Electronic structure of nanoparticles of substoichiometric hexagonal tungsten oxides

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Abstract. X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods were used to study the electronic structure of hexagonal h-WO$_3$ and h-WO$_{2.8}$ nanoparticles. For comparison, nanopowder substoichiometric monoclinic tungsten oxides with close content of oxygen atoms, namely m-WO$_3$ and m-WO$_{2.77}$ compounds, were also investigated. For the mentioned oxides, XPS valence-band and core-level spectra, XES O $K\alpha$ bands and XAS W $L_{III}$ and O $1s$ edges were derived. The XPS valence-band spectra and O $K\alpha$ emission bands in the mentioned hexagonal and monoclinic tungsten oxides were compared on a common energy scale. Both the O $K\alpha$ bands and XPS valence-band spectra broaden somewhat in the sequences h-WO$_3$ → h-WO$_{2.8}$ and m-WO$_3$ → m-WO$_{2.77}$, with the half-widths of the spectra being somewhat higher for the hexagonal oxides as compared with those for the monoclinic compounds. The effective positive charge state of tungsten atoms in h-WO$_{2.8}$ is very close to that in m-WO$_{2.77}$, but the negative charge states of oxygen atoms are close to each other for all the tungsten oxides under consideration.

1. Introduction

Tungsten trioxide crystallizes in a monoclinic structure (m-WO$_3$) and it loses oxygen readily under reducing conditions [1]. As a result, substoichiometric tungsten oxides in the intermediate region between m-WO$_3$ and tungsten dioxide, m-WO$_2$, are synthesized. Among these oxides, it is necessary to mention those in the range from WO$_3$ to WO$_{2.87}$. In the above range of compounds, m-WO$_3$ shows the tendency to form substoichiometric shear phases: tungsten oxides with crystallographic shear (CS) planes on the \{120\} planes can be ascribed by a formula W$_n$O$_{3n-1}$, but those with CS on the \{103\} planes can be ascribed by a formula W$_n$O$_{3n-2}$ [2]. Structures of the mentioned substoichiometric oxides consist of largely unchanged slabs of tungsten trioxide joined along the mentioned CS planes. A homologies series of WO$_x$ oxides in the range WO$_{2.75}$ to WO$_{2.65}$ was also observed [1].

Gerand et al. [3] were first to synthesize the hexagonal form of tungsten trioxide, h-WO$_3$, due to dry heating of the WO$_3$$^{1/3}$H$_2$O hydrate. The structure of h-WO$_3$ belongs to the space group $P6/mmm$ in which every six [W–O$_6$] octahedra linked by corner sharing form hexagonal channels oriented along the $c$ axes [3]. Hence, the structure of the hexagonal form of WO$_3$ differs essentially from that of m-WO$_3$. In the latter form of WO$_3$, each tungsten atom is surrounded by six oxygen atoms in an octahedral coordination. Every four [W–O$_6$] octahedra in the unit cell of m-WO$_3$ are slightly tilted with respect to one other, therefore, the structure of pure m-WO$_3$ is less symmetrical as compared with that of ReO$_3$ type. The hexagonal form of tungsten trioxide was found to be a very prospective material for positive electrodes of rechargeable lithium batteries: h-WO$_3$ is widely used mainly as an intercalation host of lithium for obtaining hexagonal lithium tungsten bronzes, h-Li$_x$WO$_3$. Therefore, since Gerand et al. [3] first obtained h-WO$_3$, several alternative routs for synthesis of h-WO$_3$ have been proposed (for details, see Refs. [4, 5]). On the initial stage of hydrogen reduction of h-WO$_3$, the nonstoichiometric h-WO$_{2.8}$ phase with the structure belonging to UO$_3$ type has been synthesized [6]. The h-WO$_{2.8}$ oxide was found to be a very prospective sensor material possessing excellent electrochromic properties.
Electronic structure of the monoclinic form of WO$_3$ has been extensively studied using X-ray photoelectron (XPS), emission (XES) and absorption (XAS) spectroscopy methods (detailed reviews of such studies were made in monographs [7, 8]). Band-structure calculations of WO$_3$ in the oversimplified cubic structure were made in Refs. [9-12]. The results of the above theoretical works regarding the occupation of the both valence and conduction bands of WO$_3$, as well as energy positions of the main peculiarities of the bands, are in agreement: the O 2$p$-like states dominate the valence band of cubic WO$_3$, but the conduction band of the compound is dominated by the W 5$d$-like states. The distortion of the cubic lattice of WO$_3$ to the full monoclinic structure leads to an increase of the semiconducting energy gap by 0.8 eV and causes an increase of the W 5$d$-orbital occupation [10].

