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A Study of Copper(II) Oxide and Copper(II) Acetate on Multi-Walled Carbon Nanotubes by XPS

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

We present the XPS survey and detailed element spectra of a copper-carbon nanotube composite synthesized in our laboratories. We compare the copper spectrum to a reference spectrum of copper(II) acetate measured under the same conditions to ascertain the chemical composition of the copper in the composite.ww

Keywords: Copper, XPS, Multi-walled carbon nanotubes

Acccession#:

Technique: XPS

Host Material: 1) CuAc 2) CuO on MWCNTs

Instrument: Kratos XPS Supra

Major Elements in Spectra: Cu, C

Minor Elements in Spectra: O, In

Published Spectra: 9

Spectra in Electronic Record: 15

Spectral Category: comparison

INTRODUCTION

The development of copper-carbon nanotube composites is of interest for application in ultra-conductive copper wire¹. Ultraconductive copper wire consists of a copper species and a nanocarbon, such as graphene or carbon nanotubes². The coppercarbon composites are also of interest as electrocatalysts for the electrocatalytic reduction of carbon dioxide to higher value products such as methane and ethylene³. A number of synthetic procedures are available and have been used for manufacturing such composites⁴⁻⁷. Depending on the procedure the copper can be chemically bound to the carbon nanotubes or just associated with the carbon nanotubes. The composites can be characterized using solid-state techniques such as scanning electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy (XPS). For the analysis of copper-carbon nanotube composites it is particularly important to determine the copper oxidation state. In addition, the modelling of the carbon 1s signal is non-trivial as it consists of sp2, sp3, adventitious and oxidized carbon, along with plasmon signals. We have characterized a commercial sample of copper(II) acetate as a reference sample. (XPS spectra of copper(II) acetate are uncommon in the literature to the best of our knowledge.) We have also measured the XPS spectra of a synthesized copper-carbon composite⁸. We have ascertained the chemical composition and oxidation state of the copper in the composite using our reference spectra.⁹ Following literature precedent we have modelled the carbon 1s signal using a mixed Donjiach-Sunjik Sum Gaussian Lorentzian (30) fitting¹⁰. We have found this model to be particularly effective. In this study, particular importance is given to the analysis of the C 1s and Cu 2p signals.

Host Material: CuAc

• CAS Registry #: 142-71-2

Host Material Characteristics: homogeneous; solid; polycrystalline; conductor; composite; Other

Chemical Name: Copper(II) acetate

Source: Sigma-Aldrich

Host Composition: C, Cu, H, O

Form: Polycrystalline composite

Structure: Cu(CH₃OO)₂

History & Significance: $Cu(Ac)_2$ powder was used as received.

As Received Condition: The as-received sample was a blue crystalline solid.

Analyzed Region: Same as host material.

Ex Situ Preparation/Mounting: The composite was pressed onto carbon tape.

In Situ Preparation: none

Charge Control: Charge neutralizer was used.

Temp. During Analysis: 300K

Pressure During Analysis: 4 x 10⁻⁶ Pa

Pre-analysis Beam Exposure: 0 s.

SPECIMEN DESCRIPTION (ACCESSION #00000)

Host Material: CuO/MWCNT

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; polycrystalline; conductor; composite; Other

Chemical Name: Copper(II) oxide on multi-walled carbon nanotubes.

Source: Cu(II)Ac purchased from Sigma Aldrich and used as received. MWCNTs synthesized at Rice University, Texas, USA and purified before use¹¹.

Host Composition: CuO on MWCNTs

Form: Amorphous composite

Structure: CuOC_x

History & Significance: 6 mg of powdered CuAc were added to a vial containing 10 mg of MWCNTs. 6 ml of distilled water was added and the mixture sonicated for 15 minutes in order to disperse the copper particles amongst the MWCNTs. The water was evaporated by drying the sample in the oven at 80 °C for 4 hours. The sample was then heated in the microwave for 3 x 1 minutes at 1000 W to decompose the copper(II) acetate to copper(II) oxide. The product obtained was a black powder.

As Received Condition: The as-prepared sample was a black solid.

Analyzed Region: Same as host material.

Ex Situ Preparation/Mounting: The material was pressed onto indium foil.

In Situ Preparation: none

Charge Control: Charge neutralizer was used

Temp. During Analysis: 300 K

Pressure During Analysis: 4 x 10⁻⁶ Pa

Pre-analysis Beam Exposure: 0 s.

