

Impact of Reduction Techniques on the Optical Band Gap of Defective TiO_{2-x} Nano-structures

ISSN : 2688-8394



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Submission: September 30, 2024

Published: November 27, 2024

Volume 5 - Issue 1

How to cite this article: Elham Khorashadizade*. Impact of Reduction Techniques on the Optical Band Gap of Defective TiO_{2-x} Nano-structures. Ann Chem SciRes.5(1).ACSR.000603.2024. DOI: [10.31031/ACSR.2024.05.000603](https://doi.org/10.31031/ACSR.2024.05.000603)

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Abstract

This research examines the influence of two main reduction techniques- hydrogenation and DC plasma on the band gap characteristics of defective titanium dioxide (TiO_{2-x}). Recognized for its photo-catalytic properties, TiO_2 nano-structures demonstrate improved functionality when subjected to a reduction process. Initially, TiO_2 nanoflakes were fabricated via the hydrothermal method. Then, thermal hydrogenation and DC plasma treatments were independently employed in an Ar/H_2 atmosphere (90/10 vol%) to develop defective TiO_{2-x} structures. The incident photon to current efficiency (IPCE) spectra of the treated defective TiO_{2-x} photo-anodes in 0.1 M Na_2SO_4 displayed a notable increase in photo-activity within the UV range, rising from 5% to 35% compared to the pristine TiO_2 nanoflakes. The Tauc plots were also developed for defective TiO_{2-x} samples based on the IPCE data. The findings indicate the presence of weak band tails, measuring less than 0.2eV, attributed to defect states between valence and conduction bands. Notably, these weak band tails significantly influence the electronic structures of defective TiO_{2-x} , enhancing their photo-activities up to seven-fold.

Introduction

Titanium dioxide (TiO_2) is a well-known semiconductor that finds extensive applications in photo-catalysis, solar energy conversion and environmental cleanup due to its stability, non-toxic nature and strong reactivity when exposed to ultraviolet (UV) light [1]. Nevertheless, its wide band gap of around 3.0-3.2eV limits its performance in visible light conditions, leading to significant research aimed at improving its electronic characteristics. A particularly promising strategy involves creating point defects such as oxygen vacancy or Ti^{3+} , which can notably modify the electronic configuration and optical attributes of TiO_2 , thus enhancing its photo-catalytic efficiency [2]. The creation of defective TiO_2 , particularly TiO_{2-x} , results from the removal of oxygen atoms from its lattice structure, leading to various structural and electronic modifications. Oxygen vacancies introduce additional energy levels within the band gap, improving the light absorption and aiding in the separation of charge carriers [3,4].

Various synthesis methods have been utilized to create defective TiO_{2-x} , with each method affecting the concentration and distribution of point defects in distinct ways. For instance, high energy particle bombardment [5], elevated pressure conditions [6], chemical and electrochemical methods [7] enable the incorporation of defects in the crystal structure of TiO_2 . Understanding the impact of reduction techniques on the optical band gap of defective TiO_{2-x} nano-structures is decisive for enhancing its characteristics for real-world applications. This research aims to investigate how two key reduction methods- DC plasma and thermal hydrogenation- affect the band gap of defective TiO_{2-x} nanoflakes, offering a comparative analysis of the influence of various reduction techniques on photo-activity and electronic structure. By elucidating these relationships, this can aim to guide future material design strategies to improve photo-catalytic performance and other applications.

Experimental Section

Synthesis of TiO₂ thin films

TiO₂ films exhibiting nanoflake morphologies were fabricated through hydrothermal treatment of titanium foil. Initially, titanium foils (0.10mm thick, 99.6% purity, sourced from Advent Research Materials Ltd) underwent ultrasonically cleaning in acetone, ethanol and deionized water for 15 minutes each, followed by drying with nitrogen gas. The cleaned Ti foil, serving as both substrate and titanium source, was then placed in a Teflon-lined stainless-steel autoclave (250ml) containing 1.0M solution of LiOH or CsOH, referred to as (pristine TiO₂ (LiOH) or TiO₂ (CsOH)). The hydrothermal treatment was conducted in an oven at 100 °C for 3 hours. Subsequently, the resulting samples were annealed in air at 500 °C for 3 hours, with a controlled heating and cooling rate of 2 °C/min.

