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# Exploration of one-dimensional $TiO_2$ for efficient electron transporting layer

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**Abstract.** This study explores the parameters that, regulate and impact the crystallization process and morphology of electron-transporting layers, thereby enhancing photovoltaic performance. We developed a vertically aligned $TiO_2$ nanotubes (TiNTs) electron transporting layer to facilitate electron extraction from an absorber and to inhibit recombination between electrons in the fluorine-doped tin oxide and metal Ti. The electron transporting layer is essential for photon-to-electron conversion. This abstract presents the development of an electron transporting layer through sputtering followed by anodization at different potential. The key characterization techniques were employed to study the structural and optoelectronic properties. The anodization method has been utilized to develop $TiO_2$ nanostructured electron transport layers, studied the high optical transmittance (70-80%), anatase crystalline structure, the corresponding vibration $E_g$(145cm$^{-1}$), $B_{1g}$(397cm$^{-1}$) and an extensive surface area. The oxidation states were performed using XPS analysis. To ensure uniform thickness, sputtering parameters were optimized to regulate the thickness of the electron transport layer, resulting in effective electron extraction and hole blocking in thin film solar cell. This study emphasizes the significance of ETL geometry in optimizing device performance especially for photovoltaic applications.

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## 1. Introduction

Titanium dioxide ($TiO_2$) is considered one of the most versatile semiconductor materials due to its excellent chemical stability, natural abundance, low cost, and distinctive photoelectrochemical properties. Due to the advantages, $TiO_2$ was utilized in various applications such as photovoltaics, photocatalysis, chemical sensing, and energy storage devices. Specifically, $TiO_2$ used as an electron transporting layer (ETL) in solar cells and optoelectronic devices owing to its favorable band alignment, relatively high electron mobility compared with other metal oxides, and high optical transparency in the visible region. In order to improve charge separation, reduce recombination losses, and eventually increase the power conversion efficiency of solare cell, the electron transporting layer's performance is essential.[1–3].

Morphologically $TiO_2$ tuned over one-dimensional (1D) nanostructures such as nanotubes, nanorods, and nanowires are particularly advantageous for efficient charge transport. The presence of direct electron conduction pathways along the one-dimensional axis, together with a large interfacial contact area with the active layer, helps reduce electron–hole recombination and enhances charge collection efficiency. In contrast to nanoparticle-based films, where numerous grain boundaries can act as recombination centers, one-dimensional $TiO_2$ nanostructures promote directional electron transport and enable faster charge extraction. These structural features make them highly suitable for advanced photovoltaic technologies such as dye-sensitized solar cells, perovskite solar cells, and quantum-dot-sensitized solar cells [3–7]. In addition to $TiO_2$, other metal oxides including ZnO and $SnO_2$ have also been extensively investigated and employed as efficient electron transporting materials in photovoltaic devices.

Anodization of titanium has emerged as one of the most effective and scalable methods for fabricating highly offered TiO2 nanotube arrays. This electrochemical process enables precise and control over nanotube length, diameter, and wall thickness by tunning parameters such as electrolyte composition, applied potentials, and anodization time. The resulting nanotubular $TiO_2$ film exhibits vertically aligned channels that act as direct electron highway, significantly reducing interfacial resistance. Moreover, the anodization method ensures intimate contact between the nanotubes and the underlying Ti or FTO substrates enhancing the mechanical stability and electronic couple at the interface. However, the morphology and quality of $TiO_2$ nanotubes are strongly influenced by the initial characteristics of the titanium layer subjected to anodization. Direct anodization of bulk titanium foils have studied extensively, while the thin titanium films deposited by sputtering techniques offers more advantages. Magnetron sputtering allows uniform deposition of titanium with well controlled thickness, purity, and adhesion to different substrates. Subsequent anodization of sputtered titanium films can yield highly ordered TiO2 nanotube arrays directly integrated conductive substrates, thereby expanding their applicability in next generation device. Such hybrid approaches that combine physical vapor deposition and electrochemical anodization are particularly promising for fabricating compact, tunable, and reproducible 1D $TiO_2$ nanostructures [8–10] with improved crystallinity and optical transparency.

The functionality of $TiO_2$ as an ETL is not solely dependent on its morphology but also on its crystalline phase and electronic properties. As prepared anodized $TiO_2$ nanotubes are typically amorphous and require post annealing to induce crystallization. Anatase $TiO_2$ is widely recognized for superior electron mobility and band alignment. Thermal treatment enhances the innertube connectivity, remove residual organic or fluorides from the electrolyte and its essential for achieving high performance ETLs. In recent studies on $TiO_2$ nanotubes as electron transporting scaffolds in perovskite and dye sensitized solar cells have demonstrated significant improvement in device efficiency. The aligned nanotube architecture provides efficient charge extraction from the light absorbing layer and electron transfer to the electrolyte or hole transporting medium. In addition, the tunability of nanotube dimensions enables adaptation to different device configurations. The large area fabrications, positions sputtering assisted anodized $TiO_2$ nanotube as a promising route towards high performance ETL in scalable optoelectronic devices [11,12].

