

令和 5 年 6 月 8 日現在

機関番号：12608

研究種目：若手研究

研究期間：2018～2022

課題番号：18K14085

研究課題名(和文) ワンステップ陽極酸化法によるTi-Nb-Ta-Zr-Oナノチューブ光触媒の創製

研究課題名(英文) TNTZO nanotubes photocatalyst fabricated by one-step anodization method

研究代表者

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交付決定額(研究期間全体)：(直接経費) 3,200,000円

研究成果の概要(和文)：陽極酸化プロセスにより、Ti-Nb-Ta-Zr-O ナノチューブを Ti-29Nb-13Ta-4.6Zr 合金板表面に形成し、光電気化学システムによる水分解の新規な陽極としての可能性を見極める。Nb、Ta、Zr の自己ドープ効果により、バンドギャップの狭小化、可視光吸収率及び導電性を向上させ、フォトキャリアの電荷分離過程の効率と光電流の増大を引き出す。ナノチューブの細管壁厚は、支配的に水分解効率に影響を与えることがわかっており、陽極酸化の反応条件を変えることによってナノ構造の形態最適化を図る。そして、電気化学インピーダンス解析から、新規可視光応答型光触媒の電荷キャリア移動機構を解明する。

研究成果の学術的意義や社会的意義

The present work examined the realistic hydrogen evolution by employing TNTZO as the photoanode in the photoelectrochemical(PEC) water splitting cell. This illustration reveals that the fully depleted TNTZO nanotubes can practically perform PEC water splitting to realize solar hydrogen production.

研究成果の概要(英文)：By performing electrochemical anodization on Ti₂₉Nb₁₃Ta_{4.6}Zr (TNTZ) alloys, quaternary Ti-Nb-Ta-Zr-O mixed-oxide nanotube arrays with controllable geometric features were prepared. Compared with pristine TiO₂, the TNTZO photoanodes exhibited noticeably enhanced photoactivity toward solar water splitting. The analytic results manifest that the superior photoactivity of TNTZO originated from the introduction of Nb, Ta, and Zr elements, which enhanced the amount of accessible charge carriers, modified the electronic structure, and improved the hole-transfer kinetics for expediting water splitting. Furthermore, reducing the water content of the electrolyte to 0.9 vol % generated TNTZO nanotubes that can be fully depleted during photoelectrochemical (PEC) operations, which may serve as a versatile structural backbone to construct a sophisticated photoelectrode paradigm. This work examined the realistic hydrogen evolution by employing TNTZO as the photoanode in the PEC water splitting cell.

研究分野：電気化学

キーワード：anodization nanotubes array water splitting

1. 研究開始当初の背景

TiO₂ is the most representative photocatalyst in recent decades. However, TiO₂ also suffers significant limitations. The most important drawback of TiO₂ photocatalyst is derived from the mismatch between the TiO₂ band gap energy and the sunlight spectra (key scientific question), which overlap only in the UVA and UVB ranges. Only high-energy UV irradiation sources can activate TiO₂. As a consequence, this technology can only take advantage of less than 5% of the solar energy impinging on the Earth's surface, limiting its potential as an environmentally sustainable technology. On the other hand, development of modified TiO₂ photocatalysts that can yield high reactivity under visible light allow the main part 43% of the solar spectrum (Asahi et al., Science 2001, 293, 269–271), and even poor illumination of interior lighting (our proposal), as show in Fig.1.

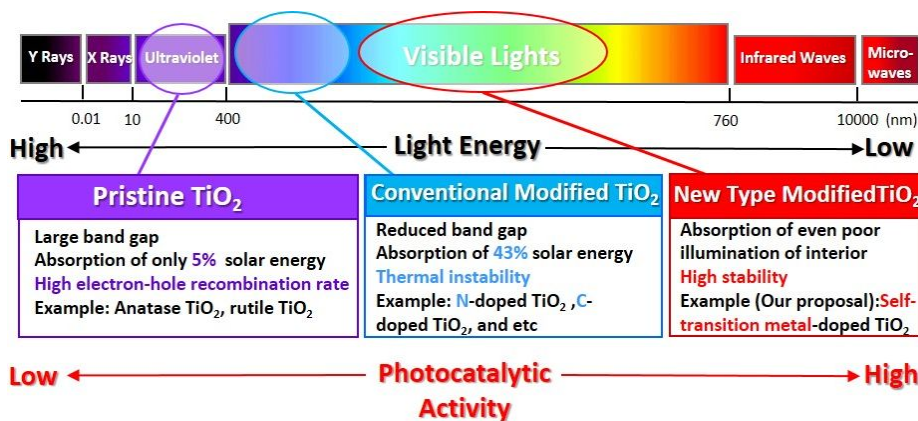


Fig.1 TiO₂ and modified TiO₂ absorption spectrum compared with solar spectrum.

