Ordered Nanotubular Titanium Disulfide (TiS₂) Structures: Synthesis and Use as Counter Electrodes in Dye Sensitized Solar Cells (DSSCs)

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TiS₂ nanotubular structures were synthesized by a high temperature H₂S treatment of anodized TiO₂ nanotube layers, and their electrochemical activity for a use as counter electrodes in dye sensitized solar cells (DSSCs) was evaluated. During conversion to TiS₂ compositional, morphological and structural transformations were monitored. The fully converted TiS₂ nanostructures show a high electrocatalytic activity for the I[−]/I₃[−] oxidation comparable to a nanoparticulate platinum layer. For a simplified model a DSSC solar cell efficiency of 6.1% was obtained using the TiS₂ nanotube layer as counter electrode, which is very close to values obtained for a Pt reference (6.2%).

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Self-organized TiO₂ nanotubular structures, prepared by anodization, are widely investigated because of their potential use in applications such as photocatalysis, dye sensitized solar cells, membranes, drug delivery systems, or electrochromic devices.^{1,2} In solar energy conversion devices, for example dye sensitized solar cells, the structures provide not only a beneficial geometry for ideal charge and ion transport pathways but provide also low cost fabrication. For DSSCs, research has been focused widely on increasing the total efficiency; only few works deal with reducing the fabrication cost. One important factor of the total cost is the classic counter electrode material, namely platinum. Platinum has two main tasks in DSSCs: i) it serves as a back contact for the transport of electrons and, ii) more importantly, it acts as an electrocatalyst for the reoxidation of the I₃[−]/I[−] couple in the electrolyte.^{3,4} In the past, several promising materials were investigated as counter electrode materials, such as stainless steel/graphite or transition metal based compounds, e.g. in form of carbides, nitrides, selenides, oxides or sulfides. Among transition metal sulfides, CoS, NiS, WS₂ and MoS₂ were considered as cost efficient counter electrode materials. In nanoparticle based DSSCs efficiencies of 6.5%, 6.8%, 7.6% and 7.7% were achieved in comparison with 10% when using platinum.^{5–15} In those assemblies, counter electrodes in form of nanoparticles or nanostructures were used to replace platinum, due to their high electrocatalytic surface area. Such counter electrode films can be fabricated by reactive sputtering, wet chemical synthesis or dip coating.^{16–18} In principle, an attractive alternative would be to use TiO₂ based aligned nanotubes as counter electrode. A drawback of TiO₂ in general is however the low intrinsic conductivity of the material and very importantly the low catalytic activity for the oxidation of the I₃[−]/I[−] couple. However, in recent years, it was demonstrated that TiO₂ nanotubes can be processed without any significant loss of the morphology by suitable high temperature treatments to change their electronic properties, e.g. TiO₂ nanotubes can be fully converted in acetylene or ammonia to conductive titanium carbide or nitride nanotubular structures, as well as modified into “doped” TiO_xS_y phases in a high temperature treatment under sulfur or hydrogen sulfide atmosphere.^{19–23} Recent reports by Li et al. suggest that TiS₂, as semi metal with a high conductivity and a high catalytic activity for the iodine couple, can increase the efficiency in solar cells with PEDOT:PSS counter electrodes.²⁴ However, Li used

a PEDOT:PSS/TiS₂ counter electrodes in a cell with a 20 μm thick absorber layer, which is 5 times thicker than the absorber layer used in our study. Furthermore Qiu used a TiS₂/graphene composite counter electrode with an efficiency of 8.8%.²⁵ In the present paper we report on a high temperature H₂S conversion of anodic TiO₂ nanotubes to TiS₂ nanotubes, and show the highly beneficial effect as a counter electrode in a DSSC configuration that reaches almost the same performance as platinum.

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 NH₄F and 1 M H₂O 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 Jaisle high voltage potentiostat 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 H₂S (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 prepared by drop coating a FTO glass with a H₂PtCl₆ solution (Solaronix) and heating it in a tube furnace in air 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 4f_{7/2} 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 Oriel 6356 150 W Xe arc lamp as light source and an Oriel 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

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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 TiO_2 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 under 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 LiClO_4 , 10 mM LiI and 1 mM I_2 (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.²⁶ A commercial I^-/I_3^- redox couple based electrolyte (Iolitec ES-004) was used. The np- TiS_2 consists of a 3 μm doctor bladed TiO_2 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 annealed TiO_2 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 H_2S 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 dichalcogenides (e.g. TiS_2).²⁷ 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 TiO_2 whereas the peaks at 15.5° and 30.4° as well as the shoulders of the peaks at 33.9° and 37.9° can be ascribed to TiS_2 .²⁸ While the anatase TiO_2 sample and the 30 min H_2S sample only show signals of the anatase phase and of the FTO substrate, the 60 min H_2S sample additionally exhibits first signals of TiS_2 , and the signals TiO_2 anatase phase show a reduced intensity. Further treatment with H_2S for 120 min leads to a full transformation from the TiO_2 anatase phase to TiS_2 . To obtain information about the chemical composition, XPS experiments were carried out. Figure 2b compares the Ti 2p peaks of anatase TiO_2 nanotubes, that were treated for 0 min, 30 min, 60 min and 120 min in H_2S . The reference anatase tubes display peaks at 464.4 eV (2 p1/2) and 458.7 eV (2 p3/2), which can be assigned to Ti^{4+} in TiO_2 . 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 Ti^{4+} in TiS_2 .^{29,30} The peak intensity for the TiS_2 signals is increased with treatment time and shows full conversion after 120 min H_2S treatment time. The S 2p XPS spectra in Figure 2c gives the data of the plain anatase TiO_2 nanotubes, as well as after the H_2S treatment for 30 min, 60 min and 120 min. While the reference air annealed TiO_2 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 TiO_xS_y compound.³¹ The S 2p XPS spectra of

Figure 1. SEM pictures of different transformation steps. A) top view and cross section (inset) of TiO_2 anatase, b) top view and cross section (inset) of 30 min H_2S treated samples, c) top view and cross section (inset) of 60 min H_2S treated samples and d) top view and cross section (inset) of 120 min H_2S treated samples.

