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Core-level Reference Spectra for Bulk Graphitic Carbon Nitride (g-C₃N₄)

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X-ray photoelectron spectroscopy (XPS) was used to characterize a graphitic carbon nitride (g-C₃N₄) sample synthesized by the high temperature treatment of urea. Core-level C(1s) and N(1s) spectra are presented to aid fitting of such materials and address inconsistencies noted within published research literature.

Keywords: C₃N₄, XPS, Carbon Nitride, Graphitic

INTRODUCTION

Graphitic carbon nitride (g-C₃N₄) is a subset of the carbon nitride family, with a structural skeleton consisting primarily of heptazine (CAS number 204-34-2) and triazine units, such as melamine (CAS number 108-78-1). The structure of such graphitic carbon nitrides may be controlled by the synthesis method (Ref. 2). By means of illustration, figure 1 shows examples of representative g-C₃N₄ structures.

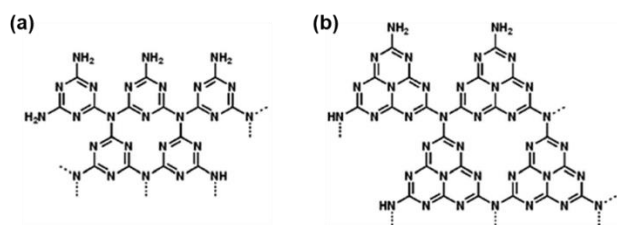


Figure 1. Structures considered representative of g-C₃N₄, where (a) triazine and (b) tri-s-triazine based

Owing to its low cost and CO₂ activation properties, g-C₃N₄ has received great attention for photocatalytic CO₂ reduction, whilst its relatively facile synthesis can be tuned using different precursors for polymerization which can strongly modify not only its electron transfer properties, but also its light absorption (Ref. 3).

Briefly, the g-C₃N₄ synthesized herein was from analytical grade urea which was heated in a muffle furnace to 550°C for 3 h as described in Ref. 4; the yellow powder formed is indicative of bulk, lamellar g-C₃N₄ (Ref.5).

Presented herein are both raw and fitted core-level data for an in-house synthesized sample, which is used as an exemplar for peak positions and assignments and appreciation of the satellite

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Accession#:

Technique: XPS

Host Material: Graphitic Carbon Nitride

Instrument: Thermo Scientific K-Alpha⁺

Major Elements in Spectra: C, N

Minor Elements in Spectra: O

Published Spectra: 7

Spectra in Electronic Record: 7

Spectral Category: comparison

structure. An in-depth analysis has not been performed on the satellite structure; however, the reported peak positions and fitting parameters should facilitate analysis for any overlapping elements or study of any perturbation which may affect the satellite structure. Furthermore, any deviation in peak ratios to those reported may be indicative of the levels of hydrogenation of some of the nitrogen species.

SPECIMEN DESCRIPTION (ACCESSION #00000)

Host Material: Graphitic Carbon Nitride

CAS Registry #: 143334-20-7

Host Material Characteristics: homogeneous; powder; unknown crystallinity; semiconductor; organic compound; -

Chemical Name: Carbon Nitride

Source: Synthesized in-house

Host Composition: C₃N₄

Form: Powder

Structure: C₃N₄

History & Significance: Synthesized during 2019 and stored in an argon purged glass sample vial

As Received Condition: The sample was received as a yellow powder after synthesis

Analyzed Region: Approximately the center of the sample was analyzed with the software 400-micron spot mode which is an elliptical area of ca. 400 x 600 microns and defines the analysis area.

Ex Situ Preparation/Mounting: The sample was mounted in air, by pressing into a sample well of a Thermo Scientific K-Alpha copper powder holder plate to reveal a relatively flat surface.

In Situ Preparation: No in-situ treatment was performed

Charge Control: Dual electron and low energy argon ion source, tuned to give a C 1s binding energy for the C-C peak in PET as 284.8 eV.

