

## Cluster cleaned HOPG by XPS

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# Cluster cleaned HOPG by XPS

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X-ray photoelectron spectroscopy was used to characterize a highly oriented pyrolytic graphite (HOPG) sample. The HOPG was freshly cleaved using Scotch tape prior in the entry lock of the spectrometer and subsequently cleaned using an argon cluster source. This method of cleaning has led to an improved definition of the C KLL Auger signal used for differentiation in the determination of  $sp^2/sp^3$  ratios according to the method of Lascovich *et al.* [Appl. Surf. Sci. **78**, 17 (1994)]. © 2017 American Vacuum Society. <https://doi.org/10.1116/1.4993771>

**Keywords:** HOPG, XPS, graphite, Auger

**Accession #:** 01421

**Technique:** XPS

**Host Material:** Highly orientated  
pyrolytic graphite

**Instrument:** Thermo Scientific K-Alpha<sup>+</sup>

**Major Elements in Spectra:** C

**Minor Elements in Spectra:** O

**Published Spectra:** 4

**Spectra in Electronic Record:** 4

**Spectral Category:** Technical

## INTRODUCTION

Highly oriented pyrolytic graphite (HOPG) is commonly used as a model carbon support for a diverse range of surface studies, including a well-defined reference material for analysis of graphite, nuclear graphite, and the functionalisation of graphitic materials (Refs. 1 and 2). Lascovich and Scaglione (Ref. 3) derived the use of the so-called D-parameter as a measure of the amount of  $sp^2$  character in a carbon material, based on the differential spectra of the C KLL Auger peak.

To date, however, the C KLL peak still shows remnants of adventitious carbon or similar as evidenced by the poor definition of the highest binding energy peak in the spectra; thus, to date the majority of x-ray induced Auger electron spectroscopy data published for HOPG is commonly that of a partially contaminated sample. The advent of cluster cleaning has allowed for a less contaminated HOPG surface to be examined.

## SPECIMEN DESCRIPTION (ACCESSION NO. 1421)

**Host Material:** Highly orientated pyrolytic graphite (HOPG)

**CAS Registry No.:** 7782-42-5

**Host Material Characteristics:** Homogeneous; solid; single crystal; conductor; inorganic compound; other

**Chemical Name:** Carbon

**Source:** SPI Supplies

**Host Composition:** Carbon

**Form:** Crystalline wafer

**Structure:** C

**History and Significance:** Newly acquired HOPG

**As Received Condition:** The sample was received as new from the supplier in a sealed plastic box.

**Analyzed Region:** Approximately the center of the sample (of dimensions ca.  $10 \times 10 \times 5$  mm) was analyzed with a  $400\text{-}\mu\text{m}$  analysis area.

**Ex Situ Preparation/Mounting:** The sample was placed directly on to the spectrometer sample plate and held with copper clips. The surface was cleaved with Scotch tape immediately before evacuation to UHV conditions.

**In Situ Preparation:** The sample was analyzed via XPS to ascertain any contamination from the scotch tape or similar. The sample was subsequently sputtered using a MAGCIS source operating at 4 kV with large argon clusters of approximately 2000 atoms and rastered over an area of ca  $2 \times 2$  mm.

**Charge Control:** No charge control was used as HOPG is a conducting sample

**Temp. During Analysis:** 300 K

**Pressure During Analysis:**  $9.33 \times 10^{-7}$  Pa

**Preanalysis Beam Exposure:** The sample was analyzed for a total of 5 min prior to sputtering. Subsequent analysis after sputtering using argon clusters involved no pre-exposures.

