Core-level Reference Spectra for Bulk Graphitic Carbon Nitride (g-C_3N_4)

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X-ray photoelectron spectroscopy (XPS) was used to characterize a graphitic carbon nitride (g-C_3N_4) 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: C_3N_4, XPS, Carbon Nitride, Graphitic

Acccession#:

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

INTRODUCTION

Graphitic carbon nitride (g-C_3N_4) 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-C_3N_4 structures.

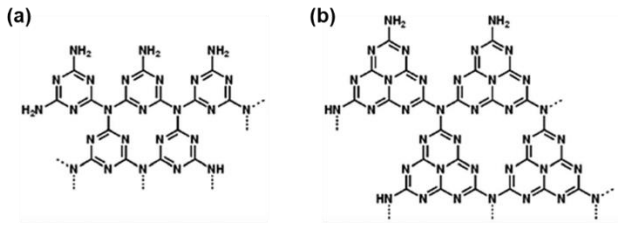

Figure 1. Structures considered representative of g-C_3N_4, where (a) triazine and (b) tri-s-triazine based

Owing to its low cost and CO_2 activation properties, g-C_3N_4 has received great attention for photocatalytic CO_2 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-C_3N_4 synthesized herein was from analytical grade urea which was heated in a muffle furnace to 550^{o}C for 3 h as described in Ref. 4; the yellow powder formed is indictive of bulk, lamellar g-C_3N_4 (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 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 indictive 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: C_3N_4

Form: Powder

Structure: C_3N_4

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

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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[peak area/(PE*XSF)] versus log(KE/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 Touggard (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 LA(α,β,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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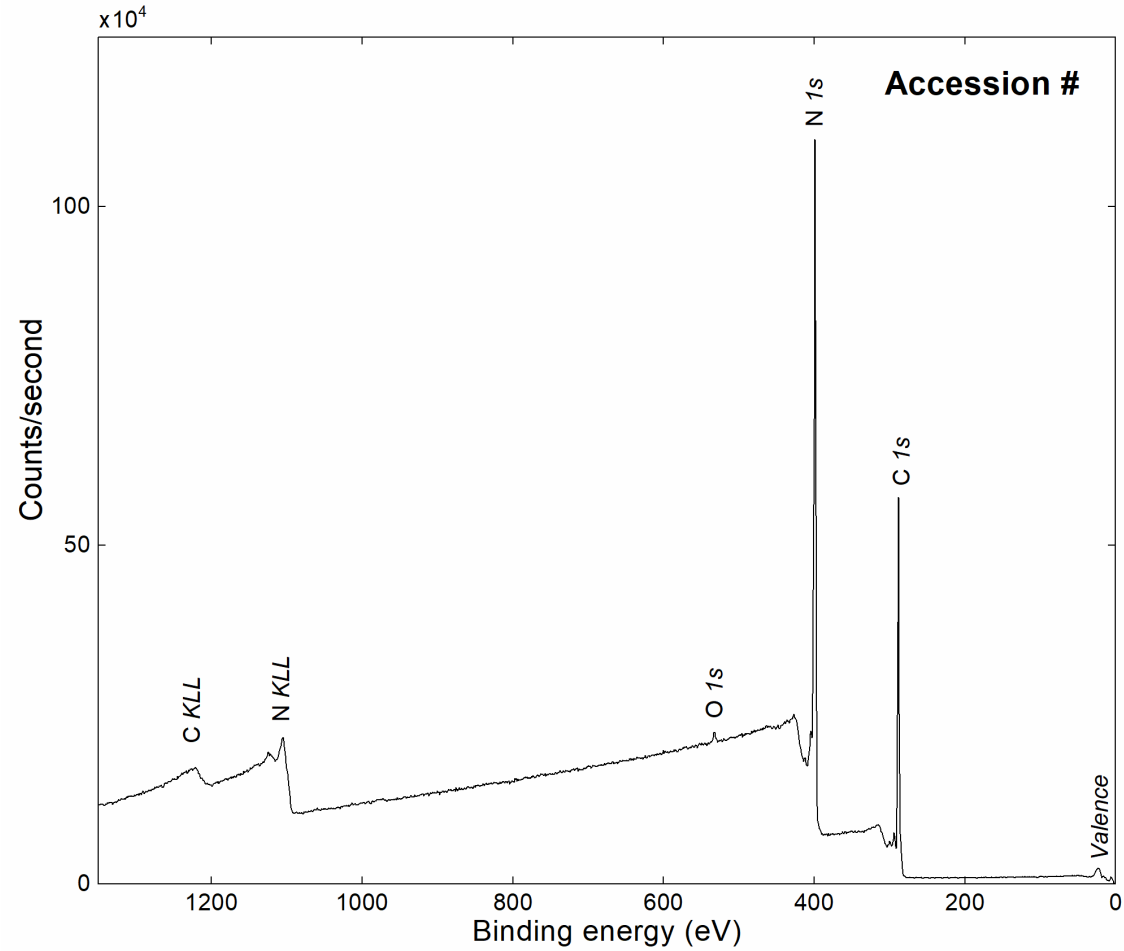
SPECTRAL FEATURES TABLE							
Spectrum ID #	**Element/ Transition**	**Peak Energy (eV)**	**Peak Width FWHM (eV)**	**Peak Area (eV x cts/s)**	**Sensitivity Factor**	**Concentration (at. %)**	**Peak Assignment**
00000-01	C 1s*	288.0		1675779.80	1.00	43.53	Total carbon in g-C_3N_4
00000-01	N 1s*	399.0		3874678.14	1.80	55.91	Total nitrogen in g-C_3N_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_3N_4
00000-01	C KLL**	265.0					C Auger in g-C_3N_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.

