

## II.H.4 Nanostructured MoS<sub>2</sub> and WS<sub>2</sub> for the Solar Production of Hydrogen

Thomas F. Jaramillo (Primary Contact),  
Zhebo Chen, Shin-Jung Choi  
Dept. of Chemical Engineering  
381 N-South Axis  
Stanford University  
Stanford, CA 94305  
Phone: (650) 498-6879; Fax: (650) 725-7294  
E-mail: jaramillo@stanford.edu

DOE Technology Development Manager:  
Roxanne Garland  
Phone: (202) 586-7260; Fax: (202) 586-2373  
E-mail: Roxanne.Garland@ee.doe.gov

Contract Number: DE-AC36-08GO28308

Start Date: December 18, 2008  
Projected End Date: December 17, 2009

### Objectives

Develop novel nanostructured dichalcogenide materials for photoelectrochemical (PEC) production of hydrogen from water:

- Synthesize nanometer-scaled MoS<sub>2</sub> and WS<sub>2</sub> as (1) nanoparticles, (2) nanowires, and (3) a 3-dimensional bi-continuous network.
- Explore and optimize bandgap and band edge position as a function of size and architecture for water splitting.
- Study photogenerated charge separation and transport in nanostructured materials.
- Investigate catalytic ability for water splitting as a function of surface structure.
- Incorporate optimized nanostructures into a PEC device and determine efficiency and durability.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

### Technical Targets

The focus of this project is the development of semiconductor materials with strong solar absorption characteristics that efficiently store energy from the sun by splitting water into hydrogen and oxygen. If successful, this project will address the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

**TABLE 1.** Progress towards Meeting Technical Targets for PEC Hydrogen Production

Characteristics	Units	2013 Target	2009 Status
Usable semiconductor bandgap	eV	2.3	1.9
Chemical conversion process efficiency (EC)	%	10	TBD
Plant solar-to-hydrogen efficiency (STH)	%	8	TBD
Plant durability	hr	1,000	TBD

TBD - to be determined

### Accomplishments

- Optimized low temperature (150°C) sulfidization of MoO<sub>3</sub>.
- Synthesized air-stable nanoscaled MoS<sub>2</sub> nanoparticles in various sizes.
- Achieved quantum confinement of MoS<sub>2</sub> nanoparticles with indirect bandgaps between 1.2–1.9 eV and direct bandgaps between 2.0–2.8 eV.
- Produced p-type MoS<sub>2</sub> to improve PEC stability.
- Produced highly stable RuO<sub>2</sub> counter electrodes for facile oxygen evolution with ~10% performance decrease over 100 cycles at 2 V vs. Ag/AgCl in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution.
- Developed nanoscaled alumina templates for nanowire synthesis with mean pore diameter of 13 nm.



### Introduction

PEC water splitting for hydrogen production was first demonstrated by Fujishima and Honda in 1972 using titanium dioxide (TiO<sub>2</sub>) [1], a material limited to a maximum solar-to-hydrogen efficiency of 1% due to its large bandgap of 3.0 eV. Since the maximum solar-to-hydrogen efficiency of a material is ultimately determined by its ability to absorb light, research efforts

have primarily focused on improving solar absorption characteristics, including the use of semiconductor doping/alloying [2-6], tandem absorbers [7,8], and dye sensitization [9,10]. However, even the best absorbers to date are compounded by problems following the initial absorption such as poor charge transport and/or poor stability [11,12]. Thus, no material system exists that can yet be considered as a wide-scale deployable solution. The world record device with 12.4% solar-to-hydrogen efficiency was developed by Khaselev and Turner over a decade ago in 1998 [13], but exhibited significant stability problems and extremely high cost [14,15]. New approaches are necessary to accelerate the development of highly efficient, durable, and low cost materials for PEC water splitting.

