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Core-level Spectra of Powdered Tungsten Disulfide, WS₂

David J. Morgan

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(Received day Month year; accepted day Month year; published day Month year)

Core level spectra, generated by monochromatic Al K α x-rays for a commercial, powdered tungsten disulfide (WS₂) specimen have been recorded and presented. The XPS spectra of WS₂ obtained include a survey scan, high-resolution spectra of W 4f, S 2p, S 2s, W 4d, W 4p, O 1s, W 4s, S LMM and the valance band. Quantitative analysis has been achieved using a 2-parameter Tougaard background and line shapes indicated for fitting; using these methods a surface composition of WS₂ is found.

Keywords: WS₂, tungsten, XPS, disulfide, dichalcogenide

INTRODUCTION

There is currently a great interest in the study of transition metal dichalcogenides (TMDs) of the type MX₂, where M is a metal atom (such as W or Mo) and where X is a chalcogen atom (S, Se or Te) (Ref. 1). Tungsten disulfide, WS₂, is one such TMD which exhibits a diverse range of applications, including catalysis in crude oil hydrotreating and carbon dioxide hydrogenation (Refs. 2 – 3) and lubrication, especially for industrial applications (Ref. 4). Many TMDs, including WS₂, exhibit a direct band gap which can be exploited in electronic transistors (Ref. 5), whilst nanostructured WS₂ is also being tested for hydrogen and lithium storage (Ref. 6). With diverse applications, the surface chemistry of such TMDs is of great interest, and it is with that in mind the spectra of WS₂ is presented herein.

SPECIMEN DESCRIPTION (ACCESSION #00000)

Host Material: Tungsten disulfide, WS₂

CAS Registry #: 12138-09-9

Host Material Characteristics: homogeneous; powder; unknown crystallinity; semiconductor; inorganic compound; Powder

Chemical Name: Tungsten disulfide

Source: Sigma-Aldrich

Host Composition: WS₂

Form: Powder

Structure: polycrystalline

History & Significance: Received direct from manufacturer

As Received Condition: Supplied as new in glass bottle

Analyzed Region: Same as host material

Ex Situ Preparation/Mounting: Mounted ex-situ by pressing in to a well of a Thermo scientific powder sample holder.

Accession#:

Technique: XPS

Host Material: Tungsten disulfide, WS₂

Instrument: Thermo Scientific K-Alpha⁺

Major Elements in Spectra: W, S

Minor Elements in Spectra: O

Published Spectra: 10

Spectra in Electronic Record: 10

Spectral Category: reference

In Situ Preparation: None

Charge Control: Combined low energy electrons and argon ions

Temp. During Analysis: 300K

Pressure During Analysis: 1.3x10⁻⁵ Pa

Pre-analysis Beam Exposure: 30 s.

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Scientific K-Alpha+

Analyzer Type: double focussing hemispherical analyser

Detector: multichannel resistive plate

Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput (T=E^N): N=0

Excitation Source Window: None

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Beam Size: 800 μ m x 400 μ m

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 60 °

Source-to-Analyzer Angle: 60 °

Emission Angle: 90 °

Specimen Azimuthal Angle: 45 °

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Acceptance Angle from Analyzer Axis: 60 °

Analyzer Angular Acceptance Width: 45 ° x 0 °

■ Ion Gun

Manufacturer and Model: Thermo Scientific MAGCIS

Energy: 1000 eV

Current: 1 mA

Current Measurement Method: biased stage

Sputtering Species: None

Spot Size (unrastered): 120 μm

Raster Size: 4000 μm x 4000 μm

Incident Angle: 58 °

Polar Angle: 58 °

Azimuthal Angle: 90 °

Comment: No in-situ cleaning was performed

DATA ANALYSIS METHOD

Energy Scale Correction: None

Recommended Energy Scale Shift: None

Peak Shape and Background Method: Background: A custom 2-parameter Tougaard (U 2) background was used, with a 'C' parameter value of -650. For W 4p peaks, the loss structure should be included in defining the background, but the loss structure given a zero sensitivity factor in quantification. Peak Shapes: Finite Lorentzian (LF), Gaussian-Lorentzian (GL) mixtures or asymmetric Lorentzian (LA) lineshape were used as follows; W 4f LF(0.7,0.9,525,280,4); S 2p LF(1,1,25,180); W 4p loss peaks and W 5p_{3/2} GL(90); S 2s LA(1,1,80); W 4p LF(0.6,1,45,80). For W 4d peaks, peaks are readily described using an asymmetric shape, modified by Gaussian-Lorentzian sum function as described by: W 4d_{5/2} A(0.3,0.53,0)SGL(75); W 4d_{3/2} A(0.3,0.1,0)SGL(75)

Quantitation Method: Quantification was performed using component definitions within CasaXPS v2.3.19rev1.2w, utilizing Scofield sensitivity factors corrected with an energy dependence of -0.6. Using this method, the ratio of S:W is found to be 1.97:1, in excellent agreement with expected 2:1 ratio.

