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Xps Study of the Oxidation State of Uranium Dioxide

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Abstract In this article we report an investigation of the oxidation state of uranium dioxide using X-Ray Photoelectron Spectroscopy, and by comparing to results obtained in previous studies. We find that uranium dioxide in powder appears to share its six valence electrons with the oxygen atoms to form crystalline UO_3.

Keywords: Uranium dioxide; XPS; Chemical shift; Oxidation states

1. INTRODUCTION

Uranium dioxide has a band gap comparable to those of semiconductors at the proper energies for absorption of solar radiation including infrared [1]. However, different uranium compounds have varying stoichiometry, and this influences its electrical properties which depend on the oxidation state of U in the compound. Here we investigate the oxidation state of uranium dioxide using X-Ray Photoelectron Spectroscopy (XPS) measurements, and by comparing to previous studies.

2. FABRICATION PROCEDURE

UO_2 has a cubic cF12 structure, with each U linked to eight O nearest neighbors. Uranium dioxide is produced by directly placing uranium in contact with oxygen. For our purposes UO_2 samples were prepared for XPS examination by combining 200 mg of UO_2 powder and 5 ml of dichloromethane (DCM, CH_2Cl_2) in a vial; the UO_2 solid was sourced from International Bio-Analytical Industries Inc, and the DCM was obtained from Fisher Scientific at 99.9% purity. A

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sonication was applied to the suspension for 10-15 minutes (see Figure 1) to promote the formation of nanoparticles, speed dissolution, to provide the energy for the endothermic U-O_2 reaction, and help initiate the crystallization process.

Drops of approximately 0.5 ml to 1 ml of the UO_2 suspension were slowly drop-casted onto the non-adhesive side of a precut ½ cm x ½ cm piece of 1 Mil Kapton polyimide tape (made of O, C, H and N). The applied suspension was allowed to dry in air on the Kapton, leaving behind a film on the tape. Tape-mounted samples were sandwiched between two glass slides for transportation. Three redundant samples were prepared using the same sonicated UO_2 suspension, see Figure 2.

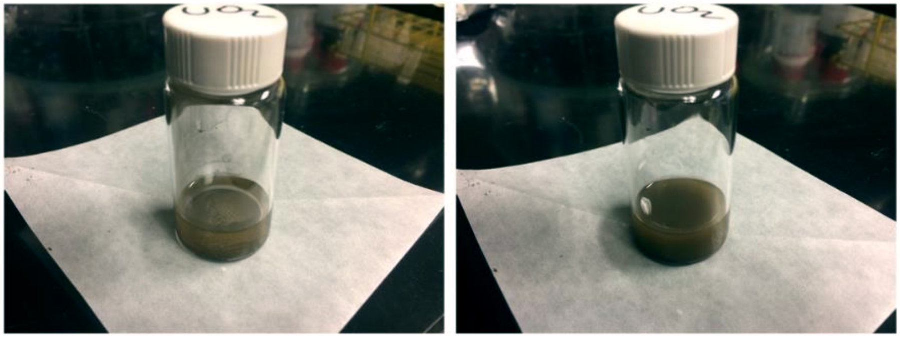

Figure 1: Solution of UO_2 in DCM before sonication (left panel), and after sonication (right panel).

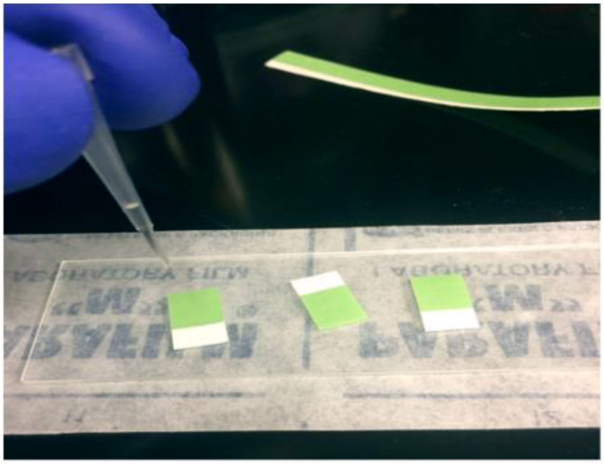

Figure 2: Drops of UO_2 being deposited on the Kapton polyimide tape. Samples were sandwiched between glass slides for transportation.

