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# **A substoichiometric tungsten oxide catalyst provides a sustainable and efficient counter electrode for dye-sensitized solar cells**

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## **Abstract**

Development of Pt-free catalyst materials for the counter electrode (CE) in dye-sensitized solar cells (DSSCs) has been regarded as one of the crucial steps to improving energy conversion efficiency and cost effectiveness of DSSCs. In this work, low cost tungsten oxide ( $\text{WO}_{3-x}$ ) counter electrodes, prepared by annealing tungsten metal sheets under an Ar and low  $\text{O}_2$  atmosphere, exhibited high catalytic activity and energy conversion efficiency. The highest efficiency achieved here for DSSCs with  $\text{WO}_{3-x}$  counter electrodes, was 5.25%, obtained from a 500 °C annealed tungsten sheet. TEM and XPS analysis suggested the formation of sub-stoichiometric tungsten oxide layer ( $\sim\text{WO}_{2.6}$ ) with the presence of  $\text{W}^{6+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{4+}$  oxidation states at the tungsten metal surface after the 500 °C annealing. Only  $\text{W}^{6+}$  and  $\text{W}^{5+}$  oxidation states were detected after a 600 °C annealing indicating the formation of a more stoichiometric tungsten oxide layer ( $\sim\text{WO}_{2.8}$ ) and resulting

in a drop in efficiency of the DSSC. We suggest that mixed valence tungsten states account for the excellent catalytic activity and good electrical conductivity as evidenced by the highest cyclic voltammetry response of  $0.76 \text{ mA/cm}^2$  and the lowest impedance value of  $44.33 \Omega$ , respectively.

**Keywords :** substoichiometric tungsten oxide, counter electrode, dye-sensitized solar cell

## 1. Introduction

The counter electrode (CE) is regarded as one of the most important components of dye-sensitized solar cells (DSSCs) since it acts as the electron collector from the external circuit and facilitates the reduction reaction of tri-iodide ions ( $I_3^-$ ) [1]. In addition, high catalytic activity and high electrical conductivity are required for a good catalyst for DSSCs. Pt is a catalyst typically used in DSSCs. However, it is costly, rare and is readily corroded by an iodide electrolyte [2]. Identifying and developing alternative materials to substitute for Pt in the CE of DSSCs is a crucial challenge and success could reduce production costs sufficiently to increase the use of DSSCs. Candidate materials already proposed as replacements for Pt CEs include carbon materials [3], CoS [4], TiN [5] and conductive polymers [6]. Recently, tungsten carbide (WC) [7] and tungsten oxide ( $WO_x$ ) [8] have been introduced as CEs and have exhibited good catalytic performance.

Wu et al. reported that the use of  $WO_2$  nanorods embedded in mesoporous carbon (MC) as the counter electrode in DSSCs generated a conversion efficiency as high as 7.76%, which is higher than that of a Pt DSSC, 7.55% [9]. This was attributed to a combination of the excellent conductivity of carbon and the high catalytic activity of  $WO_2$ . Tungsten trioxide ( $WO_3$ ) or stoichiometric tungsten oxide and substoichiometric tungsten oxide ( $WO_{3-x}$ )

nanostructures have also been intensively investigated for a wide range of applications including photocatalysis [10-12], electrochromic devices [13], gas sensors [14] and DSSC photoanodes [15]. The crystal structure of  $\text{WO}_3$  is based on corner-sharing  $\text{WO}_6$  octahedra [16]. Non-stoichiometric tungsten trioxide ( $\text{WO}_{3-x}$ , where  $0 < x \leq 1$ ), which is oxygen deficient, contains tungsten in a number of differing formal oxidation states. It has been reported that a slight deficit of oxygen i.e.  $x = 1/6$  is more energetically stable in standard atmospheric conditions than stoichiometric  $\text{WO}_3$  [17]. Stoichiometric  $\text{WO}_3$  is a wide band gap semiconductor ranging from 2.6 - 3.0 eV [13, 18], with a conductivity that increases with increasing oxygen deficiency [13].