Hjelm et al. [11] were first to calculate the electronic structure of h-WO$_3$ using the \textit{ab initio} relativistic full-potential linear muffin-tin orbital (FP-LMTO) procedure. To the best of our knowledge, no theoretical band-structure calculations have been made so far for WO$_{x<3}$ compounds.

The purpose of the present work was to fulfil a complex investigation of the electronic structure of nanopowders of the two known up to now hexagonal forms of tungsten oxides, namely h-WO$_3$ and h-WO$_{2.8}$, using XPS, XES and XAS methods. The aim was also to compare the electronic structure of the above oxides with that of nanopowders of tungsten oxides with monoclinic structure and with close O to W ratios, namely m-WO$_3$ and m-WO$_{2.77}$ compounds.

2. Experimental

The methods of synthesis and lattice parameters of hexagonal and monoclinic forms of tungsten oxides studied in the present work were reported in details previously in Refs. [5, 6, 13]. All the oxides under consideration were obtained in the form of nanoparticles (sizes in the range from 60 to 80 nm).

XPS valence-band and core-level spectra of the WO$_x$ specimens under study were derived with an ES-2401 spectrometer using Mg K$\alpha$ radiation (1253.6 eV). An ion-pumped chamber of the spectrometer was evacuated to $(1\pm2)\times10^{-7}$ Pa. The impurity C $1s$ line (285.0 eV) was taken as a reference. The X-ray emission O $K\alpha$ bands ($K \rightarrow L_{II,III}$ transition), reflecting the energy distribution of the O 2$p$-like states, were derived with the energy resolution of about 0.4 eV using an RSM-500 spectrometer. The dispersing element was a diffraction grating with 600 lines/mm and a radius of curvature of $R = 6026$ mm. When recording the O $K\alpha$ spectra, the operation conditions of the electron gun were the following: accelerating voltage, $U_a = 5$ kV; anode current, $I_a = 2.5$ mA. The W $L_{III}$ absorption spectra, reflecting the energy distribution of the unoccupied W 5$d$-like states, were obtained using a KRUS-1 spectrograph. A quartz crystal with the (1340) reflecting plane prepared according to Johann (see Ref. [8] for details) and a radius of curvature of $R = 872$ mm was used as a dispersing element. The operating conditions of the X-ray BSV-23 tube were the following: $U_a = 14$ kV, $I_a = 40$ mA. The XAS O $1s$ spectra, reflecting the energy distribution of the unoccupied O $p$-like states, were recorded with the energy resolution of about 0.6 eV using the method which was analogous to that employed in Ref. [14]. The experiments were made in a turbopumped UHV chamber with base pressure typically $2\times10^{-7}$ Pa mounted to synchrotron source. The beam-line was equipped with a plane grating monochromator.

3. Results and discussion

Results of comparison of the O $K\alpha$ emission bands and the XPS valence-band spectra for the hexagonal and monoclinic oxides under study are shown in Figure 1. The comparison was made taking into account the XPS O $1s$ core-level binding energies which were found to be within $(530.8\pm0.1)$ eV for all the compounds studied.

