Ordered Nanotubular Titanium Disulfide (TiS$_2$) Structures: Synthesis and Use as Counter Electrodes in Dye Sensitized Solar Cells (DSSCs)

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Ordered nanotubular structures were synthesized by a high temperature H$_2$S treatment of anodized TiO$_2$ nanotube layers, and their electrochemical activity for a use as counter electrodes in dye sensitized solar cells (DSSCs) was evaluated. During conversion to TiS$_2$, compositional, morphological and structural transformations were monitored. The fully converted TiS$_2$ nanostructures show a high electrocatalytic activity for the $\Gamma^+/\Gamma^-$ oxidation comparable to a nanoparticular platinum layer. For a simplified model a DSSC solar cell efficiency of 6.1% was obtained using the TiS$_2$ nanotube layer as counter electrode, which is very close to values obtained for a Pt reference (6.2%).

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Experimental

A 1 μm thick titanium layer was evaporated on fluorine doped tin oxide (FTO) glass (Solaronix) by E-beam evaporation (Balzers Pfeiffer PLS 500 Labor System). The layer was then anodized at room temperature in an ethylene glycol electrolyte containing 0.15 M NH$_4$F and 1 M H$_2$O at 60 V for 10 minutes with a sweep of 10 V/s to reach the final voltage. The anodization was performed in a two electrode arrangement (Pt as a counter) using a computer controlled anodization setup (consisting of a Jaissle high voltage potentiotstat IMP88PC-100V and Burster Digistat 6706). After anodization the layers were washed with deionized water and dried in a nitrogen stream. Afterwards the as grown amorphous material was crystallized to anatase phase in a pipe-furnace under air at 450°C for 1h. The sulfidation was carried out by a second annealing of the samples in a quartz tube under H$_2$S (Linde Purity 2.5) with a volume flow of 4 l/h at 500°C for 30 min to 120 min. The platinum counter electrode, which was used as a reference counter electrode, was coated by drop coating a FTO glass with a H$_2$PtCl$_6$ solution (Solaronix) and heating it in a tube furnace at 450°C for 20 min. The morphologies of all electrodes were characterized using field emission scanning electron microscope (Hitachi FE-SEM, 4800). The chemical composition was evaluated by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) using a PHI 5600 spectrometer. The XPS spectra were corrected for charging effects against an external Au reference using Au 4 f/72 at 84.0 eV for shifting. The crystallinity of the layers was investigated by X-ray diffraction (XRD, Philips Xpert-MPD PW3040) using Cu Kα radiation.

Photocurrent spectra were recorded with a setup consisting of an Oriol 6356 150 W Xe arc lamp as light source and an Oriol cornerstone 7400 1/8 monochromator. The measurements were carried out in 0.1 M tetrabutylammonium phosphate in acetonitrile at an applied potential of 0.5 V (three electrode configuration: Ag/AgCl as
reference electrode and Pt as counter electrode) in an electrochemical cell equipped with a quartz glass window. DSSCs were constructed using nanoparticulate Pt coated FTO glass sheets, which were sandwiched against a photoanode using a polymer adhesive spacer (25 μm, Surlyn, DuPont). The photoanode consists of a 4 μm doctor bladed TiO2 nanoparticle film (20 nm nanoparticles, Solaronix) on FTO. For dye sensitization the nanoparticle films were immersed for 24 h in a 30 mM solution of Ru-based dye (N719 Solaronix) in acetonitrile/tetra-butyl-alcohol (50:50 vol%). After sensitization the films were washed with acetonitrile to remove non-chemisorbed dye. The electrolyte ES_004 from IoLiTec, Germany, was injected into the space between the sandwiched cells. Using front side illumination the CV-characteristics were measured und AM 1.5 illumination of a solar simulator (300W Xe with filter, Opto polymers), applying an extended bias to the cell and measuring the generated photocurrent with a 4 point source meter (Keithley 2420). The cyclic voltammetry measurements were performed in a three electrode arrangement using a platinum foil as a counter electrode and an additional platinum wire as pseudo reference electrode using Autolab (PEStat302W). As electrolyte water free acetonitrile containing 0.1 M LiClO4, 10 mM LiI and 1 mM I2 (Sigma Aldrich) was used. The potential was cycled between −1.0 V and +1.3 V vs. Pt with a scan rate of 10 mV/s. The impedance spectroscopy experiments were carried out in a symmetrical cell arrangement (CE/EL/CE) using a spectrum analyzer Zahner IM6 for data acquisition at OCP. A commercial I−/I3− redox couple based electrolyte (Iolitec ES-004) was used. The np-TiS2 consists of a 3 μm doctor bladed TiO2 nanoparticle film (20 nm nanoparticles, Solaronix) on FTO, which was sulfidated under optimized conditions at 500 °C for 2h.