3. XPS ANALYSIS

The X-ray Photoelectron Spectroscopy (XPS) analyses were carried out with a PHI 5600 spectrometer with a hemispherical energy analyzer, using magnesium (MgK_α) source of 1253.6 eV at 100 Watts. No sputtering (cleaning) was performed. The pressure in the analysis chamber during XPS analysis was in the low range of 10^{-8} Torr. All spectra were recorded at 54° take off angle, the analyzed area being about 1 mm^2. All spectra were recorded with 1.0 eV step, 5 cycles, 50 sweeps and calibrated using the adventitious C1s carbon peak at 284.5 eV. XPS spectra were analyzed using CasaXPS software version 2.3.12. The Shirley method was used for extracting the background necessary for curve fitting.

The XPS spectrum for uranium oxide are shown in Figure 3. The spectra were collected in the range of 400 to 370 eV, peaks were observed from the excitations of U4f orbital. The most intense peaks correspond to the spin–orbit (L–S) split U4$f_{7/2}$ and U4$f_{5/2}$ states, respectively; Figure 3 shows the 4$f_{5/2}$ peaks for the fours samples at 381.8 eV, 382.1 eV, 382.2 eV and 382.5 eV and the 4$f_{7/2}$ peaks at 381.2 eV, 381.3 eV, 381.4 eV, and 381.5 eV.

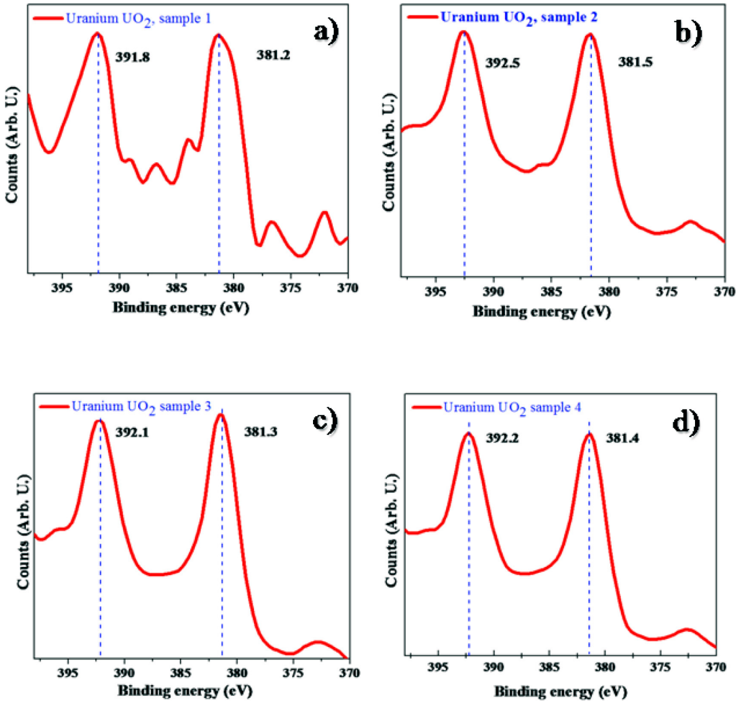

Figure 3: XPS peaks of the 4$f_{5/2}$ and 4$f_{7/2}$ peaks of UO$_2$.

Table 1: Binding energies of the U 4f5/2 and 4f7/2 peaks in different compounds.

Compound	Energy 4f5/2 (eV)	Energy 4f7/2 (eV)	4f7/2 Difference from 377.3 eV
UO_2 (U^{4+})	390.758	379.857	2.557
$NaUO_3$ (U^{5+})	391.327	380.426	3.126
KUO_3 (U^{5+})	390.947	379.857	2.557
$Ba_2U_2O_7$ (U^{5+})	391.137	380.142	2.842
$Cs_2U_4O_{13}$ (U^{6+})	392.180	381.279	3.979

4. DETERMINATION OF THE OXIDATION STATE

Published data [2] lists the $4f_{5/2}$ and $4f_{7/2}$ XPS peaks for pure U at 388 eV and 377.3 eV, respectively, it is clear that our observed values do not correspond to these values and present a shift due to oxidation. The same booklet [2] also lists the observed peaks for a variety of uranium compounds, with a range from 377 to almost 383 for the $4f_{7/2}$ peak, including oxides. The specific energy values for the binding energy shifts for different oxidation states, however, are not listed and they must be inferred from a different source.