Temp. During Analysis: 300K

Pressure During Analysis: 2.10×10^{-5} Pa

Pre-analysis Beam Exposure: The sample was illuminated by both X-ray and neutralizer for *ca.* 30 seconds before data acquisition whilst the spectrometer automatically determined the optimum analysis heights.

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 ($T=E^N$): Calculated from a polynomial fit to a plot of $\log[\text{peak area}/(\text{PE} \times \text{XSF})]$ versus $\log(\text{KE}/\text{PE})$, where PE is the pass energy, KE is the kinetic energy, and XSF is the relative sensitivity factor.

Excitation Source Window: None

Excitation Source: Al Ka monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Beam Size: 400 μm x 600 μm

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 30 °

Source-to-Analyzer Angle: 60 °

Emission Angle: 90 °

Specimen Azimuthal Angle: 45 °

Acceptance Angle from Analyzer Axis: 60 °

Analyzer Angular Acceptance Width: 45 ° x 0 °

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 v2.3.24 rev 1.1Z using a 2 parameter Tougaard (U2) background to enable determination of fitting parameters for the satellite structure to higher binding energy. The use of a Shirley-type background is possible, yielding similar results but should terminate just after the largest N1s peak. Lorentzian Asymmetric (LA) Voigt type lines shapes were used for analysis of the general form $\text{LA}(\alpha, \beta, m)$ where α and β define the spread of the tail on either side of the Lorentzian components and m is an integer between 0 and 499 defining the width of the Gaussian used to convolute the Lorentzian peak (note the β

parameter may be omitted). The fitting parameters used are: LA(1.3,243) for all peaks, including satellite structure with the exception of C(1s) and N(1s) peaks at 288.1 and 398.7 eV respectively, where LA(1.03,1.24,243) was used.

Quantitation Method: Data analysis was performed in CasaXPS V2.3.24 rev 1.1Z, using a 2 parameter Tougaard (U2) background and utilizing Scofield sensitivity factors with a kinetic energy dependence of -0.6.

ACKNOWLEDGMENTS

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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
00000-01	C 1s*	288.0		1675779.80	1.00	43.53	Total carbon in g-C ₃ N ₄
00000-01	N 1s*	399.0		3874678.14	1.80	55.91	Total nitrogen in g-C ₃ N ₄
00000-01	O 1s	533.0		63074.43	2.93	0.56	Oxygen contamination
00000-01	N KLL**	381.5					N Auger in g-C ₃ N ₄
00000-01	C KLL**	265.0					C Auger in g-C ₃ N ₄
00000-02a	C 1s	284.8	1.4	7856.03	1.00	2.48	sp ³ -carbon
00000-02a	C 1s	286.5	1.1	1365.08	1.00	0.43	C-OH
00000-02a	C 1s	288.1	1.0	112800.74	1.00	35.62	C in C-N-C
00000-02a	C 1s	293.2	1.9	5888.32	1.00	1.86	Satellite
00000-02a	C 1s	294.5	1.9	4000.98	1.00	1.26	Satellite
00000-02a	C 1s	296.4	1.9	1368.12	1.00	0.43	Satellite
00000-02a	C 1s	299.5	2.7	3798.84	1.00	1.20	Satellite
00000-03a	N 1s	398.7	1.0	106675.65	1.80	33.68	N in C-N-C
00000-03a	N 1s	399.9	1.4	26157.75	1.80	8.26	N in N-[C] ₃
00000-03a	N 1s	401.1	1.4	24054.43	1.80	7.59	N in C-N-H
00000-03a	N 1s	404.2	2.4	14275.69	1.80	4.51	Satellite
00000-03a	N 1s	406.8	2.4	4915.75	1.80	1.55	Satellite
00000-03a	N 1s	409.0	2.4	481.72	1.80	0.15	Satellite
00000-03a	N 1s	411.7	2.4	1516.85	1.80	0.48	Satellite
00000-04	O 1s	532.3	2.2	1566.37	2.93	0.49	OH (hydroxyl)
00000-05	N KLL	382.3					Nitrogen Auger
00000-06	C KLL	265.8					Carbon Auger
00000-07	Valence						Valence region