ACKNOWLEDGMENTS

XPS data collection was performed at the EPSRC National Facility for XPS ('HarwellXPS'), operated by Cardiff University and UCL, under contract No. PR16195.

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6. F. Cheng, J. Chen, *J. Mater. Res.* 21, 2744 (2016)

SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
3 ^a	W 4f _{7/2}	32.6	0.67	23466.8	9.80	30.44	W in WS ₂
3 ^a	W 4f _{5/2}	34.7	0.62	17600.1
3 ^a	W 5p _{3/2}	38.3	2.2	5361.7
4	S 2p _{3/2}	162.2	0.63	9572.3	1.68	60.20	S in WS ₂
4	S 2p _{1/2}	163.4	0.63	4786.2
5	S 2s	226.6	1.43	11901.0	1.43
6 ^b	W 4d _{5/2}	244.6	3.85	71729.7	16.33
6 ^b	W 4d _{3/2}	257.2	4.37
8 ^c	W 4p _{3/2}	425.1	5.50	27985.0	5.16
8 ^c	Loss Peak	448.6	13.1	8329.5	Satellite / loss peak
8 ^c	W 4p _{1/2}	491.9	5.50	9998.9	2.10
8 ^c	Loss Peak	514.5	13.1	3356.0	Satellite / loss peak
8 & 9	O 1s	530.9	2.93	9.36	Oxide / hydroxide species
10	W 4s	595.1	8.9	7393.6	1.81
11 ^d	S LMM	149.7	LMM Auger

^a The reported sensitivity factor for W 4f is for both 7/2 and 5/2 peaks. For quantification, the background should include the W 5p_{3/2} component, but the sensitivity factor set to zero for quantification.

^b The reported sensitivity factor for W 4d is for both 5/2 and 3/2 peaks, whilst the peak area is the total for both spin-orbit split components

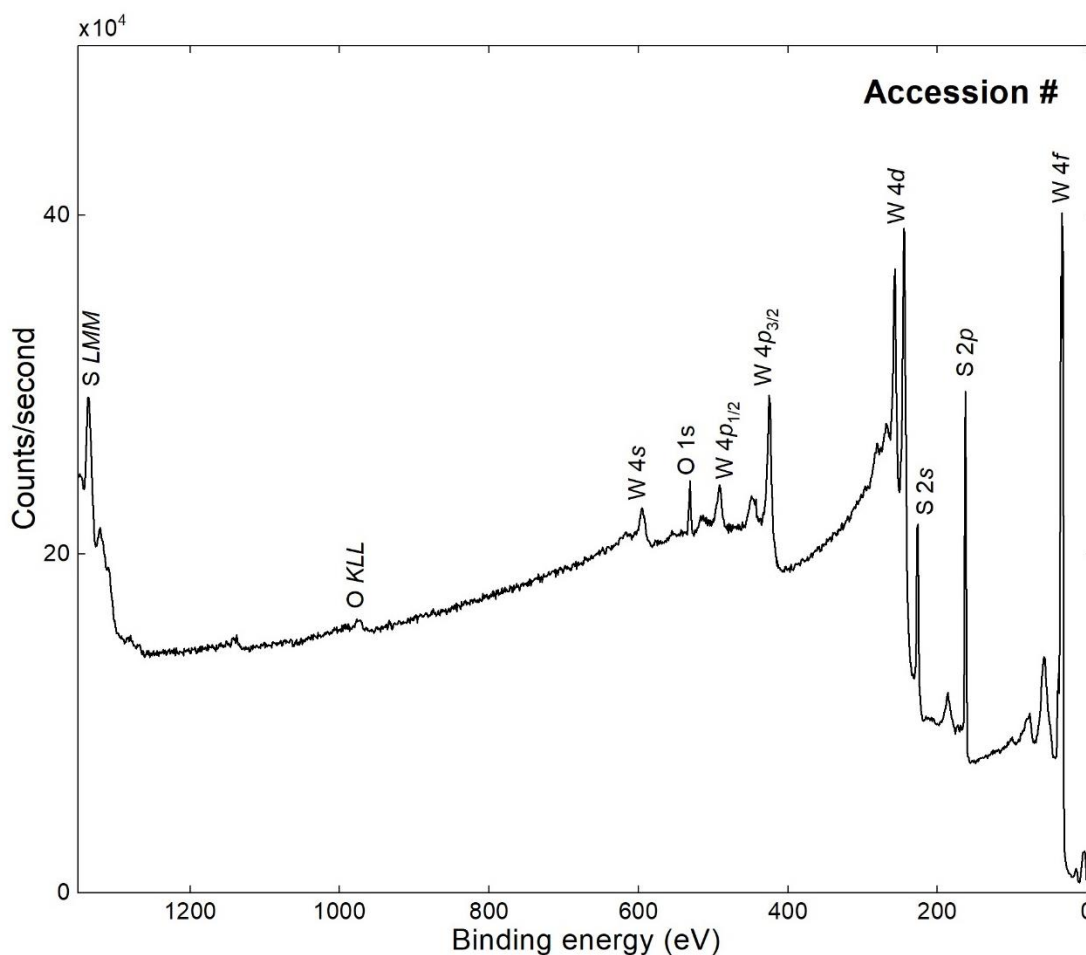
^c The reported sensitivity factors are for W 4p 5/2 and 3/2 peaks only, whilst the background is extended to include the loss structure, the sensitivity factor for the peak component is set to zero for quantification.

