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**The Importance of Oxygen Vacancies in Nanocrystalline
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The Importance of Oxygen Vacancies in Nanocrystalline WO_{3-x} Thin Films Prepared by DC Magnetron Sputtering for Achieving High Photoelectrochemical Efficiency

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ABSTRACT: The photoelectrochemical properties of tungsten oxide thin films with different stoichiometry (WO_{3-x}) and thickness were investigated. The films were sputtered in O₂/Ar gas (ratio 0.43) on glass substrates coated with fluorine doped tin dioxide at two sputter pressures, P_{tot} = 10 and 30 mTorr, yielding O/W ratios of the films, averaged over three samples, of 2.995 and 2.999 (x~0.005 and x~0.001), respectively. The films were characterized by x-ray diffraction, scanning electron microscopy and spectrophotometry. The 10 mTorr samples showed large absorption in the near infrared (NIR) range, whereas the 30 mTorr samples had a small absorption in this region. The concentration of oxygen vacancy band gap states was estimated from cyclic voltammetry, and was found to correlate with the optical absorption in the NIR region. The incident photon to current efficiency for illumination from the electrolyte side

(IPCE_{EE}) and substrate electrode side (IPCE_{SE}) showed higher efficiency for the more stoichiometric films, indicating that oxygen vacancies in the band gap act as recombination centres. Surprisingly high values of IPCE_{EE} and IPCE_{SE} were found, and it was concluded that efficient charge separation and transport takes place almost throughout the entire film even for film electrodes as thick as 2 μm . Analysis of the spectral distribution of the photo-response (action spectra) using an extended Gärtner-Butler model to calculate the IPCE, for front side and back-side illumination was performed and showed that the diffusion length is large, of the order of the depletion layer thickness.

I. INTRODUCTION

Tungsten trioxide (WO_3) is a technologically important material with a wide range of applications in photocatalysis, electrochromics, and gas sensors.¹⁻² Several phases of nanocrystalline WO_3 can co-exist close to room temperature and atmospheric pressure; often with varying oxygen vacancy concentrations.³⁻⁶ As a result, different fabrication methods have been shown to yield materials with different physical properties. For example, the role of oxygen vacancies has been extensively studied, and is known to influence the electronic, optical and transport properties of sub-stoichiometric WO_3 .⁷⁻¹² In electrochemical applications, WO_3 is known to be resistant against photo-corrosion in aqueous solutions and can be used in acidic solutions below pH 5.¹³ Most reported studies on the photoelectrochemical properties of WO_3 concern porous nanostructures.¹⁴⁻¹⁸ Only few photoelectrochemical studies have employed dense WO_3 films¹⁹⁻²¹ which is the subject of this study.

The Schottky barrier model to describe the photocurrent in a semiconductor in contact with an electrolyte was introduced by Butler in 1977,²¹ partially based on earlier work by Gärtner.²² Butler extended Gärtner's model to describe the photocurrent as a function of wavelength and voltage, and applied it to polycrystalline WO₃ thin film electrodes, in the limit where the oxygen formation kinetics at the semiconductor anode do not limit the photo-response. Information about the optical band gap, depletion layer thickness and minority carrier diffusion length were extracted, and he inferred that the hole diffusion length in low mobility semiconductors such as WO₃ was typically small compared to the depletion layer thickness.²¹

In the present work, the spectral distribution of the photo-response (action spectra) of solid nanocrystalline WO₃ thin film electrodes prepared by dc magnetron sputtering is studied. The photoelectrochemical results were analyzed and related to several measured physical properties of the films. Changes in the action spectra related to changes in stoichiometry, applied potential, film thickness, and back- and front illumination were observed. The absorption coefficients of the films were calculated based on measured transmittance and reflectance data. From cyclic voltammetry measurements the concentration of electronic trap states was estimated, and shown to correlate with the concentration of oxygen vacancies inferred from optical measurements. Finally, action spectra have been compared with theoretical models due to Butler²¹ and Lindquist et al,²² and a generalized model is introduced that, in contrast to the others, relaxes the constraint that the minority diffusion length should be much shorter than the penetration depth of light, which is found to be necessary to describe the experimental data.

II. MATERIALS AND METHOD

A. Sample preparation

The tungsten oxide (WO_3) thin films were prepared by reactive dc magnetron sputtering using a versatile deposition system based on a Balzers UTT 400 unit. WO_3 was deposited on fluorine doped tin oxide (FTO) coated glass substrates. A 5 cm diameter WO_3 sputter target with 99.95 % purity (Plasmaterials) was employed. Sputtering was conducted in Ar and O_2 plasma. The purity of the gases was 99.998 % and the sputtering power was 200 W. The O_2 /Ar gas pressure ratio was kept fixed at 0.43, and the samples were sputtered at a substrate temperature of $T_s = 553$ K and subsequently post-annealed at $T_a = 673$ K for 1 h ex situ. The FTO substrates were cleaned with de-ionized water and ethanol before sputtering. Samples were sputtered at two different working pressures, $P_{tot} = 10$ and 30 mTorr, respectively. The deposition rate varied as a function of the working pressure from 36 nm min⁻¹ at $P_{tot} = 10$ mTorr to 11 nm min⁻¹ at $P_{tot} = 30$ mTorr. Films prepared at low P_{tot} exhibited a slightly bluish color, indicating sub-stoichiometry. The samples sputtered at $P_{tot} = 30$ mTorr were slightly yellowish and red, characteristic of stoichiometric WO_3 . The physical properties of WO_3 films prepared in similar manner have been reported elsewhere.¹¹⁻¹² The WO_3 electrodes were deposited on FTO back contacts and could therefore be irradiated from both sides in the visible region down to the cut off wavelength of the FTO film around 325 nm.

B. Electrolyte and electrode preparation

A buffer solution prepared from aqueous solution of 0.2 M HAc (CH_3COOH) was titrated to pH = 4.5 by a 0.2 M NaOH solution. Electrodes with typical areas of 1 cm² were cut from large pieces of WO_3 coated FTO glass substrates, and connected to copper wires by conductive silver epoxy. Exposed FTO back contact areas and edges were carefully sealed with epoxy. The sealing

procedure was repeated several times to prevent leak currents through unsealed parts of the FTO film.