Fabrication of defective TiO_{2-x} thin films

A. Thermal hydrogenation: Defective TiO_{2-x} nanoflakes were synthesized in a tube furnace at varying temperatures of 450, 500, and 550 °C for one hour, utilizing a mixed argon/hydrogen atmosphere (90/10 vol %) with a flow rate of 2.5ml min⁻¹.

B. DC plasma reduction: This procedure was performed in an ultra-high vacuum (UHV) chamber under an Ar/H₂ atmosphere (90/10 vol%). The chamber was evacuated to a base pressure of 10⁻⁸ Torr and maintained at a pressure of 10⁻³ Torr at room temperature for 1h, employing different applied power levels of 5, 15 and 45 watts.

Results and Discussion

The morphology of the TiO₂ thin films produced through the hydrothermal treatment of titanium foils in lithium or cesium hydroxide solutions is illustrated in Figures 1a & 1b. Field emission scanning electron microscopy (FESEM) results exhibit porous structures with clear nanoflake morphologies on the surface of the thin films.

To assess the photo-activity of defective TiO_{2-x} photo-electrodes compared to pristine TiO₂, a three-electrode setup consisting of an Ag/AgCl reference electrode, a platinum counter electrode and a custom-fabricated sample as the working electrode was used. The current through the working electrode was measured every 0.2 seconds while exposed to monochromatic light across a wavelength range of 300-600nm. Light exposure followed a specific sequence: 10 seconds with the light off, 20 seconds with the light on, and then another 10 seconds with the light off. During the measurements, a constant external bias value of 0.5V vs. Ag/AgCl was applied. The incident photon to current efficiency (IPCE) of all photo-anodes was calculated for each wavelength using the appropriate formula [8]:

$$IPCE(\%) = \left(\frac{I_{ph} \times h\nu}{P \times \lambda} \right) \times 100 \quad (1)$$

Where, I_{ph} is the photo-current density in mA.cm⁻², P is the optical power density in mW.cm⁻², $h\nu$ is the photon energy (~1240eVnm), and λ is the wavelength of light in nanometer. A 0.1M sodium sulfate (Na₂SO₄) solution, with a pH of 7, served as the supporting electrolyte.