J. H. Liu et al. [3] used XPS to analyze several uranium compounds with different oxidation states. Table 1 shows their results, also listed is the difference between the observed 4f7/2 and the expected 377.3 eV value.

The oxidation state of our samples can be inferred by comparing our 4f7/2 results with those of Liu et al. Figure 4 shows the energy of the 4f7/2

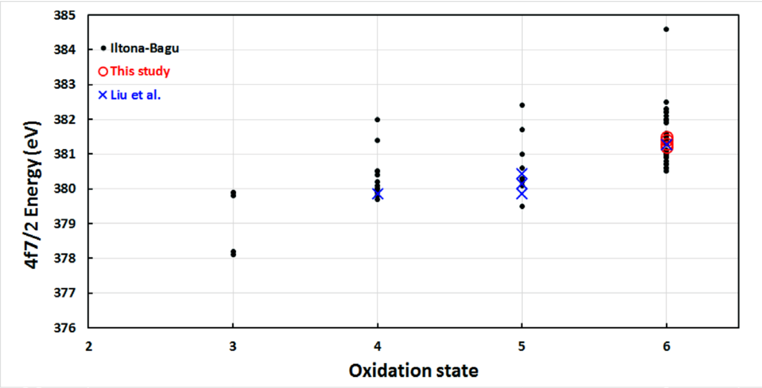

Figure 4: Energy of the 4f7/2 level of our four samples and data from several previous studies [5-11] plotted against their oxidation state. Notice that our four samples were assigned an oxidation state of 6+ to fit the trend.

level of the compounds studied by Liu et al. plotted against the oxidation states listed in the article (4+, 5+ and 6+). For comparison, the figure also lists the energies of the XPS results of our four samples (for visibility presented as enlarged hollow red circles), and those from the compilation summarized in reference [4]. It is clear that our results correspond to an oxidation state of 6+, as plotted.

Numerically, we can estimate the energy shifts incurred by the different oxidation states with respect to the expected 377.3 eV. For U^{4+} the difference is 2.557 eV; for U^{5+} the average shift is (3.126+2.557+2.842)/3 = 2.841 eV, and for U^{6+} it is 3.979 eV. For our samples the energies are 381.2 eV, 381.3 eV, 381.4 eV, and 381.5 eV, and the average difference with 377.3 eV is 4.05 eV, which is very close to the 6+ shift of 3.979 eV.

CONCLUSIONS

Uranium dioxide is usually listed with a structure O=U=O, which would imply an electronegativity of U^{4+} with O^{2-}, this, however, depends on the structure of the compound. For instance, researchers have found [5] that the U-O interactions are modified by changing the U-O distance, as in fluorite and octahedral crystal structures for U4+ oxides. In our case, UO_2 is expected to have a fluorite-like cubic 4f12 structure in which each U would be surrounded by 8 O nearest neighbors [6]. Our results, however, indicate that the degree of the shift observed in the emission lines of 4f5/2 and 4f7/2, are comparable to those of other compounds with a 6-fold valence as reported by Liu et al. [3] and Ilton and Bagus [4], and observed in the tendency of Fig. 4. Thus we conclude that uranium, with its electron configuration of [Rn] 5f3 6d1 7s2, appears to share all of its six valence electrons with the oxygen atoms to form a chemical structure of the type UO_3, stoichiometrically speaking.

In the future we expect to investigate the emission lines corresponding to 6p1/2 6p3/2, 5f, 6d and 7s which were not properly resolved in our initial experiments, but are expected to support our present arguments. Particularly the peaks corresponding to 5f, 6d and 7s are expected at very low energies, less than 4 eV, thus with disadvantages of signal-to-background ratio.

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