## INSTRUMENT DESCRIPTION

**Manufacturer and Model:** Thermo Scientific K-Alpha<sup>+</sup>

**Analyzer Type:** Double focussing hemispherical analyzer

**Detector:** Multichannel resistive plate

**Number of Detector Elements:** 128

## INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

### ■ Spectrometer

**Analyzer Mode:** Constant pass energy

**Throughput ( $T = E^N$ ):** Choose an item.

**Excitation Source Window:** None

**Excitation Source:** Al K $\alpha$  monochromatic

**Source Energy:** 1486.6 eV

**Source Strength:** 72 W

**Source Beam Size:**  $400 \times 400 \mu\text{m}$

**Signal Mode:** Multichannel direct

### ■ Geometry

**Incident Angle:**  $60^\circ$

**Source-to-Analyzer Angle:**  $60^\circ$

**Emission Angle:**  $90^\circ$

**Specimen Azimuthal Angle:**  $45^\circ$

**Acceptance Angle from Analyzer Axis:**  $60^\circ$

**Analyzer Angular Acceptance Width:**  $45^\circ \times 0^\circ$

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## ■ Ion gun

**Manufacturer and Model:** Thermo Scientific MAGCIS

**Energy:** 4000 eV

**Current:** Enter ion beam current (-)

**Current Measurement Method:** Biased stage

**Sputtering Species:** Ar cluster

**Spot Size (Unrastered):** 120  $\mu\text{m}$

**Raster Size:** 4000  $\times$  4000  $\mu\text{m}$

**Incident Angle:** 58°

**Polar Angle:** 58°

**Azimuthal Angle:** 90°

**Comment:** Argon clusters of 2000 atoms were utilized for at a voltage of 4 kV, the current was approximately 5 nA.

### DATA ANALYSIS METHOD

**Energy Scale Correction:** Not required

**Recommended Energy Scale Shift:** Not required

**Peak Shape and Background Method:** Peak analysis is performed using CASAXPS v2.3.19 using a Shirley background. Differentiation of the C KLL Auger peak is performed using a polynomial regression background type in CASAXPS with the first parameter set to 32, and the differential of this data

envelope performed using the Test data tab. The D-parameter is obtained using the “SP” background type, the value of which is found to be 23 in accordance with Ref. 3. A finite Lorentzian (LF) lineshape, as described by LF (0.75,1,100,150), was used to model the C1s asymmetry to obtain the peak FWHM, together with a mixed Gaussian-Lorentzian peaks for the satellite structure. Details of these lineshapes can be found in Ref. 4.

**Quantitation Method:** Data analysis was performed in CasaXPS using a Shirley background and utilizing Scofield sensitivity factors with an energy dependence of  $-0.6$ .

### ACKNOWLEDGMENTS

The author would like to thank P. R. Davies for the loan of the HOPG sample and the Ser Cymru capital equipment grant for help in purchase of the spectrometer.

