



# Doping of anodic nanotubular TiO<sub>2</sub> electrodes with MnO<sub>2</sub> for use as catalysts in water oxidation



Mijeong Seong, Sunkyu Kim, Hyeonseok Yoo, Jinsub Choi\*

Department of Chemistry and Chemical Engineering, Center for Design and Applications of Molecular Catalysts, Inha University, Incheon 402-751, South Korea

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## ABSTRACT

MnO<sub>2</sub> was homogeneously doped into anodic nanotubular TiO<sub>2</sub> 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 MnO<sub>2</sub> precursor solution (herein, 0.006 M KMnO<sub>4</sub>: 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. % MnO<sub>2</sub> into the high-aspect-ratio nanotubular TiO<sub>2</sub> within 10 s. The TiO<sub>2</sub> nanotubes doped with MnO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 RuO<sub>2</sub>-doped TiO<sub>2</sub> electrodes for water oxidation [20–22]. In addition, the single-step anodization in the negatively charged precursor allows the homogenous doping of RuO<sub>2</sub> in anodic TiO<sub>2</sub> nanotubes without further treatment [23].

Because of the high cost of noble metal oxide catalysts, TiO<sub>2</sub> has been studied as a cheap alternative metal oxide catalyst for water oxidation. From the perspective of density functional theory calculation, TiO<sub>2</sub> 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 MnO<sub>2</sub>/TiO<sub>2</sub> nanotube arrays, capable of decomposing acid orange II under visible illumination [28]. Several studies on MnO<sub>2</sub> itself as a catalyst for OER of water have been performed [11].

This work aims to produce anodic TiO<sub>2</sub> nanotubes doped with MnO<sub>2</sub> for use as catalysts by a simple doping process. Compared to the formation of anodic TiO<sub>2</sub> nanotubes with RuO<sub>2</sub>, MnO<sub>2</sub> doping by an electrochemical method with a negatively charged precursor is expected to be relatively difficult, since the MnO<sub>4</sub><sup>−</sup> (Mn<sup>4+</sup>) ion is easily reduced to Mn<sup>2+</sup> 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 KMnO<sub>4</sub> precursor. In this work, we demonstrate a novel

\* Corresponding author.

E-mail address: [jinsub@inha.ac.kr](mailto:jinsub@inha.ac.kr) (J. Choi).

**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 MnO<sub>2</sub> on high-aspect-ratio TiO<sub>2</sub> nanotubes, which were then successfully used as catalysts in water oxidation.

## 2. Experimental

**Fabrication of anodic TiO<sub>2</sub> 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 H<sub>3</sub>PO<sub>4</sub> (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 MnO<sub>2</sub> into anodic TiO<sub>2</sub> nanotubes:** To dope MnO<sub>2</sub> into the anodic TiO<sub>2</sub> nanotubes, KMnO<sub>4</sub> (Sigma-Aldrich) was used as the Mn source. High voltages of 80–200 V were imposed on the as-prepared TiO<sub>2</sub> nanotubes using a DC power supply (SourceMeter 2400, Keithley) for 10 s in an ethylene glycol (EG) solution containing 0.006 M KMnO<sub>4</sub> at room temperature. The MnO<sub>2</sub>-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> in an air furnace at 450 °C for 1 h.

**Structural and component analysis:** The morphological analysis of the TiO<sub>2</sub> 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-K $\alpha$  X-ray source.

The elemental concentration of the doped MnO<sub>2</sub> in the prepared TiO<sub>2</sub> 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 TiO<sub>2</sub>:** Linear sweep voltammetry (LSV) was performed to measure the water oxidation efficiency of electrodes consisting of the MnO<sub>2</sub>-doped TiO<sub>2</sub> 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

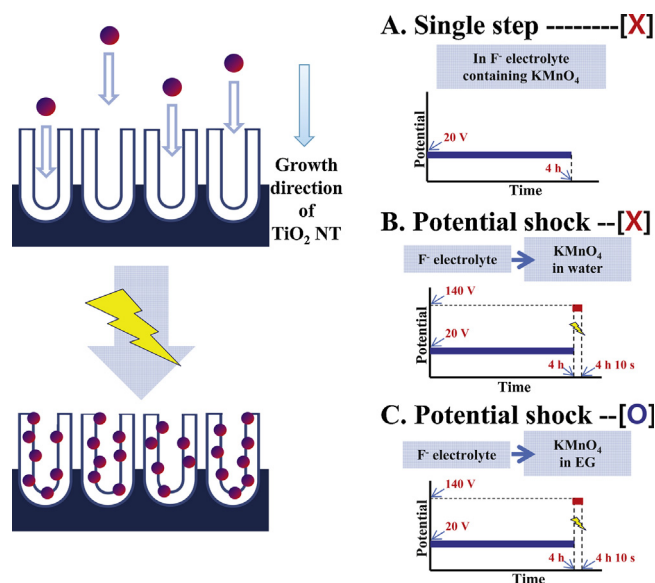
response analyzer (Autolab, PGSTAT 302 N, Netherlands) at 0.7 V over the frequency range between 100 kHz and 0.01 Hz with the amplitude of 10 mV in 1 M KOH.

## 3. Results and discussion

Several methods were attempted to fabricate homogeneously MnO<sub>2</sub>-doped TiO<sub>2</sub> nanotubes (Fig. 1). First, anodization of Ti was performed in EG containing F<sup>-</sup> with the addition of KMnO<sub>4</sub> as a source of MnO<sub>2</sub> (so-called single-step anodization). With this approach, unlike the formation of RuO<sub>2</sub>-doped TiO<sub>2</sub> by single-step anodization [23], no results showed the successful doping of MnO<sub>2</sub> into nanotubular TiO<sub>2</sub>. We suppose that anodic oxidation via F<sup>-</sup> contribution predominantly occurs as anion competition between F<sup>-</sup> and MnO<sub>4</sub><sup>-</sup>, because of the higher tendency of reduction of MnO<sub>4</sub><sup>-</sup> (Mn<sup>7+</sup>) to Mn<sup>2+</sup> in the electrolyte (+1.23 V vs. NHE). Thus, during the single-step anodization, the MnO<sub>4</sub><sup>-</sup> precursor self-reduces to Mn<sup>2+</sup>, 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 TiO<sub>2</sub> nanotubes.

As a second approach, we adopted the potential shock method, in which a high voltage was imposed on the anodic nanotubular TiO<sub>2</sub> for a short time immediately after the anodization concluded. We found that the aqueous 0.006 M KMnO<sub>4</sub> solution's conductivity (852–933  $\mu$ S/m) exceeds that of aqueous KRuO<sub>4</sub>, 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 KMnO<sub>4</sub>, with an overall conductivity of 35.5–37.5  $\mu$ S/m, instead of the aqueous solution.

Fig. 2 shows nanotubular TiO<sub>2</sub> anodized in a mixture of 1 M NaOH, 1 M H<sub>3</sub>PO<sub>4</sub>, and 0.5 wt. % HF both before and after MnO<sub>2</sub> 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 MnO<sub>2</sub> in high-aspect-ratio TiO<sub>2</sub> nanotubes. (A): single-step anodization was performed in a mixture of 1 M NaOH, 1 M H<sub>3</sub>PO<sub>4</sub>, and 0.5 wt. % HF with 0.006 M KMnO<sub>4</sub> 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 TiO<sub>2</sub> nanotubes in aqueous 0.006 M KMnO<sub>4</sub>. C: The aqueous solution mentioned in B is substituted by ethylene glycol; all other conditions are maintained from B.

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