Electrochemistry Communications 82 (2017) 112–116

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Molybdenum dichalcogenide nanotube arrays for hydrogen-evolution-reaction catalysis: Synergistic effects of sulfur and selenium in a core-shell tube wall

Xuemei Zhou[a], Jan Prikryl[b], Milos Krbal[b], Jan M. Macak[b], Patrik Schmuki[a,*]

[a] Department of Materials Science, Institute for Surface Science and Corrosion (LKO), University of Erlangen-Nuremberg, Martensstr. 7, 91058 Erlangen, Germany
[b] Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic

ARTICLE INFO

Keywords:
Anodization
Nanotube
Mo-dichalcogenide
Hydrogen evolution

ABSTRACT

The present work shows the growth and conversion of self-organized anodic Mo-oxide nanotube arrays to core-shell structures consisting of a conducting molybdenum sub-oxide core and a shell of Mo-Se/S – this structure is then investigated for electrochemical hydrogen evolution catalysis. To form the core-shell tubes, we first anneal MoO_3 nanotube arrays under vacuum conditions, to induce reduction to MoO_2. Subsequently these oxide tubes are thermally sulfurized and selenized resulting in dichalcogenide@sub-oxide structures. Under optimized conditions, the mixed dichalcogenide (selenized and sulfurized) tube walls on the conductive oxide core lead to a synergistic beneficial effect for the electrocatalytic H_2 generation from H_2SO_4 solution.

1. Introduction

Molybdenum dichalcogenides (MoX_2) have been investigated as promising functional materials for decades due to a number of unique intrinsic chemical and physical properties [1–3]. A key feature is the weak van der Waals forces between the layered Mo-X units that allows for easy ion intercalation and exfoliation of individual MoX sheets. As a result, MoX_2 structures can be used for wide range of layered devices such as transistors to lasers [4], high energy density super-capacitors [5], Li-ion batteries [6], and photocatalysts [7–8]. Moreover, recently MoX_2-functionalized electrodes have increasingly been studied for electrochemical hydrogen generation where MoX_2 structures can significantly reduce the overpotential for the hydrogen evolution reaction [9–12].

Nevertheless, MoX_2 typically has a low intrinsic electrical conductivity, thus the catalyst is often decorated as a thin layer or nanoparticle powder mixtures [13–14] on a conductive nanostructured scaffold, hence providing short charge carrier and ion diffusion pathways [9,15–16].

The use of nanostructured MoX_2 geometries additionally delivers a high specific surface area with a high density of active sites. Most investigated for HER-catalysis are MoS_2 or $MoSe_2$. However, recent investigations of molybdenum sulfoselenides have reported that such mixed MoX_2 combinations can be even more active as the free energy of the reactive sites is optimized, particularly for S/Se ratios close to 1 [17–18].

Methods to prepare Mo dichalogenide nanostructures were pioneered > 20 years ago by Tenne et al. [19]. The most common synthetic approaches include chemical vapor deposition (CVD) [20], gas-phase reactions [21], electrodeposition [22], liquid exfoliation [23], or wet-chemical template-assisted approaches [24].

A very direct way to prepare functional nano-structured oxide electrodes is by self-organized anodization of a Mo-metal sheet. Using this approach, Mo-oxide nanotube arrays can be formed as 1D scaffolds and then be converted to chalcogenides. MoO_3 oxide nanotube structures commonly show a low electron conductivity and thus are less effective as an electrode than molybdenum sub-oxide (MoO_2) that provides a drastically higher electron-conductivity [25–26].

In the present work, we form Mo-oxide nanotubular structures by self-ordering electrochemical anodization [27]. Then we anneal the as-anodized sample in vacuum to obtain molybdenum sub-oxide nanostructures. The Mo sub-oxide samples are then thermally selenized and/or sulfurized to convert the oxide tube wall partially to the desired MoX_2 species.

We show that these tubes beneficially combine the HER catalytic properties of mixed MoX_2 compounds and the conductivity of the MoO_2 scaffold.

---

* Corresponding author.
E-mail address: schmuki@ww.uni-erlangen.de (P. Schmuki).

http://dx.doi.org/10.1016/j.elecom.2017.08.004
Received 19 July 2017; Received in revised form 3 August 2017; Accepted 3 August 2017

