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journal homepage: www.elsevier.com/locate/elecomUniform ALD deposition of Pt nanoparticles within 1D anodic TiO₂ nanotubes for photocatalytic H₂ generationJeongEun Yoo^a, Raul Zazpe^b, Gihoon Cha^a, Jan Prikryl^b, Imgon Hwang^a, Jan M. Macak^b, Patrik Schmuki^{a,c,*}^a Department of Materials Science, Institute for Surface Science and Corrosion WW4-LKO, Friedrich-Alexander University, Martensstraße 7, D-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^c Chemistry Department, Faculty of Sciences, King Abdulaziz University, 80203 Jeddah, Saudi Arabia

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ABSTRACT

In the present work we investigate the utilization of Pt nanoparticles produced by atomic layer deposition (ALD) within anodic TiO₂ nanotube (NT) layers for photocatalytic H₂ production. By varying the number of ALD cycles, Pt nanoparticles with different diameters were produced, uniformly decorating the tube walls. The Pt nanoparticle size (2–15 nm), the Pt mass loading and areal density were strongly dependent on the number of Pt ALD cycles. The deposited Pt nanoparticles turned out to be highly effective as a co-catalyst for photocatalytic H₂ generation. The most effective performance for solar light photocatalysis was reached after 26 ALD cycles (yielding an optimal area coverage with particles of diameter \approx 7 nm). For UV light, the optimum photocatalytic efficiency was reached after 40 ALD cycles.

1. Introduction

Since the pioneering work of Fujishima and Honda in 1972, the production of H₂ by photocatalytic splitting of H₂O on semiconductors has been extensively investigated [1]. Among the different photocatalysts studied, titanium dioxide (TiO₂) received wide attention mainly due to its suitable conduction and valence band edge position for photogenerated charge carriers reacting with water as well as for its nontoxicity and stability against photocorrosion [2]. The TiO₂ conduction band edge lies higher than the redox potential of water (– 0.45 and 0 V vs. NHE, respectively, at pH 0) [3]. Therefore, it is possible to reduce H₂O to H₂ by photoexcited electrons that cross the TiO₂ band gap (E_{g,TiO2} \approx 3.0–3.2 eV) [4,5].

However, pristine TiO₂ shows low efficiencies for H₂ production and a kinetically slow electron transfer to reactants. Nanostructured photocatalysts can be employed in order to improve the electron transfer efficiency. In particular, one dimensional (1D) nanostructures, such as anodic TiO₂ nanotubes (NTs), have attracted significant attention in photocatalysis and photoelectrochemistry during the last decade as the growth conditions can be easily adjusted, leading to a large palette of nanotubular geometries [6–12]. 1D TiO₂ structures can promote directional charge transport and orthogonal electron-hole separation and thus enhance photocatalytic reaction rates [13]. However, except for

nanostructuring to reach reasonable H₂ evolution from TiO₂ photocatalysts, co-catalysts are usually decorated onto the substrate. These co-catalysts aid charge separation and transfer; most typical are noble metal nanoparticles (such as Au, Pd and Pt) [14,15].

Of these, Pt is the most efficient co-catalyst for the H₂ generation reaction. Pt nanoparticles at the TiO₂ surface can enable efficient electron transfer at the catalyst/environment interface by providing a favorable solid state junction to TiO₂, and additionally catalyze the hydrogen recombination reaction (2H⁰ \rightarrow H₂) [16].

In the case of TiO₂ NT layers, different Pt decoration methods have been described – the most frequently used techniques are various wet chemical routes, photodeposition methods, and conventional sputter deposition onto the NT layer [16–19]. However, these techniques often lead to a non-homogeneous particle distribution: in general, there is a higher loading at the tube mouth and a lower level of deposition deeper in the tube. This accumulation at the tube mouth becomes increasingly severe, the higher the aspect ratio of the nanotube layers [20,21].

In recent years atomic layer deposition (ALD) has become a prime method for deposition of a wide variety of materials such as oxides, sulfides and metals, among others [22–24]. In addition, it is one of the few methods enabling homogeneous and conformal deposition of secondary material into high-aspect-ratio structures [25]. The effective utilization of ALD for deposition of various materials within TiO₂

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