## Approach

The project discussed here aims to improve upon previous material deficiencies through the nanostructuring of low cost semiconductor materials – in particular, molybdenum disulfide ( $\text{MoS}_2$ ) and tungsten disulfide ( $\text{WS}_2$ ). Both materials exhibit a bandgap of  $\sim 1.2$  eV [16-19], which enables the absorption of a significant portion of the solar spectrum. However, this value is too small to provide the photovoltage necessary to drive the water splitting reaction ( $\Delta G = 1.23$  eV). The minimum bandgap must encompass that thermodynamic water splitting potential of 1.23 eV in addition to the activation energies required to drive the individual hydrogen and oxygen evolution half reactions. Thus, the optimal bandgap value will likely lie in the range of  $\sim 1.8$ -2.0 eV [20]. Nanostructuring materials can result in an effect known as quantum confinement [19,21,22], which enables widening of the bandgap to a larger, more useable value for water splitting in the case of  $\text{MoS}_2$  and  $\text{WS}_2$ . In addition, edge sites at the surface of  $\text{MoS}_2$ , which are more prominent when nanostructured, have been documented as centers of high catalytic activity for the hydrogen evolution reaction [23]. This translates into a smaller required bandgap and higher theoretical efficiency.

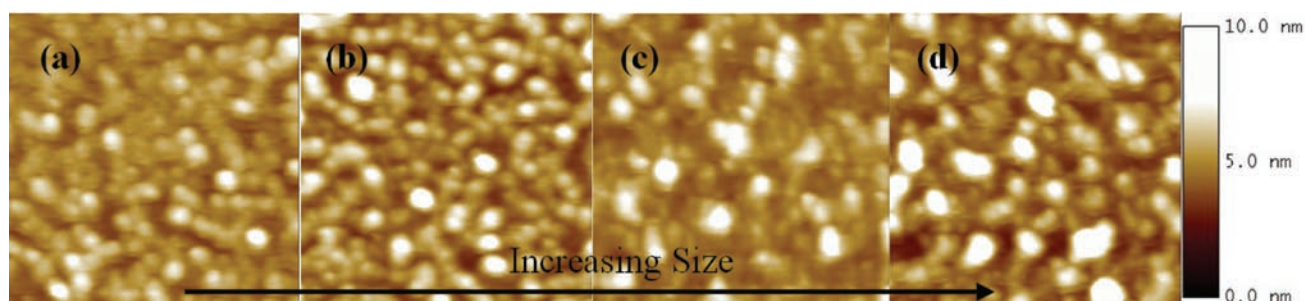
Lastly, controlling the type of conductivity has important consequences on the material's photoelectrochemical properties. By focusing on synthesizing p-type (rather than n-type)  $\text{MoS}_2$  and  $\text{WS}_2$ , the possibility of photo-oxidation is minimized and stability can be improved since the material operates as a photocathode and oxidizing holes flow away from the semiconductor-electrolyte interface [24-28].

## Results

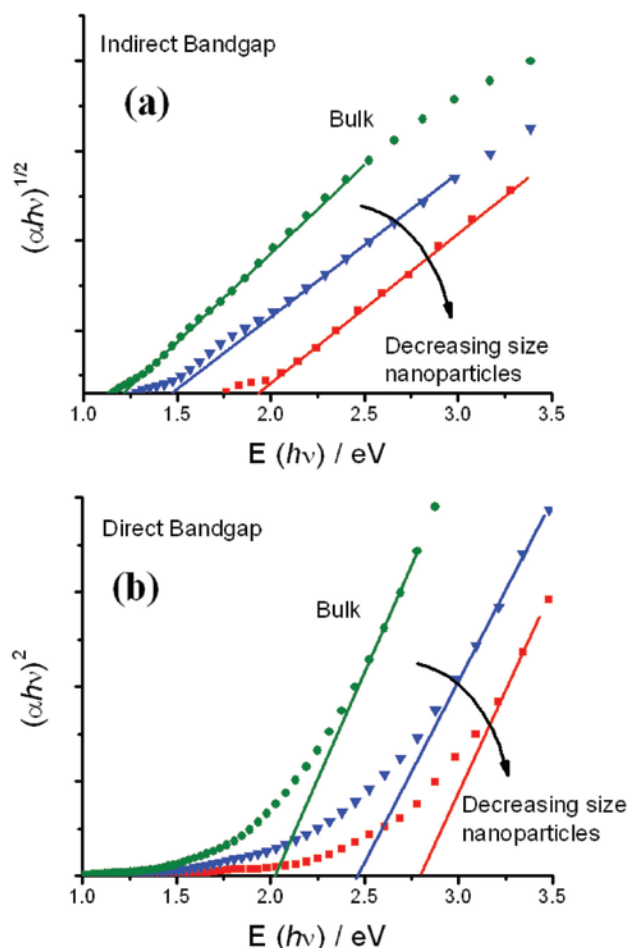
Our efforts within the first six months of the project have focused on the development of  $\text{MoS}_2$ , since it represents a material with a rich history of catalysis and photoactivity [22,29-31]. We have optimized the sulfidization of molybdenum in our laboratory using temperatures as low as  $150^\circ\text{C}$ , confirmed using ultraviolet-visible transmission (UV-Vis) spectroscopy and X-ray photoelectron spectroscopy (XPS). Electrochemical testing of  $\text{MoS}_2$  also revealed high activity for the hydrogen evolution reaction, in agreement with previous reports [23].

