Photochemical activity of TiO_2 nanotubes

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ABSTRACT

TiO_2 is well known as a low-cost, highly active photocatalyst of good environmental compatibility. Recently it was found that TiO_2 nanotubes promise to enable for high photocatalytic activity (PCA). In our experiments, we studied the photocatalytic activity and spectroscopic properties of TiO_2 nanotube arrays formed by the anodization of Ti. The PCA efficiency related to the decomposition of methylene-blue was measured. To obtain reliable data, the results were calibrated by comparing with standard materials like Pilkington Activ™ which is a commercially available self cleaning glass. The studies included a search strategy for finding optimum conditions for the nanotube formation and the investigation of the relationship between PCA and annealing temperature. TiO_2 nanotubes of different shapes and sizes were prepared by an anodization of Ti foil in different electrolytes, at variable applied voltages and concentrations. The photo-dissociation of methylene-blue was detected by UV-VIS spectroscopy. For the optimized material, an enhancement factor of 2 in comparison to the standard reference material was found. Furthermore, femtosecond-laser induced photoluminescence and nonlinear absorption of the material were investigated. Possibilities for a further enhancement of the PCA are discussed.

Keywords: Titanium oxide, nanotubes, photocatalysis, photocatalytic activity, nonlinear optics, enhancement, Raman spectroscopy

1. INTRODUCTION

TiO_2 nanostructures are well known as important functional materials because of their applications in high-efficiency photovoltaics, photocatalysis, chemical sensors, nonlinear optics, self-cleaning surfaces, water recycling and other fields [1]. Therefore, techniques for the fabrication of defined TiO_2 nanostructures on large surface areas and appropriate methods for their characterization and modification are of growing interest. Layers of TiO_2 of different surface roughness can be fabricated chemical and physical methods like sputtering [2], chemical vapor deposition [3], or sol-gel [4]. A particular, convenient method for the formation of nanotubes is the nano-anodization of Ti [5,6]. The use of TiO_2 nanotubes generated by this approach for photocatalysis applications was demonstrated by several authors [7,8].
Here we report on recent studies of the photocatalytic activity (PCA) of TiO_2 nanotubes grown on Ti bulk material at different electrolytes and compare the data with respect to the standard reference material Pilkington Activ™ [9].

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It will be shown that the best materials show a significant enhancement of the PCA (up to a factor of 2 compared to the reference). Possible reasons for the enhancement are discussed.

Beside linear absorption measurements, spectroscopic studies of femtosecond-laser induced photoluminescence and nonlinear absorption of the materials were performed to gain further insight in the relevant energy transfer mechanisms.

2. EXPERIMENTAL TECHNIQUES

2.1 Material preparation and characterization.

In our experiments, the photochemical properties of in total 4 samples with TiO_2 nanostructures were studied. For two of these samples, the electrolyte consisted of 0.25 wt% of ammonium fluoride (NH4F Fluka, 98%) solved in ethylene glycol (EG Fluka, 99.5%). The details about the preparation can be found in ref. [10]. One of the samples was annealed at 500 $^{\circ}$C. This sample will be referred to as AE with the further subdivision in unannealed and annealed samples (called "AE_unannealed" and "AE_annealed", respectively).

The other two other samples were prepared by applying a mixture of dimethyl sulphoxide (DMSO) and hydrofluoric acid as electrolyte. Analogous to the above introduced terminology these samples are referred to as DH with the subdivision in "DH_unannealed" and "DH_annealed" for the unannealed and annealed states, respectively.

The samples were characterized by scanning electron microscope (SEM) and Raman spectroscopy. SEM micrographs were obtained with a field emission SEM (JEOL, JSM-6400-F). The Raman spectra were detected with a commercial Raman spectrometer (WITec Alpha 300) at an excitation wavelength of 532 nm. The exposure times for AE and DH samples were taken to be 1.1 s and 0.64 s, respectively.

2.2 Photocatalysis experiments.

The PCA was investigated by analyzing the decomposition dynamics of methylene-blue. The coated samples were in all experiments placed in beaker glasses and completely covered by 15 ml methylene blue solution with a concentration of 0.01 mmol/l. After storing in dark for 20 minutes, the samples were irradiated for three hours with UV-light (Philips CLEO Professional broadband fluorescent tube, spectral intensity maximum at a wavelength of about 350nm) at an intensity of 5 mW/cm^2. The solution was stirred by means of a magnetically rotated stirrer. During the UV irradiation, the methylene-blue was dissociated in the presence of the photocatalytically active surfaces. The decay rate was determined by UV-VIS spectroscopy. After the irradiation, the UV-absorption of the solution was measured at a wavelength of 664 nm.