As can be seen from Figure 1, for all the compounds studied, the XPS valence-band spectra have their maxima “$A$” at about 7 eV below $E_F$. The maximum of the XPS valence-band spectrum coincides with the position of the low-energy shoulder "$D$" of the O $K\alpha$ band for every tungsten oxide studied, while the energy position of the feature "$B$" of the XPS spectrum corresponds to that of the maximum "$E$" of the O $K\alpha$ band. Therefore, the maximum of the energy distribution of the W 5$d$-like
states in the studied oxides should be positioned about 7 eV below $E_F$. According to the results of the theoretical calculations [9–12], the valence band of WO$_3$ should be dominated by the contribution of the O 2$p$-like states, nevertheless due to the fact that when using the Mg Kα excitation, the atomic subshell photoionisation cross section for the W 5$d$-like electrons is as big as the factor of 17.6 in comparison with that of the O 2$p$-like electrons (the factor is received from the atomic subshell photoionization cross section data calculated by Yeh and Lindau [15] using the Hartree-Fock-Slater one-electron central potential model). Hence, due to much higher value of the W 5$d$-like cross section as compared with that of the O 2$p$-like cross section, even small contribution of the W 5$d$-like states to the common valence band of the WO$_x$ compound gives the maximum of the XPS valence-band spectrum which does not coincide with the maximum of the band reflecting the energy distribution of the O 2$p$-like states.

It should be mentioned that, the present experimental results seem to be in good agreement with data of the theoretical calculations [10]. As shown by Bullett [10], the central part and the bottom of the valence band of cubic WO$_3$ are occupied by the O 2$p$-like states hybridized mainly with the $t_{2g}$ ($d_{xy}, d_{xz}, d_{yz}$) and $e_g$ ($d_{x^2−y^2}, d_{z^2}$) orbital components of the W 5$d$-like states, respectively. Additionally, the O 2$p$-like states are the main contributors to the top of the valence band of WO$_x$, with very small contribution of the both $t_{2g}$ and $e_g$ orbital components of the partial W 5$d$-like DOS in that region [10]. Energy differences between the maxima of the O 2$p$-like sub-band and the hybridized W 5$d$(t$_{2g}$)−O 2$p$-like sub-band on the band-structure curves calculated by Bullett [10] are about 2.5–2.8 eV being in excellent agreement with the present experimental data: as can be seen from Figure 1, in all the tungsten oxides under study, differences between the energy positions of the features "A" and "B" of the XPS valence-band spectra are within (2.5–3.0)+0.2 eV, while those between the features "D" and "E" of the O Kα band are within (2.3–2.6)+0.1 eV.

Except of the feature "B" of the XPS valence-band spectrum, the formation of a prominent sub-band "C" in the near-Fermi region of the spectrum is characteristic for the substoichiometric compounds, h-WO$_2.8$ and m-WO$_2.77$ (Figure 1). The relative intensity of the sub-band increases monotonously with increasing the O/W ratio in monoclinic WO$_x$ oxides and its creation could be explained due to contributions of the W 5$d$-like and W 6$s$-like states taking part in the formation of the shortened W–W bonds in the m-WO$_{2.3}$ compounds [13]. As can be seen from Figure 1, the relative intensities of the near-Fermi sub-band "C" of the XPS valence-band spectra are comparable for the both substoichiometric tungsten oxides studied, m-WO$_{2.77}$ and h-WO$_2.8$.

Data listed in Table 1 depict that the half-widths of the O Kα band increase in the sequences m-WO$_3$ → m-WO$_{2.77}$ and h-WO$_3$ → h-WO$_{2.8}$, being somewhat smaller for the monoclinic compounds as compared with the hexagonal oxides. An increase of the half-width of the valence band when going from cubic (monoclinic) WO$_3$ to hexagonal WO$_3$ was predicted by Hjelm et al. [11]. Due to the results of the FP-LMTO calculation [11], the O 2$p$-like states originating from the atoms in the hexagonal planes of h-WO$_3$ dominate the low-energy part of the O 2$p$-like band, while the states originating from the atoms between the planes dominate the top of the band. According to the present XES data listed in Table 1, the half-width of the O Kα band increases by 0.45±0.08 eV in the sequence m-WO$_3$ → h-WO$_3$, but that of the h-WO$_{2.8}$ compound is bigger by about 0.3 eV as compared with that of m-WO$_{2.77}$. Additionally, the half-width of the XPS valence-band spectrum increases somewhat when going from m-WO$_{2.77}$ to h-WO$_{2.8}$ (Table 1). Therefore, presence of two types of oxygen atoms in h-WO$_3$ and h-WO$_{2.8}$, to our opinion, is the main reason of the increased half-widths of the O Kα and XPS valence-band spectra in the hexagonal tungsten oxides as compared with those of the monoclinic WO$_x$ oxide possessing close content of oxygen atoms. Energy positions of the centres of gravity and the maxima “E” of the O Kα band remain constant within ±0.1 eV for all the compounds studied.

