

Effect of seed layers on the growth of novel 3D TiO₂ nanorod thin films by Hydrothermal Method

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Abstract

Titanium dioxide (TiO_2) nanostructures have attracted extensive attention due to their outstanding chemical stability and potential applications in photocatalysis, optoelectronics, and energy conversion devices. In this work, TiO_2 nanorod thin films were synthesized on fluorine-doped tin oxide (FTO) coated glass substrates using a low-temperature hydrothermal method, with and without a TiO_2 seed layer deposited via spin coating. The effect of the seed layer and hydrothermal growth temperature on the structural, morphological, and optical properties of the films was systematically investigated. Hydrothermal reactions were carried out at 160°C and 170°C for 24 h. FESEM analysis reveals that the seed layer significantly enhances nucleation density and promotes the formation of uniformly distributed nanostructures, while the absence of the seed layer leads to the growth of larger and randomly oriented nanorods due to reduced nucleation sites and enhanced anisotropic crystal growth. UV-Vis spectroscopy indicates strong ultraviolet absorption with a slight red shift in the absorption edge for seed-layer-assisted films. The optical band gap values, estimated from Tauc plots, vary between 2.70 and 3.08 eV depending on synthesis conditions. Photoluminescence studies reveal defect-related emissions associated with oxygen vacancies and surface states, while reduced PL intensity in seeded samples suggests suppressed charge carrier recombination. These results demonstrate that seed-layer-assisted hydrothermal growth is an effective strategy for tailoring TiO_2 nanorod morphology and improving their optical properties for potential applications in photocatalysis and optoelectronic devices.

Introduction

In the last few years optical and morphological properties of TiO_2 thin film have drawn a great attention in optoelectronic devices and photocatalytic applications because of large band gap of the material. TiO_2 exists in three polymorphs i.e. anatase, rutile and brookite with band gap 3.2, 3.02, and 2.96 eV respectively. Here we pay our attention more to synthesize anatase phase TiO_2 thin films. The key role of the thin film is to develop innovative technologies such as protective coatings, device fabrication etc. TiO_2 is one of the most important host materials for antibacterial activity, water treatment, dye degradation application etc. The main advantages of the thin films are high transparency, high refraction index, chemical, thermal and mechanical stability etc under UV light [1–5]. 3D nanorods, nanowires, nanotubes are very important specialized structures for DSSC, photocatalysis, gas sensing due to their large surface area which can absorb large amount of light and gas. Unfortunately, TiO_2 is an intrinsic large band gap (3.2 eV for anatase phase) semiconductor which absorbs only the UV light of the total solar energy on the earth's surface, which is 4% of the total solar radiation [6, 7]. Various seed layers on FTO or ITO glass substrate develop and control the crystalline orientation of nanorods of the thin films. These seed layers provide continuous pathway for the movement of electrons in the film and act as nucleation centers. These nucleation centers mismatch the interfacial layer between TiO_2 and seed layer which help TiO_2 nanorods to align in an array form. Literature review by the researchers shows that 1D TiO_2 nanostructures can be fabricated by using various deposition techniques such as electrochemical anodization, template assisted method, electrospinning method, vapour phase method. Among which

hydrothermal method is the low cost method by which growth of crystalline materials can be formed at relatively low temperature compared to high temperature in annealing process. For the formation of TiO_2 nanorods, crystallite nanorods can be formed by hydrothermal method on the FTO coated glass substrate. Moreover, the deposition of seed layers by spin coating technique keeping spin rotation for 3000–5000 rpm for 30–40 s can form an adhesive attachment with crystallite nanostructures which is further fabricated by hydrothermal method.

