Thin MoS₂ on TiO₂ nanotube layers: An efficient co-catalyst/harvesting system for photocatalytic H₂ evolution

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Abstract

In the present work, we decorated MoS₂ site-selectively at the top of anodic anatase TiO₂ nanotubes (TiNTs). For this we sputter-deposited a thin layer (0.5 to 10 nm) of molybdenum onto the tops of the tubes and converted it to sulfide by a thermal treatment in H₂S gas. The converted layers were characterized by SEM, XRD and XPS, and tested as an open-circuit photocatalyst for hydrogen evolution. Under AM1.5 (100 mW/cm²) illumination, strongly enhanced H₂ evolution activity can be observed using only a nominal 1 nm thick MoS₂ decoration on top of a 6 μm thick TiNT layer. We ascribe this strong beneficial effect to two factors: (i) the thin molybdenum sulfide on the top acts as an electron transfer mediator, i.e. as an H₂ evolution co-catalyst; and (ii) the underlying tube layer acts as a light-to-electron harvester.

Keywords: Titanium dioxide nanotubes, Molybdenum sulfide, Photocatalysis, Hydrogen evolution, Anodization

1. Introduction

The work of Fujishima and Honda in 1972 showed the feasibility of using a TiO_2 single crystal as a photoanode for H_2 evolution [1]. Under UV illumination and with Pt as a counter electrode, water could be split into H_2 and O_2 using an external applied bias. Intensive scientific and technological follow-up work was targeted in order to overcome the main disadvantages of TiO_2 , namely the wide band gap ($E_g \approx 3.2$ eV for anatase or $E_g \approx 3.0$ eV for rutile) and the slow kinetics of charge carrier transfer to form H_2 [2–4]. To overcome the first problem, numerous approaches based on the heavy doping of TiO_2 (e.g. with N) for band gap engineering have been reported [5–6]. Regarding the second problem, to improve the transfer and separation of charge carriers under open circuit conditions, TiO_2 is commonly modified with co-catalysts. The most effective co-catalysts for H_2 evolution are noble metals such as Pt, Pd and Au [7–9]. These can act as an electron transfer mediator for photogenerated electrons from the conduction band to the environment, e.g. water, to produce H_2 , however, the use of these noble metals raises considerable economic issues.

In order to substitute these metals, a number of plain electrocatalysts, such as various transition metal chalcogenides (MoS_2 , WS_2), have been considered, as they have been reported to show remarkable hydrogen evolution properties in electrolysis with a comparably low overpotential for H_2 evolution. Nanostructured molybdenum sulfides in particular have been identified as very promising hydrogen evolution catalysts [10–12].

Bulk molybdenum sulfide has a band gap of 1.2 eV with a conduction band close to the conduction band of TiO_2 . If nanoscale units of MoS_2 are used, the gap broadens up to 1.8 eV when reaching monolayer thickness due to quantum confinement effects. The main energetic shift by quantum confinement is ascribed to a change in the energetic position of the conduction band [13–14]. As a result, charge transfer cascades become plausible for various sizes of $\text{MoS}_2/\text{TiO}_2$ junctions, leading to possible use either as a photosensitizer or as an electron transfer mediator to electrolyte [15–21].

In contrast to previous reports (which focused mainly on fully decorated hydrothermal nanotube powder), in the present work we investigate the role of a thin MoS_2 decoration deposited only at the top of an aligned anodic nanotube layer. The thin layer of MoS_2 can be

adjusted to act as an excellent electron transfer mediator for photoelectrons generated in the underlying TiO₂ nanotube layer, i.e., photoelectrons generated in the nanotube layer can travel over micrometers to reach the thin MoS₂ layer and there successfully react to form H₂.