In recent years, electrochemical anodization is considered as an efficient method to fabricate a variety of nanostructures. Among these nanostructures, nanotubes array is the representative nanostructures fabricated by anodization. With the nanotube backbone offering spatial decoupling of light absorption from carrier collection, this nanotubular array can find potential use for energy conversion applications, such as photoelectrochemical (PEC) water splitting. Common approaches (Schmuki et al., ACS Catal. 2017, 7, 3210–3235) that target a modification of the reactivity of these TiO₂ nanotubes are illustrated in Fig.2. Such approaches include surface alterations of the chemistry and of physical properties to establish electronic heterojunctions (e.g., secondary semiconductor/metal nanoparticle decoration), to induce electronic effects (such as doping or band gap engineering), or to alter the crystallinity. Among these methods, introducing foreign elements into the crystal structure of TiO₂ to achieve doping or band gap engineering is a promising approach to foster the application deployment of TiO₂ nanotubes. Nevertheless, the progress has been retarded by the difficulties of achieving uniform and homogeneous mixing of the foreign elements with TiO₂ nanotubes.

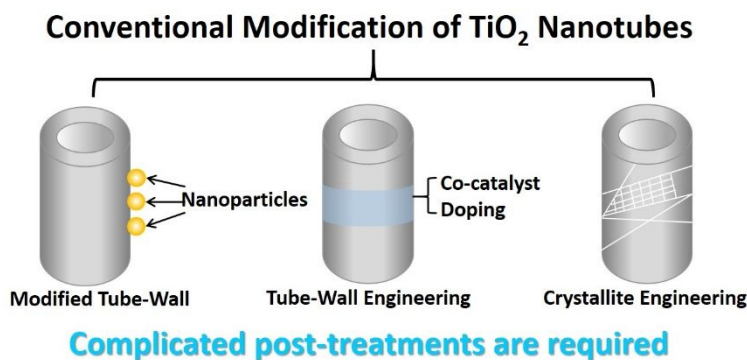


Fig.2 Conventional modification methods of TiO₂ nanotubes.

2. 研究の目的

The objective of this study is to fabricate self-doped quaternary Ti-Nb-Ta-Zr-O mixed oxide nanotubes arrays through a simple novel one-step anodization process of Ti-29Nb-13Ta-4.6Zr alloy, as shown in Fig.3. Ti-29Nb-13Ta-4.6Zr composed of non-toxic elements like Nb, Ta, and Zr, have been developed for

newgeneration biomaterials in the past. Nb oxide is a well-known material to increase the electron conductivity and mobility because of its shallow donor states. Besides, mixing with Zr and Ta oxides would also enhance the photocatalytic activity because of the narrowed band gap due to the doping effect of Nb, Ta, and Zr. There is no report of its photoactivity and PEC water splitting applications. This new Ti-Nb-Ta-Zr-O mixed oxide nanotubes are expected to effectively suppress the electron-hole pair recombination. Therefore, these attributes, together with the nanotubular architectures, make the present Ti-Nb-Ta-Zr-O nanotubes array an ideal photoanode candidate for conducting efficient water splitting. This proposal demonstrates the first example of employing quaternary mixed oxides photoelectrodes in PEC system, which paves the way for their advanced use in various photoconversion processes.

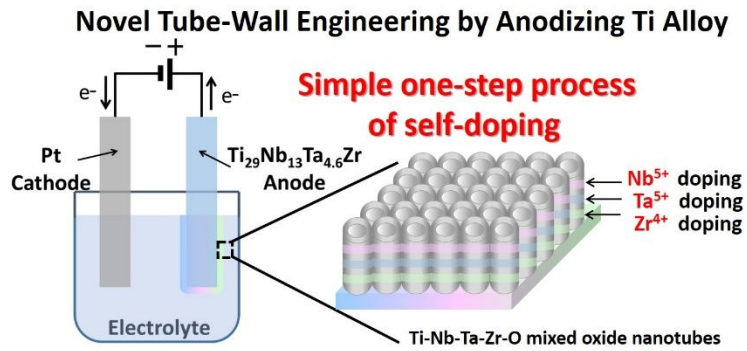


Fig.3 Novel one-step anodization of $\text{Ti}_{29}\text{Nb}_{13}\text{Ta}_{4.6}\text{Zr}$ alloy.