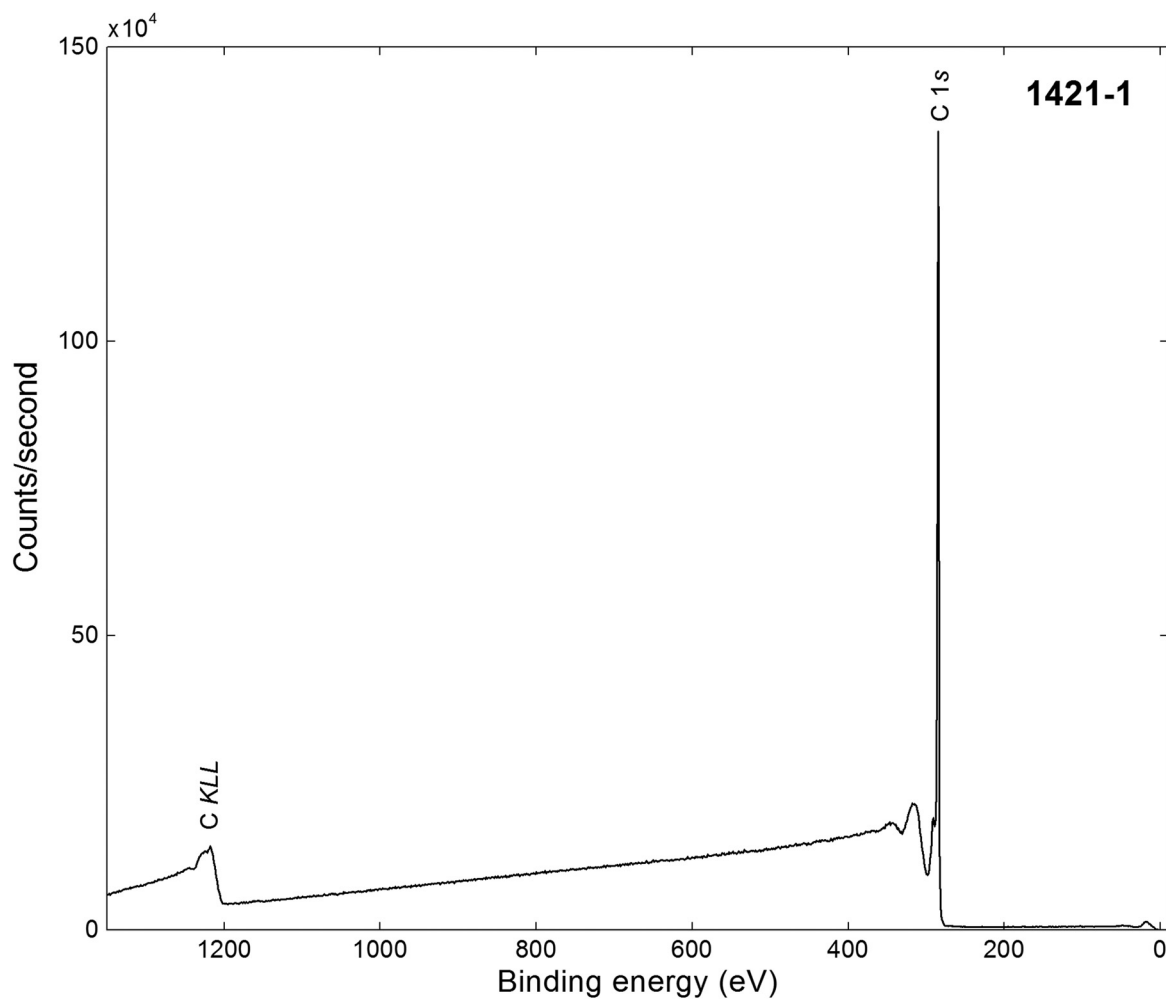
### REFERENCES

1. W. Xie, K. Mo Ng, L.-T. Weng, and C.-M. Chan, *RSC Adv.* **6**, 80649 (2016).
2. R. Burgess *et al.*, *J. Catal.* **323**, 10 (2015).
3. J. C. Lascovich and S. Scaglione, *Appl. Surf. Sci.* **78**, 17 (1994).
4. S. J. Freakley, J. Ruiz-Esquius, and D. J. Morgan, *Surf. Interface Anal.* **49**, 794 (2017).

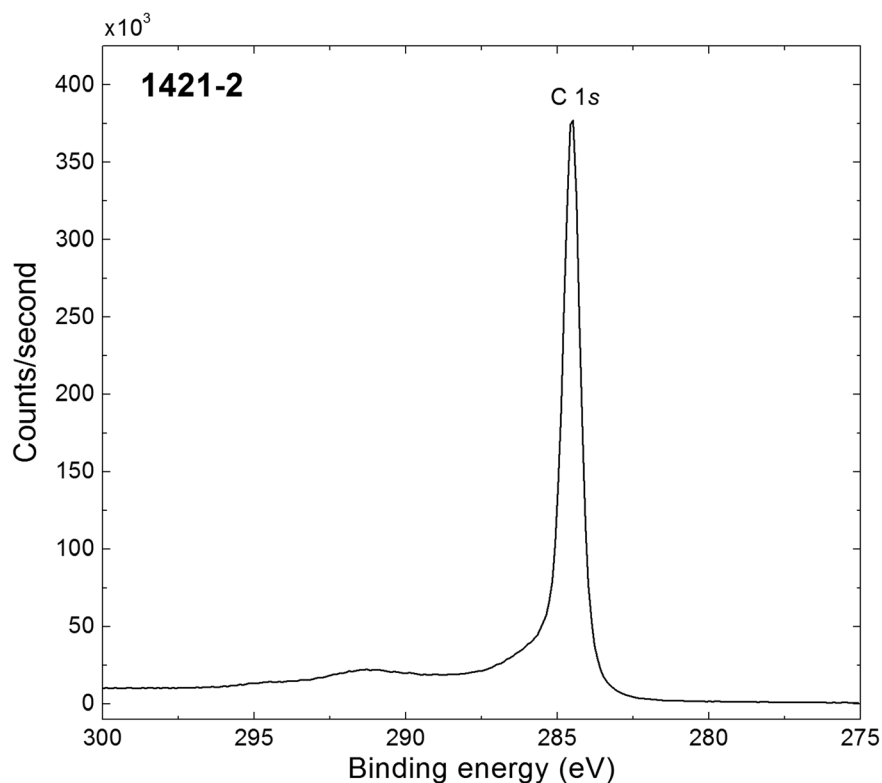
SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
1421-01	C 1s	285.0	2.1	...	1.00	100	Sp <sup>2</sup> carbon
1421-01	C KLL	1218.0	...	...	...	...	Carbon Auger
1421-02	C 1s	284.5	0.63	452747.3	1.00	99.9	Sp <sup>2</sup> carbon
1421-03	O 1s	532.7	2.0	1490.9	2.93	0.1	Oxygen bound to carbon
1421-04	C KLL	1217.9	...	...	...	...	Sp <sup>2</sup> carbon Auger