The crystallinity, morphological properties and optical properties are highly depended on the synthesis condition. In the hydrothermal technique, the parameters such as temperature, deposition timings, pressure, types of precursors highly influence the crystallite properties of the nanostructures. Up to date many reports has been published on TiO_2 nanorod arrays grown at various reaction temperatures (mostly $\leq 200^\circ \text{C}$) and durations ($\geq 2 \text{ h}$) using different precursor concentrations. The obtained nanostructures are used in various applications. Very slight variations in the parameters can show significant alternation in the properties. Moreover, for substrate-assisted growth, the type and placement of substrate acts an crucial role as the TiO_2 nanorods grow through self-assembly and the orientation of the substrate also enhances the precipitation incident. Kumar et al. reported vertical TiO_2 nanorod arrays and dandelion structure formation for vertical and horizontal orientation of the FTO substrates [11]. Tao et al showed the formation of TiO_2 nanorods on the conductive side and nanoflowers on non-conductive sides of the FTO coated glass substrate when it was placed at 30° to 40° inclination against the wall of an autoclave with the conductive side facing up [13]. Issar et al showed that the TiO_2 nanoflowers form with increasing hydrothermal temperature, where nanoflowers were observed for more than 180°C temperature [14]. Liu et al. reported precursor concentration-dependent morphology variation from nanorod arrays (for 0.045 ml TBOT) to microflowers on top of nanorod arrays (for 0.090 ml TBOT) during the hydrothermal reaction [12].

In this manuscript we have studied the growth of TiO_2 nanorods and effect of seed layer on the nanorods by hydrothermal method. The morphological and optical properties of the seed layer and TiO_2 nanorods are investigated here. Our results reveal that with seed layer the formation of TiO_2 nanorod arrays are vertically aligned but the nanorods align in a disordered manner in case of absence of seed layer. The UV-Vis absorbance spectrum shows a slight shifting to higher wavelength side after depositing with seed layer. PL spectra demonstrate quenching of emission for the film with a seed layer.

Methodology and Synthesis process

Cleaning of FTO substrate:

FTO glass substrates are washed in a soap water solution at 80°C . Next these are ultrasonicated in DI water, acetone and isopropyl alcohol for 15 minutes each and dried with a blower after each sonication. Later the substrates were kept in hot air oven for 1 hour at 60°C .

Preparation of seed layer:

TiO₂ seed layer was prepared by coating TiO₂ sol on the conductive side of FTO glass substrate with a spin coating system. Thin films were annealed for 6 hours at 400° C and they were labeled as T3. The sol used in spin coating to form seed layer was prepared by following process.

2 ml of acetic acid (99.5%) and 10 ml absolute ethanol was mixed and stirred for 10 minutes on the magnetic stirrer. Next 0.35 ml titanium butoxide was added dropwise in the beaker. The whole process was carried out in a sealed container and stirring was continued for 2 hours. Later the sealed container was kept overnight for 24 hours for aging. After the aging a transparent TiO₂ sol was formed and it was spin coated on the conductive side of the cleaned FTO glass substrate. The TiO₂ seed layer thin films prepared by this process is labelled as SL.

Preparation of TiO₂ nanorods:

The seed layer coated and without seed layer coated (bare) FTO glass substrates were placed vertically with a holder in a 100 ml Teflon beaker containing tetratitanium isopropoxide (TTIP), HCl and DI water in a volumetric ratio of 0.33:10:10. The Teflon beaker containing solution and substrate was kept in a stainless steel autoclave and the whole system was transferred to a hot air oven. The autoclave was kept in the oven at two different hydrothermal temperature 160° C and 170° C for 24 hours. The autoclave was cooled to room temperature and the substrates were washed in DI water and isopropanol for several times to remove organic compounds and uniform thin films of TiO₂ were obtained. The films synthesized on substrates with and without seed layers for 160°C hydrothermal temperature were labeled as 160SL and 160 WSL and for 170°C hydrothermal temperature were labelled as 170SL and 170WSL respectively.

