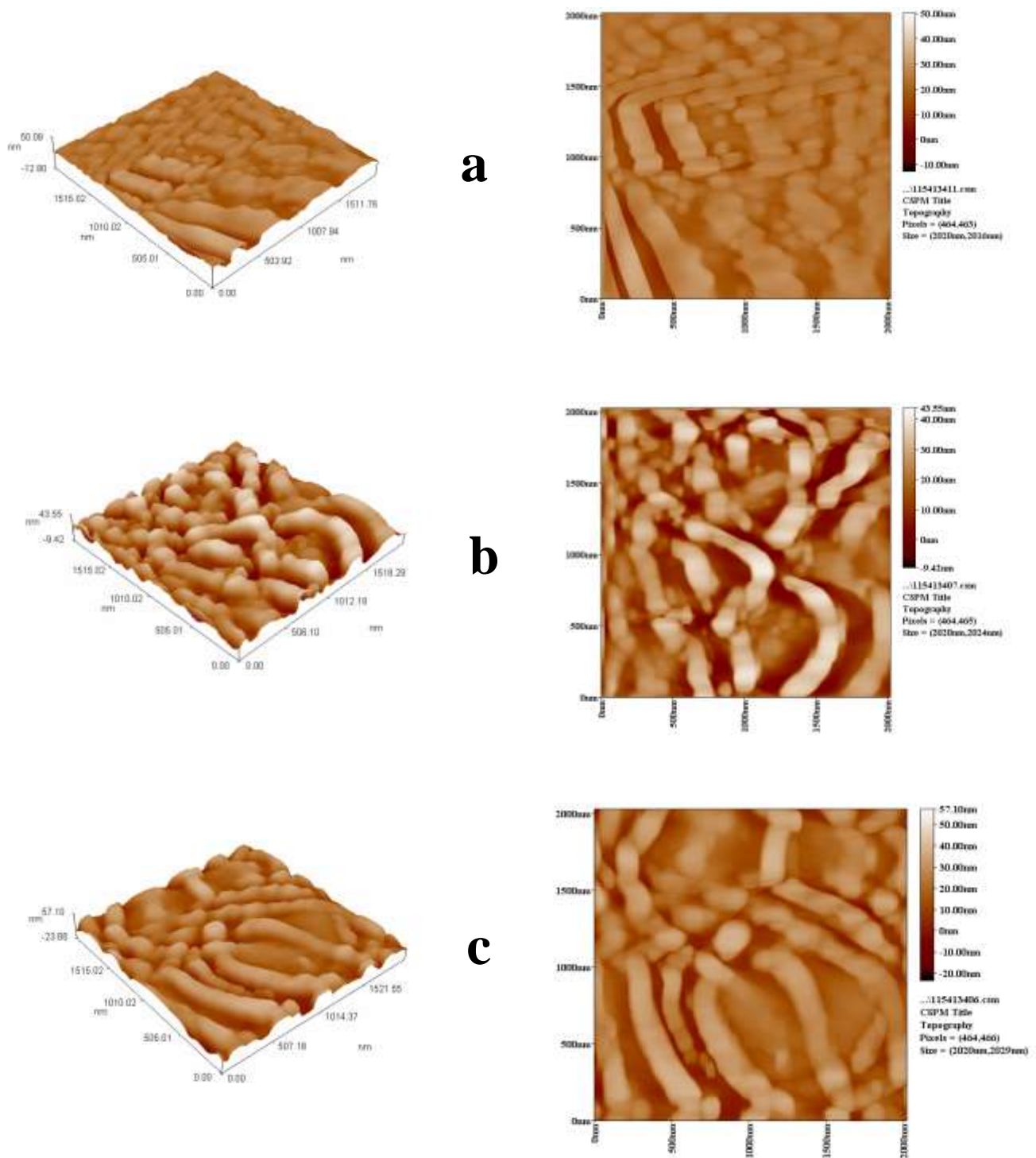


Figure (2): AFM micrographs of TiO_2 fibers prepared in different applied voltages, (a) 15 kV (b) 18 kV and (c) 21 kV.