^d The Auger peak energy is reported as a kinetic energy, the corresponding binding energy is 1336.9 eV.

ANALYZER CALIBRATION TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
1	Au 4f _{7/2}	83.99	0.76	1597652	9.580	100	Gold metal
2	Ag 3d _{5/2}	368.28	0.58	1876744	7.38	100	Silver metal
3	Cu 2p _{3/2}	932.67	0.83	2205571	16.73	100	Copper metal

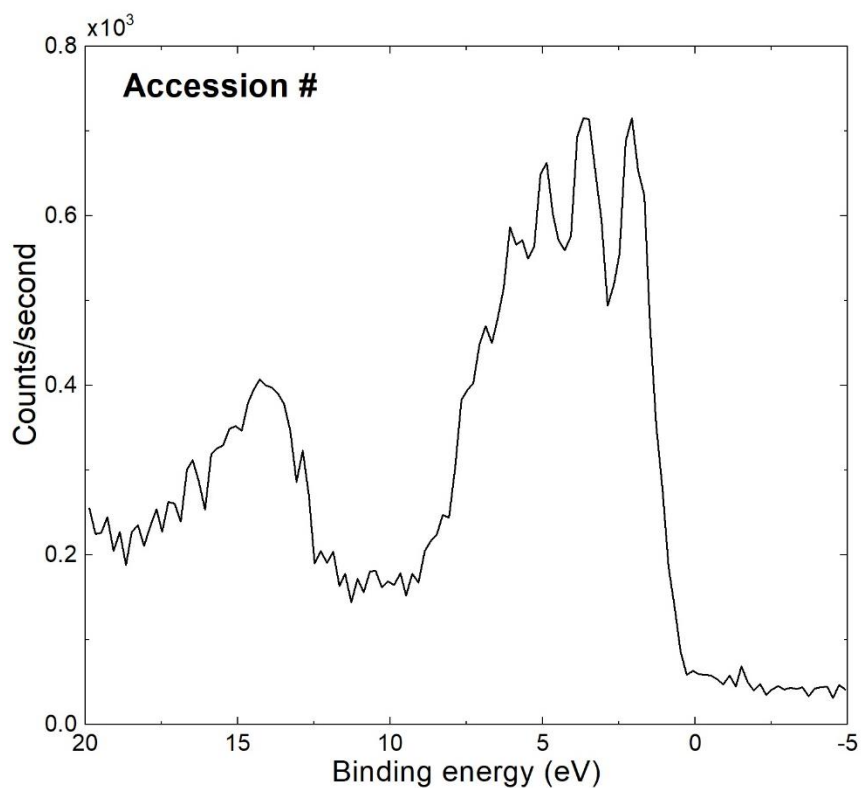
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
1	Survey	0	1	0	
2	Valence	0	1	0	
3	W 4f	0	1	0	
4	S 2p	0	1	0	
5	S 2s	0	1	0	
6	W 4d	0	1	0	
7	C 1s	0	1	0	
8	W 4p & O 1s	0	1	0	
9	O 1s	0	1	0	
10	W 4s	0	1	0	
11	S LMM	0	1	0	