Results and Discussion

Morphological studies:

The surface morphology of the TiO₂ thin films deposited on FTO substrates was examined using scanning electron microscopy. The corresponding SEM images are presented in Fig. 1 (a–e). The seed layer film (SL), shown in Fig. 1 (e), exhibits a relatively uniform and densely packed nanocrystalline structure composed of fine TiO₂ nanoparticles distributed homogeneously across the substrate surface. The particle size appears to be in the nanometer range, forming a compact layer that can effectively act as nucleation sites for subsequent crystal growth.

Figure 1 (a) represents the sample grown at 160°C with the seed layer (160SL). The micrograph reveals a dense distribution of small nanograins and short rod-like features covering the entire surface. The presence of the seed layer significantly increases the nucleation density, resulting in smaller crystallites and a relatively compact morphology. In contrast, the sample grown at the same temperature without the seed layer (160WSL), shown in Fig. 1 (b), exhibits comparatively larger and more irregular grains. The absence of pre-existing nucleation sites leads to reduced nucleation density and promotes uncontrolled crystal growth, resulting in comparatively coarser structures.

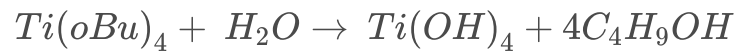
When the growth temperature is increased to 170°C, noticeable changes in the surface morphology are observed. As shown in Fig. 1 (c), the 170SL sample still maintains a dense distribution of nanostructures; however, the crystallites become slightly larger due to enhanced atomic diffusion and crystal growth at the elevated temperature. The seed layer continues to regulate nucleation and ensures relatively uniform grain distribution across the substrate. In contrast, the SEM image of the 170WSL sample (Fig. 1 (d)) clearly shows the formation of elongated rod-like structures with significantly larger dimensions. The inset further confirms the presence of well-developed TiO₂ nanorods. This morphology can be attributed to anisotropic crystal growth occurring in the absence of a seed layer, where reduced nucleation density combined with enhanced surface diffusion at higher temperature favors oriented attachment and directional growth along energetically favorable crystallographic directions.

Overall, the SEM analysis demonstrates that both the growth temperature and the presence of the seed layer play crucial roles in determining the morphology of the TiO₂ nanostructures. The seed layer promotes uniform nucleation and results in compact nanocrystalline films, whereas the absence of the seed layer allows anisotropic growth leading to the formation of larger grains and nanorod-like structures. Such morphological variations are expected to significantly influence the surface area and functional properties of the TiO₂ films.

Mechanism of seed layer formation:

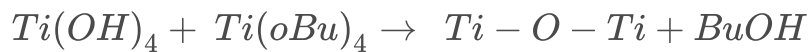
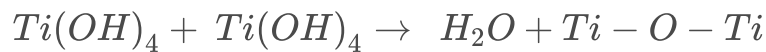
The formation of seed layer followed by hydrolysis and condensation reaction:

- Hydrolysis reaction: The precursor for TiO₂ used here is titanium butoxide which reacts with HCl medium:



The final product of this hydrolysis reaction produces titanium hydroxide

- Condensation reaction: After the production of hydroxide species which condense to form Ti-O-Ti networks



The above Ti-O-Ti networks create a colloidal TiO₂ network

- The role of Acetic Acid slows down the hydrolysis rate by decreasing the precipitation rate, which produces uniform nanoparticles by generating titanium acetate complex. The reaction is as follows:



The seed layer assisted sample has controlled crystal growth, higher density nanostructures and preferred orientation which shows uniform nanocrystalline texture.

Nucleation process:

The structures for all the samples arise from nucleation and anisotropic crystal growth. The growth mechanism includes:

$$\Delta G = \Delta G_v + \Delta G_s$$

$$\Delta G_v$$

volume free energy

$$\Delta G_s$$

surface energy

Seed layer lowers nucleation barrier

The cross sectional image of the thin film samples having seed layer and without seed layer is illustrated in the Fig. 2. From the figure it is cleared that the thickness of the seed layer increases with the increase with hydrothermal temperature. Whereas the thin film thickness increases with the increment of the hydrothermal temperature. From these figures it is also found that the adhesiveness of the TiO₂ seed layer deposited by spin coating techniques increases with hydrothermal temperature. In case of sample 170SL, it is displayed that seed layer thickness increases and some part of it tightly attached with the FTO substrate in atomic level.