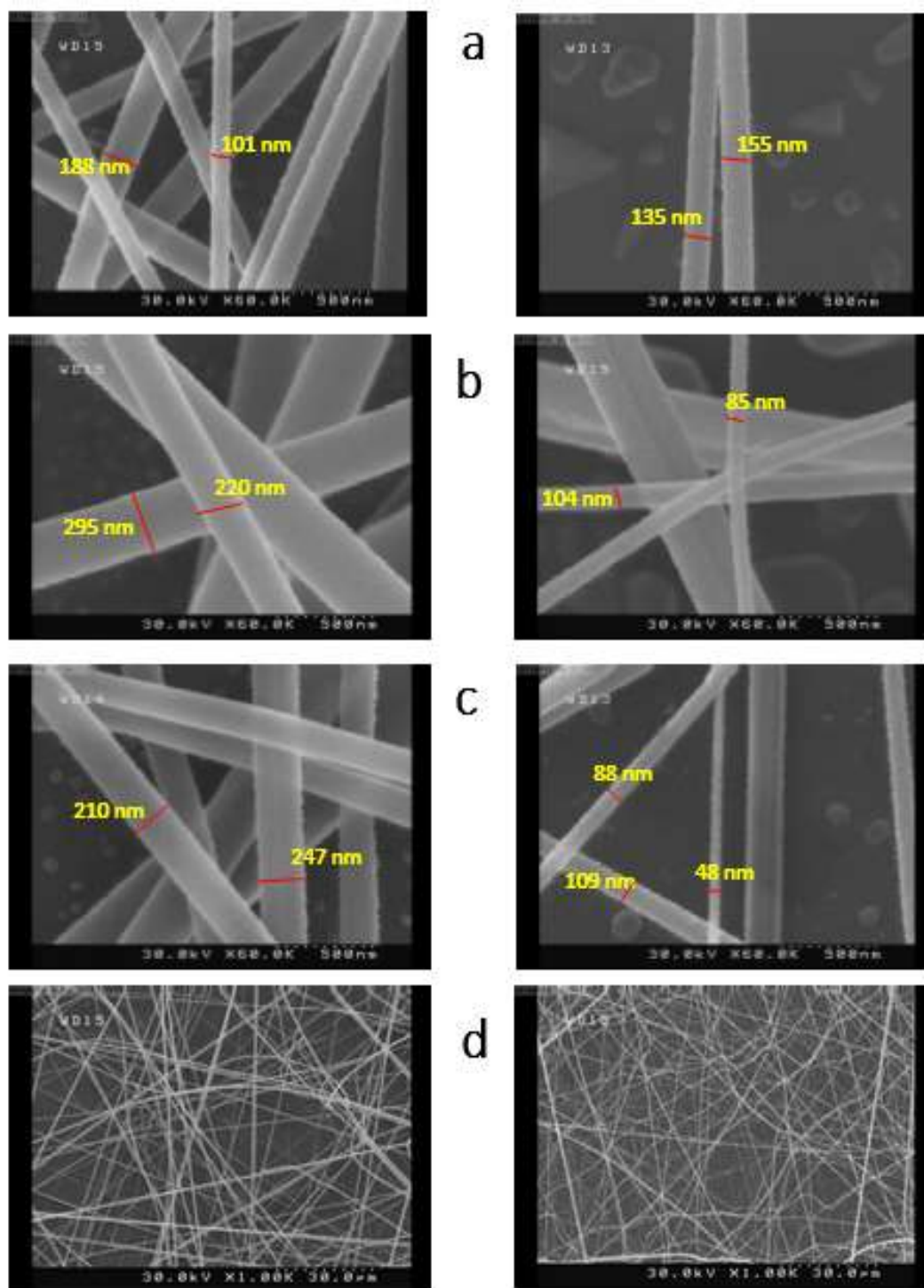


Figure (3) : FESEM images of pre-calcined as-spun fibers on left side and TiO_2 nanofibers on right side prepared in different applied voltages (a) 15 kV (b) 18 kV (c) 21 kV (d) 21 kV in smaller magnification.