Note:

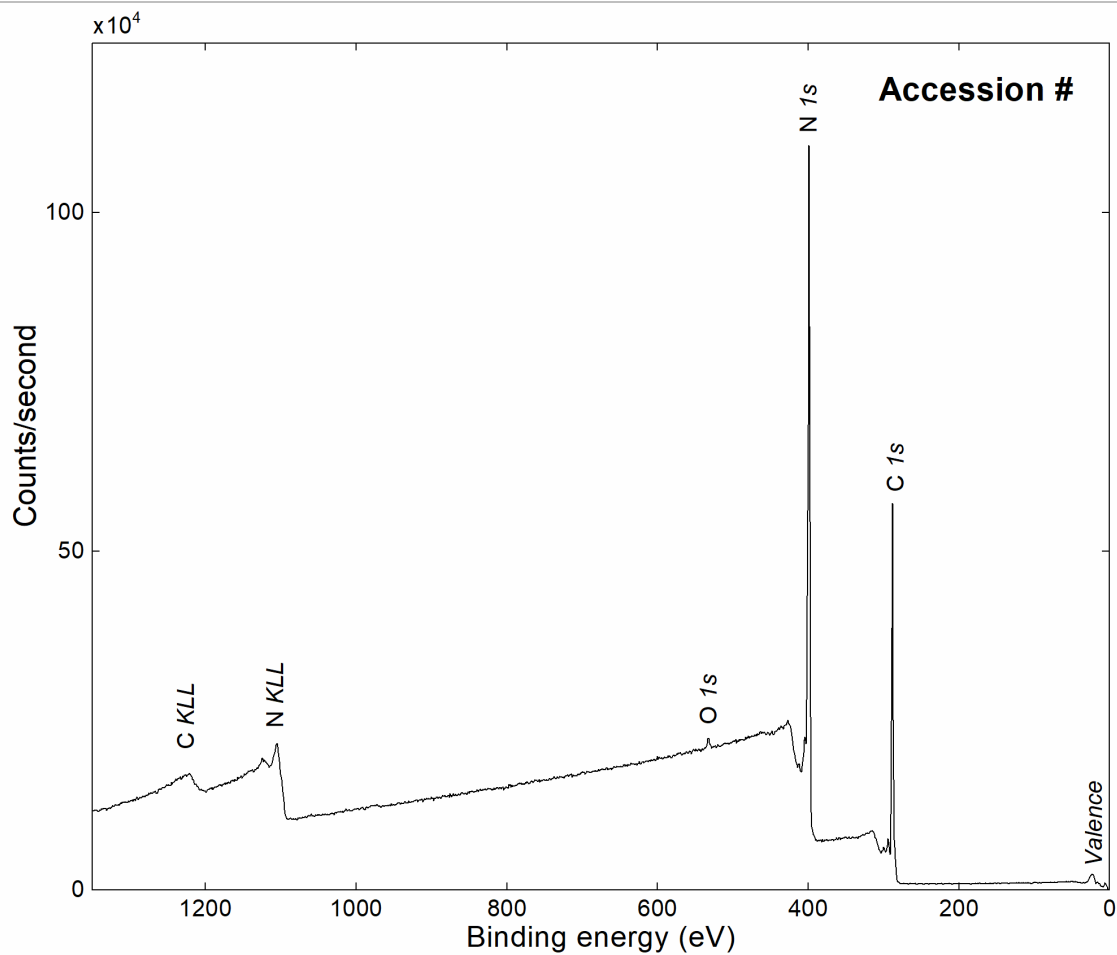
* Peak areas include satellite structure.