As Received Condition:Pre-analysis Beam Exposure:s

INSTRUMENT DESCRIPTION

Manufacturer and Model: Kratos Axis Supra

Analyzer Type: spherical sector

Detector: multichannel resistive plate

Number of Detector Elements: 3 MCP, 128 channel DLD

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■Spectrometer

Analyzer Mode: constant pass energy

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

Excitation Source Window: not specified

Excitation Source: Al Ka monochromatic

Source Energy: 1486.6 eV

Source Strength: 225 W

Source Beam Size: $700 \ \mu m \ x \ 300 \ \mu m$

Signal Mode: multichannel direct

■Geometry

Incident Angle: 54.7 °

Source-to-Analyzer Angle: 54.7 °

Emission Angle: 0 °

Specimen Azimuthal Angle: N/A °

Acceptance Angle from Analyzer Axis: 0 °

Analyzer Angular Acceptance Width: 30 ° x 30 °

∎lon Gun

Manufacturer and Model: Kratos GCIS Minibeam 6

Energy: 10 k eV

Current: 23 mA

Current Measurement Method: biased stage

Sputtering Species: Argon 1000+ ion clusters

Spot Size (unrastered): 200 µm

Raster Size: 2000 µm x 2000 µm

Incident Angle: 40 °

Polar Angle: 0 °

Azimuthal Angle: 0 °

Comment: Sputtering was carried out on reference samples only.

DATA ANALYSIS METHOD

Energy Scale Correction: The binding energy scale was referenced to C $1s = 248.8 \text{ eV}^8$

Recommended Energy Scale Shift: Spectra 5-9 have been shifted by 3.146 eV.

Peak Shape and Background Method: A Shirley background was used¹². Peak shape was Gaussian Lorentzian product formula GL(30) for all components except the dominant C (1s) peak which was fitted as a mixture of Doniach-Sunjik DS (0.03, 0) and Sum Gaussian Lorentzian SGL (30) following the protocol set by Kalbac *et. al.*¹⁰

Quantitation Method: Quantification was done using component definitions with CasaXPS version 2.3.15. Sensitivity factors supplied by Kratos Analytical.

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SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
			(eV)				
02	C 1s	284.8	1.14	17970.12	0.278	28.27	Adventitious C-C/C-H
02	C 1s	285.7	1.14	1145.73	0.278	1.80	Adventitious C-O
02	C 1s	286.6	1.14	472.52	0.278	0.74	Adventitious C=O
02	C 1s	288.7	2.13	2882.22	0.278	4.53	CH₃ C OO
03	O 1s	529.6	0.91	41263.46	0.78	23.14	Cu O
03	O 1s	531.1	1.30	20545.78	0.78	11.52	Cu O /Cu(CH ₃ C OO) ₂
03	O 1s	531.9	1.30	9273.46	0.78	5.20	Adventitious Organics
03	O 1s	533.2	1.30	2225.00	0.78	1.25	Adventitious Organics
04	Cu 2p _{3/2}	933.5	2.70	114896.4	5.321	9.44	CuO
04	Cu 2p _{3/2}	935.1	2.67	15249.3	5.321	1.25	CuAc
04	Cu 2p _{3/2}	940.3	1.48	21574.2	5.321	1.77	Satellite
04	Cu 2p _{3/2}	942.1	1.48	17964.6	5.321	1.48	Satellite
04	Cu 2p _{3/2}	943.8	1.48	23539.8	5.321	1.93	Satellite
04	Cu 2p _{1/2}	953.2	2.67	49866.98	5.321	4.10	CuO
04	Cu 2p _{1/2}	954.9	2.67	8754.96	5.321	0.72	CuAc
04	Cu 2p _{1/2}	962.1	2.40	34476.98	5.321	2.83	Satellite
06	C 1s	284.4	0.59	41401.63	0.278	72.99	MWCNT
06	C 1s	284.8	0.93	4284.43	0.278	7.55	Adventitious C-C/C-H
06	C 1s	285.8	0.93	2211.15	0.278	3.90	Adventitious C-OH/C-O-C
06	C 1s	286.7	0.93	989.36	0.278	1.74	Adventitious C =O
06	C 1s	288.6	0.93	370.2	0.278	0.65	Cu(CH3 C OO)2
06	C 1s	290.3	3.00	1987.22	0.278	3.50	$\pi \rightarrow \pi^*$ transitions
07	O 1s	530.2	1.30	2380.91	0.78	1.5	Cu O /Fe ₂ O ₃ /In ₂ O ₃
07	O 1s	531.3	1.30	2696.75	0.78	1.69	Cu(CH ₃ C OO) ₂
07	O 1s	532.1	1.30	3903.26	0.78	2.45	Adventitious C -O -C/C=O
07	O 1s	533.1	1.30	1650.75	0.78	1.04	Adventitious C- O H
07	O 1s	534.6	1.30	330.12	0.78	0.21	Chemisorbed H ₂ O
08	Cu 2p _{3/2}	934.2	3.06	5942.50	5.321	0.55	CuO
08	Cu 2p _{3/2}	941.4	2.48	1231.98	5.321	0.11	Satellite
08	Cu 2p _{3/2}	944.0	2.48	1588.81	5.321	0.15	Satellite
08	Cu 2p _{1/2}	953.9	3.44	2946.87	5.321	0.27	CuO
08	Cu 2p _{1/2}	962.6	2.57	1308.17	5.321	0.12	Satellite
09	In 3d _{5/2}	444.90	1.54	9324.94	7.265	0.63	In metal
09	In 3d _{5/2}	445.8	1.54	2074.62	7.265	0.14	In ₂ O ₃
09	In 3d _{3/2}	452.4	1.54	6204.8	7.265	0.42	In metal
09	In 3d _{3/2}	453.3	1.54	1380.45	7.265	0.09	In ₂ O ₃

