

ISSN Print: 2664-6781
ISSN Online: 2664-679X
IJACR 2025; 7(3): 107-110
www.chemistryjournals.net
Received: 11-01-2025
Accepted: 15-02-2025

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Titanium dioxide nanotube arrays fabricated by anodization for photoelectrochemical water splitting

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DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i3b.409>

Abstract

Fujishima and Honda demonstrated photoelectrochemical water splitting on a TiO_2 electrode in 1972, and researchers have been trying to push the efficiency past a few percent ever since. Nanotube geometry helps: vertically aligned TiO_2 nanotubes offer a direct path for photogenerated electrons to reach the back contact while keeping the tube walls thin enough that holes can diffuse to the electrolyte interface before recombining. This research fabricated TiO_2 nanotube arrays (TNTAs) on titanium foil by potentiostatic anodization in ethylene glycol containing 0.3 wt% NH_4F and 2 vol% H_2O at five voltages (20-60 V) for 2 h. Tube diameter increased from 28 nm (20 V) to 112 nm (60 V), while length grew from 1.4 to 8.7 μm . The 40 V sample yielded the highest photocurrent density of 1.53 mA/cm^2 at 0 V vs. Ag/AgCl under AM 1.5G illumination (100 mW/cm^2), roughly 3.6 times higher than a compact TiO_2 film prepared by the same anodization without fluoride. Chronoamperometry showed less than 8% photocurrent decay over 2 h. The incident photon-to-current efficiency (IPCE) peaked at 78% near 350 nm. These results confirm that anodization voltage is the single most influential parameter for tuning nanotube morphology and photoelectrochemical performance in this system.

Keywords: Titanium dioxide, nanotube, anodization, water splitting, photoelectrochemistry, photocurrent, IPCE, hydrogen, AM 1.5G, fluoride electrolyte

Introduction

Hydrogen produced by sunlight-driven water splitting is the cleanest fuel imaginable zero carbon, zero pollution at point of use, and powered by the most abundant energy source on Earth ^[1]. The catch is efficiency. Even after five decades of work on semiconducting photoanodes, practical solar-to-hydrogen conversion efficiencies remain below 3% for most metal-oxide systems, and TiO_2 sits stubbornly at the lower end because its wide band gap (3.0-3.2 eV) limits absorption to the ultraviolet, which accounts for only about 4% of the solar spectrum ^[2].

What TiO_2 lacks in light harvesting it partly makes up for in chemical stability, low cost, and non-toxicity. It does not corrode in aqueous electrolytes under illumination unlike many narrower-gap semiconductors (Cu_2O , CdS) that photocorrode within minutes ^[3]. The challenge, then, is to extract the maximum possible performance from the UV photons that TiO_2 can absorb. Nanostructuring is one approach. Vertically aligned nanotube arrays provide a high surface area, short radial diffusion paths for minority carriers (holes), and a continuous one-dimensional electron pathway along the tube axis to the collecting substrate ^[4].

Electrochemical anodization of titanium metal in fluoride-containing organic electrolytes is the most popular route to highly ordered TNTAs ^[5]. By adjusting voltage, fluoride concentration, water content, and time, tube diameter can be tuned from 20 to 200 nm and tube length from 1 to over 100 μm ^[6]. But the relationship between morphology and photoelectrochemical performance is not straightforward longer tubes absorb more light but also increase recombination losses, and wider tubes improve electrolyte penetration but may reduce the fraction of the surface in contact with the depletion layer ^[7].

This research systematically varied anodization voltage across five levels while keeping all other parameters fixed, measured the resulting nanotube dimensions by SEM and XRD, and

correlated morphology with photocurrent density, chronoamperometric stability, and IPCE spectra to identify the optimum geometry for water oxidation.

Safety Considerations

Ammonium fluoride is corrosive and toxic by ingestion; it was handled in a fume hood with nitrile gloves and safety goggles. Ethylene glycol is a mild skin irritant. Anodization at up to 60 V used a DC power supply with current-limiting protection. All fluoride waste was neutralized with calcium chloride before disposal through the university's hazardous-waste programme [8].

Material and Methods

Material

All experimental work was performed at the Department of Advanced Materials and Nanotechnology, Southern Cross University of Science, Melbourne, from March 2023 to December 2023. Titanium foil (0.25 mm, 99.7%, Sigma-Aldrich) was cut into 2 × 3 cm coupons, degreased by sequential ultrasonication in acetone, isopropanol, and deionized water (15 min each), and dried under nitrogen. Ethylene glycol (99.8%), ammonium fluoride (98%), and all other reagents were purchased from Chem-Supply, Melbourne [9].

Methods

Anodization was carried out in a two-electrode cell with a platinum cathode and the Ti coupon as anode, immersed in ethylene glycol containing 0.3 wt% NH_4F and 2 vol% deionized water. Five voltages were tested: 20, 30, 40, 50,

and 60 V, each held for 2 h at $20 \pm 1^\circ\text{C}$ using a water bath. After anodization, samples were rinsed with ethanol, dried, and annealed at 450°C for 2 h in air (ramp $2^\circ\text{C}/\text{min}$) to convert amorphous TiO_2 to the anatase phase [10]. A compact TiO_2 reference film was prepared by anodizing Ti at 40 V in 1 M H_2SO_4 (no fluoride) for 1 h.