Publish in *Surface Science Spectra*: Yes No

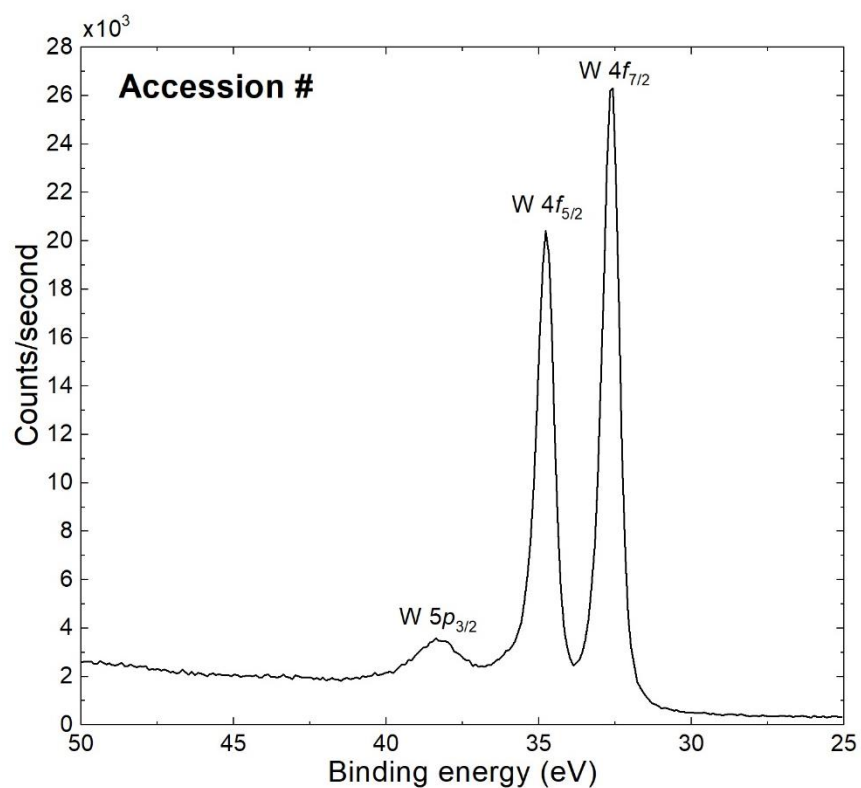
Accession #	01312-01
Host Material	Tungsten disulfide
Technique	XPS
Spectral Region	survey
Instrument	Thermo Scientific K-Alpha+
Excitation Source	Al Ka monochromatic
Source Energy	1486.6 eV
Source Strength	72 W
Source Size	0.8 mm x 0.4 mm
Analyzer Type	double focussing hemispherical analyser
Incident Angle	60°
Emission Angle	90°
Analyzer Pass Energy	150 eV
Analyzer Resolution	1 eV
Total Signal Accumulation Time	130 s
Total Elapsed Time	260 s
Number of Scans	10
Effective Detector Width	1 eV



Publish in SSS: Yes No

■ **Accession #:**
■ **Host Material:** Tungsten disulfide
■ **Technique:** XPS
■ **Spectral Region:** Valence

Instrument: Thermo Scientific K-Alpha+
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.8 mm x 0.4 mm
Analyzer Type: spherical sector
Incident Angle: 60 °
Emission Angle: 90 °
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.45 eV
Total Signal Accumulation Time: 200 s
Total Elapsed Time: 226 s
Number of Scans: 20
Effective Detector Width: 0.2 eV



Publish in SSS: Yes No

■ **Accession #:**

■ **Host Material:** Tungsten disulfide

■ **Technique:** XPS

■ **Spectral Region:** W 4f

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.8 mm x 0.4 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 60 °

Emission Angle: 90 °

Analyzer Pass Energy 20 eV

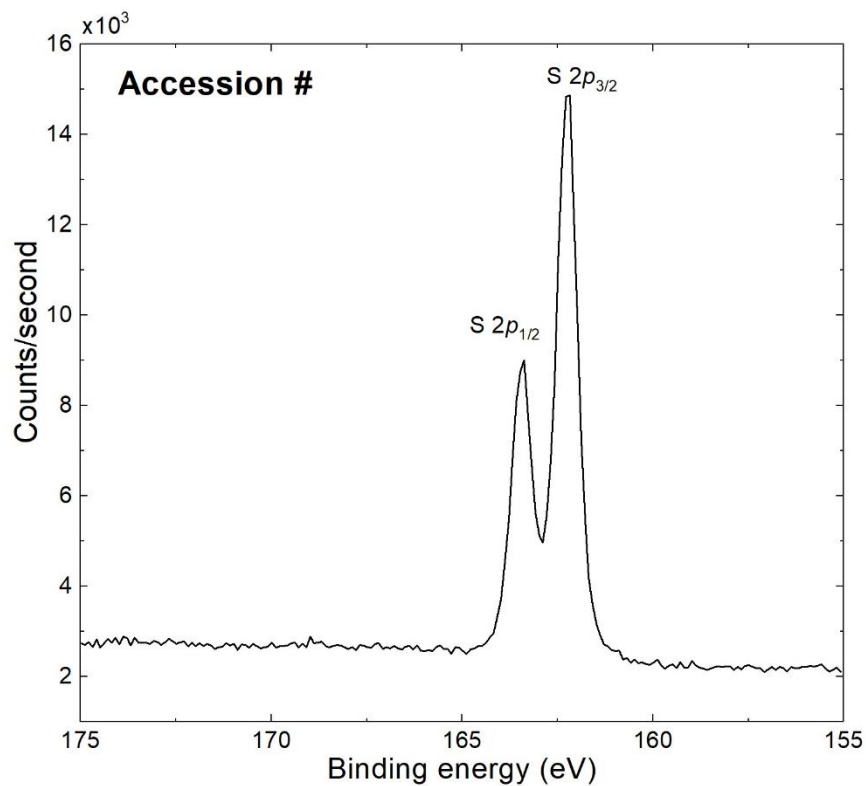
Analyzer Resolution: 0.45 eV

Total Signal Accumulation Time: 240 s

Total Elapsed Time: 251 s

Number of Scans: 20

Effective Detector Width: 0.1 eV



Publish in SSS: Yes No

■ Accession #:

■ Host Material: Tungsten disulfide

■ Technique: XPS

■ Spectral Region: S 2p

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.8 mm x 0.4 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 60°

