



Doping of anodic nanotubular TiO₂ electrodes with MnO₂ for use as catalysts in water oxidation



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ABSTRACT

MnO₂ was homogeneously doped into anodic nanotubular TiO₂ by a potential shock method, in which a high potential was imposed on the anodic nanotubes immediately after anodization process. We found that the potential shock process is inapplicable in a high-conductivity aqueous electrolyte, e.g. a MnO₂ precursor solution (herein, 0.006 M KMnO₄: 852–933 μS/m). To avoid exceeding the output compliance of the current source, the potential shock voltage was optimized in ethylene glycol for the application of water oxidation. We found an optimal potential shock voltage of 140 V, which led to the doping of 0.7 at. % MnO₂ into the high-aspect-ratio nanotubular TiO₂ within 10 s. The TiO₂ nanotubes doped with MnO₂ were successfully employed as electrodes for the non-noble catalysis of water oxidation. Although the doping concentration of Mn was found to be linearly proportional to the applied potential shock voltages, potential shocks greater than 140 V significantly increased the thickness of the barrier oxide layer, which increased the overpotential in the water oxidation process.

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1. Introduction

The anodization of metals has long been studied in order to improve the metal's surface properties, such as corrosion and abrasion, or to decorate a metal's surface with various colors [1–5]. In the past 10 years, the anodization of Ti has attracted much attention as a protocol to homogeneously produce 1 D semiconductive nano-objects for catalysis and photocatalysis, nanodevices, active components in energy storage or generation systems, smart membranes, and other purposes [6–9]. Morphological tuning for surface enlargement and bandgap tailoring by foreign elements has both been used to increase the catalytic and photocatalytic properties of anodic TiO₂ nanotubes [10–14].

Because of the high-aspect-ratio structure of nanotubes, a few successful examples exist of homogeneously doped foreign elements over the entire surface of anodic TiO₂ nanotubes without complicated processes [15–19]. Recently we have reported on the use of the potential shock method, in which an abrupt positive-biased potential is imposed on TiO₂ nanotubes in an electrolyte containing negatively charged foreign ions immediately after anodization completed. The method was shown to be an

effective and time-saving process for forming RuO₂-doped TiO₂ electrodes for water oxidation [20–22]. In addition, the single-step anodization in the negatively charged precursor allows the homogenous doping of RuO₂ in anodic TiO₂ nanotubes without further treatment [23].

Because of the high cost of noble metal oxide catalysts, TiO₂ has been studied as a cheap alternative metal oxide catalyst for water oxidation. From the perspective of density functional theory calculation, TiO₂ doped with transition metals, (such as Cr, Mo, and Mn) shows considerably enhanced oxygen evolution reaction (OER) activity as a non-noble catalyst [24–27]. Xu et al. reported the remarkably active photocatalytic properties of MnO₂/TiO₂ nanotube arrays, capable of decomposing acid orange II under visible illumination [28]. Several studies on MnO₂ itself as a catalyst for OER of water have been performed [11].

This work aims to produce anodic TiO₂ nanotubes doped with MnO₂ for use as catalysts by a simple doping process. Compared to the formation of anodic TiO₂ nanotubes with RuO₂, MnO₂ doping by an electrochemical method with a negatively charged precursor is expected to be relatively difficult, since the MnO₄[−] (Mn⁴⁺) ion is easily reduced to Mn²⁺ due to its high reduction potential (+1.23 V vs. NHE) [21]. In the case of potential shock with aqueous electrolytes, an excessively high current density is required to impose the appropriate potential shock, due to the high ionic conductivity of the KMnO₄ precursor. In this work, we demonstrate a novel

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Table 1
Analysis conditions for inductively coupled plasma mass spectrometer (ICP-MS).

ICP-MS spectrometer	PerKinElmer, ELAN 6100
RF Power	1200 W
Plasma Ar gas flow	18 L/min
Auxiliary Ar gas flow	1.2 L/min
Nebulizer Ar gas flow	0.92 L/min
Nebulizer	Meinhard type (quartz)
Spray chamber	Cyclonic
Lens voltage	13 V
Dwell time	50 ms
Replicate	3
Detector mode	Dual

potential shock method in a non-aqueous electrolyte to dope MnO₂ on high-aspect-ratio TiO₂ nanotubes, which were then successfully used as catalysts in water oxidation.

2. Experimental

Fabrication of anodic TiO₂ nanotubes: Anodic oxide films with nanotubular morphology were generated on Ti foil (0.127 mm thickness, 99.7% purity, 15 mm × 15 mm, Sigma-Aldrich) by an electrochemical method. The Ti foil was pretreated with acetone, ethanol, and distilled water (DI) for 15, 10, and 5 min, to eliminate impurities on the surface. Afterward, the foil was dried under air circulation in an oven at 60 °C for 1 h. Anodization was conducted in a mixed solution of 1 M NaOH (Daejung, South Korea), 1 M H₃PO₄ (Sigma-Aldrich) and 0.5 wt. % HF (Sigma-Aldrich) using a DC power supply (SourceMeter 2400, Keithley) at 20 V for 4 h at room temperature with a two-electrode electrochemical cell, consisting of the Ti foil as the working electrode and a Pt mesh as the counter electrode.