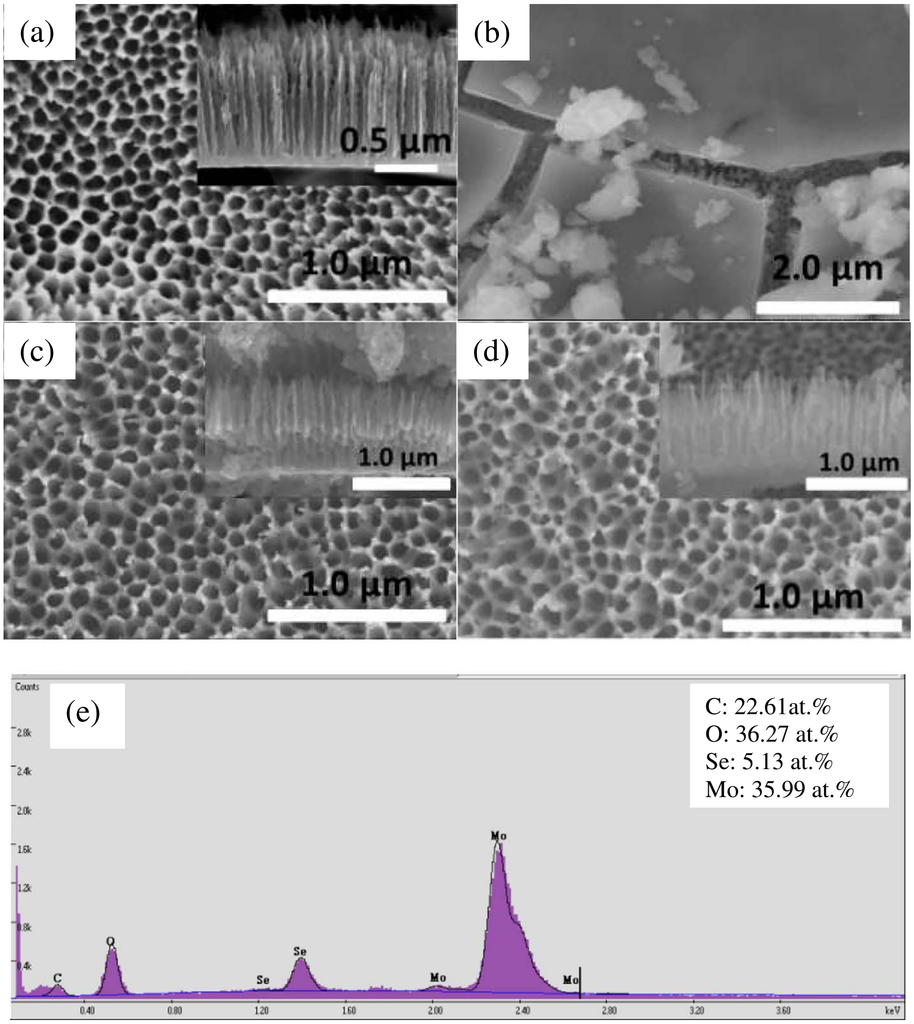

Fig. 1. SEM top and cross-sectional images for Mo-oxide nanotube arrays before and after selenization and sulfurization treatments: (a) anodic layer after annealing in vacuum at 300 °C for 1 h, (b) after selenization at 500 °C for 1 min, (c) after selenization at 350 °C for 10 min, (d) after selenization at 350 °C for 10 min and sulfurization at 300 °C for 2 min. (e) EDX results for sample treated after selenization at 350 °C for 10 min.

2. Experimental section

Self-ordered arrays of molybdenum oxide (MoO_3) nanotubes were grown on Mo foils of a 0.1 mm thickness and 99.6% purity. Before anodization, the foils were degreased by ultrasonication in acetone and ethanol successively, rinsed with deionized (DI) water, and dried in a nitrogen stream. Anodization was performed in a two-electrode system using a Pt sheet as a counter electrode. The MoO_3 nanotubes were prepared in glycerol-water electrolyte (volume ratio 9:1) containing 0.4 M NH_4F at 35 V for 1 h to achieve an approx.1 µm thick nanotubular film. After anodization the resulting layers were kept in the electrolyte for 3–5 min, then immersed into ethanol to remove the rest of electrolyte, and dried in nitrogen. To crystallize and reduce the samples, the substrates were annealed at 350 °C for 1 h in vacuum (further noted as MoO_2).

Selenization was then carried out in a tube furnace in a temperature range from 300 °C to 500 °C for 1 to 10 min. MoO_2 nanotube arrays and 0.2 g Se were placed into a quartz ampoule, evacuated to 2×10^{-4} Pa and sealed. Next, the ampoule was exposed to the target temperature with a rate 5 °C/min, equilibrated for 1 to 10 min and then gradually (within 10 h) lowered to room temperature.

After selenization, the samples were annealed in H_2S gas at 200 °C, 300 °C and 500 °C for 2 min. Sulfurization was carried out in a tube furnace (Heraeus ROK/A6/30) in a H_2S (Linde Purity 2.5) volume flow of 6 L/h.

For the morphological characterization, a field emission scanning electron microscope (Hitachi FE-SEM S4800) equipped with an energy dispersive X-ray (EDX) analyzer was used. The length of the nanotubular array was directly obtained from SEM cross-sections. The composition and the chemical state of the anodic layers were characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US). XRD patterns were collected using an X'pert Philips PMD diffractometer with a Panalytical X'celerator detector, using graphite-monochromatized Cu Kα radiation (λ = 1.54056 Å).

For the electrochemical measurements, molybdenum-oxide (or dichalcogenide) tube arrays on the Mo foil were employed as anode, a graphite rod as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. H_2 evolution measurements were carried out in 0.5 M H_2SO_4 aqueous solution. Impedance measurements were performed using a Zennium Zahner electrochemical workstation at applied voltages of 200 mV and − 400 mV (vs. RHE) The conversion of the potential from SCE to RHE is E (RHE) = E (SCE) + 0.236 V @ 25 °C, (in 0.5 M H_2SO_4).

3. Results and discussion

Self-organized Mo-oxide tubular layers were grown on Mo metal by anodizing in a NH_4F/H_2O/glycerol electrolyte as described in the experimental section. Fig. 1a shows SEM top and cross-sectional images of the ordered tube array layers that consist of tubes that have an average diameter of ~80 nm and a length of ~1 µm.

In a set of preliminary experiments, these oxide tubes were selenized followed by sulfurization in H_2S gas in a range of temperatures (see experimental section). We observed that selenization at elevated