Tungsten oxides can be synthesized by many different routes including vapor phase techniques such as physical vapor deposition (PVD) [19] including thermal evaporation [20], chemical vapor deposition (CVD) [21] or liquid phase methods such as sol-gel and hydrothermal techniques [22]. Other chemical methods for synthesizing sub-stoichiometric tungsten oxides are; for example, thermal decomposition of  $\text{W}(\text{CO})_6$  at 250–270 °C in  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  and oleylamine mixture to produce colloidal  $\text{W}_{18}\text{O}_{49}$  nanorods [23].  $\text{WO}_2$  nanorods were also produced by adding urea to a solution of  $\text{WCl}_6$  and alcohol, then the solution was dried and sintered at 800 °C for 4 hours under a  $\text{N}_2$  atmosphere [9]. In general, vapor phase routes are rapid and high-yield processes, but they usually require high temperatures 700-1400 °C and low pressures [24]. Liquid phase methods are generally more time consuming but offer lower production costs and better control of morphology; however, they suffer from impurities that require further post-synthesis treatments to eliminate them.

Development of high performance CEs by a facile synthesis route without sophisticated equipment, harsh experimental conditions or dealing with hazardous chemicals would be very beneficial to the solar cell manufacturing industry. In this work, we have prepared and characterized  $\text{WO}_{3-x}$  counter electrodes for DSSCs by direct annealing of pure

tungsten metal under an Ar atmosphere with low oxygen content. The tungsten oxide films produced were found to exhibit a good catalytic activity with  $I^-/I_3^-$  redox species and a promising DSSC energy conversion performance of 5.25%, however the performance of the resulting DSSCs was found to vary with annealing temperature. To explain the changes in DSSC efficiencies, cyclic voltammetry and electrochemical impedance spectroscopy were also conducted.

## **2. Experimental**

### *2.1 Counter electrode preparation*

DSSC counter electrodes were prepared using tungsten metal sheet with a thickness of 0.25 mm (99.95 % purity, Goodfellow) cut into pieces of 0.7 x 1.5 cm<sup>2</sup>. The tungsten foils were cleaned in a series of deionized water, ethanol and acetone solutions. After drying in air, the tungsten foils were annealed in a tube furnace under an Ar atmosphere (99.9% purity containing less than 25 ppm O<sub>2</sub> and less than 25 ppm water vapor) at 100, 200, 300, 400, 500 and 600 °C for 2 hours at a heating rate of 2 °C/min. Then the samples were allowed to cool down to room temperature under Ar atmosphere.

### *2.2 Cell assembly*

DSSCs were assembled using the pure tungsten or annealed tungsten foils as counter electrodes, TiO<sub>2</sub>-coated dye-sensitizer films on Fluorine Tin Oxide (FTO, sheet resistance 7 Ω/sq, Solaronix, USA)) were used for the working electrodes, and an  $I^-/I_3^-$  solution was used as the electrolyte. The working electrodes were prepared using a screen printing method as previously reported [25] using commercial TiO<sub>2</sub> powders: PST-18NR and PST-400C (JGC Catalysts and Chemicals Company, Japan). The TiO<sub>2</sub> films were sintered at 500 °C for 1 hour, and treated with UV radiation for 10 min and then immersed into a 0.3 mM *cis-bis-*

(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium (N-719, Solaronix) solution for 24 hours. Pt counter electrodes were prepared by spin coating 20 mM of  $\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$  (Aldrich) and 0.01 g of ethylcellulose (Aldrich) in ethanol onto FTO glass, and then annealing at 500 °C for 1 hour in an ambient environment.

### *2.3 Film characterization*

The morphology and structure of the pure (unannealed) and annealed tungsten sheets were characterized using transmission electron microscopy (TEM) (FEI Tecnai G2 20,  $\text{LaB}_6$  filament, operating at 200 kV) and X-ray photoelectron spectroscopy (XPS) (AXIS-His, Kratos Analytical with aluminum K-alpha X-ray source (1486.71 eV, 150W). The XPS spectra were fitted with asymmetric mixed Gaussian–Lorentzian sum functions using the XPS peak fitting programme XPSpeak (version 4.0). XPS analyses were undertaken on the bulk structures of the as-prepared tungsten sheets. TEM samples were prepared by scratching off the film surface, the particles being dispersed in ethanol and dropped onto TEM grids. The electrode catalytic activity was measured using Cyclic Voltammetry (CV, Gamry Instrument Reference 3000, U.S.A) with a three-compartment cell at a scan rate of 20 mV/s in solutions of 10 mM LiI, 1 mM  $\text{I}_2$ , and 0.1 M  $\text{LiClO}_4$  in acetonitrile. A Pt plate and an Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. The DSSC characteristics were analyzed using a solar simulator (PEC-L11, Japan) under an air mass of 1.5 and a light intensity of 100  $\text{mW}/\text{cm}^2$ . The impedance of the symmetric-electrode cells was measured using Electrochemical Impedance Spectroscopy (EIS, Gamry Instrument Reference 3000, U.S.A.) under dark conditions by varying the frequency from 0.1 Hz to 100,000 Hz at an AC amplitude of 10 mV.