The W L$_{III}$ absorption spectra of h-WO$_{2.8}$ and m-WO$_{2.77}$ oxides are presented in Figure 2. For comparison, Figure 2 depicts also the spectrum of pure metallic tungsten (the analogous spectra of h-WO$_3$ and m-WO$_3$ were derived in Ref. [3]). As can be seen from Figure 2, the energy position of the inflection point “a” of the W L$_{III}$ spectrum of h-WO$_{2.8}$ coincides within the experimental error with
that of the spectrum of m-WO$_{2.77}$. This fact indicates the similar displacement of the electron density from tungsten atoms to oxygen atoms in the both substoichiometric tungsten oxides studied. Additionally, the position of the inflection point of the W $L_{III}$ spectrum of m-WO$_3$ is very close to that of h-WO$_3$ [5]. Therefore, charge states of tungsten atoms do not change when going from the monoclinic to hexagonal motif of WO$_x$. The present XAS data, as well as those reported in Ref. [5], reveal that the high-energy shift of the inflection point of the W $L_{III}$ absorption edge decreases somewhat in the sequences m-WO$_3$ → m-WO$_{2.77}$ and h-WO$_3$ → h-WO$_{2.8}$. Unfortunately, due to the covering of the surfaces of substoichiometric tungsten oxides by a thin film of tungsten trioxide, it was impossible to evaluate charge states of the tungsten atoms of WO$_{x<3}$ samples using the XPS W 4f core-level measurements. As an example, Figure 3 represents the XPS W 4f core-level spectra of the hexagonal oxides under study and, for comparison, of pure metallic tungsten. It is apparent that the three-peak shape of the spectrum of h-WO$_{2.8}$ is due to superposition of the real position of the W 4f spin-doublet in this compound as well as of the W 4f spin-doublet of a thin film of WO$_3$. We could not eliminate this film on the surface of nanoparticles of h-WO$_{2.8}$. A treatment of h-WO$_{2.8}$ nanoparticles with Ar$^+$ ions leads to appearance in the W 4f core-level spectrum of two additional features with their binding energies corresponding to those of the W 4f$_{7/2,5/2}$ spin-doublet of pure metallic tungsten.

The XAS O 1$s$ spectra measured for the compounds under investigation are presented in Figure 4. The XAS O 1$s$ spectra in the energy region from 520 eV to 570 eV reveal a variety of resonance features, labelled “a–g”: six features are distinguished on the spectrum of m-WO$_3$ and four features on the spectra of h-WO$_3$ and h-WO$_{2.8}$. Energy positions of the resonance features for the compounds investigated are listed in Table 2. As Figure 4 shows, a strong resonance “a” positioned in the energy region (530.0–530.1)$\pm 0.2$ eV (Table 2) dominates the spectra of the compounds studied. Additionally, as the data listed in Table 2 reveal, the energy positions of the inflection point of the XAS O 1$s$ spectra coincide within accuracy of the measurements in the tungsten oxides under consideration. The latter fact indicates that the negative charge state of oxygen atoms does not change when going from m-WO$_3$ to h-WO$_3$ and, further, to h-WO$_{2.8}$. This statement is in agreement with the results of measurements of the XPS O 1$s$ spectra: as it was mentioned in the beginning of this section, for the studying WO$_x$ compounds, both stoichiometric and substoichiometric, the XPS O 1$s$ core-level binding energies coincide within the experimental error being within (530.8–530.9)$\pm 0.1$ eV. Hence, for the compounds studied, the charge states of the oxygen atoms remain almost constant.