** Auger energies reported as kinetic energy as convention.

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	9.58	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

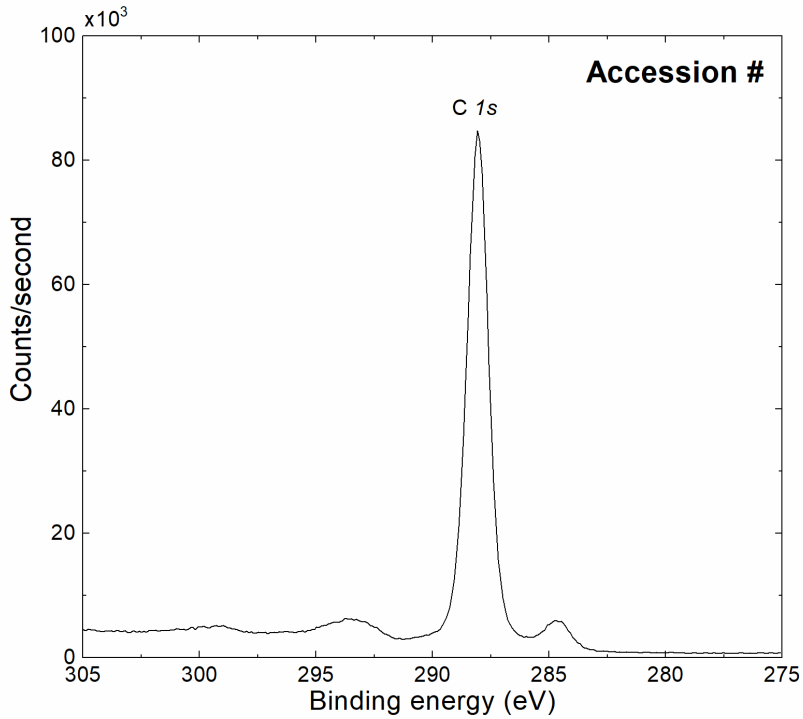
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
00000-01	Survey	0	1	0	
00000-02	C 1s	0	1	0	
00000-02a	C 1s	0	1	0	Fitted 00000-02
00000-03	N 1s	0	1	0	
00000-03a	N 1s	0	1	0	Fitted 00000-03
00000-04	O 1s	0	1	0	
00000-05	N KLL	0	1	0	
00000-06	C KLL	0	1	0	
00000-07	Valence	0	1	0	0.2 eV step size



Publish in *Surface Science Spectra*: Yes No

Accession #	00000-01
Host Material	g-C ₃ N ₄
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	0.004 mm x 0.006 mm
Analyzer Type	double focussing hemispherical analyser
Incident Angle	30°
Emission Angle	90°
Analyzer Pass Energy	150 eV
Analyzer Resolution	2.0 eV
Total Signal Accumulation Time	136 s
Total Elapsed Time	136 s
Number of Scans	10
Effective Detector Width	20 eV