3 . 研究の方法

For anodization growth of Ti-Nb-Ta-Zr-O, a customized two-electrode cell was employed to conduct electrochemical anodization at 20 V. The alloy plate was used as the working electrode, whereas a Pt foil ($1.0 \text{ cm} \times 2.0 \text{ cm}$) was used as the counter. The supporting electrolyte was prepared by mixing the NH_4F -containing (0.3 wt %) ethylene glycol solution with a given content of deionized water. Upon anodization, the samples were gently rinsed using deionized water and allowed for annealing treatment in air at $500 \text{ }^\circ\text{C}$ for 3 h. In this work, the amount of water added to the electrolyte was varied (20, 10, 0.9 vol %) to obtain TNTZO with different geometric features. For PEC measurement, a quartz-windowed cell, comprising a Ag/AgCl electrode (saturated KCl) as a reference and a Pt foil as the counter, was configured for measurements. The electrolyte was composed of NaOH aqueous solution (1.0 M, pH = 13.9). The photoanodes were assembled by attaching a copper cable to the conductive part on the sample surface, followed by jointing using Ag conducting paint and epoxy. The illumination source was provided by a xenon lamp (Newport, LCS-100, 94011A) coupled with an AM 1.5G filter, giving a 1 sun illumination of 100 mW cm^{-2} . All of the PEC data including linear-sweep voltammograms (I-V curves) and chronoamperometry scans (I-t curves) were recorded from a potentiostat (Solartron 1287A) equipped with a 1252A frequency response analyzer. The EIS Nyquist plots were collected by applying the alternating current signal (10 mV) over the frequency range (100 kHz to 0.01 Hz) under AM 1.5G illumination at open-circuit conditions. To perform the Mott-Schottky analysis, the frequency was fixed at 1 kHz. The V_{oc} decay measurements were carried out by recording the V_{oc} value under AM 1.5G illumination, followed by monitoring subsequent decay after light irradiation was turned off.

4 . 研究成果

The obtained nanotube arrays were first studied with SEM to observe the microstructure. Fig. 4 displays the SEM images for the nanotubes anodically grown from the Ti foils and $\text{Ti}_{29}\text{Nb}_{13}\text{Ta}_{4.6}\text{Zr}$ alloys. Note that the anodization time was suitably tuned to achieve a comparable nanotube length for the different samples (approximately $2 \text{ }\mu\text{m}$), which eliminated the influence of nanotube length on the resultant PEC performance. For pristine TiO_2 from the Ti foils, the organized nanotubes were tightly packed with a wall thickness of $7.3 \pm 0.8 \text{ nm}$ and an inner diameter of $54.5 \pm 4.2 \text{ nm}$. The grown TNTZO nanotubes were also highly ordered and stacked with each other. Notably, tuning the water content of electrolyte evinced the growth of TNTZO nanotube arrays with distinct geometric features, i.e., varied inner diameters and wall thicknesses. When the water content decreased from 20 to 10 vol %, the inner diameter of the TNTZO nanotubes decreased from 50.0 ± 4.0 to $45.2 \pm 2.5 \text{ nm}$. As the water content was further reduced to 0.9 vol %, the inner diameter of TNTZO largely decreased to $33.6 \pm 3.9 \text{ nm}$. Such a decrease in the nanotube size can be understood from the retarded fluoride ion diffusion at a relatively low water content condition,

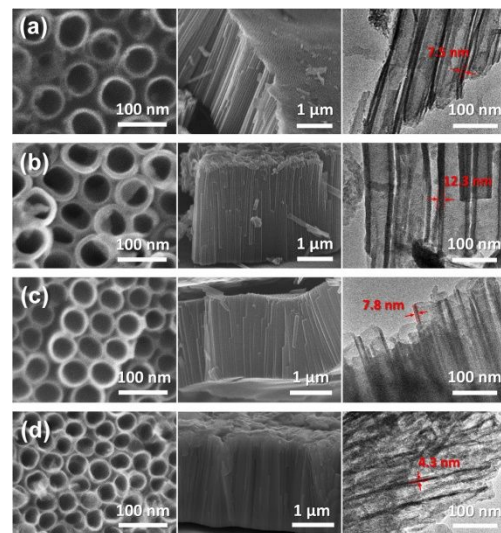


Fig.4 Top-view SEM, tilted-view SEM, and typical TEM images for (a) pristine TiO_2 , (b) TNTZO-1, (c) TNTZO-2, and (d) TNTZO-3 nanotube arrays.