Emission Angle: 90°

Analyzer Pass Energy 20 eV

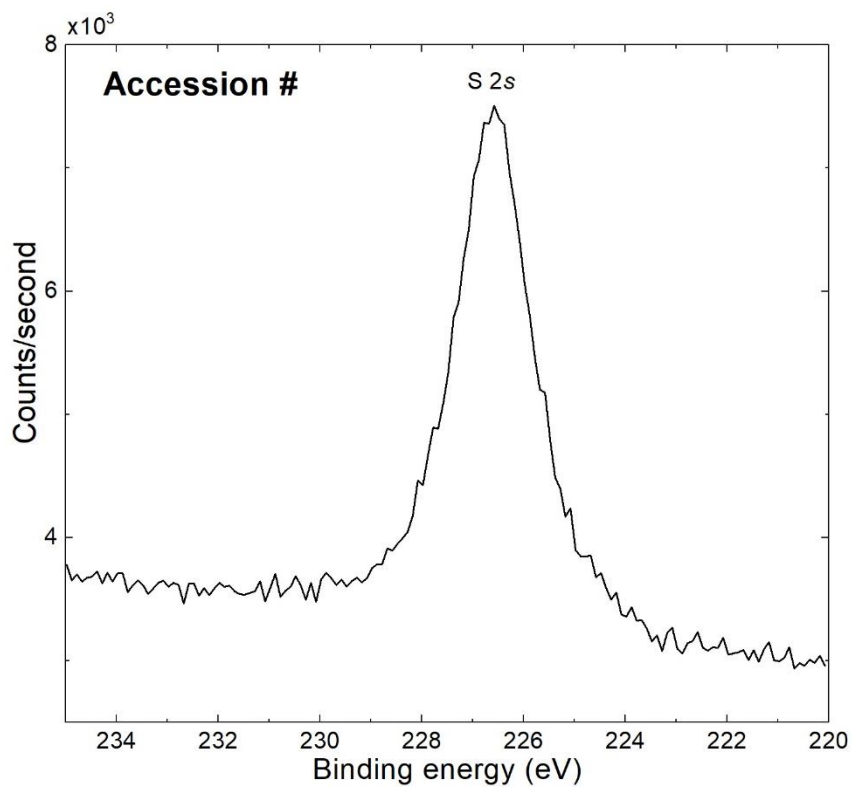
Analyzer Resolution: 0.45 eV

Total Signal Accumulation Time: 200 s

Total Elapsed Time: 226 s

Number of Scans: 20

Effective Detector Width: 0.1 eV



Publish in SSS: Yes No

■ **Accession #:**

■ **Host Material:** Tungsten disulfide

■ **Technique:** XPS

■ **Spectral Region:** S 2s

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.8 mm x 0.4 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 60°