C. Materials characterization

The surface morphology and grain sizes of the films were characterized with scanning electron microscopy (SEM) employing a LEO 1550 FEG instrument with in-lens detector operating at 10 kV. The film thickness, d , was determined from surface profilometry using a Dektak XT (Bruker) instrument. The crystalline structure was determined using grazing incidence x-ray diffraction (GIXRD) employing a Siemens D5000 with θ -2 θ goniometer and 0.3° parallel plate soller-slit collimator (Bruker AXS, Karlsruhe, Germany) using $\text{CuK}\alpha_1$ ($\lambda = 1.54056 \text{ \AA}$) radiation. Scans were recorded in the range from 10 to 90° (2 θ).

Cyclic voltammetry (CV) measurements were performed in an electrolyte with the pH 4.5 buffer solution, using the sample as working electrode, a Pt grid as counter electrode and Ag/AgCl as a reference electrode. In cyclic voltammetry (CV) the current is studied as a function of applied voltage to explore charge transfer and quantify the concentration of trap states. Throughout the CV measurement the samples were irradiated with a low intensity ($0.3 \text{ mW}\cdot\text{cm}^{-2}$) of monochromatic light at a wavelength of $\lambda = 375 \text{ nm}$. Typical forward and reverse scans were acquired in the range 0 -1.8 V vs. Ag/AgCl. In some experiments the response was measured by chopping the light beam with a period of approximately 2-3 s. The scan rate was set to 0.05 V s^{-1} .

In a CV measurement electron trap levels are drained of electrons during the forward scan direction. When the potential is swept in the reverse direction the electron traps are filled up

again. From the area between the forward and reverse scan the charge density Q (C cm^{-2}) can be determined from the equation;

$$Q = \int_U \frac{\Delta J}{2} dt \quad (1)$$

where ΔJ is the difference in current density between the forward and reverse scan (A cm^{-2}), see Supplementary information. This measurement allows us to reveal the number of trapped electrons in a cycle, Q , and is thus a measure of the electron trap states in the bandgap. As will be discussed further below the concentration of electron trap states in the band gap may be associated with the concentration of oxygen vacancies. The number of electron trap states per formula WO_3 unit determined from the CV measurements, x_{CV} , can be calculated as follows:

$$x_{\text{CV}} = \frac{QM}{eAd_f\rho N_A}, \quad (2)$$

where M is the molar mass (gmol^{-1}), N_A is Avogadro's constant, d_f is the thickness of the film (cm), ρ is the density of WO_{3-x} ,¹¹ e is the elementary charge (C) and A is the surface area (cm^2).

Transmittance, $T(\lambda)$ and reflectance, $R(\lambda)$ spectra were recorded in the wavelength range between 300 and 2500 nm, employing a Lambda 900 double-beam UV/Vis/NIR spectrophotometer equipped with an integrating sphere and a Spectralon reflectance standard. The absorption coefficient, α , was calculated from the spectral absorption according to²³

$$\alpha(\lambda) = \frac{1}{d} \ln \left(\frac{1 - R(\lambda)}{T(\lambda)} \right) \quad (3)$$

where d is the thickness. To obtain the absorption coefficient for the WO_3 thin film (α_f), the absorption from the FTO (α_{FTO}) was subtracted from the total absorption of the sample according to

$$\alpha_f d_f = \alpha d - \alpha_{\text{FTO}} d_{\text{FTO}} \quad (4)$$

where α_{FTO} was obtained from eq. (3) using measurements of $R(\lambda)$ and $T(\lambda)$ for the FTO coated substrate. The reflectance of the FTO / WO_3 interface was assumed to be close to zero. This follows from the fact that the refractive index, n , of WO_3 and FTO are very similar in the wavelength region considered here; for WO_3 n varies between 2 and 2.2,¹² and for FTO n varies between 1.9 and 2.2.²⁴ Multiple reflections can be neglected for the same reason.

D. Photoelectrochemical measurements

The experimental setup used for photoelectrochemical measurements is shown schematically in figure 1. The light source employed was a Xe arc lamp source (Oriel) operated at 300 W (1). Between the light source and the monochromator (Schoeffel GM 252) (3) a focusing lens and an 80 mm water filter (2) was placed, where the latter was used to eliminate the infrared part of the radiation. The monochromator was furnished with adjustable entrance and exit slits. The light was focused on the entrance slit. Slit width was chosen as 3 mm giving a bandwidth FWHM of 10 nm. A computer controlled filter wheel (4) was used to select long wavelength pass filters with cut-off at 400, 560 and 660 nm (Edmund Optics) to eliminate light from higher order spectra. An extra filter holder was used for measurements with band pass filters, each with FWHM approximately 10 nm (5). The light from the monochromator was focused through two lenses (6), and directed into the photoelectrochemical cell (10), after passing through a

cylindrical lens (9) to decrease the slit height to slit width ratio. A quartz window beam splitter (8) was employed to direct a minor fraction ($\sim 10\%$) of the light onto a Si photodiode (7) through a second cylindrical focusing lens (not shown in figure 1). The photodiode was used to measure the intensity from the light source when calibrating the system (see below), and to measure the diode photocurrent, I_{phd} , during the photoelectrochemical experiments to adjust for light intensity variations. The image of the exit slit was focused onto the working electrode (WE). The rectangular illuminated electrode area was typically 1 cm^2 and adjusted to fill most of the area of the electrode. The cylindrical photoelectrochemical cell consisted of a Teflon body with an O-ring sealed top lid and a 2 cm^2 circular O-ring sealed quartz window for light entry. The interior surfaces of the cell were black-coated to avoid reflections. The WE was placed close to the window inside the cell. All windows and lenses were made of high quality quartz glass. The Ag/AgCl reference electrode (RE) (Metrohm AG, Switzerland) has a potential of 197 mV versus SHE at 25°C . A platinum grid was used as a counter electrode (CE). It was encapsulated in a glass tube furnished with a glass frit. All the potentials in the experiments hereafter will be referred to a saturated silver electrode (SSE) at 25°C , which was the temperature in the cell in all the experiments within experimental error. The electrode potentials were set by a computer controlled potentiostat (CompactStat, Ivum Technologies B.V.), which was interfaced with the stepping motor on the monochromator, and allowed for fully automated wavelength and potential scan measurements.

