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Highly active titanium oxide photocathode for photoelectrochemical water reduction in alkaline solution

Xuelan Hou \textsuperscript{a,b}, Lijun Fan \textsuperscript{a,c}, Yicheng Zhao \textsuperscript{c}, Peter D. Lund \textsuperscript{b}, Yongdan Li \textsuperscript{a,c,*}

\textsuperscript{a} Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FI-00076, Aalto, Espoo, Finland
\textsuperscript{b} Department of Applied Physics, School of Science, Aalto University, FI-00076, Aalto, Espoo, Finland
\textsuperscript{c} Tianjin Key Laboratory of Catalysis Science and Technology, School of Chemical Engineering and Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin, 300072, China

**HIGHLIGHTS**

- A stepwise cathodic reduction technique turned TiO\textsubscript{2} to excellent cathode (TNT-C).
- TNT-C shows a self-improving photoelectrochemical performance for water splitting.
- The onset voltage of TNT-C displays an anodic shift from −0.79 to 0.19 V<sub>RHE</sub>.
- The overall current @ −1.0 V<sub>RHE</sub> shows an enhancement from −110.06 to −210.66 mA.
- TNT-C withstands an overall current > −100 mA in 1 M NaOH for more than 12,000 s.

**ABSTRACT**

Developing low-cost, efficient and stable metal oxide cathode catalyst for hydrogen evolution reaction (HER) is of great importance to overcome the major challenge in photoelectrochemical water splitting (PECWS) cell. Anodic titanium dioxide nanotube (TNT) as the electrode has shown promising for its flexibility, economy and efficiency. Herein, a highly active and stable photocathode for HER was achieved with a technique of stepwise cathodic reduction of anodic TNT without loading any cocatalyst. It exhibits a self-improving PECWS performance after the five-step cathodic reduction process. The onset voltage displays an anodic shift from −0.79 to 0.19 V versus the reversible hydrogen electrode (RHE) and the overall current shows an enhancement from −110.06 to −210.66 mA at −1.0 V<sub>RHE</sub> in 1 M NaOH aqueous solution (pH = 13.6). The photocathode also withstands a voltage @ −1.0 V<sub>RHE</sub> and a current @ −100 mA in the WS cell for more than 12,000 s sequentially. This work demonstrates a feasible strategy for forming a multijunction composite for efficient HER with the anodic TNT as the precursor.

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* Corresponding author. Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FI-00076, Aalto, Espoo, Finland.
E-mail address: yongdan.li@aalto.fi (Y. Li).

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1. Introduction

Solar driven water splitting (WS) to hydrogen (H₂) and oxygen is promising for solar energy harvesting and storage [1]. However, the stability of metal oxide catalysts for the cathode hydrogen evolution reaction (HER) is still insufficient for a stable, flexible, and efficient design of photoelectrochemical (PEC) aqueous reaction cell [2]. The challenge for stability of the photocathode comes from that the catalyst works in an environment with formation of atomic H⁺ and release of gaseous H₂ in some cases also with a cathodic reduction potential [3].

Most investigated photocathodes in PECWS cell are p-type semiconductors [4]. Among them, Cu₂O is promising as a single-phase photocathode catalyst [5–7]. The photocurrent density of bare Cu₂O was reported as high as −2.4 mA/cm² at 0.25 V.RE (voltage versus the reversible hydrogen electrode) in 1 M Na₂SO₄ solution buffered at a pH = 4.9, under AM 1.5 light source, i.e. 100 mW/cm², but the stable performance lasted less than 20 min in the test conditions at 0 VRHE [6]. Besides Cu₂O, other p-type semiconductors, such as p-silicon and copper based chalcogenides (Cu(In,Ga)Se₂ and Cu₂ZnSnS₄) have also been explored as the photocathode catalyst but are also unstable during the reaction [8–10]. Based on such a background, cathode designs with a passivation layer to protect the semiconductor catalyst from the attacking of the newly formed H⁺ atom as well as the reductive potential marks a breakthrough [5,11]. N-type titanium dioxide (TiO₂) has been used as the passivation layer in the design of composite cathode due to its high resistance to corrosion in alkaline media [12]. However, the passivation layer increases the overpotential and suppresses the electron exchange between the (photo)cathode and the electrolyte. To reduce the overpotential of the cathode, cocatalysts, such as Pt, RuO₂ and NiO₂, are loaded to improve the efficiency [4]. Therefore, the state-of-the-art composite cathode has a complex composite structure of a p-type semiconductor, one or two n-type semiconductor passivation layers and a metal or metal oxide cocatalyst [13].