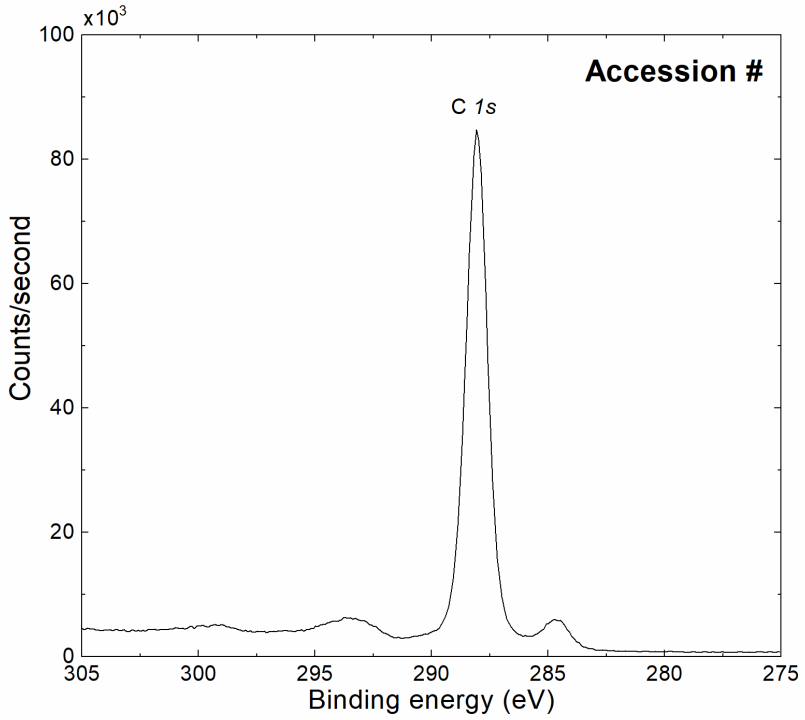
ANALYZER CALIBRATION TABLE							
Spectrum ID #	**Element/ Transition**	**Peak Energy (eV)**	**Peak Width FWHM (eV)**	**Peak Area (eV x cts/s)**	**Sensitivity Factor**	**Concentration (at. %)**	**Peak Assignment**
1	Au $4f_{7/2}$	83.99	0.76	1597652	9.58	100	Gold metal
2	Ag $3d_{5/2}$	368.28	0.58	1876744	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_3N_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-C_3N_4
- **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: 0.004 mm x 0.006 mm