Figure 1 a) Schematic drawing of the experimental setup used in the photoelectrochemical measurements (1) lamp housing for Xe-lamp, (2) water filter, (3) monochromator, (4) computer controlled filter wheel, (5) band pass filter holder, (6) two focusing lenses, (7) Light trap housing for reference photodiode, (8) quartz window beam splitter, (9) cylindrical lens and (10) photoelectrochemical cell containing working electrode (WE), counter electrode (CE) and reference electrode (RE) (only the ports for the electrodes are shown), b) A schematic drawing of the working electrode with a WO_3 thin film and a FTO coated substrate, also depicting the definition of SE and EE illumination.

The photon flux, n_{ph} , ($\text{cm}^{-2} \text{s}^{-1}$) was calibrated with a power meter (Coherent Radiation) for each wavelength. The power meter was placed at the same position as the working electrode in the photoelectrochemical cell. The illuminated area on the power meter was 1 cm^2 , n_{ph} was then calculated according to

$$n_{ph}(\lambda) = \frac{P_{\lambda} \lambda}{hc} \quad (5)$$

where P_λ is the measured photon power at wavelength λ , h is Planck's constant and c is the velocity of light.

The incident photon to current efficiency (*IPCE*) is defined as:

$$IPCE(\lambda) = \frac{n_{el}(\lambda)}{n_{ph}(\lambda)} = \frac{I_{tot}(\lambda) - I_{dark}(\lambda)}{en_{ph}(\lambda) \frac{I_{phd}(\lambda)}{I_{phd,ref}(\lambda)}}, \quad (6)$$

where the total photocurrent, I_{tot} , was measured under photostationary conditions and e is the elementary charge. In order to obtain the *IPCE*, I_{tot} was corrected by subtracting the measured dark current, I_{dark} . The photocurrent, I_{phd} , was simultaneously measured on the reference Si photodiode for each wavelength (7 in figure 1), and was normalized to the calibrated current $I_{phd,ref}$ recorded in a separate experiment with the Si photodiode placed at the same position as the working electrode in the photoelectrochemical cell (similar to the power measurement, eq. 5). Experiments were conducted employing both light incident upon the electrolyte-electrode interface (EE), and light incident upon the substrate-electrode interface (SE), see fig. 1b.²⁵ By employing EE and SE irradiation information about the minority carrier diffusion and width of depletion layer can be extracted in certain cases.^{13, 25-26} I_{tot} was corrected for reflection losses through the interfaces in EE and SE geometry, and in addition for the SE case for the FTO substrate absorption using the additional correction factor:

$$e^{-a_{FTO}d_{FTO}} = \frac{T_{FTO}(\lambda)}{1 - R_{FTO}(\lambda)} \quad (7)$$

where $T_{FTO}(\lambda)$ and $R_{FTO}(\lambda)$ are the transmittance and the reflectance, respectively, from the FTO coated glass.

For both EE and SE illumination, reflection losses at the air/quartz window and quartz window/electrolyte interfaces, respectively, were corrected for using the refractive index for the electrolyte $n = 1.34$ and for the quartz window $n = 1.46$. In the EE geometry the electrolyte/ WO_3 interface reflectance was calculated to be, $R_{w30} = 0.039$ for the 30 mTorr sample ($n = 2.01$), and $R_{w10} = 0.052$ for the 10 mTorr sample ($n = 2.14$).²⁷ The SE geometry has reflections from the electrolyte/ glass ($n = 1.53$) and the glass/FTO ($n = 2.0$) interfaces, common for both films. The total reflection losses for the EE case is $\Sigma(1-R_n) = 0.926$ for the 30 mTorr sample and $\Sigma(1-R_n) = 0.913$ for the 10 mTorr sample, and for the SE cases $\Sigma(1-R_n) = 0.943$. In both cases, multiple reflections have been neglected by the same arguments as explained in Section IIB above.

III. RESULT AND DISCUSSION

A. WO_3 electrode characterization

Optically transparent WO_3 films with thicknesses varying between 400 and 1950 nm were fabricated on FTO coated glass. Figure 2 (a and b) shows SEM images of a 917 nm WO_3 film sputtered at 30 mTorr and a 561 nm WO_3 film sputtered at 10 mTorr. The SEM images demonstrate that the films consist of densely packed grains with a rough surface morphology at the sub-micrometer scale. Samples sputtered at 10 and 30 mTorr show rather similar surface morphology, where the 30 mTorr film shows more developed crystallites with typical crystal edges visible. The 10 mTorr sample has slightly more random surface morphology with less developed, randomly oriented crystals. Structural studies employing grazing incidence x-ray diffraction (GIXRD) measurements (Fig. 2c) reveal that the WO_3 films consist mainly of the γ -

monoclinic phase²⁸ with space group $P2_1/n$. The most significant peaks has been addressed with their Miller index where the highest intensity is due to the (020) diffraction plane at $2\theta = 23.6^\circ$. The normalized diffractograms in Fig. 2c indicate that the relative intensity of reflections from the {010} planes is higher for the stoichiometric film prepared at 30 mTorr, and suggest that the crystals seen in the SEM images in Fig. 2a exhibit preferential growth direction that determines the film morphology. A detailed XRD analysis of WO_3 thin films prepared in this manner has been presented elsewhere.¹¹⁻¹² SEM images and XRD spectra of additional films are given as Supplementary Information.

Figure 2 SEM image and XRD pattern of (a) a 917 nm thick WO_3 film, $P_{\text{tot}} = 30$ mTorr, (b) a 561 nm thick WO_3 film, $P_{\text{tot}} = 10$ mTorr, deposited on a FTO coated glass substrate by DC

magnetron sputtering and (c) Normalized XRD pattern of the same WO_3 thin film samples, ISCD (01-083-0950). The diffractograms have been shifted along the y-axis for clarity, each sample has been normalized to its (020) diffraction peak.