Synthesis of supported  $\text{MoS}_2$  nanoparticles in various sizes was accomplished using a reverse micelle encapsulation method [32-34]. The low temperature sulfidization process minimized nanoparticle sintering. The nanoparticles were imaged using atomic force microscopy (AFM) as shown in Figure 1, although exact size measurements are limited due to convolution of the AFM tip. Work is currently underway to precisely determination the size distributions of such nanoparticles using transmission electron microscopy. Despite their small size, these nanoparticles are fully resistant to oxidation from exposure to air, as confirmed using XPS.

UV-Vis spectroscopy of the  $\text{MoS}_2$  nanoparticles revealed a blue-shift in their absorption onset. Furthermore, the degree of blue-shifting increased with smaller nanoparticle size. This behavior is expected and is characteristic of the quantum confinement phenomenon. Tauc plots of the direct and indirect bandgaps are shown in Figure 2.



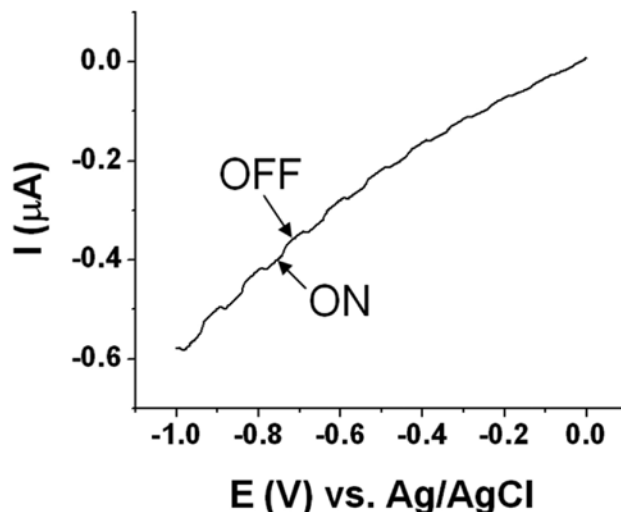
**FIGURE 1.** Atomic force microscopy of  $\text{MoS}_2$  nanoparticles in increasing size from (a)→(d), produced using an inverse micelle encapsulation method, using a poly(styrene-*b*-2-vinylpyridine) polymer and a  $\text{MoCl}_3$  precursor.