### 3. Results and discussion

#### 3.1 Tungsten oxide ( $WO_x$ ) Film characterization

Figure 1(a) shows a photograph of the pure and annealed tungsten electrodes, showing a clear color change to golden brown and dark blue at the annealing temperatures of 500 and 600 °C, respectively. This color change suggests a transformation in stoichiometry [26, 27].

The crystal structures of the films were examined by TEM analysis of the scratched surface parts of the 400, 500 and 600 °C samples. No oxide content was detected by TEM selected area electron diffraction of the 400 °C sample [Fig. 1(b)], only cubic tungsten metal was present (JCPDS file No. 47-1319). Orthorhombic  $WO_3$  and the cubic tungsten background were detected at the annealing temperature of 500 °C (JCPDS file No.20-1324) implying that annealing between 400-500 °C is sufficiently high a temperature to activate tungsten oxide formation [Fig. 1(c)]. Crystalline nanorods of various sizes were observed in the 600 °C annealed film [Fig. 1(d)]. TEM selected area electron diffraction indicated that the surface of the 600 °C sample also contained orthorhombic  $WO_3$  (diffraction pattern inset in Fig. 1(d) and indexed to JCPDS file No.20-1324) and some reflections from cubic tungsten can still be observed. Orthorhombic  $WO_3$  is typically stable at 330-740 °C [28]. The detailed indexing of the electron diffraction patterns can be found in section S1 of the supplementary material.

Fig. 1. (a) Photograph of the pristine and annealed tungsten sheets after annealing at temperatures ranging from 100-600 °C. (b), (c) and (d) are TEM images and inset selected area electron diffraction patterns of the annealed tungsten foils at 400, 500 and 600 °C, respectively.

Detection of both W metal and WO<sub>3</sub> in the 500 °C film could be due to the formation of only a thin oxide layer, with the specimen preparation route of simply scratching the film surface possibly resulting in particles of both the oxide and bulk tungsten metal being sampled [Fig. 1(c)].

To further identify the valence state and stoichiometry of the tungsten oxides, surface analysis using X-ray photoelectron spectroscopy (XPS) was performed. The W 4f spectra of the pristine tungsten and tungsten annealed at 100-300 °C (not shown) are similar, consisting of a superposition of peaks of various tungsten oxide states [Fig. (2)]. These peaks were deconvoluted into 5 doublet components as a result of spin-orbit coupling corresponding to W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> states. Binding energies of these doublet peaks are centered at ~35.7 and ~37.8 eV for W<sup>6+</sup>, at ~34.6 and ~36.7 eV for W<sup>5+</sup> and at ~33.7 and ~35.7 eV for W<sup>4+</sup> [29-31]. The peaks at 31.5 and 33.5 eV are assigned to metal tungsten peaks, which were not detectable at the annealing temperatures of 500 and 600 °C presumably due to an increase in thickness of the oxide film at these temperatures. The peaks at ~32 and 34 eV visible in the unannealed and the 400 °C annealing are suspected to be a mixture of tungsten in a low oxidation state (W<sup>2+</sup>) and possibly tungsten carbide [32].

The XPS results suggest that oxides containing W<sup>6+</sup>, W<sup>5+</sup>, W<sup>4+</sup> and W<sup>2+</sup> readily form as the native oxide at ambient temperature and remain unchanged up to an annealing temperature of 300 °C, albeit with the presence of W<sup>2+</sup>, W<sup>4+</sup> and W<sup>5+</sup> in relatively small amounts compared to W<sup>6+</sup> (Table 1). The detectable oxides presumably form a very thin layer [33] which would explain the dominance of tungsten metal in the electron diffraction patterns of specimens prepared for TEM by scratching the sample surface. After the 400 °C annealing, the ratio of total tungsten oxide peak areal intensity to tungsten metal peak areal intensity increased and at 500 °C the tungsten metal peaks almost disappeared. After the 600 °C annealing, only W<sup>6+</sup> and W<sup>5+</sup> were detected by XPS.