UV-Vis absorbance studies:

The optical absorption spectra of TiO₂ nanorod thin films SL, 160SL, 160WSL, 170SL and 170 WSL are shown in Fig. 3 in the range between 200 nm-800 nm. Absorption is observed mainly in UV region and very small absorption is shown at higher wavelengths (> 400 nm). We observe a slight shift of wavelength of T1 films with respect to T2 thin films toward higher wavelength side, i.e. red shift phenomenon is occurred. The shift occurs as the nanorod size increases in T2 while the density of nanorods is increased in T1. The shift may also arise due to the oxygen vacancies created on the seed layer coated FTO substrate after annealing. Vacancies create defect states and incorporated impurities move the absorption edge changing shape of the spectra. Band gaps of TiO₂ nanorods are calculated from Tauc plots by using the following equation.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

Where, α is absorption co-efficient, E_g is the band gap. We observe that energy band gaps for T1, T2 and T3 are 3.08 eV, 2.70 eV, and 2.72 eV respectively. The band gap decreases in T2 and T3 because of their increased crystalline structure. There are more atoms to overlap. Hence the numbers of molecular orbitals are increased and gap between conduction band and valence band is decreased. The diameter and size of nanorods and nanowires are decreased in T1 compared to T2 thin film, thus band gap energy increases.

Photoluminescence (PL) Studies:

The PL spectra of the thin film samples recorded in the range from 300 nm to 700 nm with an excitation wavelength 260 nm and they are shown in Fig. 4. TiO_2 seed layer thin film samples (SL) annealed at 400° C for 6 hours show an enhanced PL intensity, due to increase in crystallinity after annealing. Broad peaks observed in the visible region for thin film samples are attributed to the defect levels such as oxygen vacancies in the band gap region formed during hydrothermal preparation [8]. The peak at 378 nm observed for T3 thin film is due to the radiative annihilation of excitons. PL intensity decreases for the seed layer coated hydrothermally prepared TiO_2 nanorods at 160° C (160SL), which indicates that the recombination process in the film has been suppressed [9]. The PL intensity increases for samples 170 WSL and 170SL when the hydrothermal temperature increases to 170°C. The sharp peak observed at 440 nm is assigned to the radiative recombination of charge carriers by surface defect states. Several peaks are obtained in the visible regions which are attributed to various defects such as oxygen vacancies, interstitial defects and Ti vacancies [10].

Conclusions

In summary, present work demonstrates the successful synthesis of TiO_2 nanorod thin films on FTO coated glass substrates using the hydrothermal method, with and without the introduction of a TiO_2 seed layer deposited via spin coating. The results clearly show that the presence of a seed layer plays a crucial role in controlling the nucleation, growth orientation, and overall morphology of the TiO_2 nanostructures.

FESEM analysis reveals that the seed layer provides uniform nucleation sites which promote the formation of densely packed and relatively well-aligned nanostructures. In contrast, the absence of a seed layer leads to reduced nucleation density and results in the growth of larger and irregularly oriented nanorods. The increase in hydrothermal temperature from 160°C to 170°C further enhances the crystal growth and facilitates the formation of elongated TiO_2 nanorods due to increased surface diffusion and anisotropic crystal growth.

Optical characterization using UV–Vis spectroscopy shows that the TiO_2 thin films exhibit strong absorption in the ultraviolet region. A slight red shift in the absorption edge is observed for seed-layer-coated samples, which can be attributed to defect states such as oxygen vacancies generated during the annealing and hydrothermal processes. The calculated optical band gap values vary between

approximately 2.70 eV and 3.08 eV, indicating that the structural modifications and nanorod size variation influence the electronic structure of the films.