Potential shock to incorporate MnO₂ into anodic TiO₂ nanotubes: To dope MnO₂ into the anodic TiO₂ nanotubes, KMnO₄ (Sigma-Aldrich) was used as the Mn source. High voltages of 80–200 V were imposed on the as-prepared TiO₂ nanotubes using a DC power supply (SourceMeter 2400, Keithley) for 10 s in an ethylene glycol (EG) solution containing 0.006 M KMnO₄ at room temperature. The MnO₂-doped TiO₂ nanotubes were cleaned with deionized water and then dried in an oven at 60 °C for a day. Before the water oxidation experiments, thermal annealing was performed to crystallize the nanotubular TiO₂ in an air furnace at 450 °C for 1 h.

Structural and component analysis: The morphological analysis of the TiO₂ nanotubes was performed with a field-emission scanning electron microscope (FE-SEM, S-4300, Hitachi, Japan) and transmission electron microscope (TEM, JEM-2100F, JEOL) to obtain top, bottom, and cross-sectional images. Component analysis was performed by energy-dispersive X-ray spectroscopy (EDX, S-4300, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS, VGESCALAB 220i-XL spectrometer, Fison) equipped with an Al-Kα X-ray source.

The elemental concentration of the doped MnO₂ in the prepared TiO₂ nanotubes was determined by an inductively coupled plasma mass spectrometer (ICP-MS, ELAN 6100, PerkinElmer) under high-purity Ar (99.999%). Operating conditions for ICP-MS are presented in Table 1.

Water oxidation of TiO₂: Linear sweep voltammetry (LSV) was performed to measure the water oxidation efficiency of electrodes consisting of the MnO₂-doped TiO₂ nanotubes, using a three-electrode galvanostatic system (Autolab, PGSTAT 302 N, Netherlands) in 1 M KOH (OCI). The scan rate was set to 0.1 V/s in the range of 0–2.5 V. The mechanism of charge transfer at the electrode/electrolyte interface was characterized by electrochemical impedance spectroscopy (EIS) measurements using a frequency

response analyzer (Autolab, PGSTAT 302 N, Netherlands) at 0.7 V over the frequency range between 100 kHz and 0.01 Hz with the amplitude of 10 mV in 1 M KOH.

3. Results and discussion

Several methods were attempted to fabricate homogeneously MnO₂-doped TiO₂ nanotubes (Fig. 1). First, anodization of Ti was performed in EG containing F⁻ with the addition of KMnO₄ as a source of MnO₂ (so-called single-step anodization). With this approach, unlike the formation of RuO₂-doped TiO₂ by single-step anodization [23], no results showed the successful doping of MnO₂ into nanotubular TiO₂. We suppose that anodic oxidation via F⁻ contribution predominantly occurs as anion competition between F⁻ and MnO₄⁻, because of the higher tendency of reduction of MnO₄⁻ (Mn⁷⁺) to Mn²⁺ in the electrolyte (+1.23 V vs. NHE). Thus, during the single-step anodization, the MnO₄⁻ precursor self-reduces to Mn²⁺, which oxidizes other components in the electrolyte, leading to the electrochemical deposition of Mn on the counter electrode instead of the desired anodic doping of the TiO₂ nanotubes.

As a second approach, we adopted the potential shock method, in which a high voltage was imposed on the anodic nanotubular TiO₂ for a short time immediately after the anodization concluded. We found that the aqueous 0.006 M KMnO₄ solution's conductivity (852–933 μS/m) exceeds that of aqueous KRuO₄, with which we successfully used the potential shock method for doping [21]. The necessary high applied potential could not be imposed on the nanotubes using our equipment, because of the output compliance of our current source. As an alternative, the potential shock method was used with an EG solution containing 0.006 M KMnO₄, with an overall conductivity of 35.5–37.5 μS/m, instead of the aqueous solution.

Fig. 2 shows nanotubular TiO₂ anodized in a mixture of 1 M NaOH, 1 M H₃PO₄, and 0.5 wt. % HF both before and after MnO₂ doping by the potential shock method, demonstrating that the morphologies are not significantly changed with doping. From the

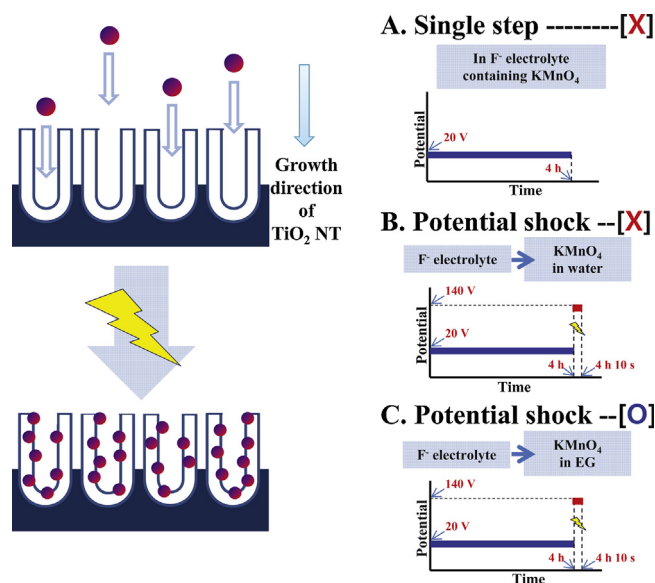


Fig. 1. Scheme of strategies for doping MnO₂ in high-aspect-ratio TiO₂ nanotubes. (A): single-step anodization was performed in a mixture of 1 M NaOH, 1 M H₃PO₄, and 0.5 wt. % HF with 0.006 M KMnO₄ at 20 V for 4 h. (B): a positively-biased potential shock with voltage varying from 80 V to 200 V was applied to anodic TiO₂ nanotubes in aqueous 0.006 M KMnO₄. C: The aqueous solution mentioned in B is substituted by ethylene glycol; all other conditions are maintained from B.

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