Journal of Power Sources 280 (2015) 339–346

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Influence of electrolyte composition on the formation of mixed oxide nanotube arrays for solar fuel production

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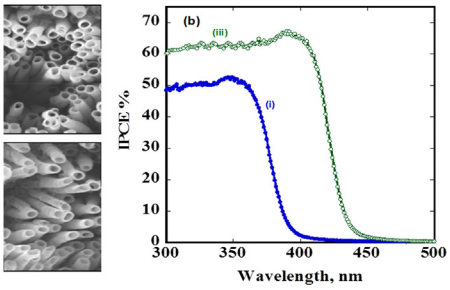
## HIGHLIGHTS

- $TiO_2$ nanotubes containing Ni and Mo were successfully produced form Ti–Ni–Mo alloy.
- The electrolyte composition determined the structural features of the resulted nanotubes.
- The Ti–Mo–Ni mixed oxide nanotubes exhibited visible light activity.
- The Ti–Mo–Ni oxide nanotubes exhibited higher IPCE values than their pure $TiO_2$ counterparts.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 4 December 2014
Received in revised form
4 January 2015
Accepted 17 January 2015
Available online 19 January 2015

*Keywords:*
Solar
Hydrogen
Photoanode
Mixed oxide
Ti–Mo–Ni
Nanotube

## ABSTRACT

Water splitting using sunlight is an important process for future energy supplies. $TiO_2$ is widely used as photoanode, but has a limited light absorption range. Here, ternary Ti–Mo–Ni mixed oxide nanotube arrays were fabricated via electrochemical anodization of Ti–Mo–Ni alloy in formamide-ethylene glycol-based electrolytes, to extend the absorption range into visible light. The electrolyte composition and anodization time were found crucial in controlling the structural features of the nanotubes. By tuning these parameters, arrays of thin walled (~9 nm) and ~8 μm long nanotubes were obtained. In photoelectrochemical water splitting, the mixed oxides showed incident photon conversion efficiency (IPCE) up to 65% for wavelengths from 300 nm to 450 nm. This enhancement in the IPCE of the mixed oxide nanotubes, compared with pure titania, can be related to synergistic effects of Mo and Ni oxides as well as to the unique structural properties of the fabricated mixed oxide nanotubes.



## 1. Introduction

Decreasing global energy resources and increasing environmental demands signify that renewable energy sources will be of great importance in the future. The main problem of using some renewable energy sources (sun and wind) is that they are not storable or transportable. Water splitting via solar energy represents an attractive route to produce hydrogen, which has high potential in the hydrogen economy as a sustainable and storable energy source [1].

Owing to their semiconducting properties, physical and chemical stability, abundance and low cost, metal oxide photoanodes are

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http://dx.doi.org/10.1016/j.jpowsour.2015.01.108
0378-7753/

mainly used in hydrogen production photoelectrochemical cells (PEC) [2,3]. Anodically fabricated $TiO_2$ nanotube arrays are extensively investigated for many applications, especially photoelectrochemical water splitting and solar cells [2,4–6]. Accurate control of the geometrical properties of the nanotubular structures facilitates the tuning of the specific light absorption and propagation characteristics [6,7]. Furthermore, the activity of the nanotubular structure as an electron infiltration pathway for vectorial charge transfer between interfaces can be controlled by the aligned porosity, crystallinity, and oriented nature of the nanotubular structure [8,9]. However, owing to its large band gap (3.2 eV), only photocatalysis using UV radiation is possible. With 3–5% UV comprises just a small fraction of the solar spectrum, compared with 45% for visible light. Therefore, any shift in the optical response of $TiO_2$ from the UV to the visible light range, while maintaining its robust properties, would render this material very efficient in water splitting.

There are several strategies in the literature to improve the absorption properties of $TiO_2$. Compositional doping of $TiO_2$ using different elements was considered as an approach for band gap engineering [10–13]. However, currently used doping methods are not without problems. Structural artifacts and defects that result in defect-dopant-lattice interactions can block the essential interactions of the dopant with the lattice. Decoration of $TiO_2$ nanotubes with metal and/or semiconductor nanoparticles has been used as an alternative approach to enhance the spectral response and catalytic properties of the material [14–17]. However, the lack of control over parameters such as particle size, cleanness, distribution on their nanotubes' surfaces/walls and the possibility of nanoparticles to aggregate limit their efficient use. The distribution of particles can be better controlled with the introduction of linker molecules that attach nanoparticles to the nanotube surface, but this presents charge carrier recombination problems [18,19].