The areal intensities and relative ratios of  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  ( $W^{6+}: W^{5+}: W^{4+}$ ) of the unannealed and the annealed tungsten sheets are presented in Table 1. When annealing above 300 °C the  $W^{6+}$  content rises sharply from ~ 45% to ~ 80 % by 600 °C. Similarly the  $W^{5+}$  content also increased sharply from ~ 5% at 300 °C to 22% at 600 °C while the  $W^{4+}$  and  $W^{2+}$  contents were at the highest in the pure W (10 and 20 % respectively) and gradually decreased with the rising annealing temperature (to 4 and 11 % respectively at 600 °C), suggesting a shift to a more stoichiometric  $WO_{3-x}$  oxide layer.

Table 1

The fitted peak area as a percentage of the total  $4f_{7/2}$  peak area and the ratio of  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  ( $W^{6+}: W^{5+}: W^{4+}$ ) of the unannealed and the annealed tungsten sheets at 100-600 °C

The combination of the TEM electron diffraction and XPS analysis suggest that a substoichiometric tungsten oxide ( $WO_{3-x}$ , containing  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  in the ratio of 5.18 : 1 : 0.24) forms and fully covers the tungsten metal foil after annealing at 500 °C. The O/W was quantified using O 1s and W  $4f_{7/2}$  XPS peak areas (the detail is described in section S2 in the supplementary material) indicating a ratio of 2.57 after the 500 °C annealing suggesting a  $WO_{3-x}$  oxide layer with  $x = 0.4$ . The 600 °C annealed tungsten contained only  $W^{6+}$  and  $W^{5+}$  ( $W^{6+}: W^{5+} = 3.46 : 1$ ) giving an O/W ratio of 2.76 suggesting the presence of  $WO_{3-x}$  with  $x \approx 0.2$  nanorods

Fig. 2. W 4f X-ray photoelectron spectra of the pristine and annealed tungsten foils at 400, 500, and 600 °C (in black) with peak fitting to metal W (grey), W<sup>2+</sup>/WC (blue), W<sup>4+</sup> (purple), W<sup>5+</sup> (green) and W<sup>6+</sup> (orange) components.

### 3.2 DSSC performance

Photocurrent ( $J$ ) - photovoltage ( $V$ ) characteristics of the tungsten and tungsten oxide DSSCs are presented in Figure 3(a). The short-circuit current density ( $J_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), the fill factor (FF), and the energy conversion efficiency ( $\eta$ ) have been extracted from Fig. 3 and are summarized in Table 2. It was found that the efficiency, short-circuit current density, open-circuit voltage, fill factor of the tungsten oxide based DSSCs depended on the annealing temperature. The efficiency dramatically increased from 0.17% for the pristine tungsten metal DSSC to 5.25% for the 500 °C annealed tungsten DSSC, which is approaching that of Pt DSSCs (6.96%). When the annealing temperature was further increased to 600 °C, the DSSC performance dropped to 4.16%.

Fig. 3. (a)  $J$ - $V$  characteristics and (b) Nyquist plot of the  $I^-/I_3^-$  symmetrical cells for the various annealing temperatures of the tungsten counter electrodes and compared to those of a Pt based DSSC. (c) The equivalent circuit used to fit the EIS spectra.

Table 2

Summary of  $J_{sc}$ ,  $V_{oc}$ ,  $FF$ ,  $\eta$ ,  $R_s$ ,  $R_{ct}$ ,  $V_{red}(1)$ ,  $I_{red}(1)$ ,  $V_{red}(2)$  and  $I_{red}(2)$  values for the tungsten CE DSSC devices annealed at the various temperatures and compared to that of a Pt CE DSSC.