3. RESULTS AND DISCUSSION

The morphology of the samples was examined by the field emission SEM. Typical images for a top view and a cross sectional view of sample AE_annealed are shown in Figures 1 (a) and 1(b), respectively. The surface owes its character by densely packed nanotubes of slightly variable diameter and eccentricity which are grown slightly tilted with respect to the normal on the foil surface. The length of the nanotubes varies around a value of about 6 µm.

In Figures 2(a) and 2(b), top view and cross sectional view for a sample of the alternative type DH_annealed are plotted, respectively. In this case, the morphology shows nanotubes standing approximately perpendicular to the foil surface. The average length of these nanotubes was about 19 µm.

Both types of nanostructures were characterized by Raman measurements. For the DH-type samples, much higher Raman signal levels were detected in comparison to the AE samples. This results in parts from the different layer thickness, however the crystal state plays an important role as well. For an excitation at a slightly different wavelength of 514 nm (as reported in literature), the TiO_2 thin film in anatase phase shows the specific Raman modes at wave numbers of 141, 194, 394, 515 and 636 cm^{-1}. Similarly, the rutile phase was reported to display the modes at 144, 235, 443, 610 and 824 cm^{-1} [11]. Most of the active Raman modes observed in our experiments were found to have energies very close to the aforementioned spectra.

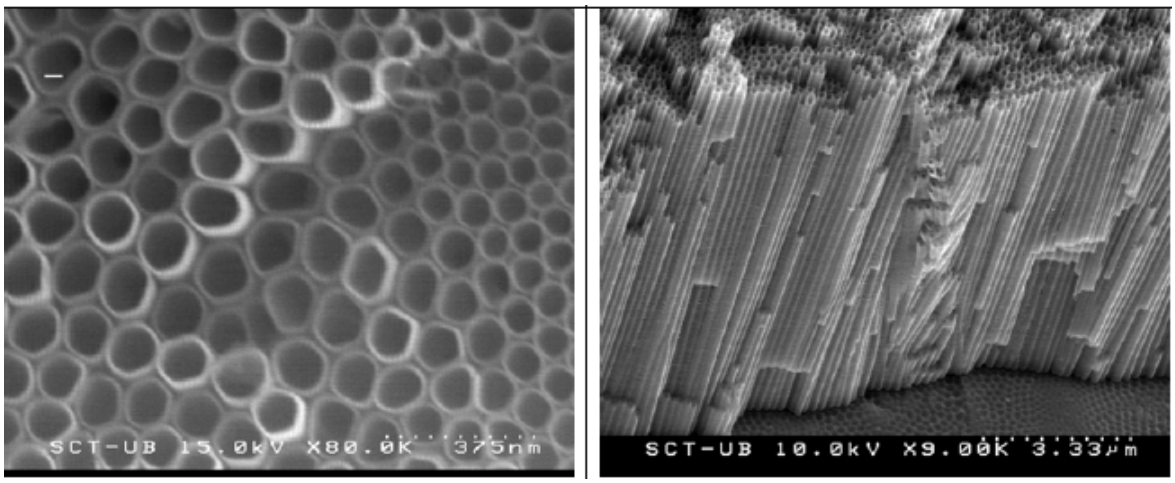

Figure 1: SEM images showing a top view (left) and a cross sectional view (right) of parts of a sample with closely packed TiO_2 nanotubes of the type AE_annealed. Please note that the scales are not identical for both pictures.

