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Soft X-ray and electron spectroscopy to determine the electronic structure of materials for photoelectrochemical hydrogen production

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ABSTRACT

To optimize materials and devices for solar photoelectrochemical hydrogen production, a detailed understanding of the chemical and electronic properties, in particular at the reactive surfaces and interfaces, is needed. In this review article we will show how electron and soft X-ray spectroscopies can provide such information. We will present exemplary studies using X-ray photoelectron spectroscopy, soft X-ray emission spectroscopy, UV photoelectron spectroscopy, and inverse photoemission. While the first two techniques mainly give insight into the chemical properties at and near the surface, the latter two methods allow us to derive the electronic levels relevant for photoelectrochemical water splitting at the surface of the investigated material. Ultimately, the ideal experiment would be performed in situ, in which the device is studied under working conditions, i.e., in a liquid environment and under illumination. We will give a short outlook on how this can be achieved experimentally under the strict requirements of the measurement environment.

1. Introduction

Successful implementation of photoelectrochemical (PEC) hydrogen production using sunlight requires significant material science breakthroughs, as a potential PEC material has to simultaneously fulfill at least three main requirements: (1) For efficient utilization of the incoming solar photon flux and its spectral distribution, the material needs to have an optimized bulk band gap. (2) For water splitting to occur, an optimized electronic structure at the interface between the material and the surrounding electrolyte must be ensured. (3) The material needs to be chemical stable to withstand extreme conditions of a very high or low pH of the electrolyte, and be durable for the lifetime of a PEC device. Even though a variety of materials have been studied [1], there is not a single material today that can fulfill those three requirements, but significant advances have been made with a variety of materials that fulfill at least two of these requirements. With the exception of the bulk band gap, the requirements above all concern the surface of the PEC material. Therefore, an in-depth knowledge of the chemical and electronic properties at the relevant surfaces and interfaces is necessary to develop a detailed understanding of the limiting factors of each material, and for their further optimization. Furthermore, the changes of these properties under the operating conditions of the PEC device are of high interest, in particular to improve the stability of the device. In this review, we present several techniques, namely X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), inverse photoemission (IPES), and soft X-ray emission spectroscopy (XES), which jointly are able to address the questions above. These techniques exhibit different degrees of surface sensitivity, following an exponential law with attenuation

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lengths ranging from a few nanometers (XPS, UPS, and IPES) up to a few hundred nanometers (XES), and directly probe the electronic structure of the investigated material. In addition to the electronic properties, a wealth of chemical information can be deduced from the data, as will also be discussed in this review.

In the next section, an XPS, UPS, and IPES study of WO_3 photoanodes will be presented as a first example. We will show how those techniques can be used to derive the electrochemically relevant electronic energy level positions, i.e., the conduction band minimum (CBM) and valence band maximum (VBM), with respect to the relevant oxidation and reduction potentials for water splitting. Furthermore, we will discuss how the incorporation of Mo into the WO_3 film can be used to tailor the electronic surface structure of WO_3. As a second example, we will show how the chemical sensitivity of XES can be used to reveal and quantify the degradation processes occurring in $ZnO:Zn_3N_2$ thin films under air exposure. Finally, we will give a short outlook on how soft X-ray spectroscopies can be used to study PEC materials in situ, i.e., under operating conditions.

2. Electronic surface level positions of WO_3 and WO_3:Mo thin films

In the following, we will demonstrate how a combination of XPS, UPS, and IPES can be used to directly derive the band edge position in vacuum and how these values can be correlated to the electrochemical energy scale relevant for a complete PEC device [2]. The discussion will exemplarily be given for WO_3, which has been studied as a photoanode material for PEC hydrogen production in recent years (e.g., [3–8]).

WO_3 is a particularly interesting example, as its optical and electronic properties strongly depend on the actual stoichiometry of the films. For example, it was found that oxygen-poor films change color and have different electrical properties compared to stoichiometric films. A detailed discussion of these effects and their origin can be found in, e.g., [9–11]. One advantage of WO_3 films is that they can be deposited by a large variety of techniques including RF- [12,13] and DC-sputtering [12,14], screen-printing [15], and thermal evaporation [16].

Stoichiometric WO_3 films studied in this chapter were deposited at the University of Hawaii, using reactive sputtering from a W metal target under an argon and oxygen ambient atmosphere [7]. To minimize unwanted surface contamination, samples were sealed under dry nitrogen without any air exposure immediately after deposition, shipped to the University of Nevada, Las Vegas (UNLV), unpacked in a nitrogen-purged glove box, and directly introduced into the vacuum chamber for measurements. UPS measurements were performed using He I and He II excitation, and for the XPS measurements a non-monochromatized Mg Kα X-ray source (15 kV with 20 mA anode current) was used. The spectra were recorded with a SPECS PHOIBOS 150 electron analyzer with a multichanneltron detector. For the IPES experiments, a low-energy electron gun (STAIB) and a dose-type detector with SrF_2 window and Ar:I_2 filling were used. All experiments were performed in ultrahigh vacuum with a base pressure below 1×10^{-10} mbar.