To explain the observed variation in efficiency, electrochemical impedance spectroscopy (EIS) was undertaken on symmetric-electrode cell, CE||electrolyte||CE, as shown in Fig. 3(b). The impedance spectra were fitted according to the equivalent circuit in Fig. 3(c). In the figure,  $R_s$ ,  $R_{ct}$  and C represent series resistance, charge-transfer resistance and interface capacitance of the electrodes, respectively.  $Z_w$  represents the Nernst diffusion impedance in the electrolyte. Electrodes with large impedance values (i.e. large  $R_s$  and  $R_{ct}$ ) indicate an inferior conductivity and electrocatalytic activity, consequently suppressing the solar cell performance [34]. The impedance of the symmetric-pure and the symmetric-annealed (at 100, 200 and 300 °C) tungsten cells were relatively large, of the order of k $\Omega$  as seen in Fig. 3(b) and Table 2. This represents low catalytic activity with  $I_3^-$ , which results in an efficiency of 0.17%-1.10%. The charge transfer resistance of the symmetric-annealed (at 400, 500, and 600 °C) tungsten cells were significantly reduced to 1.36 x10<sup>3</sup>, 44.33, and 160.15 Ohm, respectively, suggesting that the annealing process does promote the catalytic activity of the surface films, especially on annealing at 500 °C. This reduction of impedance is accounted for the enhanced cell efficiency.

Cyclic voltammetry (CV) was also conducted to analyze the CE catalytic activities. In general, two pairs of redox peaks are found in the Pt curve [Fig. 4] which can be assigned to the reaction in equation (1) and equation (2).



Reduction at the counter electrode surface is  $I_3^- + 2e^- = 3I^-$  (reduction 1) and  $3I_2 + 2e^- = 2I_3^-$  (reduction 2) as seen in Figure 4.

Fig. 4. (a) and (b) cyclic voltammetry curves of Pt, pristine tungsten and the annealed tungsten electrodes (at 100-600 °C), the measurements were performed in 10 mM LiI, 1 mM I<sub>2</sub> and 0.1 M LiClO<sub>4</sub> in acetonitrile solutions at a sweep rate of 20 mV.s<sup>-1</sup>.

There was however no reduction peak generated for the pure tungsten and 100-200 °C annealed tungsten electrodes [Fig. 4(a)]; indicating the absence of any reduction reaction on these films. The well-defined peaks detected on the 300, 400, 500 and 600 °C annealed tungsten electrodes in Fig. 4(b) imply a promotion of the I<sub>3</sub><sup>-</sup> reduction rate, i.e. an enhancement of the film catalytic activity. Taking the EIS and CV results together, one can infer that an annealing temperature between 500-600 °C would produce the greatest enhancement of the tungsten based electrode catalytic activity.

The high catalytic activity of the 500 °C annealed tungsten electrode could be attributed to the presence of W<sup>6+</sup>, W<sup>5+</sup> and W<sup>4+</sup> detected by XPS in the substoichiometric tungsten oxide surface layer. In the case of the 600 °C annealed tungsten film, only W<sup>6+</sup> and W<sup>5+</sup> were detected by XPS and its catalytic activity was found to be lower than that of the film annealed at 500 °C. Improved properties of a WO<sub>3-x</sub> oxide film over a stoichiometric WO<sub>3</sub> device has also been reported in terms of electrochromic performance [35]; the presence of W<sup>6+</sup>, W<sup>5+</sup> and W<sup>4+</sup> species in WO<sub>3-x</sub> were considered to be the key to a higher coloration efficiency than that of WO<sub>3-x</sub> with only W<sup>6+</sup> and W<sup>5+</sup> [36]. This is consistent with our findings of an inferior energy conversion efficiency for the 600 °C annealed tungsten CE DSSC which is attributed to the absence of W<sup>4+</sup> observed by XPS [Fig. 2]. This implies that the superior energy conversion efficiency of the WO<sub>3-x</sub> CE DSSC is due to an improved electrical conductivity resulting from increased oxygen vacancies in the structure [37]. The improved electrical conductivity is supported here by measurement of a low impedance value of 44.33 Ω in the 500 °C annealed tungsten or WO<sub>2.6</sub> layer (containing W<sup>6+</sup>, W<sup>5+</sup> and W<sup>4+</sup>) which rises

to 160.15  $\Omega$  in the 600 °C annealed tungsten or  $\text{WO}_{2.8}$  layer as it becomes more stoichiometric (containing only  $\text{W}^{6+}$  and  $\text{W}^{5+}$ ).