Analyzer Type: double focussing hemispherical analyser
Incident Angle: 30 °

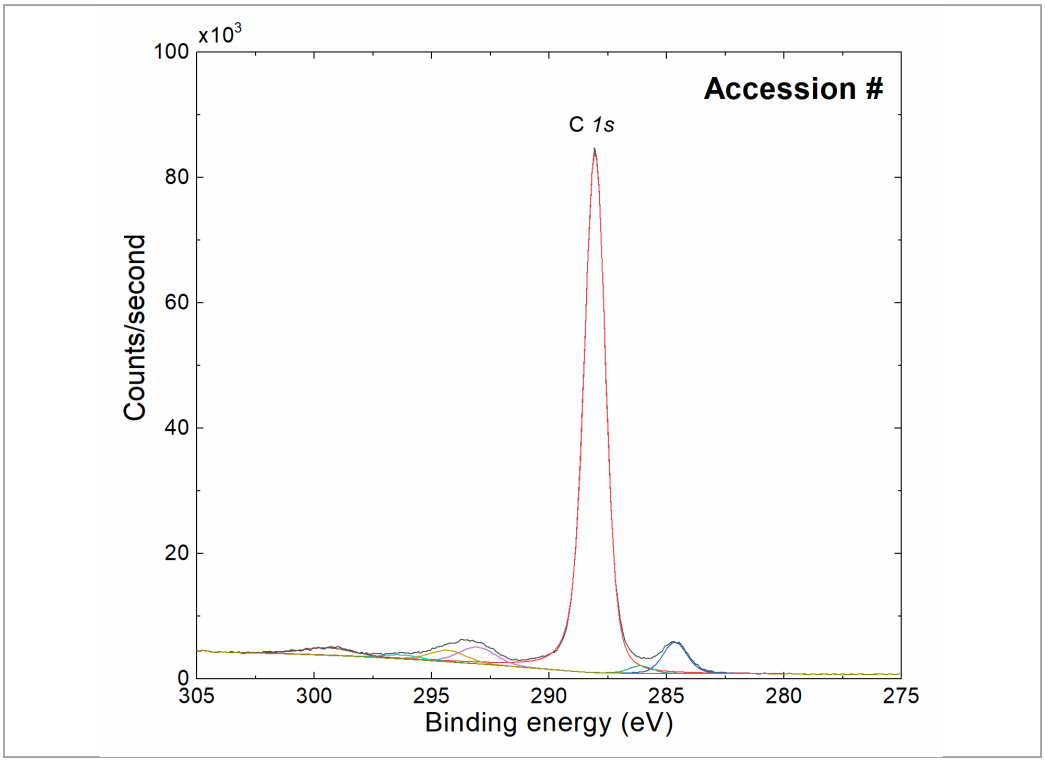
Emission Angle: 90 °

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


x10^3
100
80
60
40
20
0
Counts/second
Accession #
C 1s
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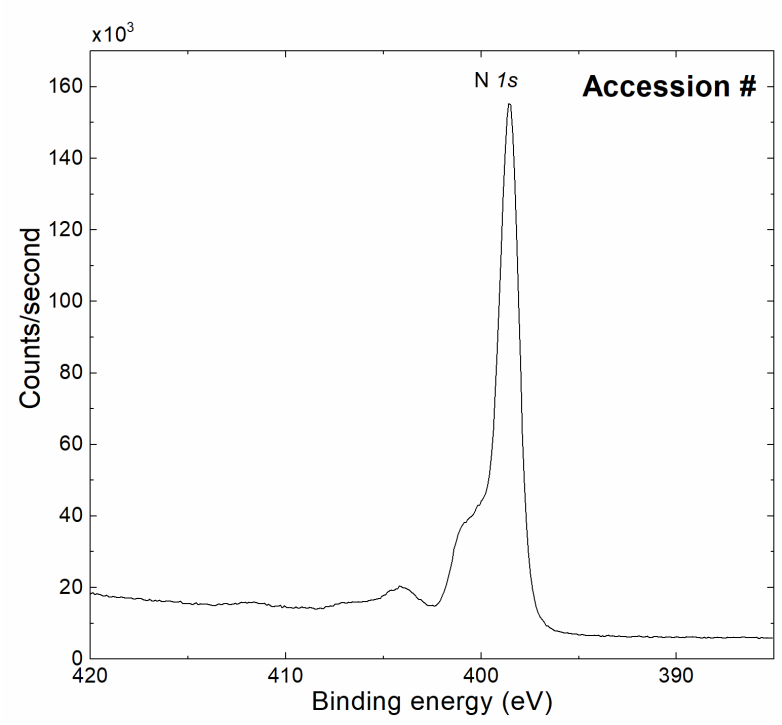
300
295
290
285
280
275
Binding energy (eV)