4. Conclusions

The half-widths of the O $K\alpha$ emission bands and XPS valence-band spectra increase somewhat in the sequences m-WO$_3$ → m-WO$_{2.77}$ and h-WO$_3$ → h-WO$_{2.8}$, being somewhat higher for the hexagonal compounds as compared with the monoclinic oxides studied. Increasing the half-widths of the above spectra when going from m-WO$_3$ to h-WO$_3$ can be explained by the fact that two types of oxygen atoms are distinguished in the structures of h-WO$_x$: the atoms belonging to the hexagonal planes and those between the planes. As a result, the O 2$p$-states originating from the atoms in the hexagonal planes dominate the low-energy part of the O 2$p$-like band, while the states originating from the atoms between the planes dominate the top of the band. Present experimental results reveal that the effective positive charge states of tungsten atoms in the oxides studied do not alter when changing the structure motif of WO$_x$ and they depend strongly on the oxygen content in m-WO$_3$ and h-WO$_x$ samples. Charge states of oxygen atoms remain constant for all the WO$_x$ compounds under study. In the sequences m-WO$_3$ → m-WO$_{2.77}$ and h-WO$_3$ → h-WO$_{2.8}$ the energy positions of the maxima and of the centres of gravity of the O $K\alpha$ bands remain constant.

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Figure captions

Figure 1. On a common energy scale the XPS valence-band spectra (solid curves) and O $K\alpha$ emission bands (dashed curves) of nanoparticles of hexagonal (h-WO$_3$ and h-WO$_{2.8}$) and monoclinic (m-WO$_3$ and m-WO$_{2.77}$) tungsten oxides studied.

Figure 2. The W $L_{III}$ absorption spectra of nanoparticles of hexagonal h-WO$_{2.8}$ and monoclinic m-WO$_{2.77}$ tungsten oxides; for comparison, the spectrum of pure metallic tungsten is also presented.

Figure 3. The XPS W 4f core level spectra of nanoparticles of hexagonal h-WO$_{2.8}$ and h-WO$_3$ tungsten oxides under study; for comparison, the spectrum of pure metallic tungsten is also presented.

Figure 4. The XAS O 1s spectra of nanoparticles of hexagonal h-WO$_{2.8}$ and h-WO$_3$ and monoclinic m-WO$_3$ tungsten oxides under study.

Table 1. Half-widths (in eV) of the XPS valence-band spectra and XES O $K\alpha$ bands of nanopowders of hexagonal and monoclinic tungsten oxides.

| Oxide      | XPS valence-band spectrum | XES O $K\alpha$ band |
|------------|---------------------------|-----------------------|
| h-WO$_3$   | 6.03                      | 4.67                  |
| h-WO$_{2.8}$ | 6.27                      | 4.98                  |
| m-WO$_3$   | 5.52                      | 4.22                  |
| m-WO$_{2.77}$ | 5.58                      | 4.70                  |
| Uncertainty | $\pm 0.08$               | $\pm 0.08$            |

Table 2. Energy positions (in eV) of some fine-structure features of the XAS O 1s spectra of nanopowders of hexagonal and monoclinic tungsten oxides.

| Oxide      | Inflection point of the O $K$ edge | Resonances |
|------------|------------------------------------|-------------|
| m-WO$_3$   | 529.1                              | 530.0       |
| h-WO$_3$   | 529.2                              | 530.1       |
| h-WO$_{2.8}$ | 529.1                             | 530.1       |

|       | a  | b  | c  | d  | e  | f  | g  |
|-------|----|----|----|----|----|----|----|
| m-WO$_3$ | 536.5 | 538.3 | 543.2 | 546.2 | –  | 558.7 |
| h-WO$_3$ | 530.1 | – | 538.2 | – | 546.0 | 553.2 | – |
| h-WO$_{2.8}$ | 538.0 | – | 545.9 | 553.4 | – | – | – |

Uncertainty