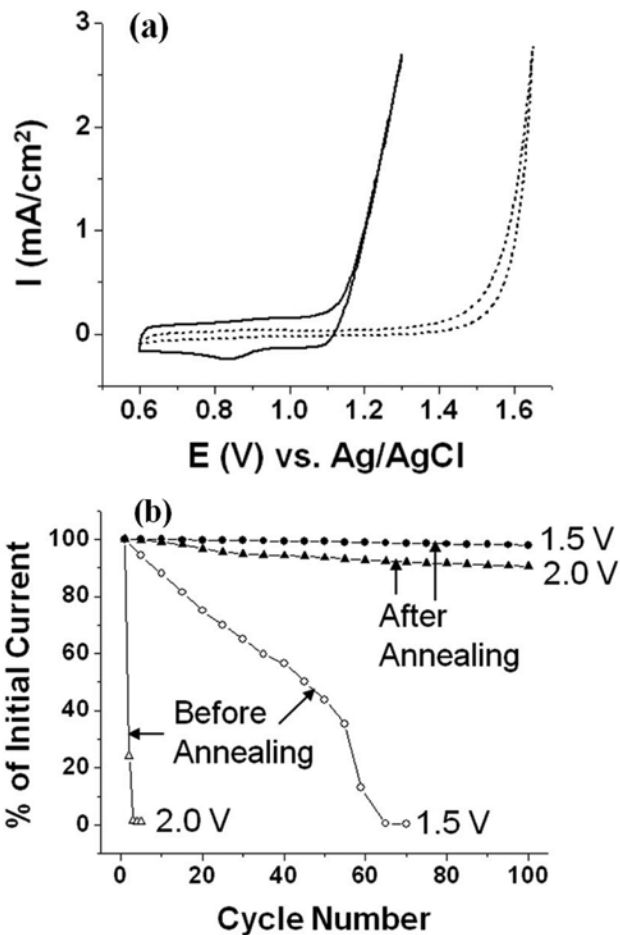
**FIGURE 2.** MoS<sub>2</sub> absorption shown in (a) allowed indirect and (b) allowed direct Tauc plots. Bulk MoS<sub>2</sub> films show an indirect bandgap of ~1.2 eV and a direct bandgap of ~2.0 eV (green circles). MoS<sub>2</sub> nanoparticles from Figure 1(d) show an indirect bandgap of ~1.5 eV and a direct bandgap of ~2.5 eV (blue triangles), while nanoparticles from Figure 1(c) show an indirect bandgap of ~1.9 eV and a direct bandgap of ~2.8 eV (red squares).

While MoS<sub>2</sub> crystals in nature can be found to have either n-type or p-type conductivity, we have synthesized consistently p-type MoS<sub>2</sub> by the addition of Nb. Conductivity type was assessed using photocurrent measurements under an applied bias in an electrochemical cell, shown in Figure 3. The observed photocurrent was negative in sign, and increased towards negative potentials, characteristic of p-type behavior.

As part of the effort to develop p-type MoS<sub>2</sub>, it is necessary to produce counter-electrodes that have low overpotentials for the oxygen evolution reaction. RuO<sub>2</sub> is a material that exhibits high conductivity, chemical and thermal stability, and catalytic activity [35-37]. Using an electrochemical deposition technique followed by a heat treatment, we produced RuO<sub>2</sub> counter-electrodes that exhibit a 400 mV earlier onset for oxygen



**FIGURE 3.** PEC response for Nb-doped MoS<sub>2</sub> thin film under chopped illumination from a ~2.5 Sun xenon lamp.



**FIGURE 4.** (a) Cyclic voltammogram of oxygen evolution reaction for a RuO<sub>2</sub> electrode (solid line) compared to a Pt electrode (dotted line). (b) Stability of RuO<sub>2</sub> electrodes unannealed and annealed at 400°C for 1 hr during 100 cyclic voltammograms between 0.5 V up to 1.5 V or 2.0 V vs. Ag/AgCl.

evolution compared to Pt as shown in Figure 4(a), and demonstrates strong stability over 100 cycles of oxygen evolution, even when subjected to a +2 V bias vs. the Ag/AgCl reference electrode in a highly acidic 0.1 M H<sub>2</sub>SO<sub>4</sub> solution as shown in Figure 4(b).

Our efforts to synthesize nanowires have been focused on the development of anodic alumina templates [38-42]. We have achieved the synthesis of templates with 13 nm pores, as imaged by scanning electron microscopy, and are continuing to optimize the synthesis towards even smaller pore sizes. We have also synthesized samples of the bi-continuous network templates using a silica template [43-45] and are continuing with further development. Following the development of these templates, we will synthesize molybdenum and tungsten nanostructures using an electrodeposition process that we optimized in our laboratory.

## Conclusions and Future Directions

We have made significant process in developing nanostructured MoS<sub>2</sub> for PEC water splitting:

- Optimized low temperature sulfidization of molybdenum.
- Synthesized air stable nanoparticulate MoS<sub>2</sub> in various sizes.
- Confirmed size-dependent quantum confinement of nanoparticulate MoS<sub>2</sub>, widening the bandgap to values of ~2 eV.
- Synthesized p-type MoS<sub>2</sub>.
- Developed anodic alumina templates with nanopores.