Photoluminescence analysis indicates that the emission behavior is strongly influenced by defect states within the TiO₂ lattice. The dominant emission peak observed around 440 nm is associated with radiative recombination through surface defect states, while additional emissions in the visible region are attributed to oxygen vacancies and other intrinsic defects. The reduction in PL intensity for seed-layer-assisted samples suggests suppressed electron–hole recombination, which is beneficial for applications involving charge transport and photocatalytic activity.

Overall, the study confirms that the incorporation of a TiO₂ seed layer significantly improves the structural uniformity, controls nanorod growth, and modifies the optical properties of hydrothermally grown TiO₂ thin films. These findings indicate that seed-layer-assisted growth is an effective approach for tailoring TiO₂ nanostructures for potential applications in photocatalysis, dye-sensitized solar cells, optoelectronic devices, and gas sensing technologies.

Declarations

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Conflicts of interest:

There are no conflicts of interest to discuss.

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Figures

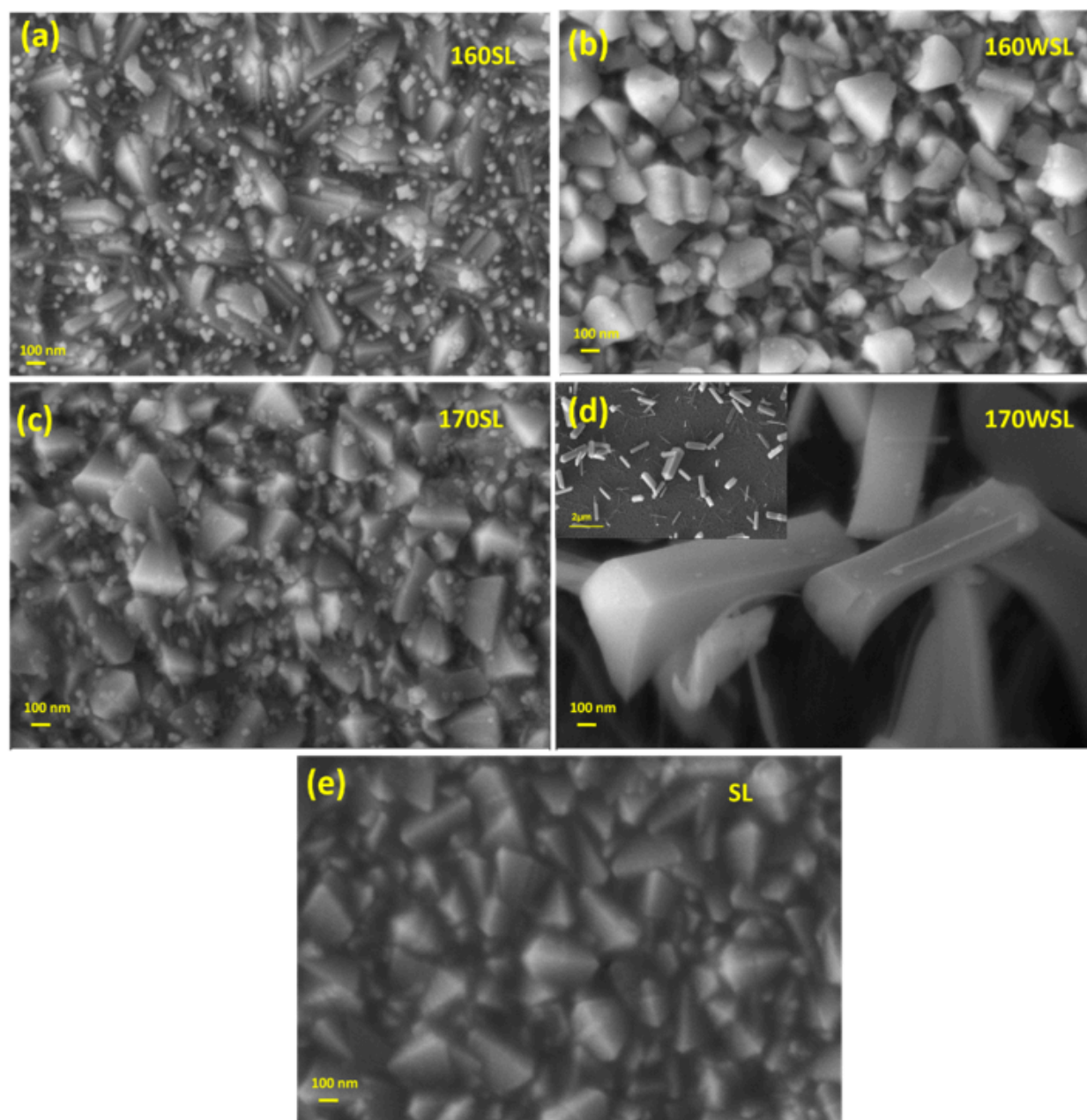


Figure 1

FESEM images of TiO₂ nanorods on, (a) & (c) FTO seed layer coated glass substrate at two different scales, (b)&(d) bare FTO coated glass substrate at two different scales and (e) seed layer of TiO₂

