



# Effect of different hole scavengers on the photoelectrochemical properties and photocatalytic hydrogen evolution performance of pristine and Pt-decorated TiO<sub>2</sub> nanotubes

Nikita Denisov <sup>a</sup>, JeongEun Yoo <sup>a</sup>, Patrik Schmuki <sup>a, b, \*</sup>

<sup>a</sup> Department of Materials Science and Engineering, WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, 91058, Erlangen, Germany

<sup>b</sup> Chemistry Department, King Abdulaziz University, 80203 Jeddah, Saudi Arabia Kingdom

## ARTICLE INFO

### Article history:

Received 4 February 2019

Received in revised form

27 June 2019

Accepted 28 June 2019

Available online 29 June 2019

### Keywords:

TiO<sub>2</sub> nanotubes

Hole scavengers

Photoelectrochemistry

Photocatalysis

H<sub>2</sub> generation

## ABSTRACT

TiO<sub>2</sub> nanotubes have been investigated in photoelectrochemistry and photocatalysis for more than a decade. However, up to now, a systematic investigation of different hole scavengers is still lacking. Here we investigate the effect of the most relevant sacrificial hole scavengers on the photoelectrochemical properties and photocatalytic H<sub>2</sub> evolution performance of pristine and Pt-decorated anodic TiO<sub>2</sub> nanotubes. We examine methanol, isopropanol, ethylene glycol, EDTA-Na<sub>2</sub>, as well as Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> and find that the incident photocurrent conversion efficiency (IPCE) of the TiO<sub>2</sub> nanotubes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolytes increases by 1.8–3.1 times, depending on the used hole scavenger. The efficiency increases in the sequence H<sub>2</sub>O<sub>2</sub> < Na<sub>2</sub>SO<sub>3</sub> < isopropanol < methanol < ethylene glycol < EDTA-Na<sub>2</sub>. In presence of any hole scavenger, for nanotubes in the length-range of 2–10 μm, the photocurrent spectra and the IPCE magnitude are independent of the tube length. The photocurrent onset potential (optical flatband potential) is significantly affected by the different type of scavengers, in line with their red-ox potential. Under open circuit conditions (photocatalytic conditions), organic hole scavengers lead to a 10.0–28.8 times higher H<sub>2</sub> production by TiO<sub>2</sub> nanotubes than the scavenger-free case, with a sequence MeOH > i-PrOH > EDTA-Na<sub>2</sub> > EG, while little or even detrimental effects of Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> are observed (note, this inactivity is in contrast to photoelectrochemical H<sub>2</sub> generation). These results are compared to results obtained for TiO<sub>2</sub> particles, and discussed in terms of various concepts in the literature.

© 2019 Published by Elsevier Ltd.

## 1. Introduction

Photocatalytic hydrogen (H<sub>2</sub>) evolution is a prospective field of research due to the current high demand for environmentally friendly energy sources, the abundance of the solar light reaching the terrestrial surface, and the availability of photocatalytically active materials which can utilize the energy of absorbed radiation to reduce the protons present in water to H<sub>2</sub>. In this respect, titanium dioxide (TiO<sub>2</sub>) has acquired wide attention from researchers, due to the high photocatalytic activity, outstanding photocorrosion resistance, nontoxicity, and economic viability of this material [1]. Nanotubular TiO<sub>2</sub> geometries are especially attractive for

photocatalytic applications due to their high surface area combined with directionality to light and charge management [2]. TiO<sub>2</sub> nanotubes can be prepared by various methods, which can be roughly divided into templating, hydrothermal, and anodic self-organization approaches [3]. Using electrochemical anodization, almost ideal hexagonally arranged tube layers can be grown to a thickness of several hundreds of micrometers on Ti surfaces of virtually any shape and a large range of properties [1,4–8]. The formed TiO<sub>2</sub> nanotubes are directly electrically back-connected to the metal substrate [5]. The anodization process also allows for many variations in tube geometries and morphologies, including the formation of bamboo morphology, stacked tube layers, branched tubes, or transferable membranes [9–12].

One of the crucial factors limiting large-scale application of TiO<sub>2</sub> nanotubes for photocatalytic H<sub>2</sub> evolution is their low photonic efficiency, due to a rapid recombination of photogenerated electron-hole pairs [13]. Since the photocatalytic H<sub>2</sub> evolution

\* Corresponding author. Department of Materials Science and Engineering, WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany.

E-mail address: [schmuki@ww.uni-erlangen.de](mailto:schmuki@ww.uni-erlangen.de) (P. Schmuki).