The high electric conductivity of the annealed tungsten sheet at 500 °C can be explained by a small polaron hopping conduction mechanism that is known to operate in  $\text{WO}_3$  [38]. S.K. Deb [39] presented a polaronic model to explain the coloring mechanism in  $\text{WO}_{3-x}$ , which is consistent with the electrical conductivity mechanism established for  $\text{WO}_3$ . The presence of oxygen vacancies in substoichiometric  $\text{WO}_{3-x}$  creates localized defect states;  $V_o^0$  ( $\text{W}^{4+}$  or  $2\text{W}^{5+}$ ),  $V_o^+$  ( $\text{W}^{5+}$ ) and  $V_o^{2+}$  ( $\text{W}^{6+}$ ), located at the top of the valence band, within the band gap and at the bottom of the conduction band, respectively (see Fig. 2. in reference [39]). These promote charge transfer and enhance the electrical conductivity in the 500°C annealed tungsten where mixed valence states of  $\text{W}^{4+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{6+}$  were shown to be present whereas in the 600°C material there were fewer mixed valence states (only  $\text{W}^{5+}$  and  $\text{W}^{6+}$ ) so the conductivity dropped accordingly (Tables 1 and 2).

To ensure reproducibility of the DSSCs, 4 cells of the tungsten oxide DSSCs were produced at each annealing condition (except for the unannealed and the 100 °C annealed tungsten DSSCs where only 2 cells each were prepared). The individual performance figures can be found in section S3 of the supplementary material. The standard errors of the measured efficiencies of almost all annealing conditions were within 10% of the mean values and those of the 400, 500 and 600 °C annealing were within less than 5% error, indicating reproducible and reliable mean values for each annealing condition.

#### 4. Conclusions

High performance  $\text{WO}_{3-x}$  counter electrodes for DSSCs have been prepared by simple, thermal annealing of tungsten foils under an Ar and low  $\text{O}_2$  atmosphere. The highest dye-sensitized solar cell performance of 5.25% energy conversion efficiency was achieved

using a 500 °C annealed containing a  $\text{WO}_{2.6}$  surface layer CE DSSC, where the oxide film structure contained  $\text{W}^{6+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{4+}$ . The reported efficiency is approaching that of a Pt DSSC (6.96%) yet the production costs would be significantly lower. The cell efficiency of a 600 °C  $\text{WO}_{2.8}$  coated CE DSSC, where the oxide film structure contained only  $\text{W}^{6+}$  and  $\text{W}^{5+}$  ( $\text{W}^{6+} : \text{W}^{5+} = 3.46 : 1$ ), was lower at 4.16% consistent with the drop in impedance expected for the more stoichiometric oxide layer. It is suggested that the presence of  $\text{W}^{6+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{4+}$  valence states in the substoichiometric  $\text{WO}_{3-x}$  produces excellent catalytic activity and electrical conductivity as inferred by cyclic voltammetry and electrical impedance spectroscopy.

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## **References**

- [1] M. Gratzel, Photoelectrochemical cells, *Nature*, 414 (2001) 338-344.
- [2] E. Olsen, G. Hagen, S. Eric Lindquist, Dissolution of platinum in methoxy propionitrile containing  $\text{LiI/I}_2$ , *Solar Energy Materials and Solar Cells*, 63 (2000) 267-273.

- [3] A. Kay, M. Grätzel, Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder, *Solar Energy Materials and Solar Cells*, 44 (1996) 99-117.
- [4] M. Wang, A.M. Anghel, B.t. Marsan, N.-L. Cevey Ha, N. Pootrakulchote, S.M. Zakeeruddin, M. Grätzel, CoS Supersedes Pt as Efficient Electrocatalyst for Triiodide Reduction in Dye-Sensitized Solar Cells, *Journal of the American Chemical Society*, 131 (2009) 15976-15977.
- [5] G.-r. Li, F. Wang, Q.-w. Jiang, X.-p. Gao, P.-w. Shen, Carbon Nanotubes with Titanium Nitride as a Low-Cost Counter-Electrode Material for Dye-Sensitized Solar Cells, *Angewandte Chemie International Edition*, 49 (2010) 3653-3656.
- [6] Q. Li, J. Wu, Q. Tang, Z. Lan, P. Li, J. Lin, L. Fan, Application of microporous polyaniline counter electrode for dye-sensitized solar cells, *Electrochemistry Communications*, 10 (2008) 1299-1302.
- [7] J.S. Jang, D.J. Ham, E. Ramasamy, J. Lee, J.S. Lee, Platinum-free tungsten carbides as an efficient counter electrode for dye sensitized solar cells, *Chemical Communications*, 46 (2010) 8600-8602.
- [8] M. Wu, X. Lin, A. Hagfeldt, T. Ma, A novel catalyst of WO<sub>2</sub> nanorod for the counter electrode of dye-sensitized solar cells, *Chemical Communications*, 47 (2011) 4535-4537.
- [9] M. Wu, X. Lin, L. Wang, W. Guo, Y. Wang, J. Xiao, A. Hagfeldt, T. Ma, In Situ Synthesized Economical Tungsten Dioxide Imbedded in Mesoporous Carbon for Dye-Sensitized Solar Cells As Counter Electrode Catalyst, *The Journal of Physical Chemistry C*, 115 (2011) 22598-22602.
- [10] C. Santato, M. Ulmann, J. Augustynski, Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films, *The Journal of Physical Chemistry B*, 105 (2001) 936-940.