TiO₂ was the first reported metal oxide in a PECWS cell, which worked as a photoanode [1]. For an high cell performance, strategies have been employed to improve optical or electrical conductivity of TiO₂ based electrode. Such as (i) Black hydrogenated TiO₂ preparation marks a breakthrough with broadening its solar absorption spectrum from 380 to 1300 nm [14], (ii) Magneli phase TiO₂, a partially reduced TiO₂ with a general formula TiₙO₂₋ₙ (n = 4–37), has been found chemically inert and has semi-metallic property possessing electrical behavior comparable to that of carbon, and therefore considered as a potentially stable powder catalyst for photocatalytic WS and a metal oxide-based catalyst for HER in water electrolysis [15–17]. (iii) A carbon rich TiOₙCₙ nanotube, showing semi-metallic conductivity, was reported in 2009 by Hahn et al. [18] and they treated the film in acetylene at 850 °C to form TiOₓCy nanotube. Anodic TiO₂ nanotube (TNT) film represents an exceptional one-dimensional structure, which also are fabricated on a conductive and flexible titanium (Ti) metal substrate [19]. It has been mostly reported as anode for oxygen evolution reaction (OER) in PECWS cells [20], even though TiO₂ is a semiconductor with its conduction band (CB) and valence band (VB) locations straddling the water reduction and water oxidation potentials. In principle, TiO₂ may act as HER catalyst due to the CB of TiO₂ is more negative than H⁺/H₂. However, the anodic TNT photocathodes have been rarely reported for HER due to the sluggish charge transfer between the anodic TNT and the aqueous solution in a PECWS cell [21]. In previously published works, TiO₂ has been used as one of the components of the cathode [22–25]. Mohapatra et al. [22] examined a Pt/TNT cathode in PECWS cell. Mor et al. [23] employed p-type Cu–Ti–O TNT as the cathode of a PECWS cell. Ye et al. [24] loaded Pd quantum dots to sensitize TNT as the cathode in a PEC cell and reported a HER rate of 592 μmol/h·cm² under 320 mW/cm². Very recently, the modified reduced anodic TNT was reported as a highly active HER catalyst in electrochemical cell in 1 M NaOH [26]. Zeng et al. [27] reported a cathodic reduction method to modify a p-type Si/GaN photocathode, which exhibited a self-improving behavior for HER, viz. the overpotential of the photocathode had an anodic-shift from −0.46 to −0.08 V.RE during the linear scan voltammery (LSV) test. In the same year 2021, a cathodic potential < −0.4 V.RE was used to modify the surface roughness of a Cu-based electrode in CO₂ reduction to CO [28].

Herein this work, a stepwise cathodic reduction approach is adopted to convert the anodic TNT sample into an efficient photocathode without loading any co-catalyst. The photocathode is also observed with both high and self-improving activity for HER in 1 M NaOH solution.

2. Experimental

2.1. Materials

Titanium foils (Ti, purity 99.5%, thickness 0.2 mm, Beijing Zhongnuo Advanced Material Technology Co., Ltd), ethylene glycol (C₂H₄O₂, EG, anhydrous 99.8%, Sigma Aldrich and Merck), ammonium fluoride (NH₄F, ACS reagent, ≥ 98.0%, Sigma-Aldrich), sodium hydroxide (NaOH, Merck KGaA, 64,271 Darmstadt Germany) and graphite rod (99.99%, Beijing HWRK Chem Co.) were used without further treatment. The aqueous solution was prepared with deionized water (DI).

2.2. Sample preparation

Prior to the anodization, the Ti foil (1.0 × 2.0 cm) was ultrasonically cleaned with acetone, ethanol and deionized water for 30 min sequentially and dried in an oven (UF 75, Memmert GmbH Co. KG) at 70 °C. The anodic oxidation growth was carried out with a two-electrode configuration in a solution of a mixture of 0.3 wt% NH₄F, DI H₂O and EG (V(EG): V(H₂O) = 3:47) under a constant voltage of 60 V for 3 h. After the growth, the sample was firstly dried in an oven at 70 °C for 30 min, then annealed at 450 °C for 30 min in air with a ramping rate of 3 °C/min [29]. The TNT sample was denoted as TNT-A (Fig. 1). This sample was reduced with a two-anode reduction (TAR) technique for 2 min under a constant voltage of 60 V in a same electrolyte as that used in the anodic growth step [20]. Afterwards, the sample was annealed again at 450 °C for 30 min in air. The sample obtained is referred to as TNT-B (Fig. 1). A stepwise cathodic reduction was done in a three-electrode electrochemical cell with TNT-B as the work electrode (WE), Pt foil as the counter electrode (CE) and Ag/AgCl as the reference electrode (RE) in an electrolyte of 1.0 M NaOH (pH = 13.6) under irradiation from one side of simulated sunlight with a Xenon lamp (94011A-ES, LCS-100, Newport, AM 1.5G, 100 mW/cm²) with a constant bias of −1.0 V.RE at room temperature, 20–22 °C. Five reduction steps at −1.0 V.RE were carried out with controlling the reduction time. 1st and 2nd steps are 1000 s, the 3rd step is 2000 s, the 4th and 5th are 3600 s, respectively. In between each two reduction steps, LSV curve was measured under the same light source with a scan rate of 10 mV/s. The sample after the 5th reduction step is referred to as TNT-C (Fig. 1).