**Results and Discussion**

Figures 1a–1d shows scanning electron microscope images of the cross-sections and top views (insets) of the nanotube layers used in the present investigation. Figure 1a shows that the air anneled TiO2 layer consists of smooth nanotubes with a layer thickness of approx. 3 μm. The top view exhibits tube openings with a diameter of 45 nm. After 30 and 60 minutes of H2S treatment at 500 °C, the tubular structure is well retained as shown in Figures 1b and 1c. With further conversion (120 min) the nanotube walls change to a flake like structure, however the overall morphology is retained (Fig. 1d). Longer treatment times lead to alterations of the morphology (see ESI S3b). Clearly a flake like morphology is formed, which is reported to be favored by transition metal dichalcogenids (e.g. TiS2). The XRD patterns in Figure 2a reveal signals of two different structures. On the one hand the peaks at 25.4° and 48.1° can be assigned to anatase TiO2 whereas the peaks at 15.5° and 30.4° as well as the shoulders of the peaks at 33.9° and 46.9° can be ascribed to TiS2. While the anatase TiO2 sample and the 30 min H2S sample only show signals of the anatase phase and of the FTO substrate, the 60 min H2S sample additionally exhibits first signals of TiS2, and the signals TiO2 anatase phase show a reduced intensity. Further treatment with H2S for 120 min leads to a full transformation from the TiO2 anatase phase to TiS2. To obtain information about the chemical composition, XPS experiments were carried out. Figure 2b compares the Ti 2p peaks of anatase TiO2 nanotubes, that were treated for 0 min, 30 min, 60 min and 120 min in H2S. The reference anatase TiO2 peaks at 464.4 eV (2 p1/2) and 458.7 eV (2 p3/2), which can be assigned to Ti4+ in TiO2. After 60 min and 120 min this spin coupling pair is complemented by a second pair at 462.4 eV (2 p1/2) and 456.5 eV (2 p3/2) which can be ascribed to TiS2. The peak intensity for the TiS2 signals increases with treatment time and shows full conversion after 120 min H2S treatment time. The S 2p XPS spectra in Figure 2c gives the data of the plain anatase TiO2 nanotubes, as well as after the H2S treatment for 30 min, 60 min and 120 min. While the reference air annealed TiO2 sample does not exhibit any signal for the S 2p spectra, a spin coupling pair of the 30 min sample appears at 163.8 eV (2 p1/2) and 162.8 eV (2 p3/2) that can be assigned to sulfur in a TiOxSy compound. The S 2p XPS spectra of the 60 min and 120 min samples show a second peak pair evolving at 162.9 eV (2 p1/2) and 160.9 eV (2 p3/2) which is assigned to TiS2. The increase of the TiS2 signal in the Ti 2p, as well as in the S 2p XPS spectra, is in line with the observations by XRD and the proposed transformation of TiO2 to TiS2. Further investigations of the chemical composition with EDX are shown in Figure 2d. The Ti concentration over treatment time stays more or less constant at about
Figure 2. a) X-ray diffraction pattern of anatase TiO$_2$ reference sample and H$_2$S treated samples after 30 min, 60 min and 120 min. The sign ♦ shows the TiS$_2$ signals, ■ is the FTO signal of the substrate and ● is the anatase TiO$_2$. b) XPS spectra in the Ti 2p region and c) XPS spectra in the S 2p region compared from anatase TiO$_2$ to the 120 min H$_2$S treated sample. d) Atomic ratio in % calculated from EDX plotted against treatment time.

33%, whereas the oxygen content of the layer is reduced over time from 66% after annealing in air to 2% after 120 min of H$_2$S treatment. The ratio for Ti to O of 1:2 obtained for the air annealed tubes from XPS and XRD data and is considered with TiO$_2$ composition. In the H$_2$S treatment the O is replaced step by step with S, leading to an atomic ratio of 1:2 for Ti:S after 120 min which is consistent with TiS$_2$.

The electrochemical and photoelectrochemical properties of the structures are summarized in Figure 3 and in the supporting information in Fig. S2b. Figure 3a shows the catalytic activity toward the

Figure 3. Cyclic voltammetry of Pt, reference compared with anatase TiO$_2$, 30 min, 60 min and 120 min H$_2$S treated samples. b) Electrochemical impedance spectroscopy for Pt reference (♦) compared to anatase TiO$_2$ (●), 30 min (∆) H$_2$S treatment, 60 min (□) H$_2$S treatment and 120 min (♦) H$_2$S treatment. Inset shows the electrical circuit. c) Photocurrent density-voltage curves of DSSCs at 100 mW/cm$^2$ (AM 1.5G) light intensity.
I\textsubscript{1}⁻/I\textsuperscript{−} redox couple of anatase TiO\textsubscript{2} nanotubes before and after different H\textsubscript{2}S treatments. In cyclic voltammograms (for comparison Pt is included) there are two redox reactions observed:

\[ \text{I}^− + 2e^− \rightarrow 3\text{I}^- \]  

\[ 3\text{I}^- + 2e^− \rightarrow 2\text{I}_2^- \]  