Emission Angle: 90°

Analyzer Pass Energy 20 eV

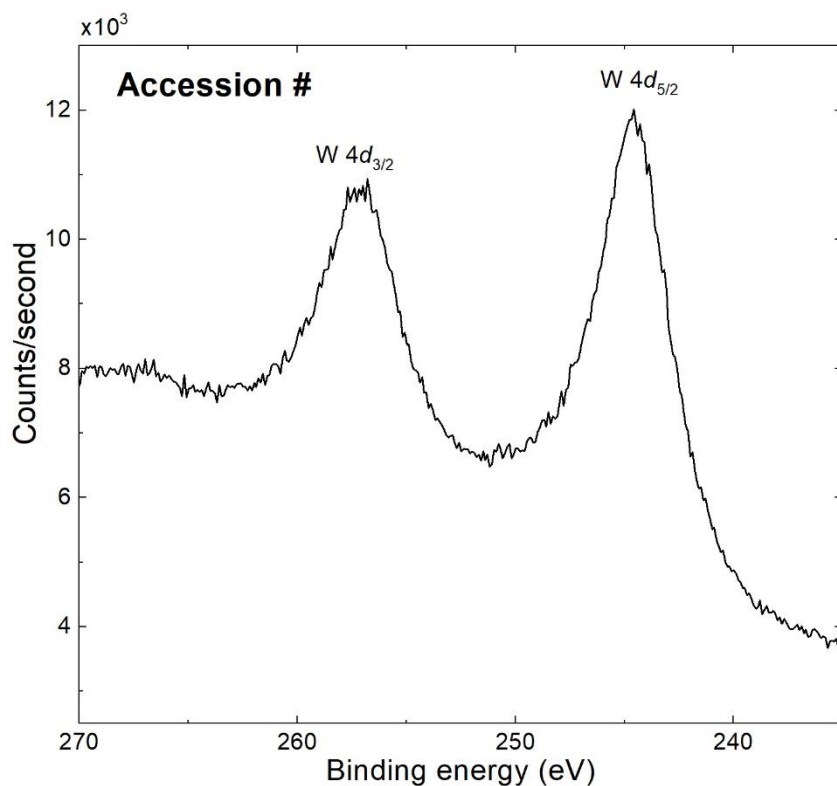
Analyzer Resolution: 0.45 eV

Total Signal Accumulation Time: 120 s

Total Elapsed Time: 131 s

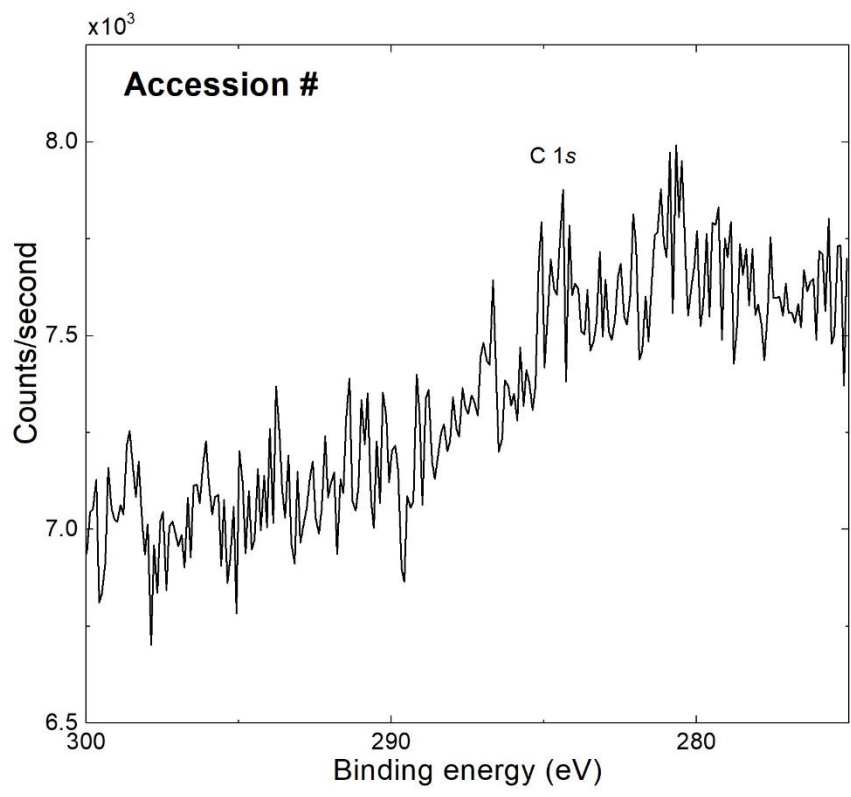
Number of Scans: 20

Effective Detector Width: 0.1 eV



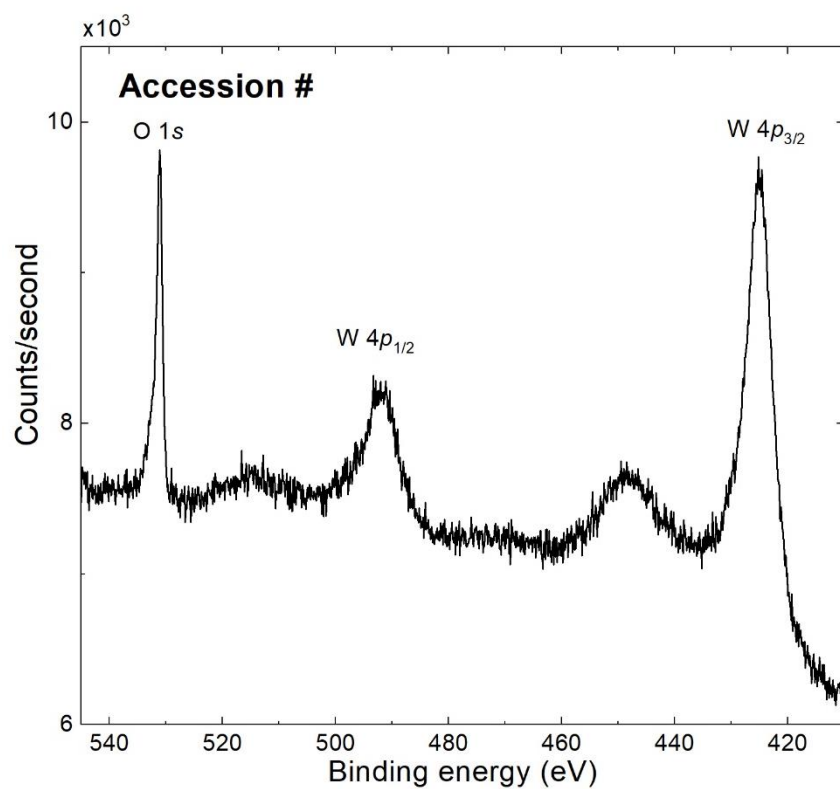
Publish in SSS: Yes No

■ **Accession #:**
■ **Host Material:** Tungsten disulfide
■ **Technique:** XPS
■ **Spectral Region:** W 4d
Instrument: Thermo Scientific K-Alpha+
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.8 mm x 0.4 mm
Analyzer Type: double focussing hemispherical analyser
Incident Angle: 60 °
Emission Angle: 90 °
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.45 eV
Total Signal Accumulation Time: 300 s
Total Elapsed Time: 351 s
Number of Scans: 20
Effective Detector Width: 0.1 eV