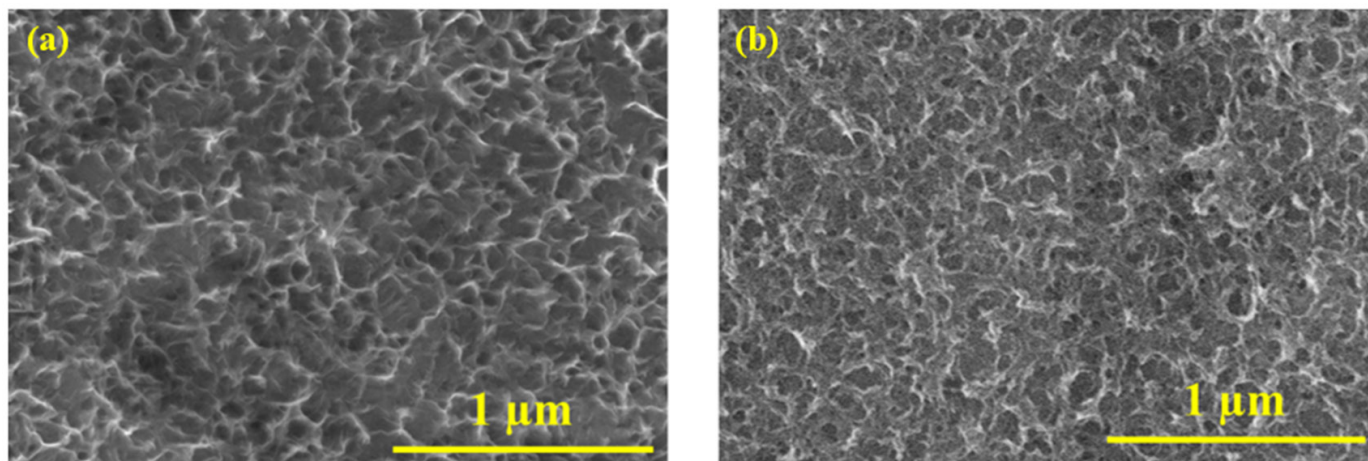


Figure 1: FESEM images of pristine TiO₂ (a) (LiOH) and (b) (CsOH).

Figures 2a & 2b illustrate the impact of hydrogenation temperature and DC plasma power on the IPCE% of the pristine TiO₂ (LiOH), respectively. All defective TiO_{2-x} photo-anodes treated in the Ar/H₂ atmosphere via thermal hydrogenation or DC plasma reduction demonstrated a significant enhancement in photo-activity across the UV spectrum. The defective TiO_{2-x} (LiOH) samples treated with Ar/H₂ at 550 °C and Plasma 5W exhibited the highest IPCE values, approximately 35% and 25%, respectively, whereas

the pristine TiO₂ (LiOH) sample achieved a maximum IPCE value of only 5%. As the temperature of hydrogenation increased, the quantity of point defects in the crystal structure rose, leading to higher IPCE values [9,10]. Meanwhile, increasing the DC plasma power and accelerating ions within the plasma could degrade surface structures at higher power levels [4]. This is evident from the decrease in IPCE values at higher power levels, as shown in Figure 2(b).

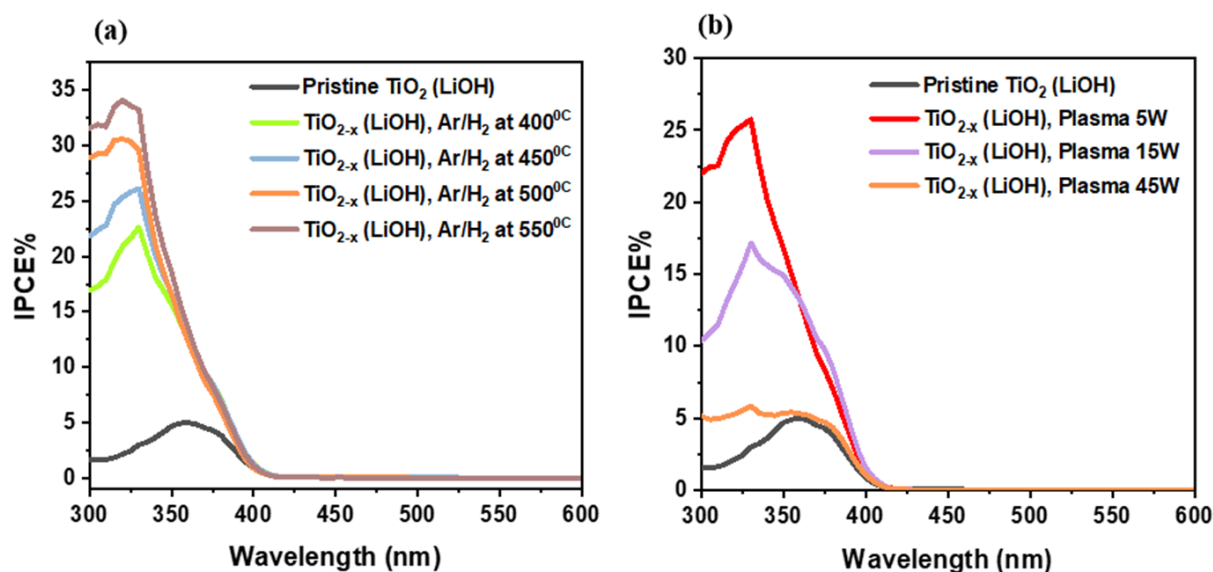


Figure 2: IPCE spectra of pristine TiO_2 (LiOH) in comparison with defective TiO_{2-x} (LiOH) nanoflakes after (a) thermal hydrogenation and (b) DC plasma reduction, under AM 1.5 illumination.