Our work on this project continues with the assessment of the valence and conduction band edges of our nanostructured MoS<sub>2</sub>, using spectroscopic techniques such as ultraviolet photoelectron spectroscopy coupled to inverse photoemission spectroscopy. We plan to assess the flat band potential using electrochemical techniques such as illuminated open circuit potential, Mott-Schottky, and photocurrent onset. This will enable determination of the surface electronic structure of our semiconductor materials and provide insight into their ability to actively split water using sunlight without an applied bias. We will also pursue PEC measurements on the supported nanostructures, measuring photocurrent with and without an applied bias and sampling the gas headspace by gas chromatography.

Work is underway to further develop the anodic alumina templates, as well as the nanoporous bi-continuous networks. The templates will enable the development of MoS<sub>2</sub> and WS<sub>2</sub> nanowires and bi-continuous networks using an electrodeposition process.

Although initial efforts have focused on MoS<sub>2</sub>, work is already underway to develop WS<sub>2</sub> nanostructures. WS<sub>2</sub> is an important avenue of study due to its structural and electronic similarities to MoS<sub>2</sub>. By studying both MoS<sub>2</sub> and WS<sub>2</sub> in multiple nanostructured forms, we address the challenge of developing a deployable PEC water splitting device using state-of-the-art techniques, with significant potential for producing knowledge that spans a large number of scientific fields, including photovoltaics and heterogeneous catalysis.

## FY 2009 Presentations

1. 2009 US DOE Hydrogen Program and Vehicle Technologies Annual Merit Review & Peer Evaluation Meeting, Arlington, VA. "Nanostructured MoS<sub>2</sub> and WS<sub>2</sub> for the solar production of hydrogen" T.F. Jaramillo, May 2009.
2. US DOE Photoelectrochemical Hydrogen Production Quarterly Meeting, San Francisco, CA. "Nanostructured MoS<sub>2</sub> and WS<sub>2</sub> for the solar production of hydrogen" T.F. Jaramillo, April 2009.
3. University of California, Berkeley, Nanosciences and Nanoengineering Institute (BNNI), Nanoscale Science and Engineering (NSE) Seminar, Berkeley, CA. "Designing nano-scaled, non-precious metal catalysts for hydrogen evolution" T.F. Jaramillo, March 2009.
4. Chevron Corporation, Richmond, CA, May 2009. "Solar Fuels by Photoelectrochemistry (PEC)" T.F. Jaramillo, March 2009.
5. US DOE Hydrogen Production Technical Team Review: Photoelectrochemical Hydrogen Production, San Francisco, CA. "Nanostructured MoS<sub>2</sub> and WS<sub>2</sub> for the solar production of hydrogen" T.F. Jaramillo, January 2009.

## References

1. A. Fujishima and K. Honda: Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37 (1972).
2. V.M. Aroutiounian, V.M. Arakelyan and G.E. Shahnazaryan: Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting. *Sol. Energy* **78**, (2005).
3. M. Anpo, S. Dohshi, M. Kitano, Y. Hu, M. Takeuchi and M. Matsuoka: The preparation and characterization of highly efficient titanium oxide-based photofunctional materials. *Ann. Rev. Mater. Res.* **35**, (2005).
4. S.U.M. Khan, M. Al-Shahry and W.B. Ingler: Efficient photochemical water splitting by a chemically modified n-TiO<sub>2</sub>. *Science* **297**, (2002).
5. T.F. Jaramillo, S.H. Baeck, A. Kleiman-Shwarsstein, K.S. Choi, G.D. Stucky and E.W. McFarland: Automated electrochemical synthesis and photoelectrochemical characterization of Zn<sub>1-x</sub>CoxO thin films for solar hydrogen production. *J. Comb. Chem.* **7**, (2005).