2.3. Photoelectrochemical measurement

The PEC performance was measured with an electrochemical workstation, ZENNIUM Pro, Zahner-Elektrik, Germany, in a three-electrode configuration with the TNT-C sample as the WE, Pt foil as the CE, Ag/AgCl as the RE, and 1.0 M NaOH (pH = 13.6) as the electrolyte under the same light irradiation from one side. Both sides of TNT-C sample were dipped in the 1 M NaOH aqueous solution and each side has an area of 1 cm². The potential versus Ag/AgCl electrode was converted into that versus RHE with Nerst equation [30]:

\[ E_{RHE} = E_{Ag/AgCl} + 0.059 \text{pH} + 0.196 \]

The LSV curves were recorded with a scan rate of 10 mV/s. A 600 s chronoamperometry (CA) test for TNT-C at −1.0 V.RE was carried out under both dark and light conditions in 1 M NaOH. A
chronopotentiometry (CP) mode test for TNT-C at −100 mA for 12,000 s and a CA mode test at a bias of −1.0 VRHE for 12,000 s were carried out sequentially in 1 M NaOH under the same light source irradiation from one side.

The electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100 kHz to 10 mHz with peak-to-peak method using an AC amplitude of 20 mV signal at open circuit potential under light. The Mott-Schottky (M – S) correlation was derived at a frequency of 1 kHz in the dark condition. The incident photon-to-electron conversion efficiency (IPCE, %) curve was measured with a QE/IPCE measurement system P211 (Zahner CIMPS-psc) with the background light on under the monochromatic light, TLS03 light source number 1974, in the range of 365–1020 nm. During the IPCE measurement, AC mode with a frequency of 10 Hz was used for lowering noise.

2.4. Characterization

After all the PEC measurements, sample TNT-C was taken for physical characterizations. The morphology was observed with a field-emission scanning electron microscope (SEM, Tescan MIRA 3, Brno, Czech Republic) and a transmission electron microscope (TEM, JEOL JEM-2200FS). The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a surface science instrument SSX-100 ESCA spectrometer with an Al-Kα X-ray excitation source. All XPS measurements were performed with Charge Neutralizer ON. X-ray diffraction (XRD) pattern was acquired with PANalytical X’PertPro instrument using Cu-Kα (λ = 1.540598 Å) radiation.

3. Results

3.1. Self-improving behavior as photocathode

The LSV curves, in Fig. 2 (A), show that the onset potential has a stepwise anodic shift and the current has an enhanced value after every cathodic reduction step. In the end, the onset shifted from −0.79 to 0.19 VRHE, meanwhile, the overall current at @-1.0 VRHE increased from −110.06 to −210.66 mA. The i-t test results of the TNT-C sample illustrated in Fig. 2 (B) were recorded under both light and dark conditions at −1.0 VRHE in 1 M NaOH for 600 s. The difference of the photo and electrochemical responses is marked with a two-way arrow (∆J = Jlight - Jdark ≈ 25 mA/cm²). Under the light condition, the photocurrent has a slight increase from −136 to −140 mA in 200–600 s, while in the dark condition, TNT-C shows a slight decrease in 0–470 s from −130 to −112 mA at 470 s. The step-change at 470 s for ca. −3 mA marked by the circle was caused by switching on of a phone camera when recording the WS phenomenon in dark (Movie S1), giving a support for the sample being sensitive to light. No surface corrosion was observed in both light and dark tests. Fig. 2 (C) plots the results of CP mode test @ −100 mA and CA mode measurement @ −1.0 VRHE of the TNT-C sample. In the 12,000 s CP mode test, the recorded potential decreased from −0.79 to −0.77 VRHE (Movie S2). The CA mode result showed a current increase from −70 to −130 mA (Movie S3). During both CP and CA tests, the
photocathode TNT-C shows self-improving performance during WS reaction.

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jpowsour.2022.231095.