Additionally, the effect of hydrogenation temperature and DC plasma power on the IPCE% of the pristine TiO_2 (CsOH) is depicted in Figures 3(a) & 3(b), respectively. The pristine TiO_2

(CsOH) displayed a similar IPCE value of around 5%, but this value increased to over 21% for TiO_{2-x} (CsOH) treated at 500 °C with Ar/ H_2 and Plasma 5W.

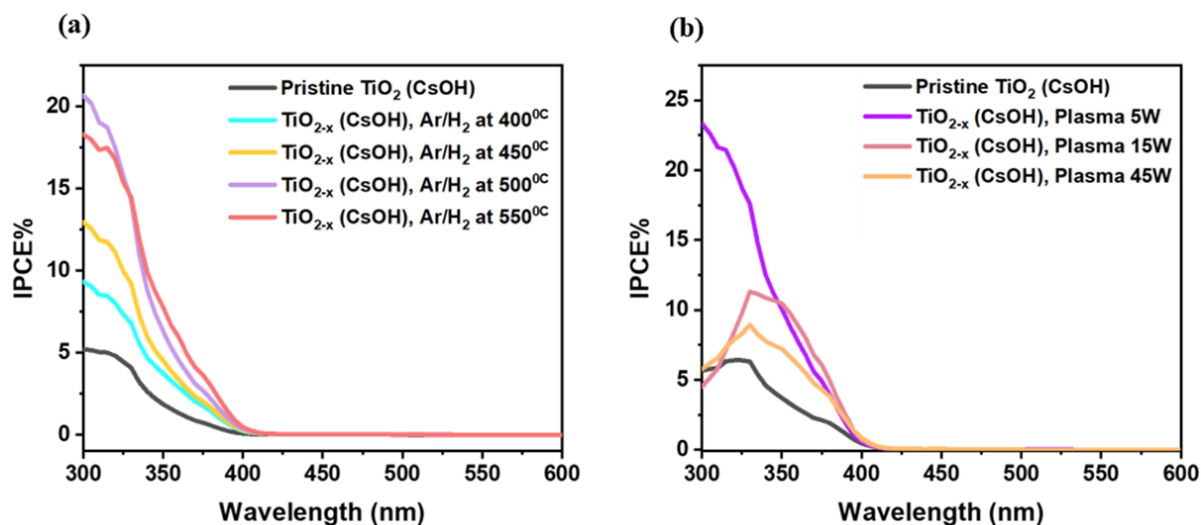


Figure 3: IPCE spectra of pristine TiO_2 (CsOH) in comparison with defective TiO_{2-x} (CsOH) nanoflakes after (a) thermal hydrogenation and (b) DC plasma reduction, under AM 1.5 illumination.

An electron transitions from the valence band to the conduction band when a photon is incident, enabling it to surpass the energy barrier of the band gap within the photo-electrodes. In the subsequent step, the optical band gap value of the photo-electrodes was determined from the IPCE data using the following equation for an indirect band to band transitions (Tauc plot) [11]:

$$\alpha(E).h\nu \alpha (h\nu - E_g)^2 \quad (2)$$

Where, $\alpha(E)$, $h\nu$, and E_g represent the absorption coefficient, photon energy and optical band gap of a semiconductor, respectively. The IPCE values instead of $\alpha(E)$ were applied to estimate the band gap of samples before and after different reduction processes.

Figures 4a-4d depict the impact of thermal hydrogenation and DC plasma reduction techniques on the optical band gap of TiO_2 (LiOH) and TiO_2 (CsOH) samples by plotting $(\text{IPCE}.h\nu)^{1/2}$ versus energy ($h\nu$).