Publish in *SSS*: Yes ☒ No ☐

- **Accession #:** 00000-03
- **Host Material:** g-C_3N_4
- **Technique:** XPS
- **Spectral Region:** N 1s

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 °

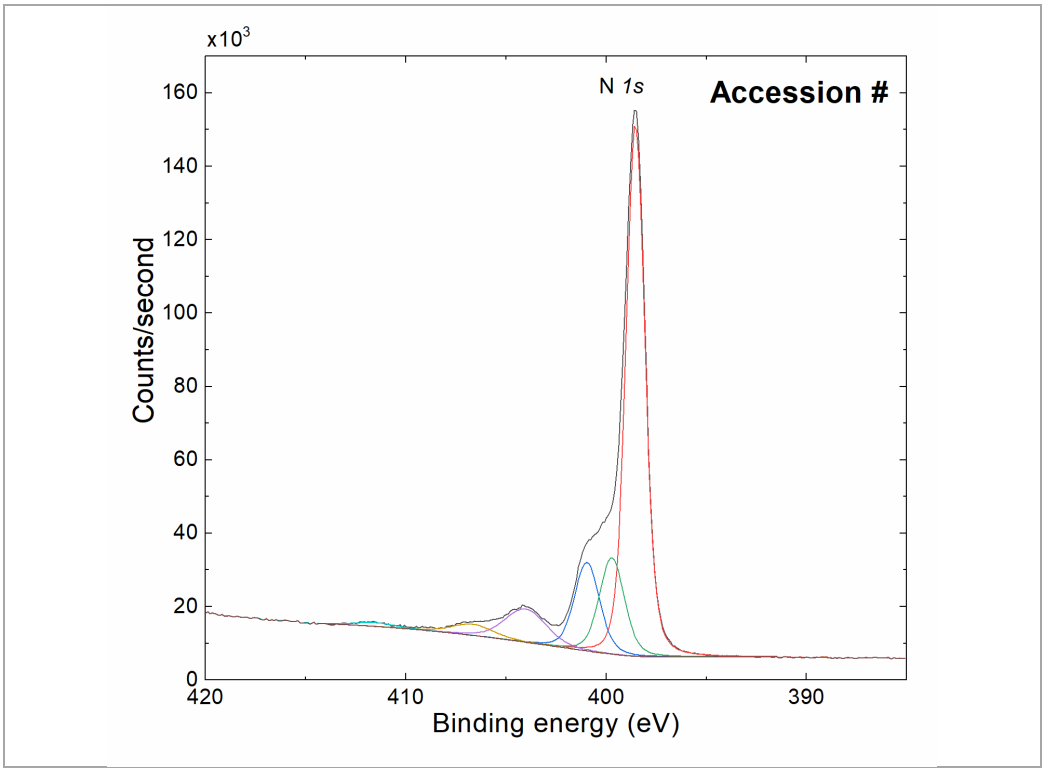
Emission Angle: 90 °

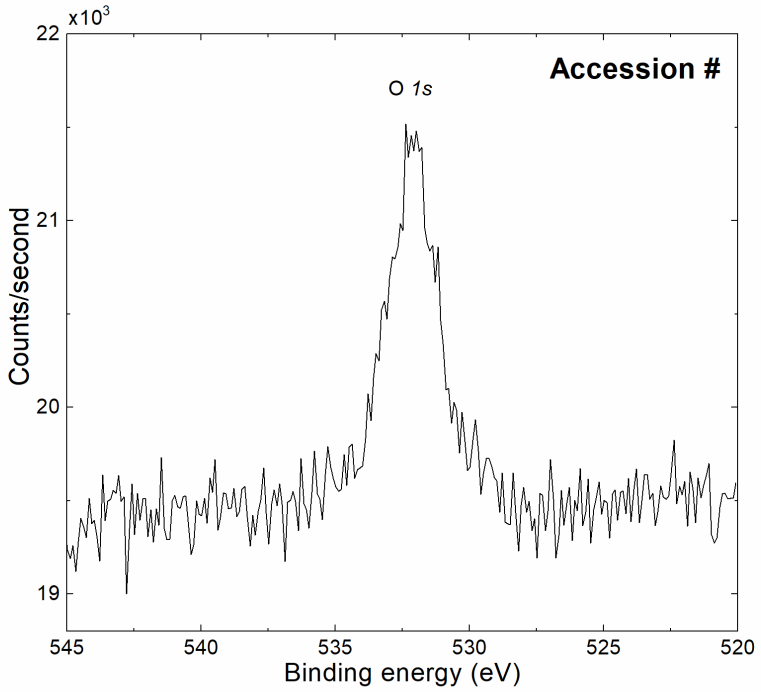
Analyzer Pass Energy 40 eV

Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 175 s

Total Elapsed Time: 175 s
Number of Scans: 10
Effective Detector Width: 5 eV


x10^3
160
140
120
100
80
60
40
20
0
Counts/second
420