- [11] R. Abe, H. Takami, N. Murakami, B. Ohtani, Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-Loaded Tungsten Oxide, *Journal of the American Chemical Society*, 130 (2008) 7780-7781.
- [12] G.R. Bamwenda, H. Arakawa, The visible light induced photocatalytic activity of tungsten trioxide powders, *Applied Catalysis A: General*, 210 (2001) 181-191.
- [13] C.G. Granqvist, Electrochromic tungsten oxide films: Review of progress 1993–1998, *Solar Energy Materials and Solar Cells*, 60 (2000) 201-262.
- [14] A. Ponzoni, E. Comini, G. Sberveglieri, J. Zhou, S.-z. Deng, N.-s. Xu, Y. Ding, Z.L. Wang, Ultrasensitive and highly selective gas sensors using three-dimensional tungsten oxide nanowire networks, *Applied Physics Letters*, 88 (2006) 203101-203101-203103.
- [15] H. Zheng, Y. Tachibana, K. Kalantar-zadeh, Dye-Sensitized Solar Cells Based on WO<sub>3</sub>, *Langmuir*, 26 (2010) 19148-19152.
- [16] C.G. Granqvist, *Handbook of inorganic electrochromic materials*, Elsevier Science B.V., Netherlands, 1995.
- [17] B. Ingham, S.C. Hendy, S.V. Chong, J.L. Tallon, Density-functional studies of tungsten trioxide, tungsten bronzes, and related systems, *Physical Review B*, 72 (2005) 075109.
- [18] P.P. Gonzalez-Borrero, F. Sato, A.N. Medina, M.L. Baesso, A.C. Bento, G. Baldissera, C. Persson, G.A. Niklasson, C.G. Granqvist, A.F. da Silva, Optical band-gap determination of nanostructured WO<sub>3</sub> film, *Applied Physics Letters*, 96 (2010) 061909-061903.
- [19] Y.B. Li, Y. Bando, D. Golberg, K. Kurashima, WO<sub>3</sub> nanorods/nanobelts synthesized via physical vapor deposition process, *Chemical Physics Letters*, 367 (2003) 214-218.
- [20] J. Thangala, S. Vaddiraju, R. Bogale, R. Thurman, T. Powers, B. Deb, M.K. Sunkara, Large-Scale, Hot-Filament-Assisted Synthesis of Tungsten Oxide and Related Transition Metal Oxide Nanowires, *Small*, 3 (2007) 890-896.

- [21] D. Davazoglou, A. Moutsakis, V. Valamontes, V. Psycharis, D. Tsamakidis, Tungsten Oxide Thin Films Chemically Vapor Deposited at Low Pressure by  $W(CO)_6$  Pyrolysis, *Journal of The Electrochemical Society*, 144 (1997) 595-599.
- [22] H. Kominami, K.-i. Yabutani, T. Yamamoto, Y. Kera, B. Ohtani, Synthesis of highly active tungsten(VI) oxide photocatalysts for oxygen evolution by hydrothermal treatment of aqueous tungstic acid solutions, *Journal of Materials Chemistry*, 11 (2001) 3222-3227.
- [23] K. Lee, W.S. Seo, J.T. Park, Synthesis and Optical Properties of Colloidal Tungsten Oxide Nanorods, *Journal of the American Chemical Society*, 125 (2003) 3408-3409.
- [24] F. Xu, S.D. Tse, J.F. Al-Sharab, B.H. Kear, Flame synthesis of aligned tungsten oxide nanowires, *Applied Physics Letters*, 88 (2006) 243115-243115-243113.
- [25] M. Towannang, S. Pimanpang, A. Thiangkaew, P. Rutphonsan, W. Maiaugree, V. Harnchana, W. Jarernboon, V. Amornkitbamrung, Chemically deposited polypyrrole-nanoparticle counter electrode for inorganic  $I^-/I^{3-}$  and organic  $T^-/T^2$  dye-sensitized solar cells, *Synthetic Metals*, 162 (2012) 1954-1960.
- [26] Y.Q. Zhu, W. Hu, W.K. Hsu, M. Terrones, N. Grobert, J.P. Hare, H.W. Kroto, D.R.M. Walton, H. Terrones, Tungsten oxide tree-like structures, *Chemical Physics Letters*, 309 (1999) 327-334.
- [27] H. Kim, K. Senthil, K. Yong, Photoelectrochemical and photocatalytic properties of tungsten oxide nanorods grown by thermal evaporation, *Materials Chemistry and Physics*, 120 (2010) 452-455.
- [28] E. Cazzanelli, C. Vinegoni, G. Mariotto, A. Kuzmin, J. Purans, Raman study of the phase transitions sequence in pure  $WO_3$  at high temperature and in  $H_xWO_3$  with variable hydrogen content, *Solid State Ionics*, 123 (1999) 67-74.