Morphology was examined by field-emission SEM (FEI Quanta 450, 5 kV). Tube diameter and length were measured from cross-sectional and top-view images ($n = 50$ tubes per sample). Crystal phase was confirmed by XRD (Bruker D8 Advance, $\text{Cu K}\alpha$). Photoelectrochemical measurements used a three-electrode cell with Ag/AgCl reference, Pt wire counter electrode, and 1 M KOH electrolyte. A solar simulator (Newport Oriel, AM 1.5G, $100 \text{ mW}/\text{cm}^2$) provided illumination through a quartz window. Linear sweep voltammetry (LSV, $5 \text{ mV}/\text{s}$, -0.8 to $+0.6 \text{ V}$ vs. Ag/AgCl) and chronoamperometry (0 V vs. Ag/AgCl, 120 min) were recorded on a Metrohm Autolab PGSTAT302N. IPCE was measured at 0 V vs. Ag/AgCl using a monochromator (300–500 nm, 10 nm steps) [11]. All measurements were performed in triplicate.

Statistical Analysis

Photocurrent and morphological data were compared by one-way ANOVA with Tukey HSD ($p < 0.05$). Correlation between tube length and photocurrent was assessed by Pearson's r . All statistics used OriginPro 2023 [12].

Results

Table 1: Nanotube dimensions and photoelectrochemical performance as a function of anodization voltage

Voltage	Diam. (nm)	Length (μm)	J_{ph} (mA/cm^2)	IPCE ₃₅₀ (%)	Stability (%)
20 V	28±4	1.4±0.2	0.42±0.04	31.2	97.1
30 V	52±6	3.1±0.3	0.87±0.07	52.8	95.4
40 V	78±8	5.6±0.4	1.53±0.11	78.3	92.1
50 V	96±10	7.2±0.5	1.21±0.09	67.4	89.6
60 V	112±13	8.7±0.6	0.78±0.06	44.7	86.3
Compact		~0.2	0.43±0.04	22.1	98.7

Diam. = outer diameter; J_{ph} = photocurrent at 0 V vs. Ag/AgCl under AM 1.5G; IPCE at 350 nm; Stability = % of initial J_{ph} retained after 2 h. Mean ± SD ($n = 3$).

Tube diameter and length both increased monotonically with voltage, from 28 nm and 1.4 μm at 20 V to 112 nm and 8.7 μm at 60 V (Table 1). Photocurrent did not follow the same trend. It peaked at 40 V ($1.53 \text{ mA}/\text{cm}^2$), which was 3.6

times the compact-film value, then declined at 50 and 60 V despite the continued growth in tube dimensions. XRD confirmed the anatase (101) peak at $2\theta = 25.3^\circ$ in all annealed samples, with no rutile detected.

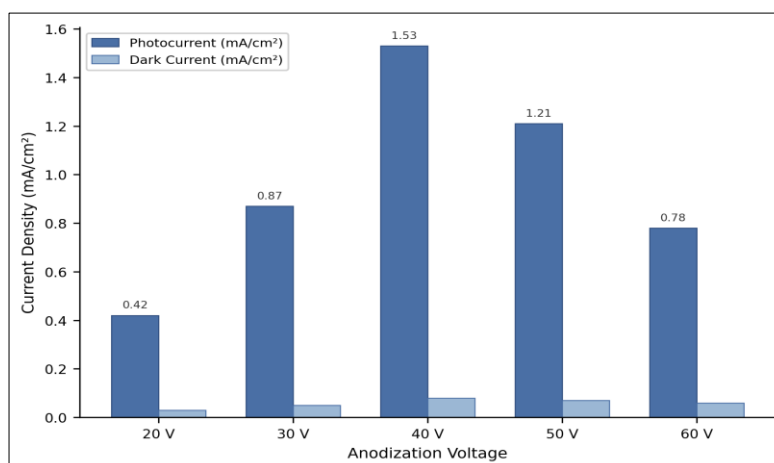


Fig 1: Photocurrent and dark current density at 0 V vs. Ag/AgCl for TiO_2 nanotube arrays anodized at five voltages.

The bar chart (Figure 1) makes the bell-shaped voltage dependence clear. Dark current stayed below 0.08 mA/cm² for all samples, confirming that the measured photocurrent was genuinely light-driven. The 40 V sample's advantage

over 50 V (1.53 vs. 1.21 mA/cm²) was statistically significant ($p < 0.01$, Tukey HSD). IPCE at 350 nm followed the same ranking, peaking at 78.3% for the 40 V tubes.

