DESCRIPTION OF DOCTORAL DISSERTATION

Title of doctoral dissertation: Scalable modifications of optical and electronic properties of TiO_2 nanotubes for solar electrochemistry

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Abstract: TiO_2 is one of the most studied compound in the world. Owing to its unique properties, it is used in photoelectrochemical systems, for instance, in photocatalysis and dye-synthesized solar cells. It can be obtained using chemical and physical methods, including sol-gel, hydrothermal, electrochemical, or chemical vapor deposition. However, many of them result in a product in the form of slurry, and further separation of the titanium dioxide from by-products and purification are required. Optimized electrochemical anodization of titanium allows the growth of highly ordered arrays of TiO_2 nanotubes already on the stable and conducting substrate. The geometric features of the nanotubes can be precisely tailored by the processing parameters such as electrolyte composition, voltage, or time. Moreover, anodization as a galvanic process can be realized on a technological scale in a cost and energy-efficient way. However, the wide band gap and indirect nature of dominating transition limit the commercial application of titania nanotubes in photoelectrochemical devices. One promising way of improving the electronic properties of TiO_2 nanotubes is defect introduction which can provide additional carriers for photon absorption. Another way is the formation of heterojunction. The resulting potential bias at the interface can facilitate the separation of excitons. The deposited species can also incorporate into titania, provide additional states deep within the band gap and contribute to the absorption of visible light. Nevertheless, to take an advantage of anodization as a fabrication process, any further modifications should be designed to make the technological scale easy to achieve. Taking into account the limitations of titanium dioxide and the challenges that it has to face to be widely applied in photoelectrochemical systems, the aim of this work is the elaboration and optimization of easily scalable methods improving the optical and electronic properties of TiO_2 nanotubes.

The basis of this doctoral dissertation is a series of four articles published in journals indexed in the Journal Citation Reports list in the field of mechanical engineering.

The first part of the thesis presents a scalable method for pulsed laser-induced structure modulation of TiO_2 nanotubes towards superior photoresponse. Controlled degradation of the

crystal structure along with beam energy fluence leading up to a 1.45-fold increase in photoresponse was found. The novel approach concerns the optimization of the laser processing parameters in the system equipped with a beam homogenizer and motorized table which allows for modification of both precisely selected as well as any large area without the need for liquid media. These advances will hopefully enrich a state-of-the-art in the field of production engineering and bridge the gap between research and successful industrial application of laser technology for the modifications of functional materials.

The second part of the thesis reports a study of the optical and electronic properties of TiO_2 nanotubes combined with thin films of chromium, molybdenum, and tungsten oxides using magnetron sputtering technology followed by thermal annealing. Because of the contradiction in the literature reports regarding the transition types occurring in the investigated metal oxides, a precise systematized method allowing for the determination of the Tauc exponent and corresponding transition types was elaborated. In particular, Taylor series expansion was applied to the logarithmic version of the Tauc equation, which after solving, allowed for determining the Tauc exponent directly from the experimental absorption data without any assumptions regarding the investigated material, such as band gap width. A further study showed an unambiguous correlation between the estimated transition types and sample photoresponse. The obtained results demonstrate that the transition type estimated based on the Tauc exponent is a crucial predictor for sample photoresponse, even better than the optical band gap width. This framework may help for a more precise determination of the optical band gap. The above considerations were supported by a theoretical study.

According to the gathered results, it was shown that optimized laser modification of titania nanotubes in a system equipped with a beam homogenizer and motorized table, as well as the formation of heterojunction with chromium oxides using magnetron sputtering technology, allow for the fabrication of materials exhibiting superior photoresponse compared to bare TiO_2 nanotubes. Moreover, the elaborated method for determining the Tauc exponent and corresponding transition type (or transition types) can be widely used in the detailed analysis of optical and photoelectrochemical properties of functional materials.

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