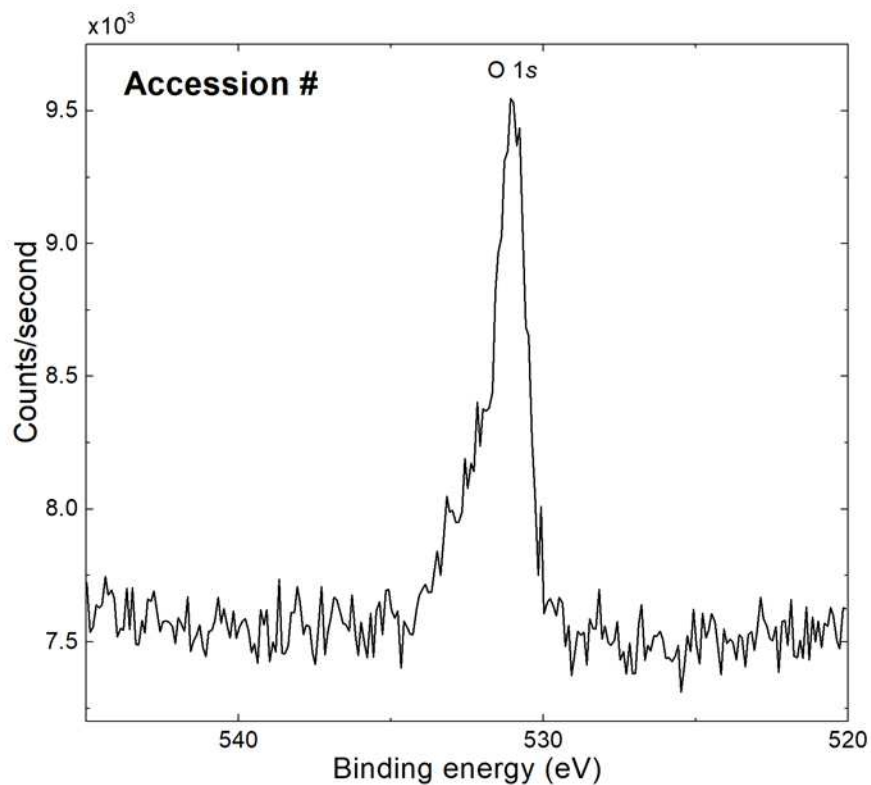
Publish in SSS: Yes No

- **Accession #:**
- **Host Material:** Tungsten disulfide
- **Technique:** XPS
- **Spectral Region:** C 1s
- Instrument: Thermo Scientific K-Alpha+
- Excitation Source: Al Ka monochromatic
- Source Energy: 1486.6 eV
- Source Strength: 72 W
- Source Size: 0.8 mm x 0.4 mm
- Analyzer Type: double focussing hemispherical analyser
- Incident Angle: 60 °
- Emission Angle: 90 °
- Analyzer Pass Energy 20 eV
- Analyzer Resolution: 0.45 eV
- Total Signal Accumulation Time: 120 s
- Total Elapsed Time: 131 s
- Number of Scans: 20
- Effective Detector Width: 0.1 eV