Publish in SSS: Yes No

■ Accession #: 00000-02

■ Host Material: g-C₃N₄

■ Technique: XPS

■ Spectral Region: C 1s

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

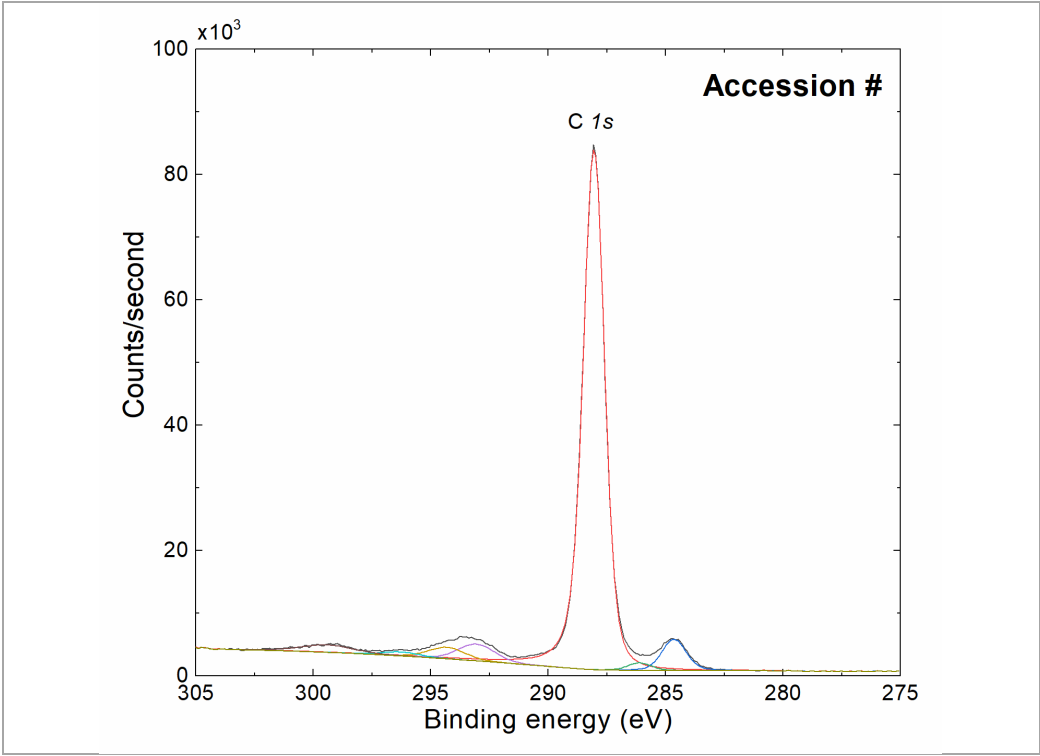
Analyzer Resolution: 0.6 eV

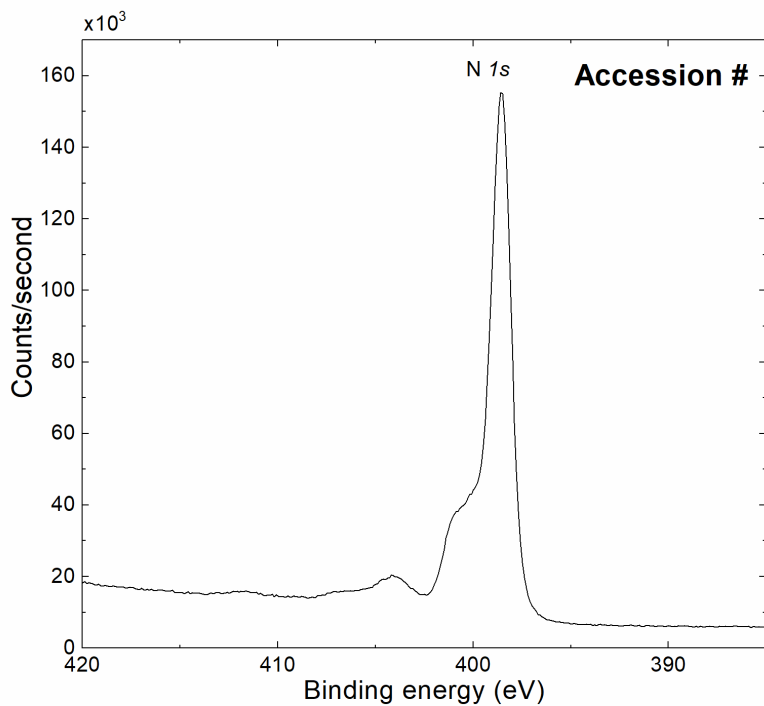
Total Signal Accumulation Time: 151 s

Total Elapsed Time: 151 s

Number of Scans: 10

Effective Detector Width: 5 eV





Publish in SSS: Yes No

■ Accession #: 00000-03

■ Host Material: g-C₃N₄

■ Technique: XPS