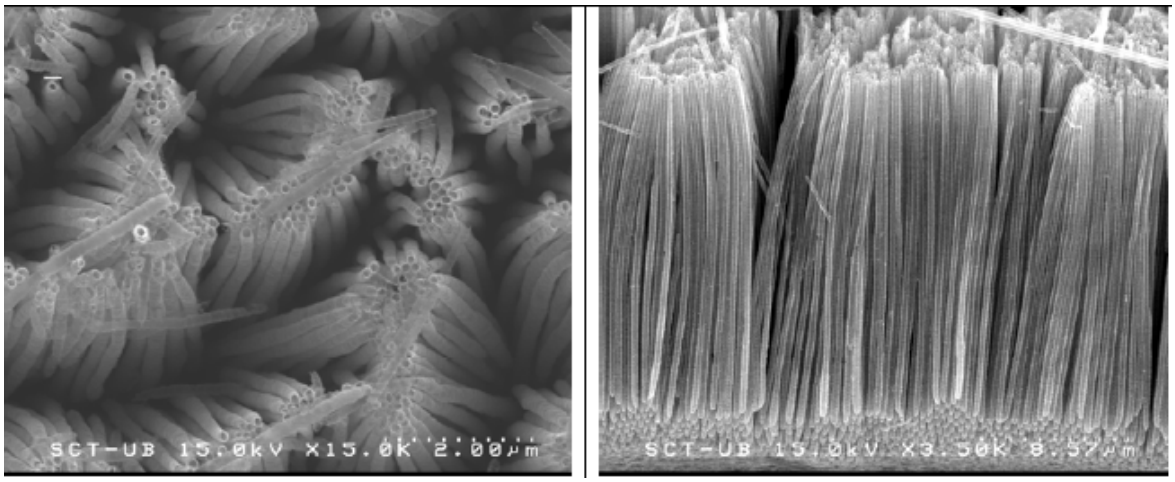

Figure 2: SEM images showing a top view (left) and a cross sectional view (right) of parts of a sample with closely packed TiO_2 nanotubes of the type DH_annealed. Please note that the scales are not identical for both pictures and also differ from the scales as applied in Fig. 1.

Representative Raman spectra of all types of samples are shown in Fig 3. The sample AE_unannealed was found to be of very weak crystallinity. For this reason, no strong Raman peaks were indicated (Fig. 3a).

After annealing (AE_annealed, Fig. 3b), the modes 255, 435 and 610 cm^{-1} were identified as the dominant peaks in the Raman spectrum. This indicates that these samples preferentially appear in rutile phase after changing to the crystalline state.

Other the other hand, both unannealed and annealed DH samples exhibit a distinct crystallinity. The unannealed sample DH_unannealed approximates the pure anatase state due to presence of the modes at 149, 200, 396, 512 and 634 cm^{-1} (Fig. 3c). The Raman spectrum of the annealed DH sample (DH_annealed) indicates in good approximation a mixed phase of anatase (148, 200, 513 cm^{-1}) and rutile (257, 431 and 615 cm^{-1}) (Fig 3d).

The photochemical activities (PCA) of all samples together with that of Pilkington Activ™ are compared in Fig. 4.

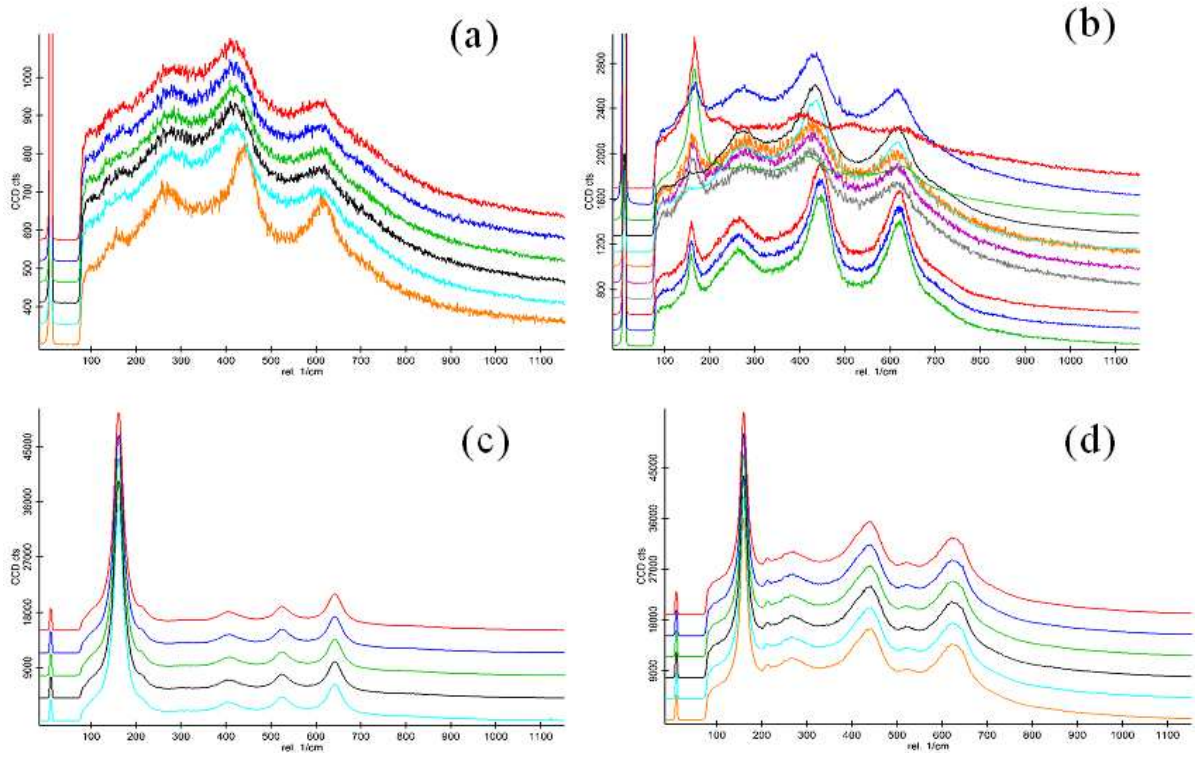

Figure 3: Raman spectra for the samples (a) AE_unannealed, (b) AE_annealed, (c) DH_unannealed, and (d) DH_annealed. Different curves within the same figure correspond to data taken at different locations on the sample surface.