Figure 3 shows the measured absorption coefficient calculated by eqn. 3 in the range 350 to 2250 nm. The absorption from the FTO glass was subtracted from the total absorption by means of eqn. 4. Films sputtered at 10 mTorr show a pronounced near infrared (NIR) absorption, which extends into the visible regime, and obscures the fine structure just below the absorption edge. The NIR absorption is due to polaron absorption and is related to oxygen vacancies.^{10, 29} Below the absorption edge an Urbach tail is discernible,³⁰ which is separated by the demarcation energy E_d from interband absorption. The position of E_d is clearly seen in the inset in Figure 3, although at $P_{tot} = 10$ mTorr the polaron absorption interferes with the Urbach tail. The demarcation energy is approximated to $E_d \approx 2.64$ eV (470 nm). We can see that the films sputtered at 30 mTorr have higher absorption coefficients in the visible range. Simple analysis of the optical band gap for WO_3 is difficult because of mixed contributions to the optical absorption from closely separated energy bands due to direct and indirect transitions.¹¹ In a previous study we have shown that the interband absorption involves direct allowed transitions with onset at ≈ 3.8 eV (326 nm), and direct forbidden transitions with onset at ≈ 3.0 eV (413 nm).¹² The reason for the difference between these values and the demarcation energy is not clear and one may hypothesize that other contributions to the optical absorption exist in the band edge region. As will be seen below, the character of the optical transitions near the band edge is important when interpreting the spectral distribution of the IPCE (action spectra) of the WO_3 electrodes. We note that our recent finding that the absorption near the band gap ($E_g \approx 3.0$ eV, or $\lambda = 413$ nm) is governed by direct

forbidden transitions is at variance with previous reports which usually describe the near edge absorption as due to indirect allowed transitions.^{21, 31}

Figure 3 Absorption coefficients, α , between 380 and 2250 nm for two WO_3 films sputtered at 10 mTorr, and two films sputtered at 30 mTorr, with different thicknesses as indicated in the figure. The inset shows a semi-logarithmic plot of α as a function of wavelength in a narrow region close to the band edge region demonstrating the exponential Urbach tail and the demarcation energy.

B. Cyclic voltammetry

Cyclic voltammetry measurements were performed under monochromatic illumination at wavelength $\lambda = 375$ nm. WO_3 is reported to have its conduction band level at about 0.53 V vs. SSE in a pH = 0 solution.³¹⁻³² The flat band potential, U_{fb} , of a semiconductor oxide in aqueous solution is at room temperature shifted by -59 mV/pH, similarly to the electrode potential of the

hydrogen electrode. Thus at pH = 4.5 the CB level will be up-shifted to $U_{fb} = 0.26$ V versus SSE.³³

Figure 4 CV curve vs. Ag/AgCl (SSE) of a 917 nm thick WO₃ electrode film sputtered at 30 mTorr, and illuminated with continuous and chopped (0.5 Hz) monochromatic light at $\lambda = 375$ nm from the front-side (EE). A scan rate of 0.05 Vs⁻¹ was used. An onset of the photocurrent is observed at $U_{on} = 0.1$ V. The curves correspond to continuous illumination in the forward (red curve 1), and reverse (2) scan direction, and the chopped illumination in the forward (black 3), and continuous illumination in the reverse (4) scan direction, respectively. Note that curve 2 and 4 almost completely overlap. The numbers also indicate the sequence in which the CV curves were acquired.

The photocurrent as a function of applied potential is shown in figure 4 for continuous and chopped illumination, respectively. From the onset potential, $U_{on} \approx 0.1$ V the photocurrent increases steadily and continues to rise until the photocurrent saturates at potentials above ~ 0.7 V. In the plateau region, between 0.7 and 1.5 V, the reaction with the redox system is sufficiently fast, and the generation of charge carriers is the rate-determining step. The current increases above ~ 1.7 V in both dark and under illumination. The dark current at this high potential indicates that the band bending is large enough to force electrons through the WO_3 film electrode.

Due to the low electric field in the depletion layer at potentials close to U_{fb} , the charge separation is incomplete, and charge carriers are lost in recombination processes. In an n-type semiconductor U_{on} is therefore shifted to somewhat higher potentials, and, in general $U_{on} > U_{fb}$. However, since we do not know the shift of U_{fb} due to recombination processes, a reasonable estimate is $U_{fb} \approx U_{on}$. In our analysis in Section IIIC below we find evidence that in our case this approximation is good since the minority charge carrier (hole) diffusion length, L_p , in WO_3 is long, and of the order the depletion layer width, $L_p \sim w$. In addition, previous measurements of open circuit voltages for a sputtered polycrystalline WO_3 thin film in a Li^+ -electrolyte gave a value of 0.05 V vs. SSE,³⁴ in fair agreement with our U_{on} . Comparing this estimate of U_{fb} with the estimated value from the pH shifted literature value of WO_3 vs SSE ($U_{fb} = 0.26$ V), we thus infer a discrepancy of at least 0.16 eV for U_{fb} obtained in this manner, which indicates that the value of U_{fb} from the literature data above depends highly on sample preparation conditions.³¹⁻³²

From the results presented in figure 4 we conclude that with applied potentials in the range 0.6 to 1 V, the reactions will be dominated by the transport properties of the photo-generated electron-hole pairs, and thus the physical properties of the semiconductor, and not by the oxygen

evolution reaction kinetics. The photocurrent reaches the dark current very fast when it is chopped, which again indicates that the sample contains only a very small concentration of trap states. The holes will then reach the semiconductor electrode surface, and rapidly capture electrons from the electrolyte, without recombining.

Figure 5 Cyclic voltammetry diagram showing the photocurrent density as a function of applied potential measured vs Ag/AgCl (SSE) for two WO_3 electrodes, deposited at 10 and 30 mTorr. A scan rate of 0.05 V s^{-1} and $\text{pH} = 4.5$ was employed.

Figure 5 shows two cyclic voltammetry curves for films sputtered at 10 mTorr and 30 mTorr, respectively. It is evident that their I - V characteristics are different. The film sputtered at 10 mTorr yields more negative photocurrent density when the potential sweep is reversed compared to the film sputtered at 30 mTorr. We attribute this behaviour to the sub-stoichiometry in the 10 mTorr films and its higher concentration of oxygen vacancies. We propose that the oxygen vacancies introduce trap states in the band gap. The level to which the electronic trap states are

filled depends on the position of the Fermi level E_F . The concentration and the distribution of these band gap states, which act as electron traps can be mapped by cyclic voltammetry. From the area between the forward and reversed scan, the accumulated charge density Q during a potential sweep and the number of trap states per formula unit, x_{CV} , can be calculated by eqns. 1 and 2, see also supplementary information.