410
400
390
Binding energy (eV)
N 1s
Accession #



Publish in *SSS*: Yes ☒ No ☐

- **Accession #:** 00000-04
- **Host Material:** g-C_3N_4
- **Technique:** XPS
- **Spectral Region:** O 1s

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 °

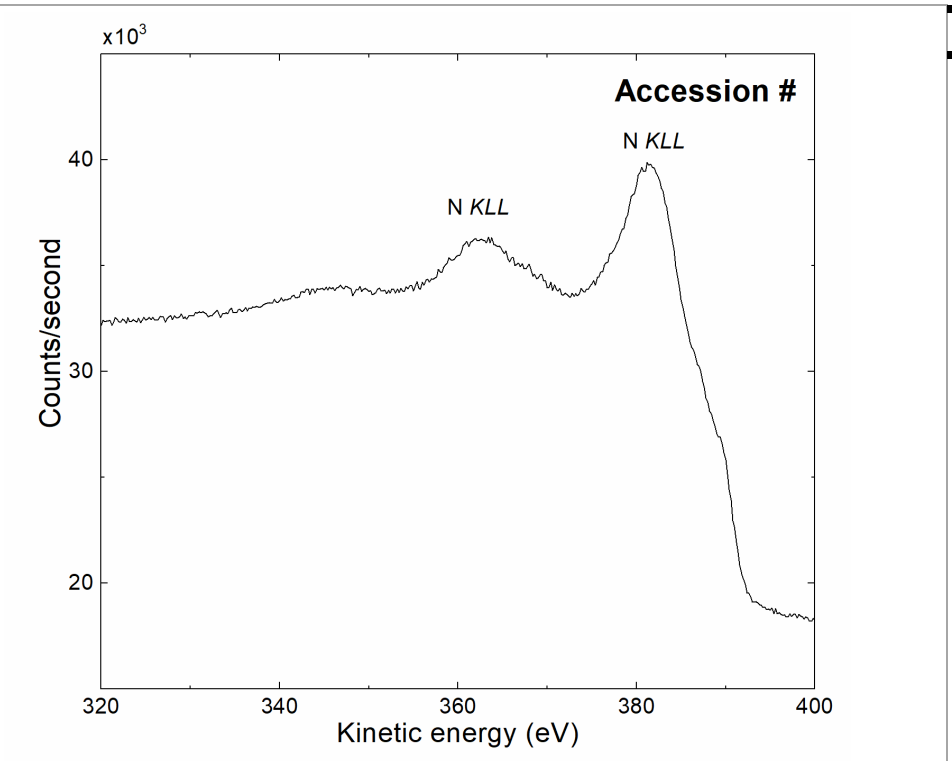
Emission Angle: 90 °

Analyzer Pass Energy 40 eV

Analyzer Resolution: 0.6 eV

Total Signal Accumulation Time: 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-C_3N_4
- **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 °