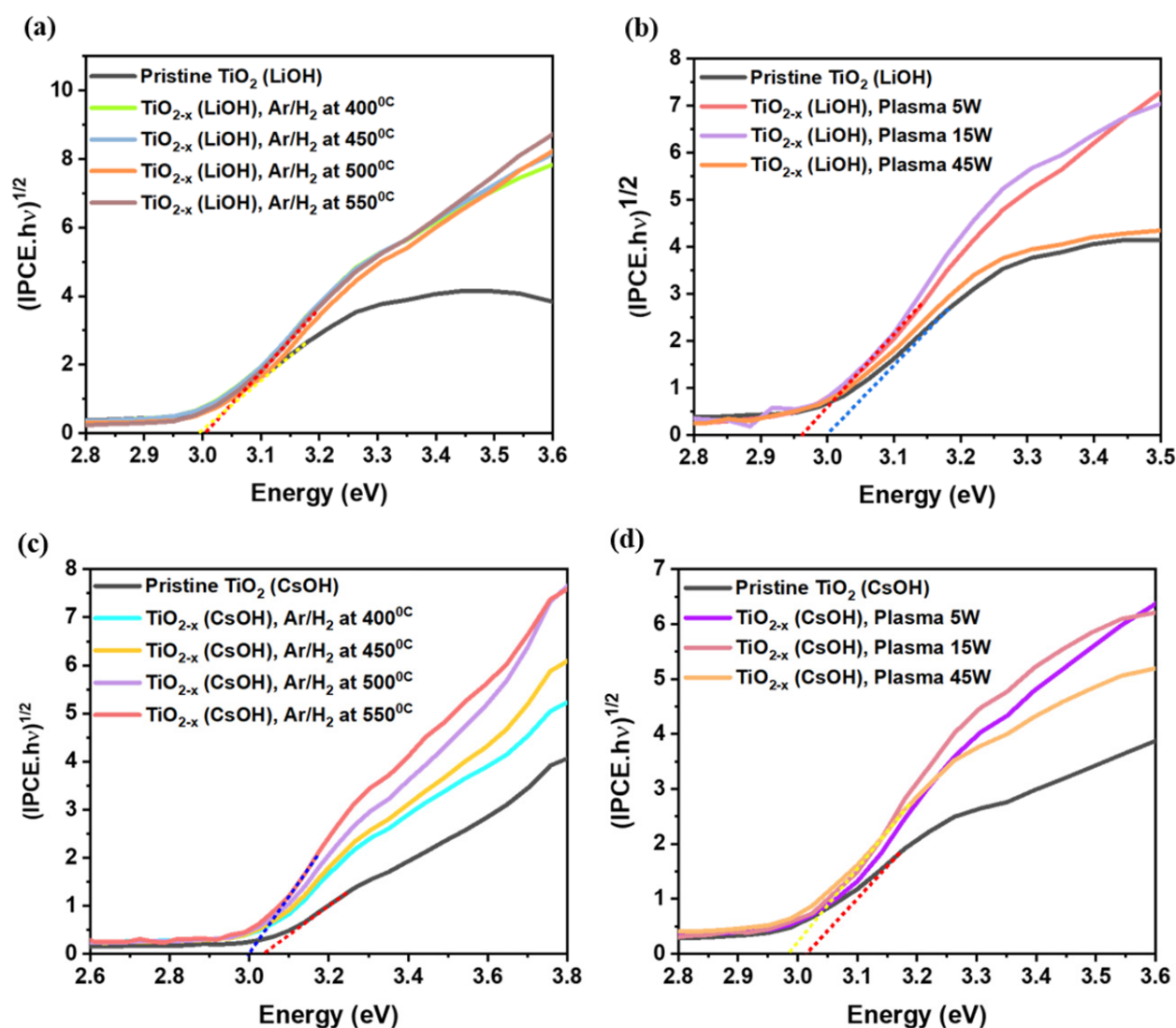


Figure 4: The impact of thermal hydrogenation and DC plasma reduction treatments on the optical band gap of (a), (b) TiO_2 (LiOH) samples, and (c), (d) TiO_2 (CsOH) samples derived from IPCE spectra.