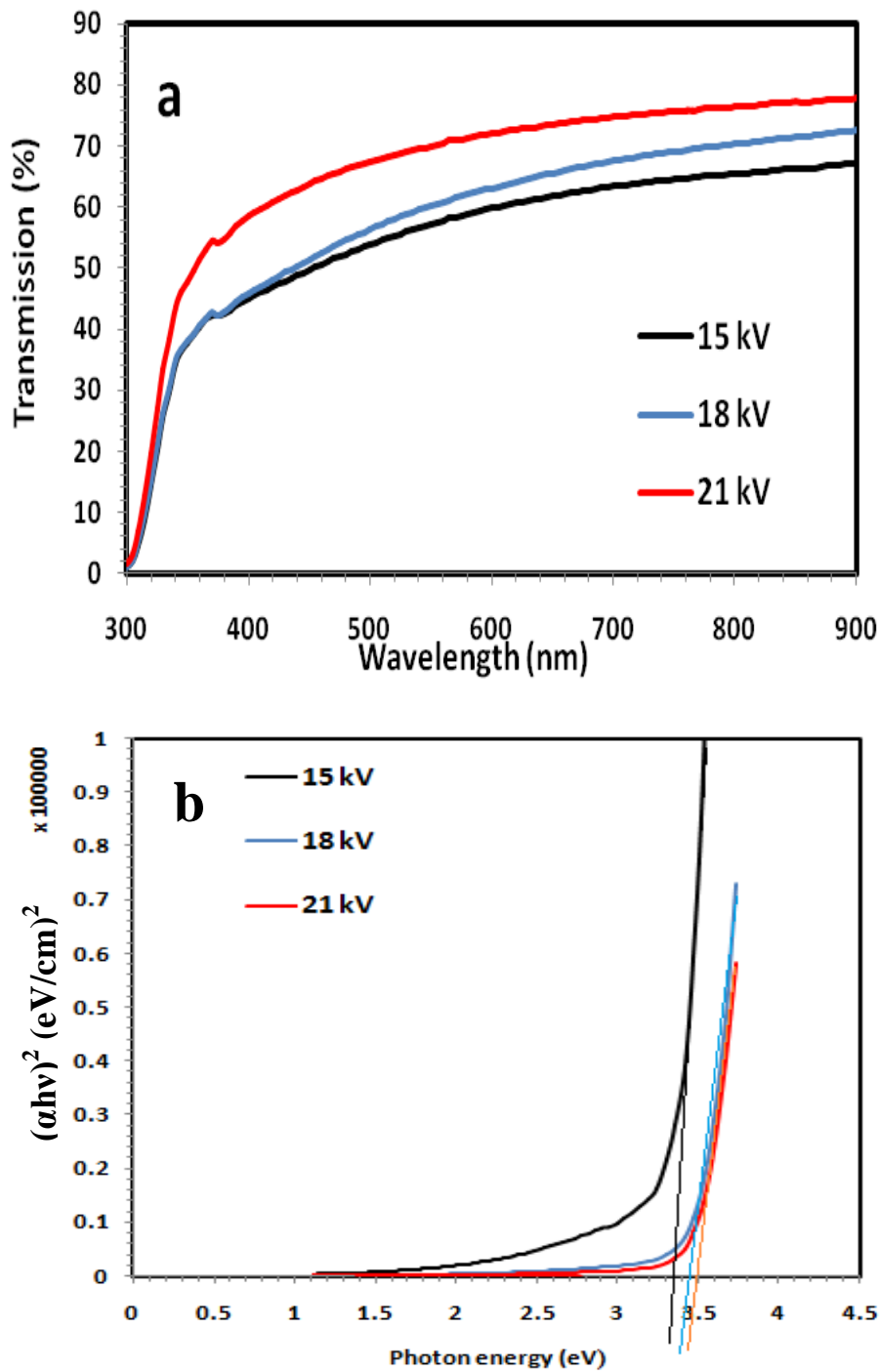


Figure (4): (a) Transmittance vs. wavelength of TiO₂ nanofibers prepared in different applied voltages. (b) The allowed direct band gap prepared in different applied voltages.

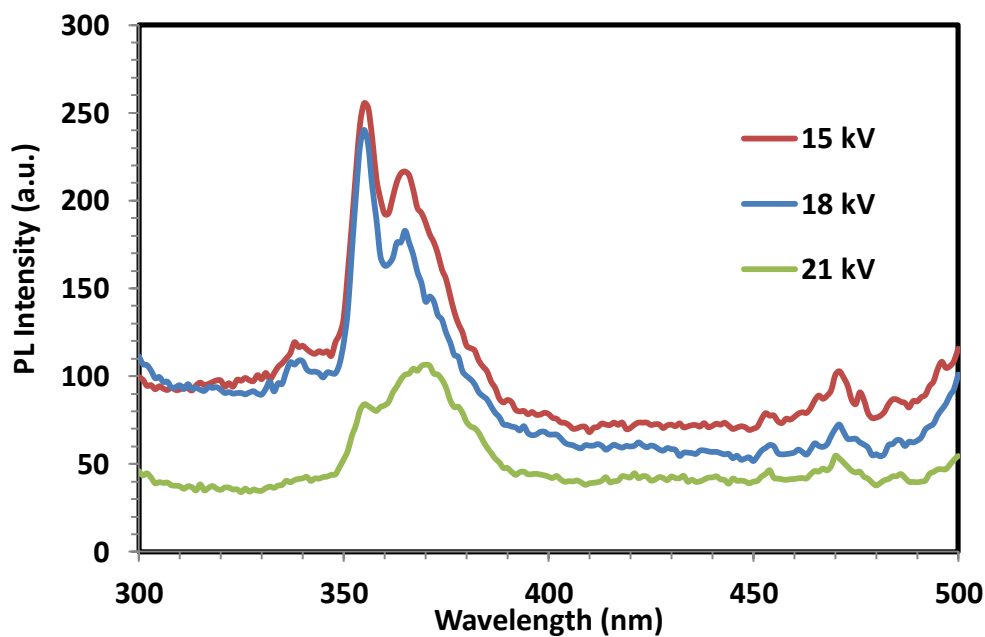


Figure (5): PL spectra of TiO₂ nanofibers prepared in different applied voltages.

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