These values can be compared with oxygen vacancy concentrations, x_{NIR} , deduced from the maximum absorption in the NIR region, $\alpha_{\max,NIR}$, calculated by means of eqn. 3 (see figure 3). By comparing our measured values with $\alpha_{\max,NIR}$ for Li^+ intercalated WO_3 thin films as previously reported,^{12, 29} assuming a similar absorption strength for Li^+ intercalation and oxygen vacancies, we can estimate x_{NIR} . In figure 6 we show x_{NIR} as a function of the number of electron trap states per formula unit, x_{CV} , from eqn. 2. A linear correlation between x_{NIR} and x_{CV} can be discerned, despite the inherent uncertainties underlying the assumptions behind this comparison. The correlation gives further support to the assignment of the electron trap states to O vacancies, and that they are associated with the polaron absorption peak between 1000 and 2000 nm in Figure 3. It is also seen in figure 6 that both the CV and the α_{NIR} -method show that the concentration of oxygen vacancies is significantly higher in the films prepared at $P_{tot} = 10$ mTorr than in those prepared at 30 mTorr.

The upper left part of the forward scan shows a small peak in the current. We propose that this current peak is either due to rapid de-trapping of electron trap states close to the conduction band,²⁷ or with re-oxidation of hydrogen present in the film from previous proton intercalation. This peak is more pronounced for the 10 mTorr electrode compared to the 30 mTorr electrode, which is consistent with the de-trapping model, since O vacancy concentrations is higher in the former samples.

Figure 6 Number of oxygen vacancies per formula unit, x_{NIR} , calculated from the NIR absorption maximum as a function of number of electron trap states per formula unit WO_3 , x_{CV} determined from CV measurements for WO_{3-x} thin films prepared at $P_{tot} = 10$ mTorr and 30 mTorr. The solid lines shows a linear fit to the data ($R = 0.85$).

C. Action spectra

Action spectra were obtained by measuring the photocurrent at three electrode potentials: $U = 0.6$, $U = 0.8$ and $U = 1$ V, respectively, as a function of wavelength at room temperature. Reflection losses were corrected for and the SE illumination was corrected for absorption losses in the FTO coated glass substrate as described in Section II. In nanoporous materials the charge

transport is limited by the diffusion of the electrons (expressed by the diffusion length L_e) through the semiconductor film,^{13, 35-36} and then the $IPCE$ value for SE illumination is generally higher than for EE illumination. In contrast to nanoporous films, dense film electrodes, such as the WO_3 and WO_{3-x} film electrodes in this study, are limited by the diffusion length of the hole L_p . This is because, in the case of SE illumination, the hole has to travel through the entire compact film before reaching the electrolyte, whereas in a nanoporous film the electrolyte can penetrate all the way to the FTO glass and L_p only need to be of the order of the semiconductor grain size.

Figure 7 shows experimental data for $IPCE_{EE}$ and $IPCE_{SE}$ for three films prepared in identical manner at $P_{tot} = 30$ mTorr, where only the thickness of the WO_3 thin films has been varied. The $IPCE$ approaches zero for wavelengths >475 nm. Both $IPCE_{EE}$ and $IPCE_{SE}$ increase with applied voltage ($U = 0.6, 0.8$ and 1 V) indicating an increasing band bending and larger w with increasing potential (eqn. 9). The depletion layer width w is given by

$$w = \left(\frac{2\epsilon\epsilon_0}{eN_D} \right)^{\frac{1}{2}} (U - U_{fb})^{\frac{1}{2}} = w_0 (U - U_{fb})^{\frac{1}{2}}, \quad (9)$$

where ϵ is the relative dielectric constant, ϵ_0 is the permittivity in free space, N_D is the donor concentration, and U the electrode potential. The band bending is given by the difference between the two potentials U and U_{fb} . As can be seen from eqn. 9 the depletion layer w is only affected by the applied potential U . Hence variations of U will give information about w . The high $IPCE_{SE}$ values even for the thickest film in Fig. 7a, indicate that charge separation close to the back-contact and hole transport is efficient and consistent with $w + L_p \sim d_f$ (see Supplementary Information). Figure 7b shows that the maximum efficiency for EE and SE illumination with $IPCE_{EE} = 0.97$ occurs for a film with $d_{WO_3} = 917$ nm at $U = 1$ V. The thinner film with $d_{WO_3} = 400$

nm shows lower efficiency for both EE and SE illumination, which is partly due to less light being absorbed. It is seen in all three samples that the $IPCE_{SE}$ reaches a maximum at a wavelength in the range 360 to 380 nm, while, $IPCE_{EE}$ reaches the highest efficiency in the range 330 – 350 nm. We also observe that the onset of the photocurrent occurs at ~ 475 nm, which is approximately the same value as the E_d value deduced from the demarcation energy in Figure 3. However, the $IPCE$ values fall off much faster than the absorptance above ~ 470 nm, which suggests that absorption in this region does not lead to charge separation and photocurrent, but rather involve electronic transitions to/from localized band gap states, i.e. transitions that do not contribute to the photocurrent. All the 30 mTorr thin films in figure 7 have a low number of electron trap states, x_{CV} (per formula unit WO_3), in the range $0.77 \cdot 10^{-3}$ - $1.47 \cdot 10^{-3}$. The lowest trap state density is found in the $d = 917$ nm film. As can be seen in fig 7a and 7b the efficiency follows very well the density of traps; the highest efficiency is from the film with lowest number of traps.

Figure 7 Action spectra of WO_3 thin film electrodes sputtered at $P_{\text{tot}} = 30$ mTorr with film thicknesses: (a) $d = 1949$ nm, $x_{\text{CV}} = 1.47 \cdot 10^{-3}$ (b) $d = 917$ nm, $x_{\text{CV}} = 0.77 \cdot 10^{-3}$, and (c) $d = 400$ nm, $x_{\text{CV}} = 0.88 \cdot 10^{-3}$, at EE and SE illumination and at applied potentials $U = 0.6, 0.8$ and 1 V, plotted together with the optical absorbance $1 - e^{(-\alpha d)}$. The lines are least square best fits to the experimental data points.