Redox couple (1) has a more negative redox potential and is the main reaction occurring at the counter electrode of a DSSC. Platinum is the standard material used as the counter electrode in DSSCs. On Pt all four peaks for the redox couples (1) and (2) are apparent. Two characteristic values can be extracted from the CV. The first one is the peak to peak distance ΔE of the redox couple (1), which describes the reversibility of a system. The second value is the current density at the peak maximum, which is directly correlated to the catalytic activity.\cite{18,32,33} In the CV curves of the platinum reference sample both redox couples are visible and a ΔE of 0.55 V is observed for redox couple (1). The current density for couple (1) has a maximum value of 1.0 mA/cm\textsuperscript{2} at −0.5 V. The anatase TiO\textsubscript{2} sample has no detectable signals as expected from literature, due to its very low conductivity and electrocatalytic activity.\cite{4,8} The 30 min H\textsubscript{2}S treated sample also delivers no signal, but after 60 min of H\textsubscript{2}S treatment first signs of redox reactions become visible. After 120 min H\textsubscript{2}S treatment time redox peaks are clearly visible and the best results can be achieved for the fully converted TiS\textsubscript{2} structures which exhibit a ΔE of 0.54 V and a current density of 1.05 mA/cm\textsuperscript{2}. These results indicate a stronger increased catalytic activity for the I\textsubscript{1}⁻/I\textsuperscript{−} redox couple compared to TiO\textsubscript{2} anatase, the not fully converted layers, as well as a similar or even slightly better catalytic activity than Pt. Nevertheless, it has to be considered that the TiS\textsubscript{2} is present as nanotubular morphology. Furthermore nanotubular TiS\textsubscript{2} and TiS\textsubscript{2} nanoparticles were compared by cyclic voltammetry and a longterm stability test was performed for the nanotubular TiS\textsubscript{2}, which are shown in the supporting information S1c/S2a. The advantage of the nanotubular structure over the nanoparticulate one was demonstrated and longterm stability was proved successfully for the nanotubular TiS\textsubscript{2}. In order to test the TiS\textsubscript{2} counter electrode in a full DSSC we assemled symmetrical cell as described in the experimental section. Figure 3b shows electrochemical impedance spectra (EIS) of the symmetric cells. For DSSCs the commonly used equivalent circuit (inset Fig. 3b) contains a constant phase element which is placed parallel to the charge transfer resistance and a Warburg resistance and is connected in series with the serial resistance.\cite{9,10} For a better visualization, the fitted circles for Pt and the 120 min H\textsubscript{2}S treated sample were added in the graph. The data for platinum and tubes after 120 min H\textsubscript{2}S treatment deliver the expected flattened semicircle shape. Here the TiS\textsubscript{2} (3.4 cm\textsuperscript{2}) shows 6.1% efficiency with comparable in Isc, V\textsubscript{oc} and FF compared by cyclic voltammetry and a longterm stability test was performed for TiS\textsubscript{2}. In order to test the TiS\textsubscript{2} as efficient counter electrode material, DSSCs were constructed and tested under AM 1.5 conditions. Figure 3c displays the photocurrent-voltage curves obtained with a platinum reference and samples treated with H\textsubscript{2}S for 120 min, 60 min and 30 min as counter electrode. The anatase TiO\textsubscript{2} nanotubes as starting material and the 30 min H\textsubscript{2}S treated sample show a very low performance, which can be expected for TiO\textsubscript{2}. The values of the sulfidated materials in view of efficiency (η), open circuit voltage (V\textsubscript{oc}), short circuit current density (J\textsubscript{sc}) and fill factor (FF) are listed in Table 1b. It is obvious that with increasing sulfidation time the efficiency of the DSSC is increasing. The fully converted TiS\textsubscript{2} nanotubes show 6.1% efficiency with comparable in J\textsubscript{sc}, V\textsubscript{oc} and FF to platinum.

| Sample | R\textsubscript{s} Ω cm\textsuperscript{2} | R\textsubscript{ct} Ω cm\textsuperscript{2} | CPE μF |
|--------|----------------|----------------|---------|
| Pt reference | 5.3 | 2.4 | 4.8 |
| 120 min H\textsubscript{2}S | 5.4 | 3.4 | 26.3 |
| 60 min H\textsubscript{2}S | 5.2 | 7.5 | 33.1 |
| 30 min H\textsubscript{2}S | 5.7 | 24.4 | 35.1 |

\begin{table}[h]
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\begin{tabular}{ccc}
\hline
Sample & J\textsubscript{sc} mA/cm\textsuperscript{2} & V\textsubscript{oc} mV & FF & η %
\hline
Pt reference & 13.8 & 763 & 0.58 & 6.2
120 min H\textsubscript{2}S & 14.4 & 716 & 0.58 & 6.1
60 min H\textsubscript{2}S & 9.6 & 716 & 0.54 & 3.7
30 min H\textsubscript{2}S & 2.4 & 252 & 0.1 & 0.06
TiO\textsubscript{2} anatase & 0.1 & 252 & 0.04 & 0.001
\hline
\end{tabular}
\end{table}

Conclusions

Overall, we demonstrate the successful transformation of TiO\textsubscript{2} nanotube arrays into highly catalytic active and conductive TiS\textsubscript{2} phases by a simple high temperature treatment in H\textsubscript{2}S and demonstrate its potential use in a DSSC.

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