2. Experimental section

TiO₂ nanotube (TiNTs) layers were grown as described before (see ref. 22) to a length of 2 μ m or 6 μ m. TiO₂ compact oxide (50 nm) is produced by anodization in 1 M H₂SO₄ at 20 V for 10 min. In order to convert the amorphous tube layer to anatase, thermal annealing was performed in air using a rapid thermal annealer (Jipelec JetFirst100) at 450 °C for 3 h with a temperature ramp rate of 0.5 °C/s.

The decoration of Mo on TiO₂ nanotubes with a nominal Mo layer thickness of 0.5 to 10 nm was performed using a plasma sputter device (EM SCD500, Leica) operated at 25 mA and a pressure of 10⁻² mbar. Ar was used as the moderating gas and sputtering was carried out at a small angle. After deposition, the samples were annealed in air at 350 °C for 1 h. Sulfurization was carried out in a tube furnace with H₂S (Linde Purity 2.5). Samples were inserted into the furnace heated under N₂ flow up to 500 °C, exposed to H₂S flow (6 L/h) for 30 min and cooled to RT under N₂ flow.

An X-ray photoelectron spectrometer (XPS, PHI 5600 XPS spectrometer, US) was used for compositional analysis as described previously (see ref. 22). All the XPS element peaks were shifted to the C 1s standard position (284.8 eV). For morphological characterization of the TiNT layers, we used a field emission scanning electron microscope (Hitachi S4800). XRD patterns of the crystallized TiNT layers were collected using an X-ray diffractometer (X'pert Philips PMD diffractometer) with a Panalytical X'celerator detector and Cu K α radiation (λ = 1.54056 Å).

For open circuit photocatalytic H₂ evolution measurements the TiNT layers were immersed in an aqueous methanol (50 vol%) solution (exposing an area of 0.785 cm²) and illuminated with an AM 1.5 (100 mW/cm²) solar simulator for 12 h. A gas chromatograph (GCMS-QO2010SE, SHIMADZU) with TCD detector was used to detect the amount of H₂ generated from the different TiNT samples.

Photoelectrochemical characterization was carried out using a Zahner IM6 (Zahner

Elektrik, Kronach, Germany) with a tunable TLS03 UV and visible light source in a 0.1 M aqueous Na_2SO_4 solution at +0.5 V (vs. Ag/AgCl). The illuminated area was 1 cm^2 .

3. Results and discussion

Fig. 1. (a) Illustration of the process to decorate MoS_2 on TiNT layers. (b) SEM images of the cross-section and (c) the top of the 6 μm bare TiO_2 nanotube layer. SEM images of (d) the top and (e) cross-section for TiO_2 NT layer with 10 nm Mo decoration. SEM image of (f) top and (g) cross-section of TiO_2 NT layer with 10 nm Mo decoration after H_2S treatment.

Fig. 1a shows an overview of the experimental process used to fabricate the thin MoS₂ layer on top of the TiNT layers. Firstly, the nanotube arrays were prepared and converted to anatase as described in the experimental section, and molybdenum was then sputtered under a shallow angle as a thin layer on top of the TiNT samples. Afterwards the layers were first annealed in air to oxidize the molybdenum to Mo oxide, and were then treated in H₂S to convert the Mo oxide to Mo sulfide.

Fig. 1b and c shows cross-sectional and top view SEM images of the TiNT layers before molybdenum deposition. The individual tubes have an average diameter of ~ 85 nm and a length (layer thickness) of ~ 6 μm. TiO₂ nanotubes with various lengths were prepared by controlling the anodization time. From the SEM images one can also see that the TiNTs (used in this work) carry a thin initiation layer on the top (Fig. 1c) which acts as a partial cap to prevent deeper penetration of sputtered Mo into the tube layer. As the amount of sputtered Mo increases, the tube morphology shows an increasingly decorated opening. At a nominal Mo thickness of 10 nm (Fig. 1d), some Mo aggregates (composed of particles) can be seen on the tube top. The cross sectional image in Fig. 1e shows that the majority of Mo clusters are present at the top of tube and the Mo coating penetrates to a depth of ~100 nm from the top of the TiO₂ nanotube. After H₂S treatment, the molybdenum deposits converted to MoS₂ show a more layer-like morphology (Fig. 1f–g).