- [29] M. Deepa, D.P. Singh, S.M. Shivaprasad, S.A. Agnihotry, A comparison of electrochromic properties of sol-gel derived amorphous and nanocrystalline tungsten oxide films, *Current Applied Physics*, 7 (2007) 220-229.
- [30] J. Zhang, J.P. Tu, X.H. Xia, Y. Qiao, Y. Lu, An all-solid-state electrochromic device based on NiO/WO<sub>3</sub> complementary structure and solid hybrid polyelectrolyte, *Solar Energy Materials and Solar Cells*, 93 (2009) 1840-1845.
- [31] C. Guo, S. Yin, M. Yan, M. Kobayashi, M. Kakihana, T. Sato, Morphology-Controlled Synthesis of W<sub>18</sub>O<sub>49</sub> Nanostructures and Their Near-Infrared Absorption Properties, *Inorganic Chemistry*, 51 (2012) 4763-4771.
- [32] N.B. Srinivasan, T.B. Thiede, T. de los Arcos, V. Gwildies, M. Krasnopolski, H.W. Becker, D. Rogalla, A. Devi, R.A. Fischer, Transition metal nitride thin films grown by MOCVD using amidinato based complexes [M(N<sup>t</sup>Bu)<sub>2</sub>{(i<sup>Pr</sup>N)<sub>2</sub>CMe<sub>2</sub>}<sub>2</sub>] (M=Mo, W) as precursors, *Surface and Coatings Technology*, 230 (2013) 130-136.
- [33] A. Warren, A. Nylund, I. Olefjord, Oxidation of tungsten and tungsten carbide in dry and humid atmospheres, *International Journal of Refractory Metals and Hard Materials*, 14 (1996) 345-353.
- [34] T. Makris, V. Dracopoulos, T. Stergiopoulos, P. Lianos, A quasi solid-state dye-sensitized solar cell made of polypyrrole counter electrodes, *Electrochimica Acta*, 56 (2011) 2004-2008.
- [35] Y.-S. Lin, Y.-L. Chiang, J.-Y. Lai, Effects of oxygen addition to the electrochromic properties of WO<sub>3-x</sub> thin films sputtered on flexible PET/ITO substrates, *Solid State Ionics*, 180 (2009) 99-105.
- [36] S.-H. Lee, M.C. Hyeonsik, J.-G. Zhang, A. Mascarenhas, D.K. Benson, S.K. Deb, Electrochromic mechanism in a-WO<sub>3-y</sub> thin films, *Applied Physics Letters*, 74 (1999) 242-244.

- [37] J.M. Berak, M.J. Sienko, Effect of oxygen-deficiency on electrical transport properties of tungsten trioxide crystals, *Journal of Solid State Chemistry*, 2 (1970) 109-133.
- [38] R.S. Vemuri, K.K. Bharathi, S.K. Gullapalli, C.V. Ramana, Effect of Structure and Size on the Electrical Properties of Nanocrystalline WO<sub>3</sub> Films, *ACS Applied Materials & Interfaces*, 2 (2010) 2623-2628.
- [39] S.K. Deb, Opportunities and challenges in science and technology of WO<sub>3</sub> for electrochromic and related applications, *Solar Energy Materials and Solar Cells*, 92 (2008) 245-258.