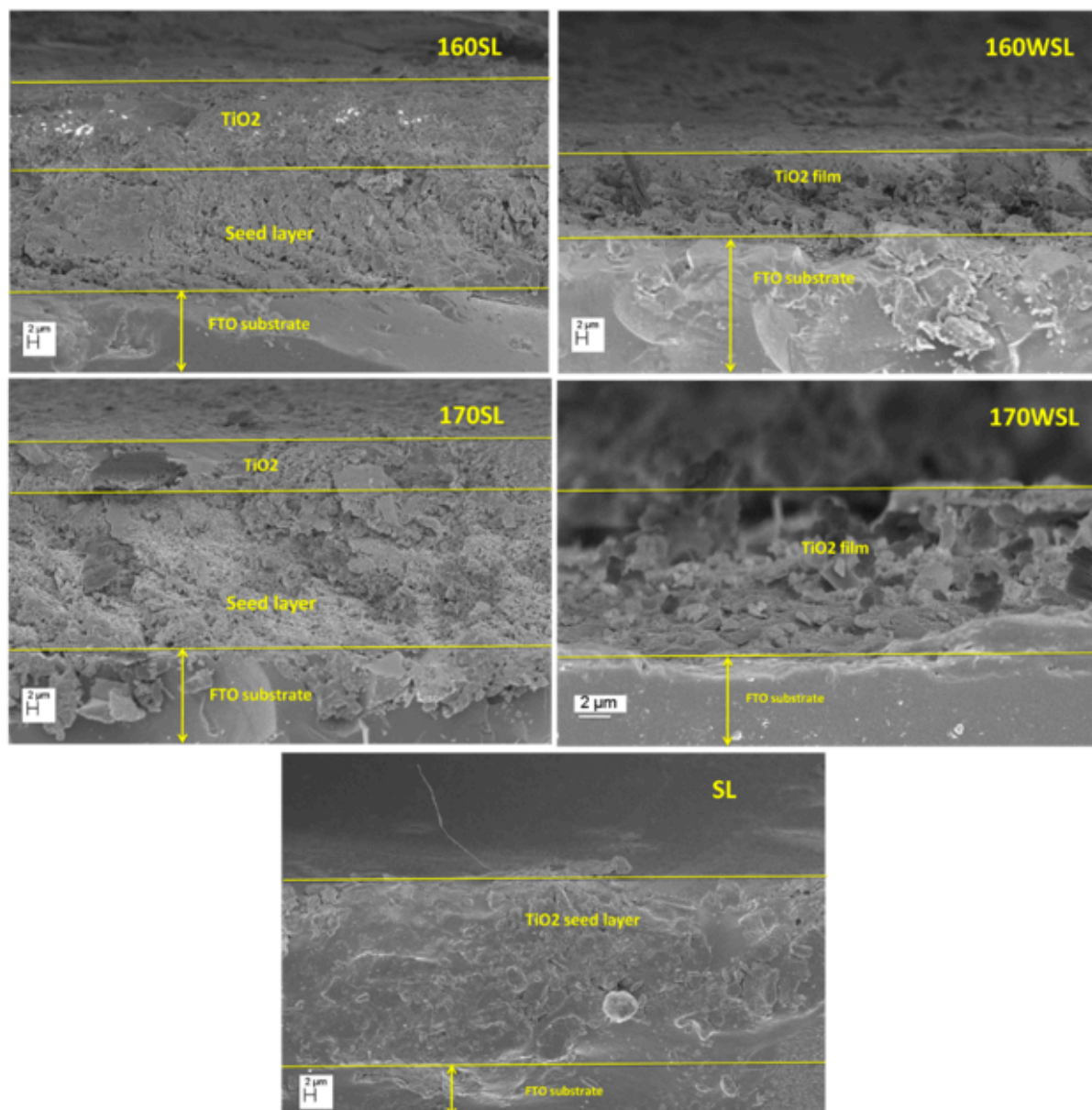


Figure 2

Cross sectional image of the thin film samples deposited with varying hydrothermal temperature 160° C and 170° C in the presence of seed layer and without seed layer