■ Spectral Region: N 1s

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

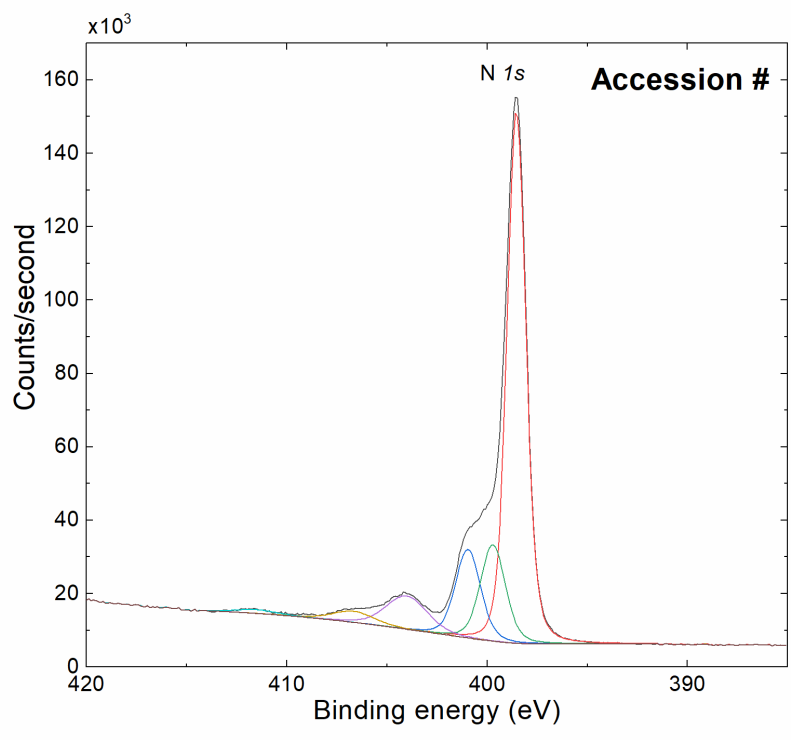
Analyzer Resolution: 0.6 eV

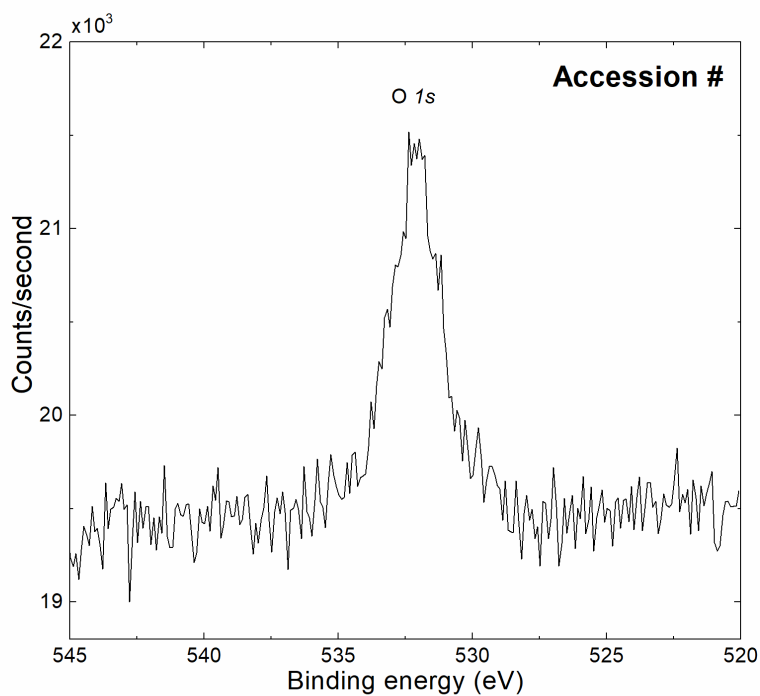
Total Signal Accumulation Time: 175 s

Total Elapsed Time: 175 s

Number of Scans: 10

Effective Detector Width: 5 eV





Publish in SSS: Yes No

■ Accession #: 00000-04

■ Host Material: g-C₃N₄

■ 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: 0.004 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