6. I. Cesar, A. Kay, J.A.G. Martinez and M. Gratzel: Translucent thin film Fe<sub>2</sub>O<sub>3</sub> photoanodes for efficient water splitting by sunlight: Nanostructure-directing effect of Si-doping. *J. Am. Chem. Soc.* **128**, (2006).
7. M. Gratzel: Photoelectrochemical cells. *Nature* **414**, (2001).
8. O. Khaselev, A. Bansal and J.A. Turner: High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. in 127-132 (2001).
9. M. Gratzel: Mesoscopic solar cells for electricity and hydrogen production from sunlight. *Chem. Lett.* **34**, (2005).
10. W.J. Younplblood, S.H.A. Lee, Y. Kobayashi, E.A. Hernandez-Pagan, P.G. Hoertz, T.A. Moore, A.L. Moore, D. Gust and T.E. Mallouk: Photoassisted Overall Water Splitting in a Visible Light-Absorbing Dye-Sensitized Photoelectrochemical Cell. *J. Am. Chem. Soc.* **131**, (2009).
11. W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S.H. Baeck and E.W. McFarland: A CU<sub>2</sub>O/TiO<sub>2</sub> heterojunction thin film cathode for photoelectrocatalysis. *Sol. Energy Mater. Sol. Cells* **77**, (2003).
12. J.A. Glasscock, P.R.F. Barnes, I.C. Plumb and N. Savvides: Enhancement of photoelectrochemical hydrogen production from hematite thin films by the introduction of Ti and Si. *J. Phys. Chem. C* **111**, (2007).
13. O. Khaselev and J.A. Turner: A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. *Science* **280**, 425 (1998).
14. O. Khaselev and J.A. Turner: Electrochemical stability of p-GaInP<sub>2</sub> in aqueous electrolytes toward photoelectrochemical water splitting. *J. Electrochem. Soc.* **145**, (1998).
15. X.P. Gao, S. Kocha, A.J. Frank and J.A. Turner: Photoelectrochemical decomposition of water using modified monolithic tandem cells. in 319-325 (1999).
16. C.B. Roxlo, R.R. Chianelli, H.W. Deckman, A.F. Ruppert and P.P. Wong: Bulk and surface optical absorption in molybdenum disulfide. *J. Vac. Sci. Technol. A-Vac. Surf. Films* **5**, (1987).
17. O.C. Monteiro and T. Trindade: Synthesis of molybdenum (IV) disulfide using a single-source method. *Mater. Res. Bull.* **39**, (2004).
18. J.A. Baglio, G.S. Calabrese, E. Kamieniecki, R. Kershaw, C. P. Kubiak, A. J. Ricco, A. Wold, M. S. Wrighton and G. D. Zoski: Characterization of n-type semiconducting tungsten disulfide photo-anodes in aqueous and non-aqueous electrolyte solutions - photooxidation of halides with high efficiency. *J. Electrochem. Soc.* **129**, (1982).
19. J.P. Wilcoxon and G.A. Samara: Strong quantum-size effects in layered semiconductor - MoS<sub>2</sub> nanoclusters. *Phys. Rev. B* **51**, (1995).
20. J. Nowotny, C.C. Sorrell, L.R. Sheppard and T. Bak: Solar-hydrogen: Environmentally safe fuel for the future. *Int. J. Hydrog. Energy* **30**, (2005).
21. A.J. Nozik and R. Memming: Physical chemistry of semiconductor-liquid interfaces. *J. Phys. Chem.* **100**, (1996).
22. T.R. Thurston and J.P. Wilcoxon: Photooxidation of organic chemicals catalyzed by nanoscale MoS<sub>2</sub>. *J. Phys. Chem. B* **103**, (1999).
23. T.F. Jaramillo, K.P. Jorgensen, J. Bonde, J.H. Nielsen, S. Horch and I. Chorkendorff: Identification of active edge sites for electrochemical H<sub>2</sub> evolution from MoS<sub>2</sub> nanocatalysts. *Science* **317**, (2007).
24. A. Jager-Waldau, M.C. Lux-Steiner, E. Bucher, L. Scandella, A. Schumacher and R. Prins: MoS/sub 2/ thin films prepared by sulphurization. *Appl. Surf. Sci.* **66**, (1993).
25. J.J. Devadasan, C. Sanjeeviraja and M. Jayachandran: Electrodeposition of p-WS<sub>2</sub> thin film and characterisation. *J. Cryst. Growth* **226**, (2001).
26. T. Moehl, M. Kunst, F. Wunsch and H. Tributsch: Consistency of photoelectrochemistry and photoelectrochemical microwave reflection demonstrated with p- and n-type layered semiconductors like MoS<sub>2</sub>. *J. Electroanal. Chem.* **609**, (2007).
27. C. Sourisseau, F. Cruege and O. Gorochoy: In-situ raman investigation of photo corrosion processes at p-type and n-type WS<sub>2</sub> electrodes in acid solutions. *J. Electroanal. Chem.* **308**, (1991).
28. R. Schlaf, D. Louder, M.W. Nelson and B.A. Parkinson: Influence of electrostatic forces on the investigation of dopant atoms in layered semiconductors by scanning tunneling microscopy/spectroscopy and atomic force microscopy. in 1466-1472 (1997).
29. H. Tributsch and J.C. Bennett: Electrochemistry and photochemistry of MoS<sub>2</sub> layer crystals. *J. Electroanal. Chem.* **81**, (1977).
30. R.R. Chianelli, M.H. Siadati, M.P. De la Rosa, G. Berhault, J.P. Wilcoxon, R. Bearden and B.L. Abrams: Catalytic properties of single layers of transition metal sulfide catalytic materials. *Catal. Rev.-Sci. Eng.* **48**, (2006).
31. B.L. Abrams and J.P. Wilcoxon: Nanosize semiconductors for photooxidation. *Crit. Rev. Solid State Mat. Sci.* **30**, (2005).
32. J.P. Spatz, S. Mossmer, C. Hartmann, M. Moller, T. Herzog, M. Krieger, H.G. Boyen, P. Ziemann and B. Kabius: Ordered deposition of inorganic clusters from micellar block copolymer films. *Langmuir* **16**, (2000).
33. T. F. Jaramillo, S.H. Baeck, B.R. Cuenya and E.W. McFarland: Catalytic activity of supported au nanoparticles deposited from block copolymer micelles. *J. Am. Chem. Soc.* **125**, (2003).
34. Y.L. Gu, J. St-Pierre and H.J. Ploehn: Pt/Glassy Carbon Model Catalysts Prepared from PS-b-P2VP Micellar Templates. *Langmuir* **24**, (2008).
35. H.J. Lewerenz, S. Stucki and R. Kotz: Oxygen evolution and corrosion - XPS investigation on Ru and RuO<sub>2</sub> electrodes. *Surf. Sci.* **126**, (1983).