ANALYZER CALIBRATION TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
1	Au 4f <sub>7/2</sub>	83.99	0.76	1597652	9.58	100	Gold metal
2	Ag 3d <sub>5/2</sub>	368.28	0.58	1876744	7.38	100	Silver metal
3	Cu 2p <sub>3/2</sub>	932.67	0.83	2205571	16.73	100	Copper metal

GUIDE TO FIGURES					
Spectrum (Accession) #	Spectral Region	Voltage Shift	Multiplier	Baseline	Comment #
1421-01	Survey	0	1	0	...
1421-02	C 1s	0	1	0	...
1421-03	O 1s	0	1	0	...
1421-04	C KLL	0	1	0	...



Accession #	1421-01
Host Material	HOPG
Technique	XPS
Spectral Region	Survey
Instrument	Thermo Scientific K-Alpha <sup>+</sup>
Excitation Source	Al Ka monochromatic
Source Energy	1486.6 eV
Source Strength	72 W
Source Size	0.004 × 0.004 mm
Analyzer Type	Double focussing hemispherical analyzer
Incident Angle	60°
Emission Angle	90°
Analyzer Pass Energy	150 eV
Analyzer Resolution	0.1 eV
Total Signal Accumulation Time	130 s
Total Elapsed Time	260 s
Number of Scans	10
Effective Detector Width	1 eV



■ Accession #: [1421-02](#)  
 ■ Host Material: HOPG  
 ■ Technique: XPS  
 ■ Spectral Region: C 1s

Instrument: Thermo Scientific  
 K-Alpha<sup>+</sup>

Excitation Source: Al K $\alpha$   
 monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004  $\times$  0.004 mm