3.2. Photoelectrochemical property

The EIS curve, presented in Nyquist plot, is shown in Fig. 3 (A) with an overall curve in major chart and a zoom-in of the low resistance end in an insert one. TNT-C exhibits two arcs, a smaller one in low resistance end and a larger one in high resistance range, indicating the sample has two electroactive interfaces with different kinetics [31]. The smaller one corresponds to a resistance of ca 1 Ohm, comparable to metallic conductivity. The larger one indicates the semiconductor behavior part of the sample, but the radius of curvature is 10-time smaller than that of the anodic TNT without reduction [32]. The M – S plot gives the information of the type of semiconductor conductivity. A straight line with positive slope indicates n-type characteristics and a negative slope reflects a p-type feature [33]. Here, TNT-C has two positive slopes and one negative slope, as shown in Fig. 3 (B), indicating the formation of n-p-n junctions. The IPCE curve, Fig. 3 (C), is measured in the range of 365–1020 nm under a voltage of −0.5 V_RHE and gives a response in the whole spectrum range, with six peaks locating at 395, 476, 563, 648, 765 and 836 nm. In contrast, TNT-A has an absorption edge at ca. 430 nm, see Fig. S1.

3.3. Morphology

The micrograph of Fig. 4 (A) shows that the nanotubes in TNT-A are well-aligned, with a smooth top surface and an average tube length of 10 μm. After TNT-A blackened with the TAR technique, the sample turns to TNT-B, see Fig. 4 (B), in which the nanotubes are shorter than in TNT-A with an average length of 8.8 μm [20]. Besides, uniform nanotube photonic crystals (NTPCs) and nanoparticles are observed on the outer-wall of the tubes in inset of Fig. 4 (B) [20,34,35]. The NTPCs and particles enhance light harvesting and weaken gas bubble adhesion to the electrode surface [36]. Below the bottom of the tubes, circles of 100–150 nm in diameter are observed on the substrate. TNT-C has a blue color, shown in Fig. 1, under the simulated sunlight in 1 M NaOH. New rod-like structures, growing out of the nanotube arrays after all the PEC tests, were observed, but the tubular array morphology retained for the rest of the film. The TEM images in Fig. 4 (D&E) show the existence of a starfish morphology, indicating the novel multi-phase composite structure of TNT-C. The electron diffraction pattern, Fig. 4 (F), of the starfish like structure indicates that the material includes both the features of amorphous and polycrystalline domains, meaning that even the starfish like structure is a composite instead of a single crystal.

3.4. Surface state and crystal structure

Fig. 5(A)–(C) plot the comparison of the C 1s, Ti 2p and O 1s XPS spectra of the three samples. All the three spectra of TNT-A are quite similar to the pure anodic TNT [20]. When comparing with TNT-A, the C 1s, Ti 2p and O 1s XPS spectra of TNT-B show slight differences in both peak locations and intensities due to the partial reduction during the TAR step [20,37]. The peak locations, widths and intensities of TNT-C in Fig. 5(A)–(C) show remarkable differences with those in the TNT-A and TNT-B samples. The details of the three spectra of TNT-C sample are illustrated in (D)–(F). The C1s spectrum is resolved into six components (Fig. 5(D)), A = C–C bond at 284.8 eV, and other carbon species of C–C, C–N, C–F, O–C–=O and –CO2 are also observed and marked [20,38]. The Ti 2p XPS core spectrum, Fig. 5(E), is deconvoluted into six peaks [38]. Two peaks locating at 464.47 and 458.52 eV are ascribed to Ti 2p1/2 and Ti 2p3/2 of typical Ti–O bond, while the peaks at 463.84 and 458.16 eV are attributed to Ti–C bond [39]. Meanwhile, Ti3d peaks at 463.19 and 457.81 eV are also observed. The percentages of these Ti species have been calculated and summarized in Table S1. The O 1s core level spectrum, Fig. 5(F), supports the existence of Ti–O–H, Ti–O–Ti, C–O, Ti3d–O and C=O [14,20,38,40].

Fig. 6 depicts the XRD patterns of the TNT-B and TNT-C samples. The TNT-B sample exhibits a typical crystal structure of anatase phase (JCPDS: 21–1272) [10]. The peaks of Ti metal, belong to a close packed hexagonal crystal a phase structure (JCPDS: 74–1294), appear in both patterns [29]. The XRD pattern of TNT-C shows new peaks, which are absent in the pattern of the TNT-B sample. Two new peaks at 2θ 33.73◦ and 57.32◦ are assigned to TiC (JCPDS: 74–1219), and the other two at 36.57◦ and 51.49◦ are assigned to Ti3C2(OH)2 [41].