36. C.C. Hu, C.F. Lee and T.C. Wen: Oxygen evolution and hypochlorite production on Ru-Pt binary oxides. *J. Appl. Electrochem.* **26**, (1996).
37. D.T. Shieh and B.J. Hwang: Oxygen evolution on PTFE-modified ruthenium oxide electrodes investigated by CV techniques. *J. Electroanal. Chem.* **391**, (1995).
38. A. Jagminas, I. Valsiunas, B. Simkunaite and R. Vaitkus: Peculiarities of Bi-0 nanowire arrays growth within the alumina template pores by ac electrolysis. *J. Cryst. Growth* **310**, (2008).
39. J.P. O'Sullivan and G.C. Wood: The Morphology and Mechanism of Formation of Porous Anodic Films on Aluminium. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **317**, (1970).
40. W. Chen, J.-S. Wu and X.-H. Xia: Porous Anodic Alumina with Continuously Manipulated Pore/Cell Size. *ACS Nano* **2**, (2008).
41. G. Ferrara, R. Inguanta, S. Piazza and C. Sunseri: Characterization of Sn-Co Nanowires Grown into Alumina Template. *Electrochem. Solid State Lett.* **12**, (2009).
42. A. Michailowski, D. AlMawlawi, G. Cheng and M. Moskovits: Highly regular anatase nanotubule arrays fabricated in porous anodic templates. *Chemical Physics Letters* **349**, (2001).
43. V.N. Urade, T.C. Wei, M.P. Tate, J.D. Kowalski and H.W. Hillhouse: Nanofabrication of double-gyroid thin films. *Chem. Mat.* **19**, (2007).
44. V.N. Urade, L. Bollmann, J.D. Kowalski, M.P. Tate and H.W. Hillhouse: Controlling interfacial curvature in nanoporous silica films formed by evaporation-induced self-assembly from nonionic surfactants. II. Effect of processing parameters on film structure. *Langmuir* **23**, (2007).
45. L. Bollmann, V.N. Urade and H.W. Hillhouse: Controlling interfacial curvature in nanoporous silica films formed by evaporation-induced self-assembly from nonionic surfactants. I. Evolution of nanoscale structures in coating solutions. *Langmuir* **23**, (2007).