In the Gärtner-Butler model²¹⁻²² IPCE is determined by integrating the photocurrent generated at a certain depth over the film thickness, as governed by the absorption coefficient, minority carrier diffusion length and depletion layer width. In the original model the minority carrier diffusion length is assumed to be much smaller than the penetration depth of light, $L_p \ll \alpha_f^{-1}$. In our case we find that we must relax this constraint, and allow for large L_p of the order of α_f^{-1} to be able to describe the wavelength (eqn. 6) and voltage (eqn. 9) dependence of the photocurrent seen in Fig. 7. In the Supplementary information we derive a generalization of the Gärtner-Butler model where the $\alpha_f L_p \ll 1$ constraint is relaxed. The EE illumination $IPCE_{EE}$ is in this model expressed as:

$$IPCE_{EE} = 1 - e^{-\alpha_f(w+L_p)} \quad (10)$$

Similarly, for back-side SE illumination $IPCE_{SE}$ can be expressed as:

$$IPCE_{SE} = e^{-\alpha_f d_f} \left(e^{\alpha_f(w+L_p)} - 1 \right) \quad (11)$$

From eqns. 10 and 11 we see that $IPCE_{EE}$ and $IPCE_{SE}$ only depend on $(w+L_p)$, since in our case α_f is known from a separate experiment. If the minority charge carrier diffusion length L_p is a constant for each film eqns. (9) – (11) imply that w and L_p can be determined from the wavelength and voltage dependent $IPCE_{EE}$ and $IPCE_{SE}$ data. With $U_{fb} = 0.1$ V we find for example that the ratio $w(U=1 \text{ V})/w(U=0.6 \text{ V}) = 1.34$ for the stoichiometric film with $d = 917$ nm, for which the IPCE data are shown in figure 7b. Thus with constant L_p , and $w = w(U)$ from eqn. (9), the set of IPCE curves at different voltages can be uniquely determined. It is seen in figure 7b that the $IPCE_{EE}$ curve approaches the optical absorptance in the short wavelength range and that even the $IPCE_{SE}$ data for $U=1$ V do not fall far away from this curve. Hence, in order to

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3 qualitatively reproduce the magnitudes of the IPCE curves in the short wavelength region eqns.
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6 (10) and (11) require that $w+L_p \approx d$, and hence that L_p is large. In particular, we find that a value
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8 of L_p of the order ~ 400 nm, is able to qualitatively reproduce the $IPCE_{EE}$ and $IPCE_{SE}$ data and
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10 their voltage dependence (see Supplementary information).
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14 The model correctly reproduces a maximum of $IPCE_{SE}$ at wavelengths below the band gap,
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16 although it is more pronounced than in the experimental spectra. The model also yields too low
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18 values at the maximum, which may be attributed to uncertainties in the estimation of α_f but
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20 could also point to other contributions to $IPCE_{SE}$ that are not accounted for by the simple
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22 description of transport processes employed here for w and L_p . The model presented here also
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24 assumes that all photo-excited holes give rise to a photocurrent, and does not take into account
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26 contributions to the optical absorption originating from localized band gap states that do not
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28 generate photocurrent. Thus the model yields higher IPCE values around E_g , and non-zero values
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30 at wavelengths above the band gap due to the non-zero experimental value of α_f from the data in
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32 Figure S4. In contrast, at short wavelengths below around 400 nm the model predicts too small
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34 $IPCE_{SE}$ values, which suggests additional contributions to the photo-current at these higher
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36 energies that cannot be accounted for by hole diffusion to the electrolyte side (which limits IPCE
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38 in the model above the bandgap when the penetration depth decreases dramatically).
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40 Nevertheless, the maximum in $IPCE_{SE}$ can within the extended Gärtner-Butler model be
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42 explained by competing effects of high absorption and hole diffusion length. We note that
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44 maximum in $IPCE_{SE}$ cannot be reproduced by the original Gärtner-Butler approximation,
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46 ($\alpha_f L_p \ll 1$), which is not valid for thin compact films that are limited by hole diffusion.
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In figure 8 *IPCE* spectra for both EE and SE illumination for two films are compared, which were sputtered at two different pressures $P_{tot} = 10$ and 30 mTorr, respectively. The spectra in Figure 8 indicate generally that the *IPCE* for the 10 mTorr sample, which has a higher concentration of O vacancies, is lower than the spectra for the electrodes prepared at 30 mTorr. We can ascribe the difference to the fact that electron-hole pair recombination is more efficient in the former case, which we attribute to hole recombination at O vacancy sites. However, it could also be due to the fact that N_D is increasing with increasing concentration of O vacancies which in turn would make w_o smaller (See eqn. 9), and consequently w smaller. Very small w values would however show up in the action spectrum as a distinct maximum in the SE spectrum located at the band gap energy, together with a rapid fall off with decreasing wavelength (see Supplementary information). We therefore favour electron-hole pair recombination at O vacancies as the main cause of the lower *ICPE* in sub-stoichiometric WO_{3-x} electrodes. Similar to the film prepared at 30 mTorr, we see in figure 8 that the onset for photocurrent occurs close to E_d , at ~ 475 nm also for the sub-stoichiometric films prepared at 10 mTorr.

Figure 8 IPCE of two WO_3 thin film electrodes sputtered at $P_{\text{tot}} = 10$ and 30 mTorr, with $d_{\text{film}} = 561$ nm, $x_{\text{CV}} = 7.6 \cdot 10^{-3}$ and $d_{\text{film}} = 917$ nm, $x_{\text{CV}} = 0.77 \cdot 10^{-3}$, respectively, at the applied potentials of $U = 0.6$ and 1 V and at pH = 4.5: (a) EE illumination, and (b) SE illumination. The lines are fitted to the experimental data points using a 10th grade polynomial.

It is clear from figures 7 and 8 that not all states giving rise to optical absorption are active photoelectrochemically and give rise to a measurable IPCE signal. This is clearly so for the localized band tail states giving rise to optical absorption in the “Urbach tail” at wavelengths above 470 nm, as mentioned above. However, also at shorter wavelengths the shape of the absorbance displays differences from the shape of the IPCE spectra. This is probably due to the complicated nature of optical absorption processes close to the band gap in WO_3 and the difficulty to make a consistent subtraction of absorption due to localized states in the Urbach tail and possibly also at the band edge. Hence quantitative fitting of the experimental IPCE data with eqs. (10) and (11), in order to find a unique value of $w+L_p$, is difficult, but a test of the

consistency of these two theoretical expressions is feasible. As we demonstrate in Supplementary information, by combining eqns. 9-11 we find relations between the IPCE values obtained in the EE and SE geometries that reasonably reproduce the relative magnitude of the IPCE data for EE and SE illumination, as well as give a physical explanation of their spectral and voltage responses.