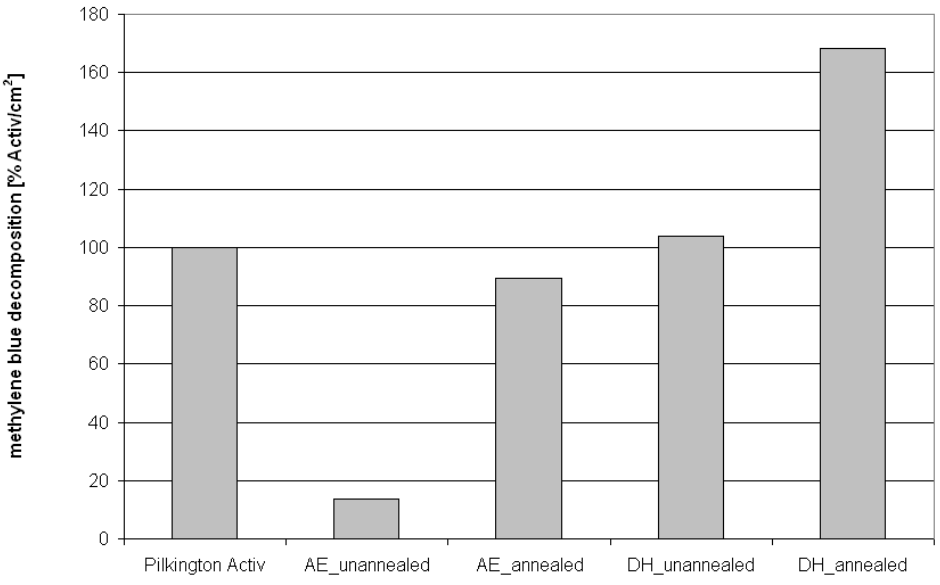

Figure 4: Photocatalytic activities (PCA) of all investigated samples compared to the PCA of a standard reference material (Pilkington Activ^{TM}).

4. CONCLUSIONS AND OUTLOOK

To conclude, different types of densely packed TiO_2 nanotubes formed by the anodization of Ti with and without thermal annealing were characterized with respect to their structure-function-relationships.

The anodization was performed with two distinct types of electrolytes: (i) ammonium fluoride solved in ethylene glycol (AE-type samples) and (ii) a mixture of dimethyl sulphoxide and hydrofluoric acid (DH-type samples).

Particular emphasis was laid on potential applications of such nanostructures in high-efficiency photocatalysis. Therefore, the photochemical activity (PCA) of the different types of samples was studied with standard methods of photochemistry. In particular, the dissociation of methylene-blue was used as a measure of the PCA. Crystalline states and induced changes of crystallinity were analyzed by Raman spectroscopy. The unannealed specimen were found to show much less photocatalytic activities than their corresponding annealed counterparts. The annealed AE-type TiO_2 sample was found to have a photocatalytic activity comparable to that of the standard reference material Pilkington Activ™. On the other hand, a 2-fold higher photochemical activity compared to the reference was indicated for the annealed DH sample. The enhancement is explained by the larger longitudinal dimensions of the DH sample (thicker layer) together with specific modifications of the crystalline structure.

The results of the PCA analysis were found to be consistent with the indications of the Raman spectroscopy data.

Furthermore, femtosecond-laser induced photoluminescence and nonlinear absorption of the material were investigated. Recently some of the authors published the results of the femtosecond-laser induced multiphoton excitation of similar large-bandgap nanomaterials like ZnO [12]. These studies were now also extended to TiO_2. For TiO_2 layers with nanogranular surfaces, a significant enhancement of third harmonic generation was reported [13]. Currently, the specific mechanisms of such surface enhanced nonlinear processes are still not completely understood. A closely related topic is the formation of appropriate templates for surface enhanced Raman spectroscopy (SERS) which promises to be another complimentary application of the TiO_2 nanostructures studies here. An additional enhancement of the PCA by laser postprocessing, the combination with metallic nanostructures [14] and a related theoretical design optimization will be the subject of further activities in future.

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