A recent and promising approach to overcome the above-mentioned limitations, as they pertain to photocatalytic properties and applications, is to employ semiconductor materials with 1D nanoarchitectures of mixed oxides. The anodization process has shown its effectiveness in fabricating several kinds of mixed oxide nanotubes. Mor et al. [20] fabricated Ti–Fe–O mixed oxide nanotube arrays with enhanced photoelectrochemical water splitting performance. Allam et al. [21] fabricated Ti–Nb–Zr–O nanotubes through one-step anodization, which showed a ~17.5% increase in photoelectrochemical water splitting efficiency compared with pure $TiO_2$ nanotube arrays. Also, Allam et al. [22] reported the fabrication of Ti–Pd oxynitride nanotube arrays, which demonstrated a photocurrent density of 1.9 mA $cm^{-2}$ and a 5-fold increase in the photoconversion efficiency under AM 1.5 illumination compared with pure $TiO_2$ nanotubes.

Interesting for the present study are the findings by Liang et al. [23] and Zhang et al. [24], who reported that Ni and Mo doping could enhance the optical absorption ability of $TiO_2$ with enhanced photocurrent. The enhanced photocatalytic activity was attributed to NiO and $MoO_3$, which help to slow down charge recombination and assist the hole diffusion to the material/electrolyte interface [25]. Motivated by these results, we studied the preparation and photoelectrochemical properties of Ti–Ni–Mo oxide nanotube arrays, prepared from formamide-based electrolytes [25]. These mixed oxide nanotube arrays were shown to have improved absorption and photocurrent efficiency, compared with pure $TiO_2$ [25]. In the present study we investigate the influence of ethylene glycol in the formamide based electrolyte on the morphology and photoelectrochemical properties of Ti–Ni–Mo oxide nanotube arrays.

## 2. Experimental section

### 2.1. Fabrication of Ti–Mo–Ni oxide nanotubes

Prior to anodization, Ti-0.3Mo-0.8Ni alloy samples (purchased from Firmetal Co., Ltd.) were ultrasonically cleaned with acetone followed by a deionized water rinse. The anodization was performed in a two-electrode electrochemical cell with the alloy as the working electrode and platinum gauze as the counter electrode. The experiments were conducted at room temperature in formamide (FA) and ethylene glycol (EG)-based electrolytes containing 0.2 M $NH_4F$, and 3 vol % $H_2O$. Anodization was carried out for 3–18 h at 20 V for 50:50 FA:EG and 40 V for 75:25 FA:EG mixtures. After anodization, the samples were rinsed thoroughly with acetone and deionized water. The as-anodized samples were annealed in air for 5 h at 500 °C with a heating and cooling rate of 20 °C/min.

### 2.2. Morphological, structure and compositional characterization

The morphology of the anodized samples was examined using a JEOL-JSM7000F field emission scanning electron microscope (FE-SEM). The crystalline phases were measured and identified by X–ray diffraction (XRD, Diffractometer Bragg Bantano, Bruker D500, Germany). The surface composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 5600. Spectra were charge-referenced to O 1s at 532 eV.

The $TiO_2$ nanotube length, diameter and wall thickness and their standard deviation were calculated from approximately 30 nanotubes on three different SEM images taken at different locations of each sample.

### 2.3. Photoelectrochemical characterization

The incident photon conversion efficiency (IPCE) experiments were performed in a two-electrode arrangement with the nanotube array films as the working photoelectrode and platinum foil as a counter electrode at 0.6 V applied dc bias in 1.0 M KOH solution. Sunlight was simulated with a 300 W xenon lamp and AM 1.5G filter at 100 mW $cm^{-2}$.

## 3. Results and discussion

### 3.1. Morphological characterization

The anodization of Ti–Mo–Ni alloy samples has been performed in formamide (FA) and ethylene glycol (EG)-based electrolytes because the anodization of titanium [6] and its alloys [26] in aqueous electrolytes usually results in the formation of short nanotubes with irregular outer diameters that contain ridges and circumferential serrations. Anodization in formamide and ethylene glycol, on the other hand, is well-known to result in the formation of smooth nanotubes several microns in length [2,20].

We previously presented the successful preparation of photoelectrochemically active Ti–Ni–Mo oxide nanotubes from formamide-based electrolytes [25]. Additionally, preliminary studies showed that the anodization of our Ti–Ni–Mo alloy in ethylene glycol resulted in smooth nanotube arrays that poorly adhered to the substrate. Therefore, mixtures of formamide and ethylene glycol were studied to optimize the nanotube preparation. Initially a 50:50 mixture was tested at an anodization voltage of 20 V.

Fig. 1 shows FE-SEM top-view and cross-sectional images for Ti–Mo–Ni oxide nanotubes prepared using 50% formamide (FA) and 50% ethylene glycol (EG)-based electrolytes containing 0.2 M $NH_4F$, 0.1 M $H_3PO_4$ and 3 vol % $H_2O$ at 20 V for different times. The