In this study, explores the fabrication of one-dimensional $TiO_2$ nanostructures via sputtering of titanium followed by anodization, aiming to evaluate their potential as efficient electron transporting layer exhibiting preferential (101) orientation. This approach integrates the uniformity and controllability of sputter deposition with the self-organizing capacity of electrochemical anodization, yielding vertically aligned $TiO_2$ nanotubes anchored to the substrate. The investigation focusses on the structural, morphological and optical properties of the resulting nanotubular films and their relevance to electron transport applications. Optimizing the fabrication conditions, such nanostructured $TiO_2$ ETL could play a transformative role in advancing next generation energy conversion systems.

## 2. Materials and Methods

Thin films of Ti were deposited over cleaned FTO substrates using DC magnetron sputtering. Prior to deposition, the substrates were ultrasonically cleaned in standard protocol followed by drying in nitrogen. Ti target with high purity was sputtered under an argon atmosphere at $5*10^{-6}$ mbar (base pressure) and $3*10^{-3}$ mbar (working pressure). The sputtering power was maintained at 100W, and a consistent Ti layer with a thickness of roughly 1 μm was achieved by varying the deposition duration. The deposited Titanium films were subjected to electrochemical anodization to form $TiO_2$ nanostructures. Ti-coated FTO was used as the working electrode and graphite as the counter electrode in a two-electrode anodization setup as described in figure 1. The electrolyte consisted of an ethylene glycol solution containing 0.5wt ammonium fluoride and 2 vol deionized water. Anodization was performed at different applied potentials ranging from 10V to 60V for 30 min at the interval of 10V under constant stirring to ensure uniform pore formation. Following anodization, the samples were dried under nitrogen and thoroughly washed with deionized water. Experiments were conducted using varying electrolyte concentrations and anodization potentials to assess the synthesis process's repeatability. The resulting films were annealed at 450◦C for 3hr in tubular furnace to achieve crystalline $TiO_2$. Based on the change in anodization potential utilized during the production process, the materials were systematically labeled B0–B6.

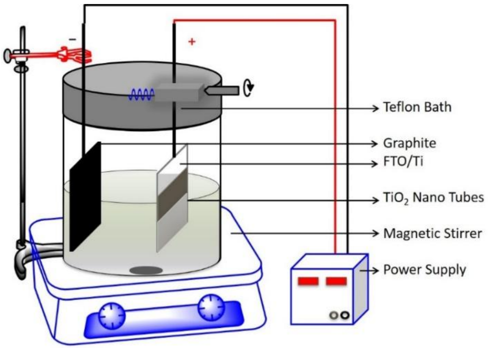

Figure 1. (a) Overview of electrochemical anodization setup

## 3. Results

Figure 2 illustrates the unique reflection feature of the anatase in the X-ray diffraction of $TiO_2$ thin films made by Ti sputtering and electrochemical anodization. The most prominent diffraction feature corresponds to the (101) plane, while additional weaker peaks such as those assigned to the (004), (200) and (105) confirming a predominantly anatase phase rather than amorphous or rutile structure. The positions and intensity of these reflections were analyzed using Braggs law ($n\lambda=2d\sin\theta$), evaluated the crystalline size of the materials using Debye-Scherrer equation, and the calculated interplanar spacing (d) values were found in good agreement with standard crystallographic data for anatase $TiO_2$. As the anodization potential is increase, the anatase peaks become progressively sharper and more intense, indicative of enhanced crystallinity, reduced macrostrain are listed in table 1. The overall, XRD indicates anodization voltage effectively tunes the oxide growth, promoting improved phase purity and structural ordering of the $TiO_2$ films. Figure 3 shows the Raman spectra of anodized $TiO_2$ films, illustrate strong and well resolved vibrational modes characteristic of the anatase phase Eg is $145 cm^{-1}$, B1g is mode near 397 $cm^{-1}$ for phase determination. The sharpening of Raman peaks at higher anodization potential further reflects improved structural ordering and reduced defect density in the oxide lattice [13].

| Sl. No | $NH_4F$ (%) | Voltage | 2θ in deg. | | (hkl) | Crystalline size ($10^{-9}$ nm) | d-spacing (A˚) | | Lattice parameter (A˚) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Exp | | Cal | |
| | | | Exp | Cal | | | Exp | Cal | a | c | a | c |
| 1 | 0.5 | 10 | 25.62 | 25.32 | 101 | 14.65 | 3.472 | 3.517 | 3.925 | 9.873 | 3.785 | 9.513 |
| 2 | | 25 | 25.36 | | 101 | 20.19 | 3.509 | | 3.810 | 9.537 | | |
| 4 | | 30 | 25.33 | | 101 | 23.57 | 3.512 | | 3.804 | 9.514 | | |
| 5 | | 40 | 25.30 | | 101 | 23.55 | 3.513 | | 3.776 | 9.520 | | |
| 6 | | 50 | 25.33 | | 101 | 23.57 | 3.509 | | 3.840 | 9.555 | | |
| 7 | | 60 | 25.33 | | 101 | 23.09 | 3.511 | | 3.822 | 9.508 | | |

