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Original Research Article

Disordered driven electrical transport in TiO_2 nanowires for dye-sensitized solar cells

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ABSTRACT

TiO_2 nanowires fabricated on ITO (Indium tin oxide)-coated glass substrate using sol-gel method and integrated into an electrochemical anodization system for transport characterization. Temperature dependent conductivity was investigated in the range of 200-500°C. Structural phase evolution from amorphous state to crystalline anatase phase was confirmed by transmission electron microscopy (TEM). The conduction barrier in the temperature range of 225-400°C was determined to be 0.9eV indicating thermally assisted transport through the disordered nanostructured network. The obtained transport parameters show good agreement with reported values for other nanostructured systems confirming the reliability, reproducibility of synthesis technique and demonstrated the potential of these sol-gel derived nanowire architectures for their candidature as photoanode in Dye-Sensitized Solar Cells.

1. Introduction

The increasing global demand for clean and sustainable energy has driven extensive research into alternative photovoltaic technologies that can complement or replace conventional silicon-based solar cells. Among the emerging approaches, dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their low production cost, simple fabrication procedures, and ability to operate efficiently under low and diffuse light conditions. Unlike traditional p–n junction solar cells, DSSCs rely on a photoelectrochemical process in which light absorption, charge separation, and charge transport occur in distinct components, making the design and optimization of each element critically important for overall device performance [1].

The photoanode is one of the most crucial components in DSSCs, as it serves multiple functions including dye adsorption, light harvesting, and electron transport. Titanium dioxide (TiO_2) has been widely adopted as a photoanode material because of its wide band gap, excellent chemical stability, suitable energy level alignment with commonly used dyes, and environmental compatibility. Conventionally, TiO_2 nanoparticle films have been employed to achieve high surface area for dye loading. However, the random arrangement of nanoparticles often leads to tortuous electron transport pathways, resulting in increased recombination losses and reduced charge collection efficiency [2].

To overcome these limitations, one-dimensional nanostructured forms of TiO_2, such as nanowires, nanorods, and nanotubes, have been explored as alternative architectures. In particular, TiO_2 nanowire-based thin films offer direct and continuous pathways for electron transport, thereby minimizing scattering events and enhancing carrier mobility. These aligned or semi-aligned nanostructures can significantly improve charge transport kinetics while maintaining adequate surface area for dye adsorption. When integrated onto conductive substrates such as indium tin oxide (ITO)-coated glass, these nanowire films form an efficient electron-collecting network suitable for photoanode applications.

Despite these advantages, the electrical transport properties of TiO_2 nanowire networks are strongly influenced by structural disorder, grain boundaries, and defect states introduced during synthesis. Such imperfections can give rise to localized trapping centers and potential barriers that hinder smooth electron flow. As a result, charge transport in these systems often deviates from ideal band conduction and instead exhibits thermally activated behavior. Understanding the role of these disordered features and the associated conduction mechanisms is essential for improving the functional efficiency of DSSC photoanodes [3-5].

Temperature-dependent electrical characterization provides a powerful means to probe these transport phenomena. By analyzing conductivity variations over a wide temperature range, it is possible to extract key parameters such as activation energy and identify dominant conduction mechanisms, including hopping transport or barrier-limited conduction. These insights are particularly important in nanostructured systems, where electron movement is governed not only by intrinsic material properties but also by interfacial and morphological factors [6-9].

In addition to electrical measurements, detailed structural characterization is necessary to establish a correlation between microstructure and transport behavior. Techniques such as transmission electron microscopy (TEM) offer high-resolution information regarding morphology, crystallinity, and phase composition. Of particular relevance is the transformation of TiO_2 from an amorphous phase to a crystalline anatase phase upon thermal treatment, which is known to significantly influence electronic properties. The degree of crystallinity, grain connectivity, and presence of defects collectively determine the efficiency of electron transport within the nanowire network [10-12].

In this context, the present study focuses on the synthesis and investigation of TiO_2 nanowire thin films deposited on ITO-coated glass substrates using a sol–gel approach. The films are evaluated as potential photoanodes for dye-sensitized solar cells, with emphasis on their electrical transport characteristics. A systematic study of temperature-dependent conductivity is carried out to elucidate the conduction mechanism and estimate the associated energy barriers. Furthermore, structural analysis using TEM is employed to examine phase evolution and nanoscale features, enabling a direct correlation between structural properties and electrical performance. The outcomes of this work provide valuable insights into disordered transport phenomena in TiO_2 nanowire systems and contribute toward the optimization of nanostructured photoanodes for enhanced DSSC efficiency.

2. Experimemtal

Materials required

- Titanium Source: Titanium (IV) isopropoxide (TTIP)
- Solvent: Isopropanol.
- Morphology Modifier/Catalyst: Glacial Acetic Acid
- Hydrolysis Agent: Deionized Water
- Substrate: Cleaned Indium Tin Oxide (ITO) coated glass sheet

Experimental procedure

Step 1: Preparation of the Sol

Mixing: Dissolve 5mL of TTIP into 30 mL of anhydrous ethanol.