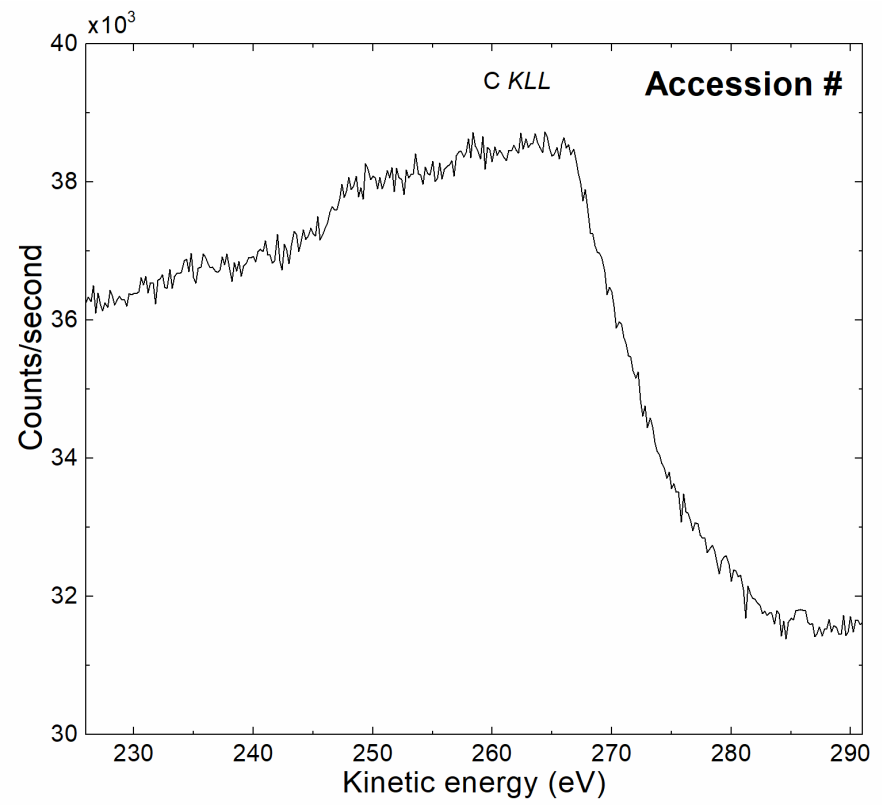
Emission Angle: 90 °

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-C_3N_4
- **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 °

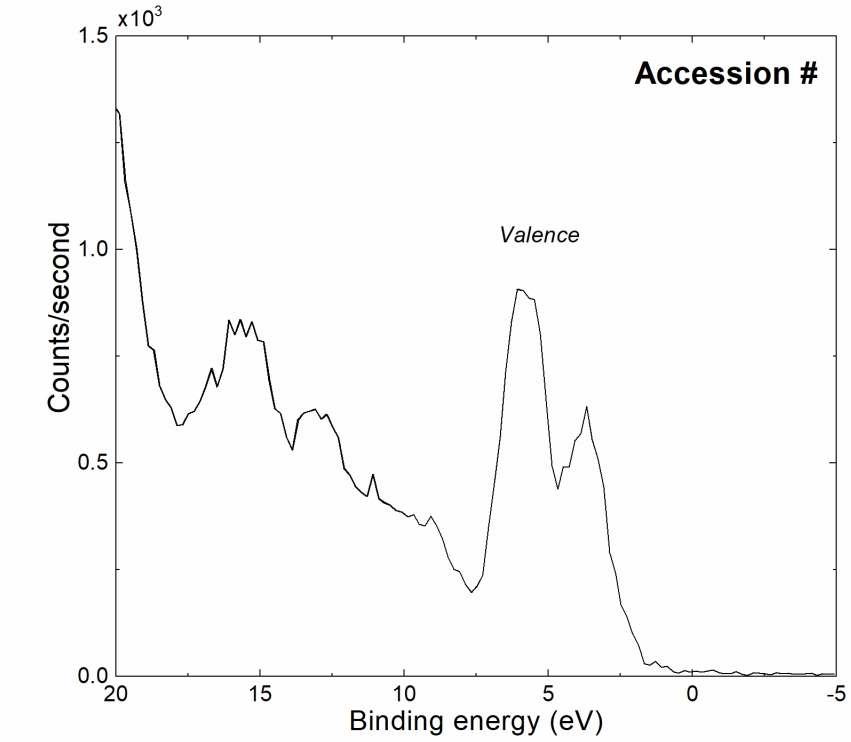
Emission Angle: 90 °

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-C_3N_4
- **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: 0.004 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