which suppressed chemical dissolution for the grown oxides. The wall thicknesses of the grown nanotubes decreased monotonically with decreasing water content. As the water content was reduced from 20, 10, to 0.9 vol %, the wall thickness of TNTZO decreased from 12.6 ± 1.0 (TNTZO-1) to 7.7 ± 0.8 (TNTZO-2) and then 3.5 ± 0.5 nm (TNTZO-3). Such an observation was in line with literature reports on the anodization of Ti, in which the nanotube wall thickness of the grown TiO_2 decreased with decreasing water content in the electrolyte. Importantly, a reduction in the wall thickness to less than 5 nm has significant implications for advancing the PEC properties of semiconductor nanotubes because the kinetics of hole transportation from semiconductor to electrolyte can be facilitated under such a confined size regime, which will be demonstrated later in the charge dynamics measurements. The structural porosity was further determined to better describe the distinct geometric features for the present TNTZO nanotube arrays, which was 49.4, 59.7, and 71.5% for TNTZO-1, TNTZO-2, and TNTZO-3, respectively.

To examine the composition of the samples, we subsequently performed XRD and STEM-EDS analyses. In Fig.5 (a), the inserted marks (*) represent the signals of the Ti foil, and the inset shows the schematic crystal structure of TNTZO. Intensity ratios quite close to those of pristine TiO_2 , reflecting that pristine TiO_2 and TNTZO nanotubes grown from the current electrochemical anodization process shared identical crystallographic orientations. Compared with pristine TiO_2 , the (101) diffraction peak of TNTZO, however, slightly shifted to a lower 2θ value, pointing out an increase in the interlayer spacing for TNTZO as a result of the substitutional replacement of Ti^{4+} with Nb^{5+} , Ta^{5+} , and Zr^{4+} , which have larger atomic sizes. In Fig.5 (b), the STEM-EDS line-scan analysis taken across several compacted nanotubes of TNTZO further reveals the uniformity of the elemental compositions. This outcome correlated to the result of XRD characterization, which reflects a homogeneous distribution of Ti, Nb, Ta, Zr, and O within the TNTZO lattice. According to the EDS result, the content of Ti, Nb, Ta, and Zr was, respectively, determined to be 24.79, 11.65, 2.59, and 0.78 at. %, similar to the composition of the starting $\text{Ti}_{29}\text{Nb}_{13}\text{Ta}_{4.6}\text{Zr}$ alloy.

Fig.6 (a) shows the typical I-V curves for pristine TiO_2 and TNTZO electrodes, which displayed several important features. First, the dark scans exhibited a fairly low current density (approximately $10^{-7} \text{ A cm}^{-2}$), revealing that both TiO_2 and TNTZO were considerably stable during their operation in an alkaline electrolyte. Second, compared with pristine TiO_2 , the three TNTZO electrodes displayed higher saturated photocurrent densities, disclosing the intriguing photoactive nature of TNTZO. Here, we attributed the enhanced photoactivity of TNTZO to the introduced Nb, Zr, and Ta elements, which not only induced shallow donor states to increase the carrier concentration, but also suppressed trap states formation to facilitate charge carrier transfer. Third, among the three TNTZO electrodes tested, TNTZO-3 attained the highest photocurrent generation of 0.28 mA cm^{-2} at 0 V versus Ag/AgCl (+1.02 V vs RHE). In practice, nanotube arrays possessing a wall thickness substantially smaller than the hole diffusion length (around 10 nm for TiO_2) are highly desired for the design of sophisticated photoanodes because the possible hole loss along the radial direction can be minimized. On the other hand, the large structural porosity may equip the nanotube arrays with abundant inner space for accelerating molecular migration inside the tube, which also helps to enhance the kinetics of water oxidation reaction. Because the geometric feature of TNTZO-3 was characteristic of the thinnest wall thickness (3.5 nm) and the largest structural porosity (71.5%), the resultant PEC performance was predominant over TNTZO-1 and TNTZO-2. To investigate the instant photoresponse behavior, the I-t curves were measured under chopped light irradiation. As Fig. 6(b) shows, the photocurrent generation of TNTZO quickly reached a steady state without any accompanying spikes; under the light-off condition, the photocurrents were quickly reduced to nearly zero without exhibiting a photocurrent tail. This phenomenon signified that the photocurrent generation of TNTZO was instantaneous without the occurrence of carrier trapping events, which is an important merit for consideration as a