Chelation: Add 15 mL of glacial acetic acid under vigorous stirring. The acetic acid acts as a "morphology modifier," binding with the titanium to slow down the rapid hydrolysis.

Controlled Hydrolysis: Mix 10 mL of deionized water with 20mL of ethanol. Add this mixture dropwise to the TTIP/acetic acid mixture while stirring constantly.

Aging: Allow the resulting transparent sol to stir for 12–24 hours at room temperature to obtain a clear, stable sol with increased viscosity (gelation).

Step 2: Film Deposition (Dip-Coating)

1. Cleaning: Clean substrates with deionized water, followed by ultrasonication in acetone and then ethanol for 15 min each to remove contaminants and improve adhesion.
2. Coating: Dip the clean glass sheet into the stabilized TiO_2 sol.
3. Withdrawal: Withdraw the substrate from the sol at a controlled, slow speed 2 cm/min.
4. Drying: Dry the films in an oven at 100°C–120°C for 30 minutes to evaporate solvents. Repeat dipping and drying 3–5 times to reach the desired thickness.

Step 3: Calcination (Nanowire Formation)

1. Annealing: Place the dried films in a muffle furnace.
2. Heat Treatment: Heat the samples at a rate of 1°C/min to 400°C-500°C and Maintain the final temperature for 1–2 hours

Characterization

The structural properties of the TiO_2 thin films were analyzed using transmission electron microscopy (TEM) to investigate morphology and phase evolution. Electrical transport properties were studied by measuring temperature-dependent conductivity over a specified temperature range. The activation energy associated with charge transport was determined from the Arrhenius behavior of conductivity.

3. Results and discussion

3.1 Structural analysis

The XRD patterns of TiO_2 thin films annealed at different temperatures are presented in Fig. 1. At lower annealing temperatures (100–200°C), the diffraction patterns exhibit broad and weak peaks, indicating the presence of an amorphous or poorly crystalline phase. As the annealing temperature increases to 300°C and above, distinct diffraction peaks begin to emerge, suggesting the onset of crystallization.

For the sample shown in Fig. 1(b), the diffraction peaks become more intense and sharper with increasing temperature, confirming enhanced crystallinity. The prominent peak observed around $2\theta \approx 25°$ corresponds to the (101) plane of anatase TiO_2. Additional peaks at higher angles further support the formation of the anatase phase.

At higher annealing temperatures (400–500°C), the peaks become well-defined and narrow, indicating significant grain growth and improved structural ordering. This enhancement in crystallinity is expected to facilitate better electron transport by reducing grain boundary scattering and defect density, which is consistent with the observed electrical behavior.

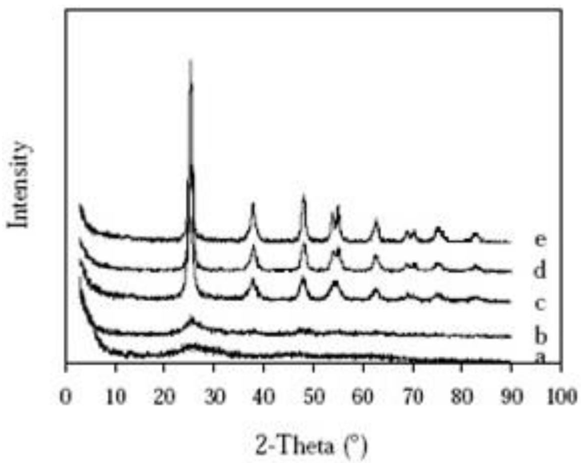

Figure 1: XRD patterns at different annealing temperatures.

The structural characteristics of the synthesized TiO_2 nanowire thin films were also examined using transmission electron microscopy (TEM).

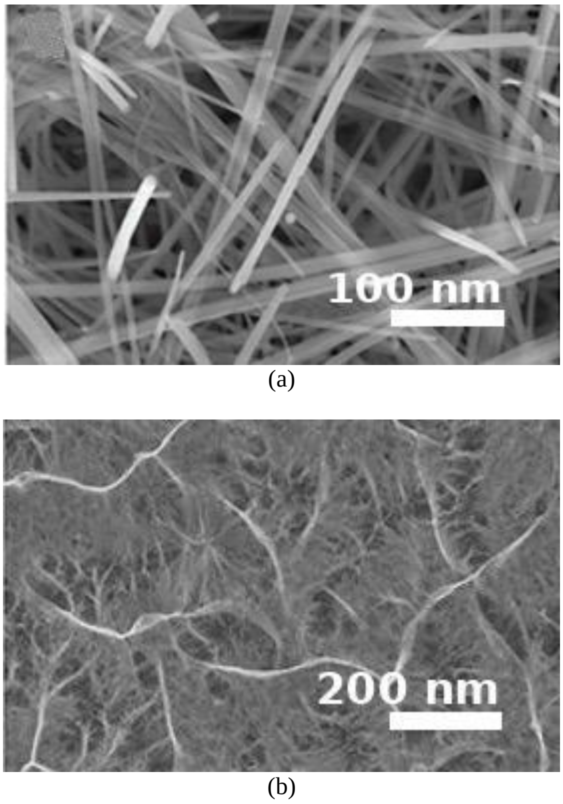

Figure 2: (a and b) TEM images of obtained nanowires structures.