4. Discussion

4.1. The synergy of photo and electric inputs

To enable the optional switching between photo and electric energy inputs of the electrodes in PECWS cell are remarkably useful nowadays because of the great demand of the storage of the intermittent renewable energies, like wind and solar powers. The highly active TNT-C photocathode enables the synergy of photo and electric inputs.

The current responses of the TNT-C sample to the photo and electric energy inputs are different in nature. Fig. 7 illustrates the cathode function of TNT-C in PECWS cell. TNT-C has two identical TNT films on both sides, with one side under the irradiation of the light source, marked as ‘front’, and the other side without irradiation but under the same condition, noted as ‘back’. The functions of Ti foil in the TNT-C sample as both the supporting substrate and as the conductor between the two identical catalyst films ‘front’ and ‘back’. In the PECWS cell, HER happens on TNT-C to reduce H+ to H2, and the OER takes place on the Pt anode with oxidizing OH− to O2. When a bias is applied or a photovoltage exists, electric gradient forms at the metal oxide interfaces
Here the metal layer serves as the depletion region, which effectively provides high electron density and prolongs the charge carrier lifetime, both superior to the cases with a direct contact junction of two semiconductors. When the cathode is irradiated with a substantial bias, e.g. $-1.0 \text{ V}_{\text{RHE}}$, the photovoltage and the applied voltage combines to generate electrons for the reduction of $\text{H}^+$. As a consequence, the

Fig. 4. (A) Cross section of TNT-A. (B) Cross sections of TNT-B. (C) Top view of TNT-C after stability test. (D) The TEM image of TNT-C after all the PEC tests. (E) The TEM image of a starfish morphology in TNT-C. (F) The selected area, marked in (E), electron diffraction pattern.

Fig. 5. (A)-(C) A comparison of C 1s, Ti 2p and O1s XPS spectra of the TNT-A, TNT-B and TNT-C samples. (D)-(E) The fitting and analysis of C 1s, Ti 2p and O1s XPS spectra of TNT-C.
overall current is enhanced and the reactions at both the cathode and the anode are accelerated, but the synergy of the photo and electric inputs cannot be described with a simple sum.

In literature up to now, when anodic TNT was used as the photo-anode in PECWS cells, the dark current density with a high positive bias up to 1.23 V_RHE is often negligible [43,44]. The TNT-C sample has an ineligible dark current from both sides in this work because it is used as the cathode. The photo response of the TNT-C as cathode is illustrated as a curve in Fig. 7(B), which is derived with a direct subtraction of the data of with light irradiation and in dark as presented in Fig. 2(B). The calculated “photocurrent density” increased from −21.5 to −27.1 mA/cm² during 470 s of the CP mode test. The photo energy utilization of TNT-C sample as cathode is remarkable.

4.2. The self-improving performance

The self-improving PEC performance of TNT-C cathode was observed for the first time in this work. The electrochemical tests were carried out to find the reasons behind the outstanding HER performance of TNT-C. TNT-A in this work is well grown TNT array and exhibits as anatase supported on Ti metal [45,46]. TNT-C has a multi-phase texture in the morphology observations. The XRD result shows that the TNT-C sample has many component phases, including metal Ti, metal oxide TiO₂, (oxy) carbides as TiC, Ti₃C₂(OH)₂, and semi-metallic TiOₓCᵧ [47]. The existence of C and Ti species on TNT-C surface is supported by the XPS results. The new phase of TiC and TiOₓCᵧ in TNT-C are likely to be responsible to the semi-metallic behavior of the sample in EIS test and improve carrier separation and charge transfer in the catalyst [42]. It is noted that, the EIS spectrum of TNT-A, Fig. 52, does not show the smaller semi-circle as in Fig. 3 (A), indicating that the smaller semi-circle is not the property of the metallic Ti. It should be also mentioned that, the phase evolution of the TNT array is sensitive to the light irradiation. In our recent work, the samples, prepared with a similar cathodic reduction process but without one side irradiation, give XRD patterns with only two phases, i.e., metallic Ti and anatase TiO₂ [26].

The IPCE spectrum of TNT-C has six peaks, providing evidence that TNT-C is a multiphase nanomaterial. The peak of TNT-C at 395 nm is due to the existence of anatase TiO₂. The absorption at ca. 470 nm may be
introduced by C, N and F doping during the TAR step in which the weak photon absorption in the visible-light range (420 nm) due to its phase composition and crystal orientation during anodic growth of TiO2 nanotubes, Electrochem. Commun. 134 (2022) 107168.