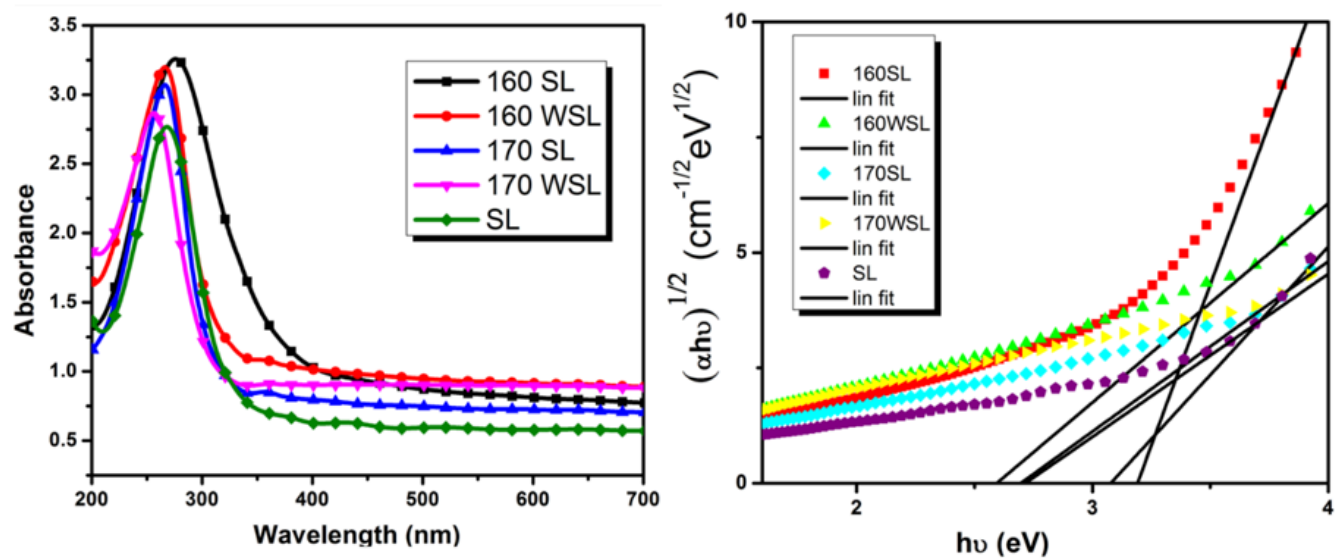


Figure 3

(a) UV-Vis spectra, (b) Tauc plot of the thin film samples deposited with varying hydrothermal temperature 160° C and 170° C in the presence of seed layer and without seed layer