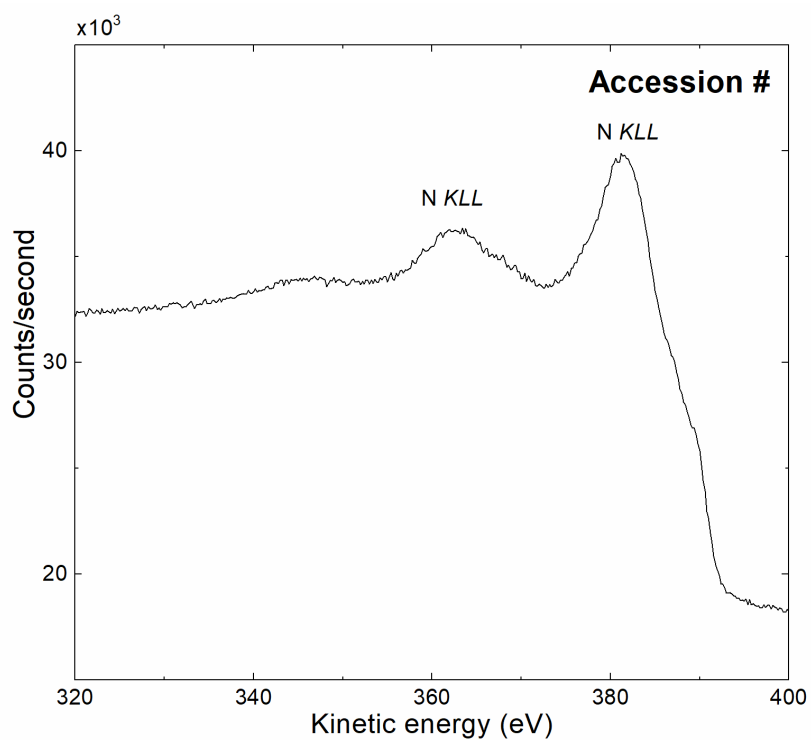
Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 251 s

Total Elapsed Time: 251 s

Number of Scans: 20

Effective Detector Width: 5 eV



Publish in SSS: Yes No

■ Accession #: 00000-05

■ Host Material: g-C₃N₄

■ Technique: XAES

■ Spectral Region: N KLL

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al Ka
monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004 mm x 0.006 mm

Analyzer Type: double focussing
hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

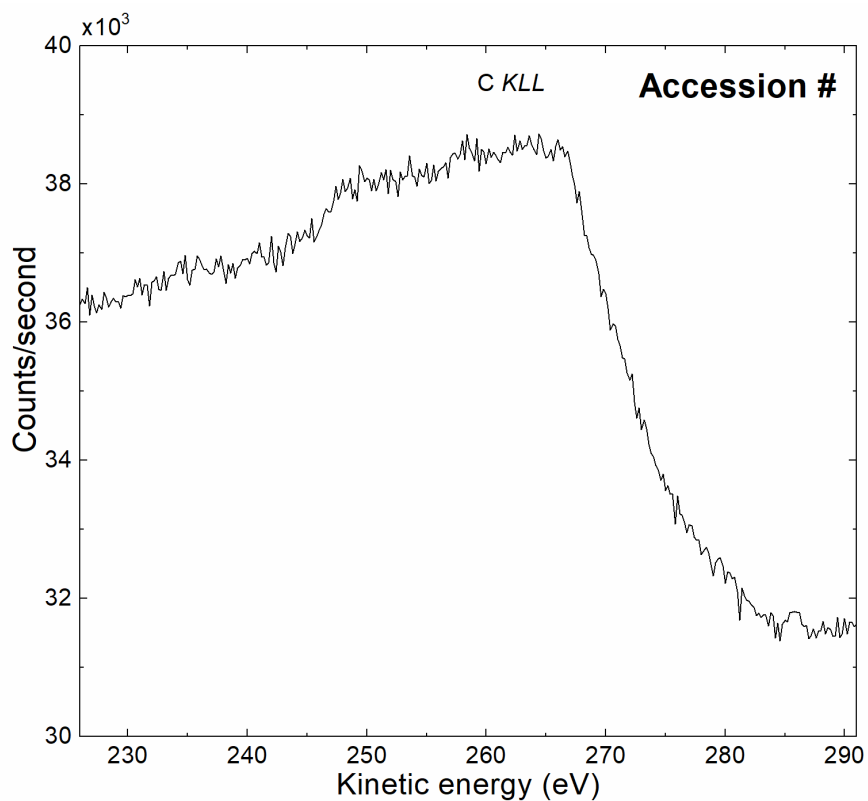
Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 1003