According to the Tauc plots, introducing structural defects in the crystal lattice of TiO_2 (LiOH) and TiO_2 (CsOH)—achieved via thermal hydrogenation at elevated temperatures (400, 450, 500 and 550 $^{\circ}C$) and DC plasma treatment at varying power levels (5, 15 and 45W)—caused minor band gap narrowing ($\sim 0.1eV$). This narrowing can be attributed to the creation of weak band tails near the band edges, caused by defect states within the band gap of the samples [11]. As a result, the lowest energy transitions no longer occur between the valence band (VB) and the conduction band (CB) of defective TiO_{2-x} (LiOH) and (CsOH), but between defect mid-gap states and the band energy levels. These transitions can increase the IPCE value up to seven-fold in this study. However, as structural defects increase, further narrowing the optical band gap, the defect-induced energy levels may act as recombination centers, reducing

the photo-catalytic activity of the defective TiO_{2-x} samples [4,9-10]. To investigate the effect of these two reduction techniques on the band gap of TiO_2 nano-structures synthesized using a different hydrothermal solution (1.0M NaOH) and other morphologies, such as nanotubes, a summary of this group's work, including the band gap reductions, is provided in Table 1. The information presented in Table 1 indicates that employing hydrogenation and plasma techniques to reduce TiO_2 nano-structures has at its most effective, decreased the band gap by $\sim 0.20 eV$ (Table 1: pristine TiO_2 nanotubes, DC plasma technique). However, when a synergistic effect with ruthenium doping is considered [10], the band gap has been narrowed by $0.25eV$ (Table 1: Ru-doped TiO_2 nanotubes, hydrogenation technique).

Table 1: A summary of the influence of thermal hydrogenation and DC plasma reduction treatments on the optical band gap narrowing of different TiO₂ nano-structures.

Base Structure	Reduction Technique	Band Gap Narrowing (eV)	Ref
TiO ₂ (NaOH) nanoflakes	Hydrogenation	~0.10	[9]
TiO ₂ (NaOH) nanoflakes	DC Plasma	~0.08	[9]
TiO ₂ (LiOH) nanoflakes	Hydrogenation	~0.02	This work
TiO ₂ (LiOH) nanoflakes	DC Plasma	~0.05	This work
TiO ₂ (CsOH) nanoflakes	Hydrogenation	~0.05	This work
TiO ₂ (CsOH) nanoflakes	DC Plasma	~0.05	This work
TiO ₂ nanotubes	Hydrogenation	~0.15	[4]
TiO ₂ nanotubes	DC Plasma	~0.20	[4]
Ru-doped TiO ₂ nanotubes	Hydrogenation	~0.25	[10]

Conclusion

This study highlights the effects of hydrogenation and DC plasma reduction techniques on the optical band gap and photo-catalytic performance of defective TiO_{2-x} nano-structures. By employing thermal hydrogenation at elevated temperatures and DC plasma treatments with different applied power in an Ar/H₂ atmosphere (90/10vol%), defective TiO_{2-x} nanoflakes with enhanced photo-activity were successfully fabricated. The incident photon to current efficiency (IPCE) spectra demonstrated a substantial increase in photo-activity, reaching up to 35% in the UV range, compared to 5% in pristine TiO₂ nanoflakes. The introduction of defect states in defective TiO_{2-x} samples can lead to weak band tails near the valence and conduction bands, which played a crucial role in improving the photo-catalytic performance, enhancing the IPCE value by up to seven-fold.

However, as the defect concentration increased, the risk of defects acting as recombination centers also rose, potentially reducing the overall photo-catalytic efficiency. This trade-off between band gap reduction and defect-induced recombination highlights the need for careful control of defect engineering during the reduction process. Overall, the findings provide valuable insights into the optimization of reduction techniques for improving the photo-activity of TiO₂ nano-structures, with potential implications for advancing photo-catalytic applications in environmental remediation and solar energy conversion.

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