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 TiS_2 . The increase of the TiS_2 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 TiO_2 to TiS_2 . 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 TiO₂ reference sample and H₂S treated samples after 30 min, 60 min and 120 min. The sign ◆ shows the TiS₂ signals, ■ is the FTO signal of the substrate and ● is the anatase TiO₂. b) XPS spectra in the Ti 2p region and c) XPS spectra in the S 2p region compared from anatase TiO₂ to the 120 min H₂S 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 H₂S 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 TiO₂ composition. In the H₂S 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 TiS₂.

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. a) Cyclic voltammetry of Pt, reference compared with anatase TiO₂, 30 min, 60 min and 120 min H₂S treated samples. b) Electrochemical impedance spectroscopy for Pt reference (☆) compared to anatase TiO₂ (○), 30 min (Δ) H₂S treatment, 60 min (□) H₂S treatment and 120 min (◇) H₂S treatment. Inset shows the electrical circuit. c) Photocurrent density-voltage curves of DSSCs at 100 mW/cm² (AM 1.5G) light intensity.

I_3^-/I^- redox couple of anatase TiO_2 nanotubes before and after different H_2S treatments. In cyclic voltammograms (for comparison Pt is included) there are two redox reactions observed:

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_p 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.^{18,32,33} In the CV curves of the platinum reference sample both redox couples are visible and a ΔE_p of 0.55 V is observed for redox couple (1). The current density for couple (1) has a maximum value of 1.0 mA/cm² at -0.5 V. The anatase TiO_2 sample has no detectable signals as expected from literature, due to its very low conductivity and electrocatalytic activity.^{34,35} The 30 min H_2S treated sample also delivers no signal, but after 60 min of H_2S treatment first signs of redox reactions become visible. After 120 min H_2S treatment time redox peaks are clearly visible and the best results can be achieved for the fully converted TiS_2 structures which exhibit a ΔE_p of 0.54 V and a current density of 1.05 mA/cm². These results indicate a stronger increased catalytic activity for the I_3^-/I^- redox couple compared to TiO_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_2 is present as nanotubular morphology. Furthermore nanotubular TiS_2 and TiS_2 nanoparticles were compared by cyclic voltammetry and a longterm stability test was performed for the nanotubular TiS_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_2 . In order to test the TiS_2 counter electrode in a full DSSC we assembled 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.^{36,37} For a better visualization, the fitted circles for Pt and the 120 min H_2S treated sample were added in the graph. The data for platinum and tubes after 120 min H_2S treatment deliver the expected flattened semicircle shape. Here the TiS_2 (3.4 Ω cm²) sample shows an only slightly higher charge transfer resistance than the platinum reference (2.4 Ω cm²) – this is additionally demonstrating the high catalytic activity of TiS_2 . The 60 min H_2S treated sample with 7.5 Ω cm² still displays a better charge transfer resistance in comparison to the pure anatase TiO_2 (380 Ω cm²) and the 30 min H_2S treated sample (24.4 Ω cm²). These results are in line with the results in the CVs, in which especially the TiO_2 and the 30 min sample did not show a convincing catalytic performance.

Finally, to demonstrate the suitability of TiS_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_2S for 120 min, 60 min and 30 min as counter electrode. The anatase TiO_2 nanotubes as starting material and the 30 min H_2S treated sample show a very low performance, which can be expected for TiO_2 . The values of the sulfidated materials in view of efficiency (η), open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) are listed in Table Ib. It is obvious that with increasing sulfidation time the efficiency of the DSSC is increasing. The fully converted TiS_2 nanotubes show 6.1% efficiency with comparable in J_{sc} , V_{oc} and FF to platinum.

Table I. a) Fitted EIS parameters. b) Photocurrent density performance values for various counter electrode materials.

a) Sample	R _s Ω cm ²	R _{ct} Ω cm ²	CPE μF	
Pt reference	5.3	2.4	4.8	
120 min H ₂ S	5.4	3.4	26.3	
60 min H ₂ S	5.2	7.5	33.1	
30 min H ₂ S	5.7	24.4	35.1	
TiO ₂ anatase	5.6	380	41.5	
b) Sample	J _{sc} mA/cm ²	V _{oc} mV	FF	η %
Pt reference	13.8	763	0.58	6.2
120 min H ₂ S	14.4	716	0.58	6.1
60 min H ₂ S	9.6	716	0.54	3.7
30 min H ₂ S	2.4	252	0.1	0.06
TiO ₂ anatase	0.1	252	0.04	0.001

Conclusions

Overall, we demonstrate the successful transformation of TiO_2 nanotube arrays into highly catalytic active and conductive TiS_2 phases by a simple high temperature treatment in H_2S and demonstrate its potential use in a DSSC.

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