Total Elapsed Time: 1003 s

Number of Scans: 50

Effective Detector Width: 5 eV



Publish in SSS: Yes No

■ Accession #: 00000-06

■ Host Material: g-C₃N₄

■ Technique: XAES

■ 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 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

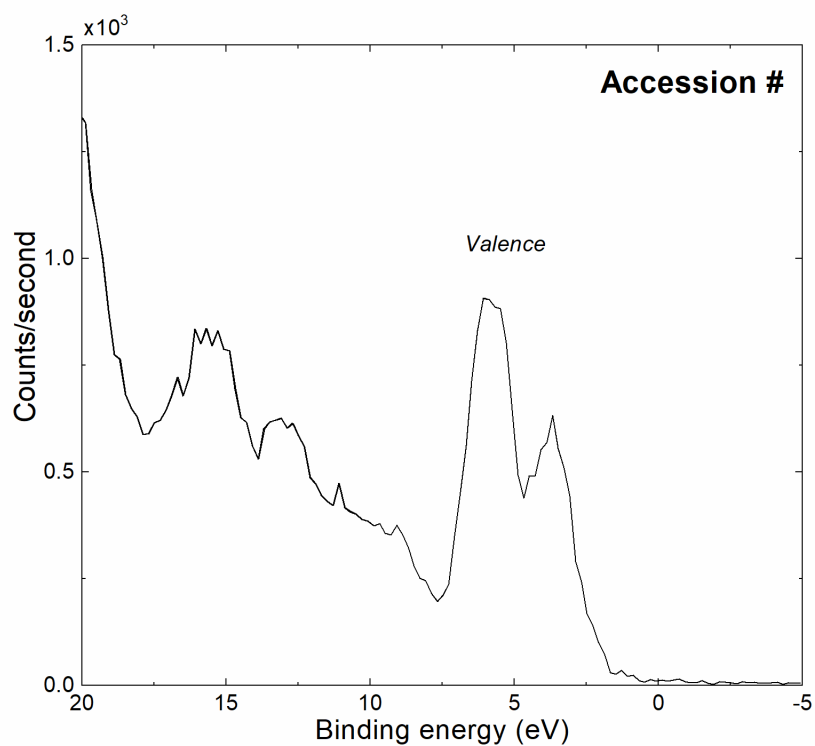
Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 815 s

Total Elapsed Time: 815 s

Number of Scans: 50

Effective Detector Width: 5 eV



Publish in SSS: Yes No

■ Accession #: 00000-07

■ Host Material: g-C₃N₄

■ Technique: XPS

■ Spectral Region: Valence

Instrument: Thermo Scientific K-Alpha+

Excitation Source: Al K α monochromatic

Source Energy: 1486.6 eV

Source Strength: 72 W

Source Size: 0.004 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser

Incident Angle: 30 °

Emission Angle: 90 °

Analyzer Pass Energy 40 eV

Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 75 s

Total Elapsed Time: 75 s

Number of Scans: 20

Effective Detector Width: 5 eV