The TEM images of the synthesized TiO_2 thin films are shown in Fig. 2. The low-magnification image (Fig. 2a) reveals a highly interconnected and disordered network structure, indicating the formation of a porous framework. Such a structure is beneficial for dye adsorption in photoanode applications due to the increased surface area.

The high-magnification image (Fig. 2b) clearly shows the formation of one-dimensional nanowire-like structures with relatively uniform diameter and random orientation. These nanowires provide direct pathways for electron transport, which can significantly reduce recombination losses compared to nanoparticle-based systems.

3.2 Temperature-dependent electrical conductivity

The electrical conductivity of the TiO_2 nanowire thin films was investigated over a temperature range of 200°C to 500°C. The conductivity was found to increase with temperature, indicating semiconducting behavior. This trend suggests that charge transport in the films is thermally activated.

The variation of conductivity with temperature follows an Arrhenius-type relationship, which can be expressed as:

$$\sigma = \sigma_0 e^{\left(\frac{-E_a}{kT}\right)}$$

where σ is the electrical conductivity, E_a is the activation energy, k is the Boltzmann constant, and T is the absolute temperature.

A linear relationship between ln(σ) and 1/T was observed within the temperature range of 225°C to 400°C, indicating a dominant thermally activated conduction mechanism in this region.

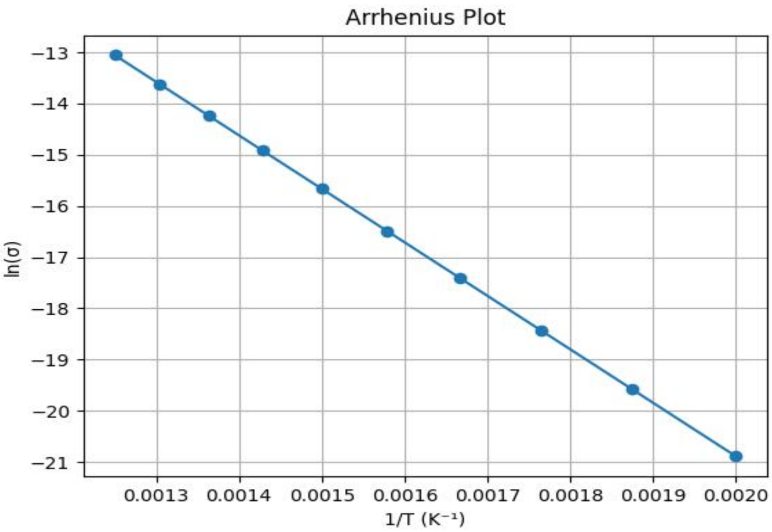

Figure 3: Conduction plot.

From the slope of the Arrhenius plot, the activation energy for conduction was determined to be approximately 0.9 eV. This relatively high value suggests that charge transport is governed by barrier-limited conduction rather than free band conduction.

The presence of such a conduction barrier can be attributed to structural disorder, grain boundaries, and localized defect states within the nanowire network. These features act as trapping centers, requiring thermal energy for charge carriers to overcome potential barriers and contribute to conduction. The disordered nature of the nanostructured film leads to a hopping or thermally assisted transport mechanism.

Furthermore, the transition from amorphous to crystalline anatase phase contributes to improved transport properties by reducing defect density and enhancing carrier mobility. However, residual disorder within the network continues to influence conduction behavior.

Correlation Between Structure and Transport

A strong correlation between structural evolution and electrical transport behavior is observed. At lower temperatures, the amorphous structure leads to higher resistance due to limited carrier mobility and increased trapping. As the films undergo crystallization, improved ordering results in enhanced conductivity.

The interconnected nanowire architecture provides continuous pathways for electron transport, which is advantageous for photoanode applications in dye-sensitized solar cells. However, the presence of conduction barriers indicates that further optimization of synthesis conditions is necessary to minimize defects and improve charge transport efficiency.

4. Conclusions

In this study, TiO_2 nanowire thin films were successfully synthesized on ITO-coated glass substrates using a sol–gel technique and investigated for their structural and electrical transport properties. TEM analysis confirmed the evolution of the crystalline anatase phase with increasing annealing temperature, accompanied by improved structural ordering.

The temperature-dependent conductivity measurements revealed semiconducting behavior with a thermally activated conduction mechanism. An activation energy of approximately 0.9 eV was determined, indicating the presence of conduction barriers associated with structural disorder and defect states within the nanowire network.

The results demonstrate a clear relationship between microstructural features and electrical performance, highlighting the importance of controlling crystallinity and defect density in nanostructured TiO_2 films. The synthesized nanowire architecture shows potential for application as a photoanode in dye-sensitized solar cells, although further optimization is required to enhance charge transport and reduce recombination losses.

Authors' contributions

The author reviewed and approved the final version of the manuscript for publication.

Conflicts of interest

The author declares no conflict of interest.

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Data availability

No new data were created.

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