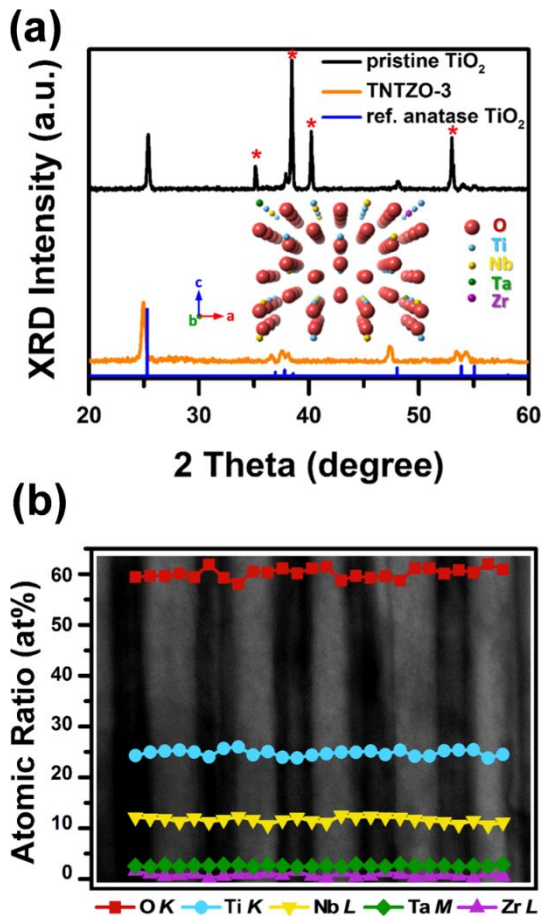


Fig.5 (a) XRD patterns for pristine TiO_2 and TNTZO nanotubes. (b) STEM-EDS line-scan analysis taken on the lateral side of TNTZO nanotube arrays.

practical photoelectrode.

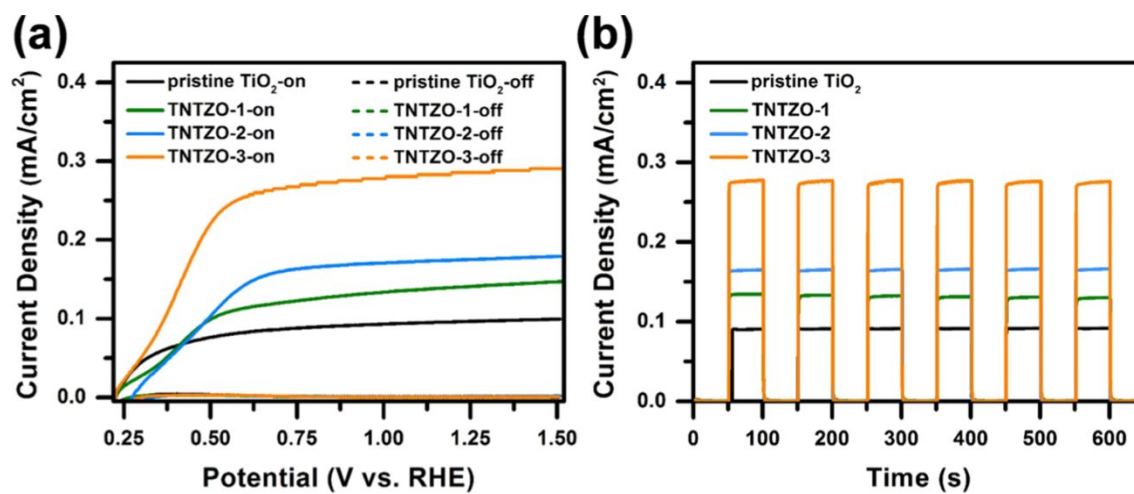


Fig.6 (a) I–V curves of pristine TiO₂ and the three TNTZO electrodes recorded under darkness and AM 1.5G illumination. (b) The corresponding I–t curves obtained at 0 V vs Ag/AgCl (+1.02 V vs RHE) under chopped light irradiation.

5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

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8 . 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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