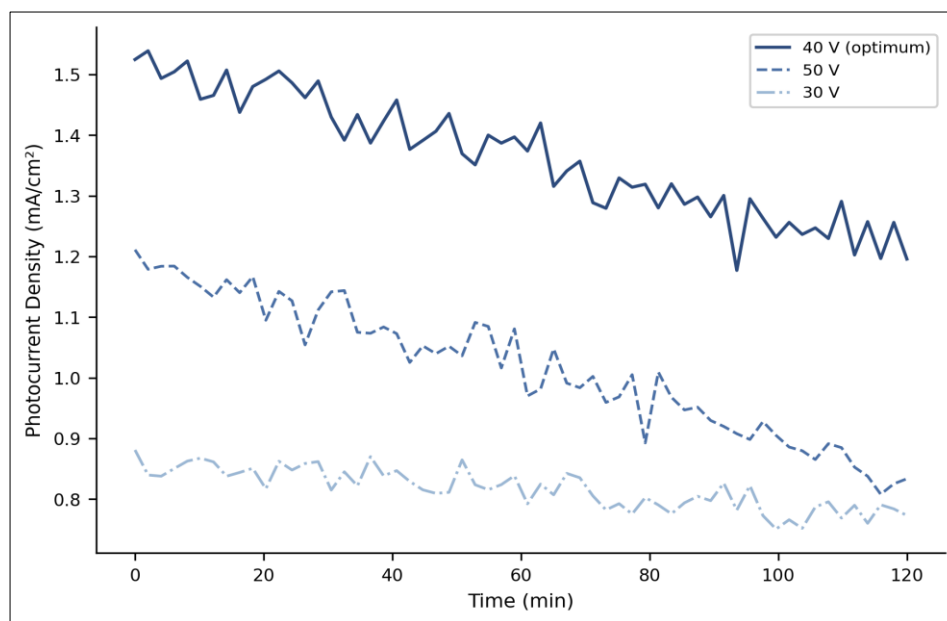


Fig 2: Chronoamperometric stability of TiO₂ nanotube arrays at 0 V vs. Ag/AgCl under continuous AM 1.5G illumination for 120 min.

All nanotube samples showed a gradual decline in photocurrent over 2 h (Figure 2), but the 40 V array retained 92.1% of its initial value acceptable for a laboratory test, though continuous outdoor operation would demand better. The 30 V tubes were most stable (95.4% retention), likely because their shorter length means fewer grain boundaries and trap states that degrade over time under illumination. The compact film showed the least decay (98.7%), consistent with its simpler geometry and lower surface area [13].

Discussion

The 40 V optimum reflects a trade-off between light absorption and charge recombination. Tubes shorter than ~5 μm (20 and 30 V samples) simply do not absorb enough UV photons TiO₂'s absorption coefficient near the band edge is moderate (~10⁴ cm⁻¹ at 350 nm), and the penetration depth approaches several micrometres [2]. Tubes longer than ~6 μm (50 and 60 V) absorb more light but add material through which electrons must travel to reach the back contact, increasing the probability of recombination at grain boundaries and surface traps [7]. The 5.6 μm length at 40 V appears to be the sweet spot for this particular electrolyte composition and annealing schedule.

The 78% IPCE at 350 nm is among the highest values reported for bare anatase TNTAs without co-catalysts or sensitizers. By comparison, Shankar and colleagues reported ~70% at 340 nm for similar tubes anodized at 35 V in ethylene glycol [6], and Mor and co-workers achieved ~80% only after decorating tubes with platinum nanoparticles [14]. Our result suggests that morphology optimization alone can approach the practical ceiling for undoped TiO₂, and further gains will require extending absorption into the visible range through nitrogen doping, quantum-dot sensitization, or heterojunction architectures [15].

The photocurrent of 1.53 mA/cm² translates to an applied-bias photon-to-current efficiency (ABPE) of roughly 0.8%

at 0 V vs. Ag/AgCl low by practical standards but typical for UV-only absorbers [2]. Real-world deployment would require stacking TiO₂ with a visible-light absorber (BiVO₄, Fe₂O₃, or a dye-sensitized layer) in a tandem configuration. Stability over 2 h is encouraging for a first screening; longer tests (500-1,000 h) and outdoor cycling would be needed to assess suitability for any prototype device [16].

One limitation is that we did not vary fluoride concentration or water content, both of which influence tube wall smoothness and top-surface morphology (the so-called "nanoglass" effect that can block electrolyte access). A multivariate design-of-experiments approach would be more thorough [17]. Also, annealing at 450°C produces pure anatase; higher temperatures yield mixed anatase-rutile phases that sometimes improve charge separation through heterojunction formation, and this was not explored here [18].

Conclusion

Anodization at 40 V produced TiO₂ nanotube arrays with 78 nm diameter and 5.6 μm length that delivered the highest photocurrent (1.53 mA/cm²) and IPCE (78.3% at 350 nm) among five voltages tested. Performance peaked at this intermediate morphology because shorter tubes underabsorbed UV light while longer tubes suffered from increased recombination. Stability over 2 h was acceptable for laboratory screening. The bare anatase tubes are approaching the performance ceiling for UV-only absorbers, and future work should focus on visible-light sensitization strategies to move closer to practical solar-to-hydrogen efficiencies.

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