As noted above, samples were kept under an inert or vacuum environment at all times to minimize surface contamination. This is particularly important for investigations using techniques as surface sensitive as XPS, UPS, or IPES, where even a thin layer of contaminants can obscure the measurement. In the present case, a look at the XPS survey spectrum (see Ref. [2]) confirms that the sample handling procedure was successful and only a small contamination signal (of carbon) can be found on the sample surface. Therefore, no additional cleaning of the surface, e.g., using Ar^+ ions, was performed. This is desirable to avoid changes of the actual surface structure induced by such cleaning steps and is especially important in the case of WO_3, for which strong changes in the spectra upon Ar^+ treatment were reported by Dixon et al. [10].

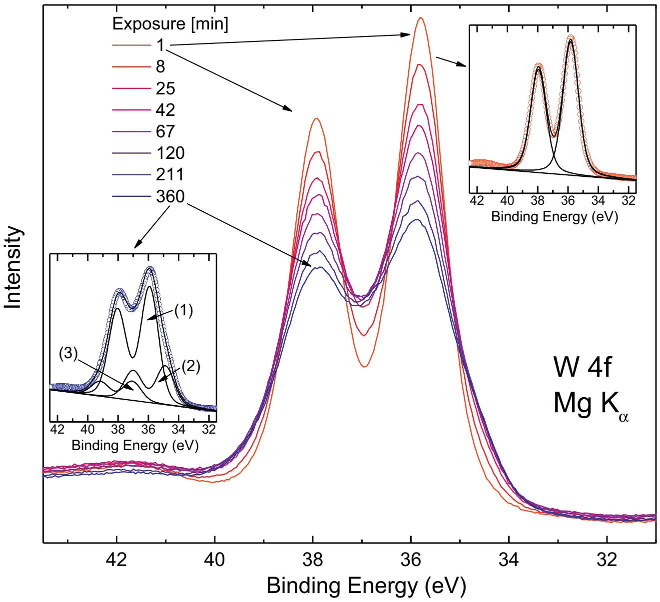

Fig. 1. W 4f XPS lines excited with Mg Kα radiation as a function of exposure time. The insets show fits of the spectra after 1 min and 6 h of exposure. While initially only one chemical species is present, we find (at least) three species after an exposure time of 6 h, marked with (1) through (3).

In addition to the careful sample handling discussed above, WO_3 requires special caution during measurement: it shows a significant sensitivity to X-ray and electron irradiation. It is necessary to carefully monitor any changes induced by the excitation sources and to minimize the experiment duration such that any irradiation-induced effects on the WO_3 surface can be neglected. Fig. 1 shows the W 4f spectrum after increasing exposure time to non-monochromatized Mg Kα radiation ($h\nu = 1253.6$ eV). The first of the recorded spectra (exposure time about 1 min) consists of two symmetric peaks [W $4f_{5/2}$ at 37.92 (±0.02) eV and W $4f_{7/2}$ at 35.80 (±0.02) eV], which are representative of W atoms with an oxidation state of +6 (as expected for the WO_3 environment) [9–11,15–18]. The presence of (only) two peaks is illustrated by the fit in Fig. 1 (top right). Upon further exposure to Mg Kα radiation, the spectra change drastically. The fit on the bottom left in Fig. 1 shows how the spectrum now consists of (at least) three different components. It is generally agreed that the low binding energy component [(2) in Fig. 1] is due to a loss of O at the surface and corresponds to W atoms in a +5 oxidation state [9–11,15–18], while the high binding energy component (3) has been attributed either to surface defects [15,18] or a plasmon loss peak [17]. Further experiments show that the UV radiation used to measure the UPS spectra (He I and He II radiation) does not affect the WO_3 surface, while the low-energy electrons used for the IPES measurements do (on a timescale of a few tens of minutes). Thus care is taken to provide an accurate picture of the conduction band of WO_3 while minimizing exposure to electrons in the IPES experiment.

Taking the findings of the previous paragraphs into account, it is possible to derive an undisturbed electronic picture of the WO_3 surface. This was achieved by using a fresh film (prepared under the same conditions) for each of the experiments (XPS, UPS, and IPES) and keeping the total exposure (measurement) time short enough for the above-described changes to be negligible. In Fig. 2 the UPS spectrum representing the valence band electronic structure (left) is shown together with the IPES spectrum of the conduction band (right) on a common energy scale. In addition, the secondary