The crystalline structure of the different samples was characterized by XRD (Fig. 2a). Clearly, anatase (PDF card No. 00-021-1272) and substrate Ti metal peaks (PDF card No. 00-044-1294) can be identified for all samples. No clear MoS₂ peaks (e.g. $2\theta \approx 14.3^\circ$) can be seen from the XRD patterns; this can be ascribed to the low loading of MoS₂ [19].

Nevertheless, the successful deposition of Mo on the layer of TiO₂ NTs and its chemical conversion can be followed by X-ray Photoelectron Spectroscopy (XPS) (Fig. 2b–f). The as-deposited Mo on TiO₂ consists of Mo⁶⁺ with a peak position of 236.6 eV for Mo 3d_{3/2} and 233.4 eV for Mo 3d_{5/2} respectively, combined with Mo⁴⁺ and Mo⁵⁺ at lower binding energies [23]. After annealing in air at 350 °C for 1 h, the Mo 3d peak in Fig. 2b (lower) shows Mo to be fully converted to Mo⁶⁺ [23]. After H₂S treatment Fig. 2c shows an obvious alteration of Mo 3d peak that mainly is dominated by Mo⁴⁺ with a binding energy of 232.8 eV for Mo 3d_{3/2} and 229.6 eV for Mo 3d_{5/2}, respectively. A clear S 2s peak at 226.9 eV can also be observed [24]. The S 2p peak (Fig. 2d) has two doublets, where

the $2p_{1/2}$ at 163.4 eV and $2p_{3/2}$ at 162.1 eV are ascribed to Mo-S, and the $2p_{1/2}$ at 164.9 eV and $2p_{3/2}$ at 163.6 eV are ascribed to Mo-S-O. A small additional peak at a higher binding energy of 168.8 eV is possibly due to the formation of molybdenum sulfate. The Ti 2p peak (Fig. 2e) shows that Ti is in the form of Ti^{4+} , as observed for the original TiNT layer.

Fig. 2. (a) XRD patterns for 6 μm TiO₂ nanotube layers with different MoS₂ loading. (b–c) XPS spectra for Mo 3d peaks for a sample with 1 nm MoS₂ on 6 μm TiO₂ NTs after different treatment steps: (b) as deposited and annealed in air and (c) after H₂S treatment and H₂ evolution reaction. (d) S 2p peak and (e) Ti 2p peak of MoS₂ on

TiO₂ NTs layer. (f) XPS depth profile of 6 μ m TiO₂ nanotube layer with 10 nm MoS₂ decoration after H₂S treatment for 2 h at 500 °C.

In order to explore the distribution of Mo along the tube walls, XPS sputter depth profiles were measured (Fig. 2f). On the outer part, Mo and S are present in a ratio of 1:2, confirming the formation of MoS₂. The depth profile shows a steep decrease of Mo and S within the first $\sim$ 30 nm, followed by a slow decrease until $\approx$ 400 nm. The amount of Mo and S are below 2% at a depth of 100 nm, and deeper inside the TiNT layers they are below the detection limit of XPS. This shows that Mo is preferentially deposited on the top and in the outmost part of the tubes (top 400 nm) — this is in line with the SEM cross-sectional image (Fig. 1g).