SUMMARY AND CONCLUSIONS

Sub-stoichiometric WO_{3-x} thin films with different thicknesses have been sputtered at $P_{\text{tot}} = 10$ and 30 mTorr under O_2/Ar atmosphere (ratio 0.43) onto glass substrates furnished with a transparent conducting oxide (FTO). The 10 mTorr samples showed high absorption in the NIR range, which was associated with oxygen vacancies. The number of oxygen vacancy band gap states per formula unit was estimated from cyclic voltammetry and average values were found to be $x \sim 0.005$ for the 10 mTorr samples and $x \sim 0.001$ for the 30 mTorr samples. These values were found to give an acceptable correlation with the optical absorption in the NIR region and previous values of the oxygen vacancy concentration, calculated using as reference NIR absorption spectra from Li intercalated WO_3 films. Photoelectrochemically recorded incident photon to current efficiencies for front side (EE) and backside (SE) illumination, IPCE_{EE} and IPCE_{SE} , showed high efficiency for the WO_3 samples sputtered at $P_{\text{tot}} = 30$ mTorr. The fact that IPCE generally is higher in films sputtered at $P_{\text{tot}} = 30$ mTorr compared to films sputtered at $P_{\text{tot}} = 10$ mTorr indicates that the oxygen vacancies in the band gap act as recombination centers. Analysis of the spectral distribution of the IPCE_{EE} and IPCE_{SE} adopting a generalized Gärtner-Butler model²¹⁻²² indicates that the sum of the diffusion and depletion layer ($w + L_p$) is the important quantity that determines the spectral distributions of IPCE_{EE} and IPCE_{SE} for the WO_3

films electrodes, and that in our case $w + L_p$ is of the order of the film thickness. It is estimated that L_p is large for the stoichiometric film (of the order 400 nm), so that the assumption $\alpha_f L_p \ll 1$ is not valid. It is further concluded that accurate modelling of the IPCE data is complicated due to electronic excitations not leading to photocurrent, which is particularly severe in the case of the sub-stoichiometric films. Surprisingly high values of *IPCE* were however found for the stoichiometric films sputtered at $P_{tot} = 30$ mTorr, and it was concluded that efficient charge separation takes place almost throughout the entire film even for film electrodes as thick as 2000 nm.

ASSOCIATED CONTENT

Supporting Information.

Structural characterization

Description of a cyclic voltammetry sweep: Derivation of Equation 5.

Absorption coefficient for a nearly stoichiometry WO_3 film

Generalized Gärtner-Butler model for IPCE when $L_p \sim \alpha_f^{-1}$

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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REFERENCES

- (1) Niklasson, G. A.; Granqvist, C. G., Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these. *J. Mater. Chem* **2007**, *17*, 127-156.
- (2) Granqvist, C. G.; Azens, A.; Heszler, P.; Kish, L. B.; Österlund, L., Nanomaterials for benign indoor environments: Electrochromics for “smart windows”, sensors for air quality, and photo-catalysts for air cleaning. *Solar Energy Mater. Solar Cells* **2007**, *91* (4), 355-365.
- (3) Jiménez, I.; Arbiol, J.; Dezanneau, G.; Cornet, A.; Morante, J. R., Crystalline structure, defects and gas sensor response to NO₂ and H₂S of tungsten trioxide nanopowders. *Sens. and Actuators B* **2003**, *93*, 475-485.
- (4) Souza-Filho, A. G.; Freire, V. N.; Pilla, O.; Saski, J. M.; Mendes-Filho, J.; Juião, J. F.; Gomes, U. U., Coexistence of triclinic and monoclinic phases in WO₃ ceramics. *J. Raman Spec.* **2000**, *31*, 451-454.
- (5) Schirmer, O. F.; Salje, E., Conduction bipolarons in low-temperature crystalline WO_{3-x}. *J. Phys. C: Solid State. Phys.* **1980**, *13*, L1067-72.
- (6) Lee, S.-H.; Deshpande, P. A.; Parilla, P. A.; Jones, K. M.; To, B.; Mahan, H.; Dillon, A. C., Crystalline WO₃ nanoparticles for highly improved electrochromic applications. *Adv. Mater.* **2006**, *18*, 763-766.
- (7) Karazhanov, S. Z.; Zhang, Y.; Wang, L.-W.; Mascarenhas, A.; Deb, S., Resonant defect states and strong lattice relaxation of oxygen vacancies in WO₃. *Phys. Rev. B* **2003**, *68*, 233204-1.