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
11	Ag 3d _{5/2}	368.4	0.51	71961	5.987	100	Ag
13	Au 4f _{7/2}	84.0	0.60	314838	6.250	100	Au
15	Cu 2p _{3/2}	933.0	0.80	401503	5.321	100	Cu

GUIDE TO FIGURES						
Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #	
01	Survey	-0.009	1	0	1	
02	C 1s	-0.009	1	0	1	
02	C 1s	-0.009	1	0	1	
03	O 1s	-0.009	1	0	1	
03	O 1s	-0.009	1	0	1	
04	Cu 2p	-0.009	1	0	1	
04	Cu 2p	-0.009	1	0	1	
05	Survey	-3.146	1	0	2	
06	C 1s	-3.146	1	0	2	
06	C 1s	-3.146	1	0	2	
07	O 1s	-3.146	1	0	2	
07	O 1s	-3.146	1	0	2	
08	Cu 2p	-3.146	1	0	2	
08	Cu 2p	-3.146	1	0	2	
09	In 3d	-3.146	1	0	2	
09	In 3d	-3.146	1	0	2	
10	Survey	0.000	1	0	4	
11	Ag 3d _{5/2}	0.000	1	0	4	
12	Survey	0.000	1	0	5	
13	Au 4f _{7/2}	0.000	1	0	5	
14	Survey	0.000	1	0	6	
15	Cu 2p _{3/2}	0.000	1	0	6	

*Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon

- 1. CuAc.
- 2. CuO on MWCNTs.
- 3. Ag calibration.
- 4. Au calibration.
- 5. Cu calibration.



1

16 eV

Number of Scans

Effective Detector Width











Publish in SSS: Yes ⊠ No □

Accession #:

- Host Material: CuAc
- Technique: XPS

■ Spectral Region: Cu 2p

Instrument: Kratos Axis Supra Excitation Source: Al Ka monochromatic Source Energy: 1486.6 eV Source Strength: 225 W Source Size: 0.7 mm x 0.3

mm

Analyzer Type: spherical sector

Incident Angle: 54.7 °

Emission Angle: 0 °













Publish in SSS: Yes ⊠ No Accession #: ■ Host Material: CuO on **MWCNTs** Technique: XPS ■ Spectral Region: 0 1s Instrument: Kratos Axis Supra Excitation Source: Al Ka monochromatic Source Energy: 1486.6 eV Source Strength: 225 W Source Size: 0.7 mm x 0.3 Analyzer Type: spherical sector Incident Angle: 54.7 ° Emission Angle: 0 ° Analyzer Pass Energy 20 Analyzer Resolution: 0.616 **Total Signal Accumulation** Time: 347 s Total Elapsed Time: Not Specified s Number of Scans: 1 Effective Detector Width: 2









Publish in SSS: Yes 🛛 No

On a stand De mis and in Or

Spectral Region: In 3d Instrument: Kratos Axis Supra Excitation Source: Al Ka monochromatic Source Energy: 1486.6 eV Source Strength: 225 W Source Size: 0.7 mm x 0.3 mm Analyzer Type: spherical sector Incident Angle: 54.7 ° Emission Angle: 0 ° Analyzer Pass Energy 20 eV Analyzer Resolution: 0.616 eV **Total Signal Accumulation** Time: 116 s Total Elapsed Time: Not Specified s Number of Scans: 1

Effective Detector Width: 2

eV



Accession #		
Host Material	Ag calibration	
Technique	XPS	
Spectral Region	survey	
Instrument	Kratos Axis Supra	
Excitation Source	Al Ka monochromatic	
Source Energy	1486.6 eV	
Source Strength	15 W	
Source Size	0.7 mm x 0.3 mm	
Analyzer Type	spherical sector analyzer	
Incident Angle	54.7°	
Emission Angle	0°	
Analyzer Pass Energy	160 eV	
Analyzer Resolution	1 eV	
Total Signal Accumulation Time	120 s	
Total Elapsed Time	120 s	
Number of Scans	1	
Effective Detector Width	16 eV	





54.7°

0°

160 eV

1 eV

120 s 120 s 1 16 eV

Total Elapsed Time	
Number of Scans	
Effective Detector Width	

Incident Angle

Emission Angle

Analyzer Pass Energy

Total Signal Accumulation Time

Analyzer Resolution





Accession #		
Host Material	Cu calibration	
Technique	XPS	
Spectral Region	survey	
Instrument	Kratos Axis Supra	
Excitation Source	Al Ka monochromatic	
Source Energy	1486.6 eV	
Source Strength	15 W	
Source Size	0.7 mm x 0.3 mm	
Analyzer Type	spherical sector analyzer	
Incident Angle	54.7°	
Emission Angle	0°	
Analyzer Pass Energy	160 eV	
Analyzer Resolution	1 eV	
Total Signal Accumulation Time	120 s	
Total Elapsed Time	120 s	
Number of Scans	1	
Effective Detector Width	16 eV	