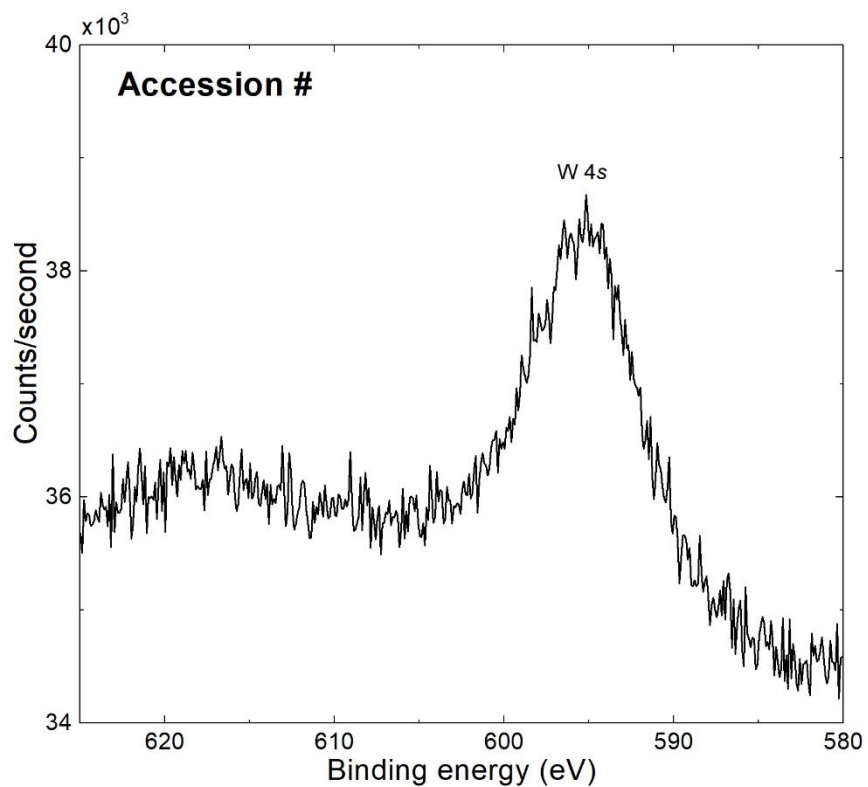
Publish in SSS: Yes No

■ **Accession #:**
■ **Host Material:** Tungsten disulfide
■ **Technique:** XPS
■ **Spectral Region:** W4p & O 1s
Instrument: Thermo Scientific K-Alpha+
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.8 mm x 0.4 mm
Analyzer Type: double focussing hemispherical analyser
Incident Angle: 60 °
Emission Angle: 90 °
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.45 eV
Total Signal Accumulation Time: 900 s
Total Elapsed Time: 935 s
Number of Scans: 20
Effective Detector Width: 0.1 eV



Publish in SSS: Yes No

■ **Accession #:**
■ **Host Material:** Tungsten disulfide
■ **Technique:** XPS
■ **Spectral Region:** O 1s
Instrument: Thermo Scientific K-Alpha+
Excitation Source: Al K α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.8 mm x 0.4 mm
Analyzer Type: double focussing hemispherical analyser
Incident Angle: 60 °
Emission Angle: 90 °
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.45 eV
Total Signal Accumulation Time: 900 s
Total Elapsed Time: 935 s
Number of Scans: 20
Effective Detector Width: 0.1 eV



Publish in SSS: Yes No

■ **Accession #:**

■ **Host Material:** Tungsten disulfide

■ **Technique:** XPS

■ **Spectral Region:** W 4s

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al Ka monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.4 mm x 0.4 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 60 °

Emission Angle: 90 °

Analyzer Pass Energy 20 eV

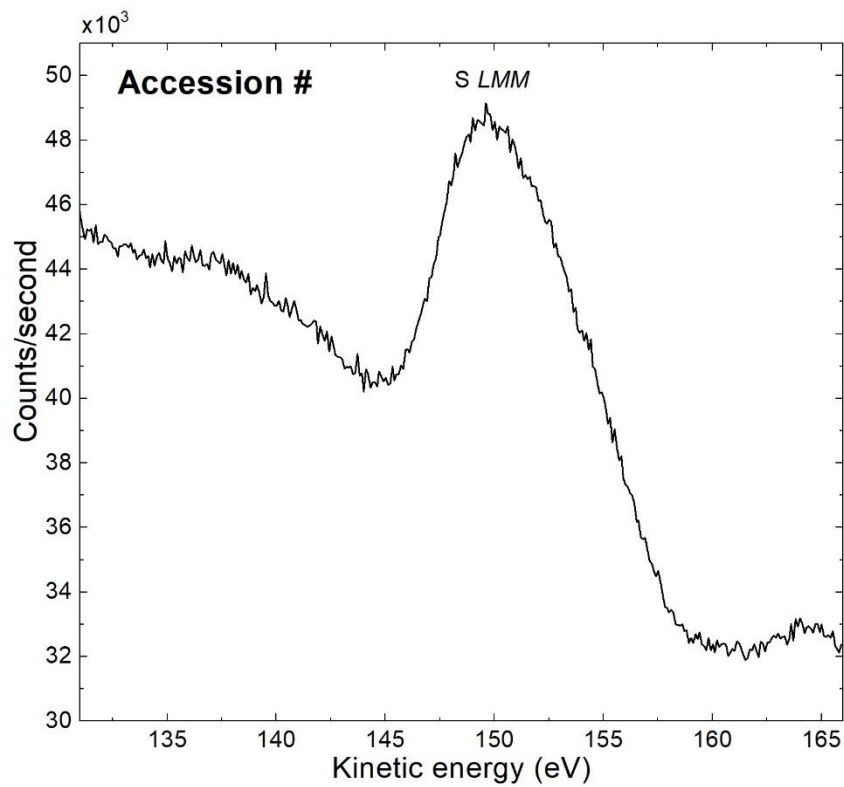
Analyzer Resolution: 0.45 eV

Total Signal Accumulation Time: 420 s

Total Elapsed Time: 451 s

Number of Scans: 20

Effective Detector Width: 0.1 eV



Publish in SSS: Yes No

■ Accession #:

■ Host Material: Tungsten disulfide

■ Technique: XPS

■ Spectral Region: S LMM

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al Ka
monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.4 mm x 0.4 mm

Analyzer Type: double focussing
hemispherical analyser

Incident Angle: 60 °

Emission Angle: 90 °

Analyzer Pass Energy 20 eV

Analyzer Resolution: 0.45 eV

Total Signal Accumulation Time: 900 s

Total Elapsed Time: 935 s

Number of Scans: 20

Effective Detector Width: 0.1 eV