- (8) Chatten, R.; Chadwick, A. V.; Rougier, A.; Lindan, P. J. D., The oxygen vacancy in crystal phase of WO_3 . *J. Phys. Chem. B* **2005**, *109*, 3146-3156.
- (9) Wang, F.; Di Valentin, C.; Pacchioni, G., Semiconductor-to-metal transition in WO_{3-x} : Nature of the oxygen vacancy. *Physical Review B* **2011**, *84*, 073103-1--073103-5.
- (10) Deb, S. K., Opportunities and challenges in science and technology of WO_3 for electrochromic and related applications. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 245-258.
- (11) Johansson, M. B.; Niklasson, G. A.; Österlund, L., Preparation and characterization of visible light active photocatalytic WO_3 thin films prepared by reactive dc magnetron sputtering. *J. Mater. Res.* **2012**, *27* (24), 3130-3140.
- (12) Johansson, M. B.; Baldissera, G.; Valyukh, I.; Persson, C.; Arwin, H.; Niklasson, G. A.; Österlund, L., Electronic and optical properties of Nanocrystalline WO_3 thin films studied by optical spectroscopy and density functional calculations. *J. Phys.: Condens. Matter* **2013**, *25*, 205502.
- (13) Wang, H.; Lindgren, T.; Jianjun, H.; Hagfeldt, A.; Lindquist, S.-E., Photoelectrochemistry of nanostructured WO_3 thin film electrodes for water oxidation: Mechanism of electron transport. *J. Phys. Chem. B* **2000**, *104*, 5686-5696.
- (14) Barczuk, P. J.; Krolikowska, A.; Lewera, A.; Miecznikowski, K.; Solarska, R.; Augustynski, J., Structural and photoelectrochemical investigation of boron-modified nanostructured tungsten trioxide films. *Electrochim. Acta* **2013**, *104*, 282-288.
- (15) Solarska, R.; Santato, C.; Jorand-Sartoretti, C.; Ulmann, M.; Augustynski, J., Photoelectrolytic oxidation of organic species at mesoporous tungsten trioxide film electrodes under visible light illumination. *Journal of Applied Electrochemistry* **2005**, *35*, 715--721.
- (16) Alexander, B. D.; Kulesza, P. J.; Rutkowska, I.; Solarska, R.; Augustynski, J., Metal oxide photoanodes for solar hydrogen production. *J. Mater. Chem.* **2008**, *18*, 2298-2303.
- (17) Hill, J. C.; Choi, K.-S., Effect of electrolytes on the selectivity and stability of n-type WO_3 photoelectrodes for use in solar water oxidation. *J. Phys. Chem. C* **2012**, *116*, 7612-7620.
- (18) Li, W.; Da, P.; Zhang, Y.; Wang, Y.; Lin, X.; Gong, X.; Zheng, G., WO_3 nanoflakes for enhanced photoelectrochemical conversion. *ACS Nano* **2014**, *8*, 11770-11777.
- (19) Vidyarthi, V. S.; Hofmann, M.; Savan, A.; Sliozberg, K.; König, D.; Beranek, R.; Schuhmann, W.; Ludwig, A., Enhanced photoelectrochemical properties of WO_3 thin films fabricated by reactive magnetron sputtering. *Int. J. Hydrogen Energy* **2011**, *36*, 4724-4731.
- (20) Qin, D.-D.; Tao, C.-L.; Friesen, S. A.; Wang, T.-H.; Varghese, O. K.; Bao, N.-Z.; Yang, Z.-Y.; Mallouk, T. E.; Grimes, C. A., Dense layers of vertically oriented WO_3 crystals as anodes for photoelectrochemical water oxidation. *Chem. Commun.* **2012**, *48*, 729-731.
- (21) Butler, M. A., Photoelectrolysis and physical properties of the semiconducting electrode WO_3 . *J. Appl. Phys.* **1977**, *48*, 1914-1920.
- (22) Gärtner, W. W., Depletion-layer photoeffects in semiconductors. *Phys. Rev.* **1959**, *116*, 84-87.
- (23) Hong, W. Q., Extraction of extinction coefficient of weak absorbing thin films from spectral absorption. *J. Phys. D: Appl. Phys.* **1989**, *22*, 1384-1385.
- (24) Rakhshani, A. E.; Makdisi, Y.; Ramazaniyan, H. A., Electronic and optical properties of fluorine-doped tin oxide films. *Journal of Applied Physics* **1998**, *83* (2), 1049-1057.
- (25) Lindquist, S.-E.; Finnström, B.; Tegnér, L., Photoelectrochemical properties of polycrystalline TiO_2 thin film electrodes on quartz substrates. *J. Electrochem. Soc.* **1983**, *130*, 351-358.

- (26) Gomez, R.; Salvador, P., Photovoltage dependence on film thickness and type of illumination in nanoporous thin film electrodes according to a simple diffusion model. *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 377-388.
- (27) Johansson, M. B.; Zietz, B.; Niklasson, G. A.; Österlund, L., Optical properties of nanocrystalline WO₃ and WO_{3-x} thin films prepared by DC magnetron sputtering. *J. Appl. Phys.* **2014**, *115*, 213510.
- (28) Woodward, P. M.; Sleight, A. W.; Vogt, T., Structure refinement of triclinic tungsten trioxide. *J. Phys. Chem. Solids* **1995**, *56* (10), 1305-1315.
- (29) Larsson, A. L.; Sernelius, B. O.; Niklasson, G. A., Optical absorption of Li-intercalated polycrystalline tungsten oxide films: comparison to large polaron theory. *Solid State Ionics* **2003**, *165* (1-4), 35-41.
- (30) Urbach, F., The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. *Phys. Rev.* **1953**, *92*, 1324-1324.
- (31) Lohmann, F., Fermi-Niveau und Flachbandpotential von Molekulkristallen Aromatischer Kohlenwasserstoffe. *Zeitschrift für naturforschung part a Astrophysik physik und Physicalische Chemie A* **1967**, *22* (5), 843.
- (32) Xu, Y.; Schoonen, M. A. A., The absolute energy position of conduction and valence bands of selected semiconducting minerals. *Am. Mineralogist* **2000**, *85*, 543-556.
- (33) Dung, D.; Ramsden, J.; Grätzel, M., Dynamics of interfacial electron-transfer processes in colloidal semiconductor systems. *J. Am. Chem. Soc.* **1982**, *104*, 2977-2985.
- (34) Strömme, M.; Ahuja, R.; Niklasson, G. A., New probe of the electronic structure of amorphous materials. *Phys. Rev Lett.* **2004**, *93*, 206403.
- (35) Abe, R.; Takami, H.; Murakami, N.; Ohtani, B., Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-Loaded Tungsten Oxide. *J. Am. Chem. Soc.* **2008**, *130*, 7780-7781.
- (36) Södergren, S.; Hagfeldt, A.; Olsson, J.; Lindquist, S.-E., Theoretical Models for the Action Spectrum and the Current-Voltage Characteristics of Microporous Semiconductor Films in Photoelectrochemical Cells. *J. Phys. Chem* **1994**, *94*, 5552.

TOC Graphic

Figure 2 SEM image and XRD pattern of (a) a 917 nm thick WO₃ film, $P_{\text{tot}} = 30$ mTorr, (b) a 561 nm thick WO₃ film, $P_{\text{tot}} = 10$ mTorr, deposited on a FTO coated glass substrate by DC magnetron sputtering and (c) Normalized XRD pattern of the same WO₃ thin film samples, ISCD (01-083-0950). The diffractograms have been shifted along the y-axis for clarity, each sample has been normalized to its (020) diffraction peak.

234x192mm (150 x 150 DPI)