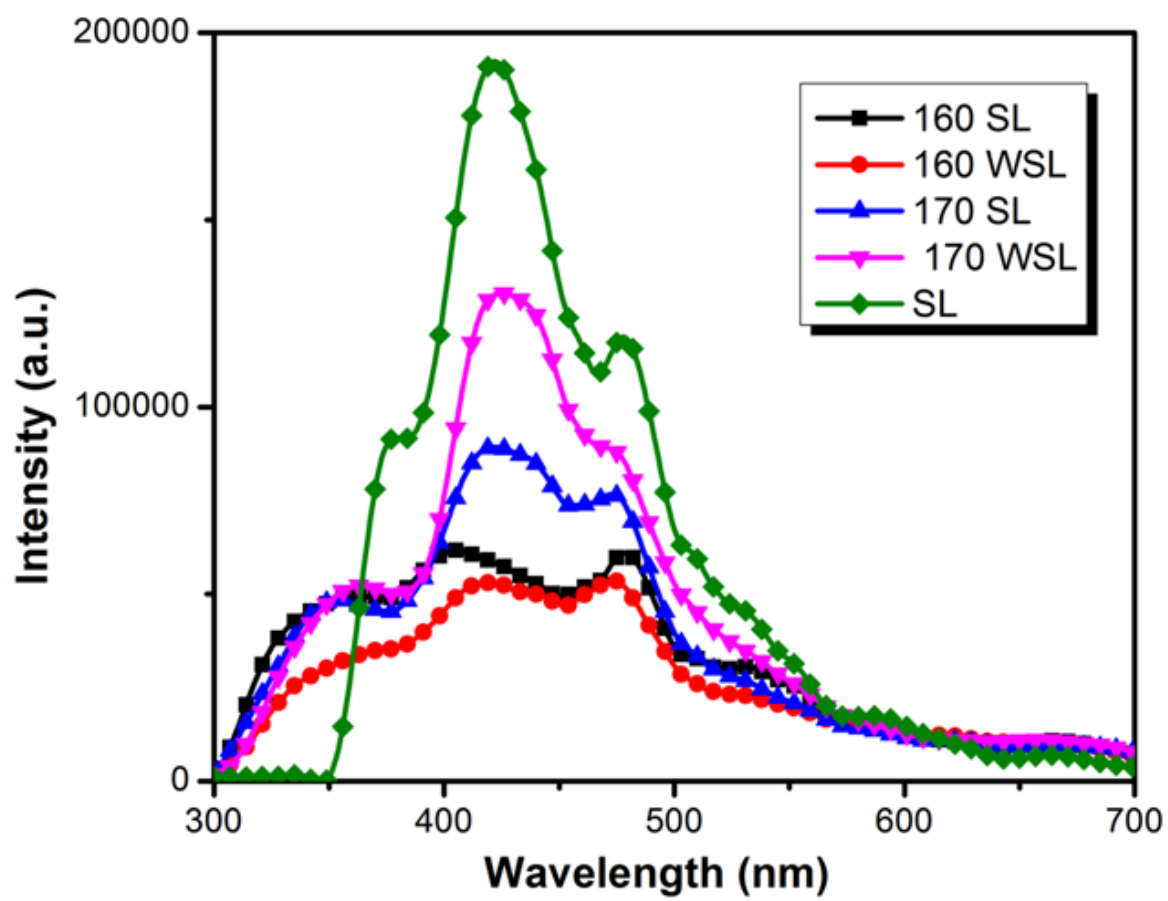


Figure 4

PL spectra of TiO₂ thin films