Analyzer Type: Double focussing  
 hemispherical analyzer

Incident Angle: 60°

Emission Angle: 90°

Analyzer Pass Energy: 40 eV

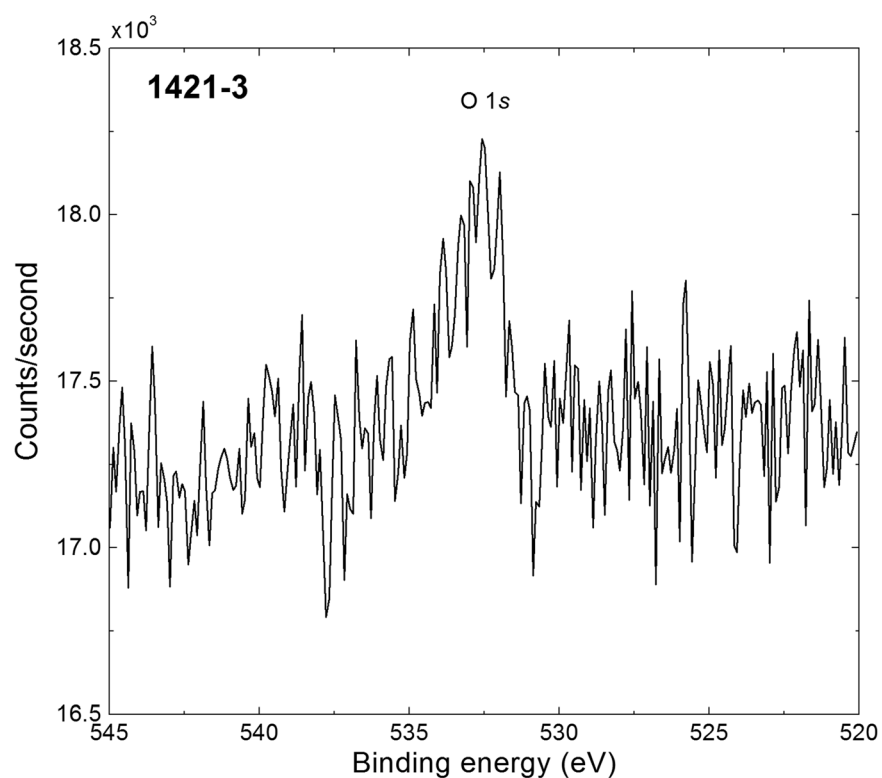
Analyzer Resolution: 0.1 eV

Total Signal Accumulation Time: 120 s

Total Elapsed Time: 153 s

Number of Scans: 10

Effective Detector Width: 0.1 eV



■ Accession #: [1421-03](#)  
 ■ Host Material: HOPG  
 ■ Technique: XPS  
 ■ Spectral Region: O 1s

Instrument: Thermo Scientific  
 K-Alpha<sup>+</sup>

Excitation Source: Al K $\alpha$   
 monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004  $\times$  0.004 mm

Analyzer Type: Double focussing  
 hemispherical analyzer

Incident Angle: 60°

Emission Angle: 90°

Analyzer Pass Energy: 40 eV

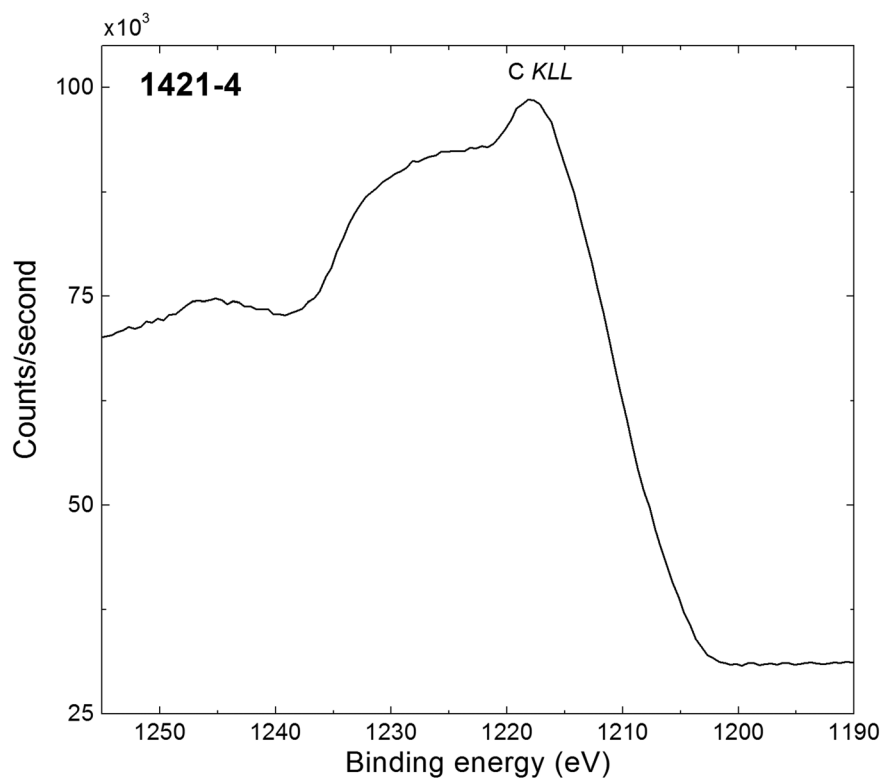
Analyzer Resolution: 0.1 eV

Total Signal Accumulation Time: 125 s

Total Elapsed Time: 133 s

Number of Scans: 10

Effective Detector Width: 0.1 eV



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■ Accession #: 1421-04  
■ Host Material: HOPG  
■ Technique: XPS  
■ Spectral Region: C KLL

Instrument: Thermo Scientific  
K-Alpha+

Excitation Source: Al Ka  
monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size:  $0.004 \times 0.004$  mm

Analyzer Type: Double focussing  
hemispherical analyzer

Incident Angle:  $60^\circ$

Emission Angle:  $90^\circ$

Analyzer Pass Energy: 100 eV

Analyzer Resolution: 0.5 eV

Total Signal Accumulation Time: 327 s  
526 s

Number of Scans: 50

Effective Detector Width: 0.1 eV

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