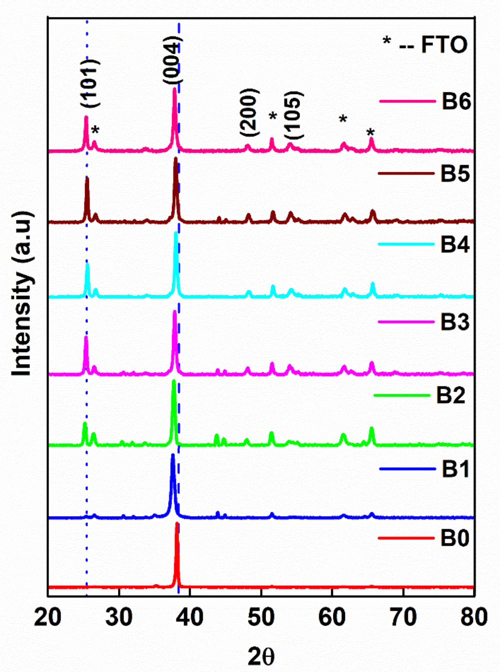

Figure 2: XRD of (B0) Ti thin film and (B1-B6) Electrochemical Anodized TiO2 at different potential

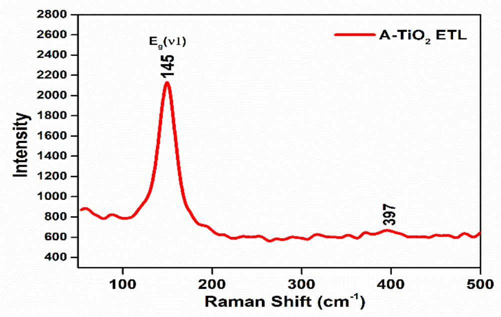

Figure 3: Raman spectra of Electrochemical Anodized $TiO_2$ at higher potential

The UV-Vis absorption spectra revealed a strong absorption edge in an ultraviolet region, characteristic of anatase $TiO_2$. The sharp onset of absorption confirmed the direct relationship between structural crystallinity and photoelectron interaction with films. The maximum optical transparency 70-80% was shown in figure 4. The broad band gap, excellent transparency in the visible spectrum, and tunable defect-related luminescence of anodized $TiO_2$ thin films make them ideal for use as electron transporting layers in energy harvesting devices, according to optical analysis. The XPS results of electrochemically anodized $TiO_2$ confirm the successful formation. The characteristic biding energy peaks corresponding to Ti 2p and O 1s core level. The Ti 2p spectrum typically exhibits two prominent peaks at 458.6 and 464.4, attributed to $Ti2p_{3/2}$ & Ti $2p_{1/2}$ respectively, Indicating the presence of $Ti^{4+}$ oxidation states. The O 1s peak appears at 529.9 e, corresponding to lattice oxygen (Ti-O) bonds [14].

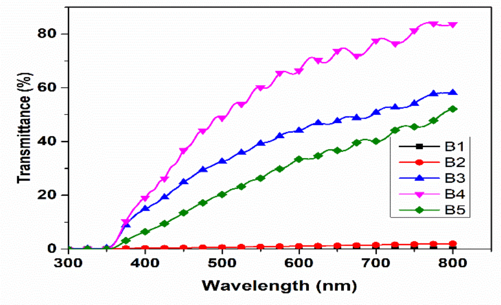

Figure 4: Optical study of Electrochemical Anodized $TiO_2$ at different potential

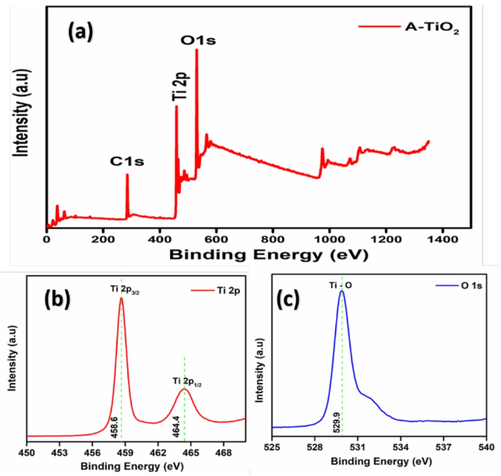

Figure 5 (a-c): XPS of Electrochemical Anodized $TiO_2$ at higher potential

## Conclusion

Sputtering and anodization were used to successfully fabricate vertically aligned $TiO_2$ electron carrying layers under regulated conditions. Comprehensive XRD Raman and optical analysis reveal that anodization not only governs the phase stability of $TiO_2$ but also acts as a tunable parameter for modifying structural integrity, defect states, and crystallite size in thin films meant for an effective electron-transporting layer. XPS analysis confirms the formation of high-purity $TiO_2$ with controlled surface states. These results highlight the crucial role that ETL geometry and crystallinity make its influence in charge transport dynamics, highlighting the possibility of tailored TiO2 nanostructures for use in next-generation thin-film solar cells.

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