Following their successful fabrication and characterization, the MoS₂ decorated TiO₂ nanotube arrays were studied to determine their photo- chemical response (Fig. 3a–b) and their ability to generate H₂ under bias-free (open-circuit) conditions (Fig. 3c). The photocurrent spectra (Fig. 3a) all show the typical UV response of TiO₂ anatase, but an additional, strong visible response is observed for the MoS₂ decorated tubes. If the band gap E_g is evaluated (Fig. 3b), then except for the primary gap of TiO₂ anatase at 3.1 eV, a secondary E_g can be determined in the range of 1.2 eV to 1.8 eV. The values depend on the nominal amount of MoS₂ deposited, i.e. $E_g \approx$ 1.2 eV, 1.3 eV, 1.8 eV for 10 nm MoS₂, 3 nm MoS₂, 1 nm MoS₂. This illustrates that all the MoS₂ deposits used here can act as a photosensitizer. The shift in the band gap suggests that the amounts deposited here are sufficiently low that quantum size effects can occur for deposits with a nominal thickness of 3 nm and 1 nm (Fig. 3d).

Fig. 3c shows the results of H₂ evolution activity when different tube and MoS₂ combinations are investigated under open-circuit conditions. It can be seen that 1 nm MoS₂ decorated on a 6 μ m TiNT layer shows the strongest H₂ evolution activity. Samples that are decorated with thinner or thicker MoS₂ layers show a lower activity for H₂ evolution. Importantly, samples with longer TiO₂ NTs show an increasing activity (when decorated with the same amount of 1 nm MoS₂). For tubes longer than 6 μ m no further increase is observed. Please note that after H₂ evolution tests the Mo 3d peak (Fig. 2c lower) does not change significantly, which suggests that MoS₂ is stable under the present experimental

conditions.

Fig. 3. (a) Photocurrent spectra for reference TiNTs layers of 6 μm, 1 nm MoS₂, 3 nm MoS₂ and 10 nm MoS₂ on the surface, respectively. (b) Evaluation of the band gap values from photocurrent spectra in panel a. (c) H₂ evolution activity for different MoS₂ thickness and different TiO₂ nanotube length with 1 nm MoS₂ under AM1.5 conditions. (d) Calculated band gap positions for different thicknesses of MoS₂ by

DFT/PBE. Reprint from Physical Review B 83, 245213 (2011), copyright 2011 American Physical Society [13]. (e) Illustration for photogenerated charge transfer mechanism in the MoS₂/TiO₂ NT samples. (f) Band gap alignments of TiO₂ and MoS₂ with different thickness.

The results thus show that MoS₂ deposited on top of TiO₂ nanotubes can act as a suitable charge transfer mediator (Fig. 3e) (co-catalyst) for H₂ evolution. Considering both the photocurrent spectra and the photocatalytic H₂ evolution measurements, one can conclude that MoS₂ can have a dual effect on TiO₂ NTs: as photosensitizer (as illustrated in Fig. 3f-A) and as H₂ evolution co-catalyst (Fig. 3f-B).

This suggests that the distribution of particle sizes present in MoS₂ provides a range of states with energies close to the conduction band of TiO₂ that act according to scheme A or B (Fig. 3f). The findings that samples carrying nominally 1 nm of MoS₂ are the most efficient H₂ evolution catalysts is ascribed to the shadowing that increases with the increasing amount of MoS₂ (light is increasingly blocked from the underlying TiO₂ layer).

It is important to note that the length of the nanotube beneath the MoS₂ layer plays a significant role in the efficiency of H₂ evolution. The tubes thus act as light harvesters and generated photoelectrons can reach the top catalyst layer by diffusion over several μm . This is in line with literature showing that for TiO₂ nanotubes the electron diffusion length is of the order of 10 μm [25–27] i.e. the longer the tube, the higher the response, as long as the tubes are not longer than the electron diffusion length. Due to the typically assumed charge distribution within the tube wall, photogenerated holes are driven to the surface and react with sacrificial agents directly (holes have a short diffusion length in TiO₂ as illustrated in Fig. 3e).

The present work therefore shows that under open-circuit conditions, due to the synergetic effect of a thin MoS₂ layer and TiO₂ nanotubes, significantly improved photocatalytic H₂ evolution activity can be observed. This effect is largely based on an optimized co-catalyst/ light harvesting combination.

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