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A study of Pt-/alpha-Fe_2O_3 nanocomposites by XPS

SECTION A - Authors

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SECTION A - Overview

A-3. Abstract: alpha-Fe_2O_3 matrices were deposited on Fluorine-doped Tin Oxide (FTO) substrates by Plasma Enhanced-Chemical Vapor Deposition (PE-CVD) from Fe(hfa)_2TMEDA (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; TMEDA = N,N,N',N'-tetramethylethylenediamine). The obtained nanosystems were subsequently functionalized by platinum nanoparticles (NPs) via Radio Frequency (RF)-sputtering, exposing samples either to a pre- or post-sputtering thermal treatment at 650 {deg}C for one hour in air. Interestingly, Pt oxidation state in the final composite systems strongly depended on the adopted processing conditions. In this work, a detailed X-ray Photoelectron Spectroscopy (XPS) analysis was carried out in order to investigate the material chemical composition, with particular regard to the relative Pt(0)/Pt(II)/Pt(IV) content. The obtained results evidenced that, when annealing is performed prior to sputtering, only PtO and PtO_2 are revealed in the final Pt/alpha-Fe_2O_3 nanocomposite. In a different way, annealing after sputtering results in the co-presence of Pt(0), Pt(II) and Pt(IV) species, the former arising from the thermal decomposition of PtO_2 to metallic platinum.

A-3a. Introduction: In the last decade, various metal oxide-based nanosystems have attracted a lot of research efforts as photocatalysts for solar fuel generation (Refs. 1-5), for instance in photocatalytic water splitting to yield hydrogen, a promising energy vector (Refs. 2, 4, 5). Among the various candidates, hematite (alpha-Fe_2O_3) stands as a preferred choice thanks to its abundance, low band-gap (E_G = 2.2 eV), enabling Vis light harvesting, and chemical stability in aqueous environments (Refs. 3, 6, 7).

Notwithstanding such favorable properties, water splitting efficiency over hematite is limited by its short hole diffusion length, slow water oxidation kinetics, poor charge carrier transport, and conduction band position that does not straddle with the reversible hydrogen potential (Refs. 6-9). These drawbacks can be at least partially circumvented by nanostructuring hematite, developing alternative Fe_2O_3 polymorphs (e. g. beta- or epsilon-Fe_2O_3), or by chemical modification through doping or functionalization, yielding specific nanocomposites (Refs. 3, 6-11).

In this context, our previous works have focused on the chemical modification of various Fe_2O_3 matrices (alpha-, beta- or epsilon-Fe_2O_3) by fluorine doping or decoration with CuO, Ag_2O/Ag, Pt, Au and particles (Refs. 8, 10-14). In Ref. 10, 13 it was found that the sputtering of platinum from Ar plasmas over alpha-Fe_2O_3 resulted in an uniform decoration of the oxide matrix by Pt(0) nanoparticles, whose metallic state was retained even after annealing in air. In the present contribution, alpha-Fe_2O_3 matrices were sputtered with Pt exposing samples either to a pre- or post-sputtering thermal treatment at 650 {deg}C in air. It will be shown that when air annealing is performed before sputtering, only Pt(II) and Pt(IV) species from PtO and PtO_2 are present in the resulting composites, suggesting that hematite plays an active role in the oxidation of platinum. In a different way, when annealing is carried out after sputtering, Pt(0), Pt(II) and Pt(IV) in comparable amount are detected on the sample surface, indicating the occurrence of a partial PtO_2 thermal reduction to metallic Pt.

In the following, two selected Pt/alpha-Fe_2O_3 samples on FTO substrates are investigated by XPS, with particular focus on the material surface composition as a function of annealing. To this aim, special attention is given to the analysis of the O 1s, Fe 2p, and Pt 4f signals employing a non-monochromated Al Kalpha X-ray excitation source.

A-6a. # of digitally submitted specimen spectra for SSS publication: 10

A-6b. # of digitally submitted specimen spectra for electronic database only: 0

A-6c. # of digitally submitted calibration spectra: 2

A-7. Publish Auger Derivative Spectra: N/A

A-9. Spectra Category: technical

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Submission Publication & Review Info

A-12. Publication Notes for Editors: References have been uploaded as a separate file.
Due to problems in the in the Proof Report with the spectra images uploading, all the pertaining figures have been also uploaded as separated files.
Could it be possible for you to generate a complete proof report and send it to us?
Many thanks

A-13. Comments on WCF:

A-14. Digital Data Format:

Suggested Reviewers

A-15a. Reviewer 1: 1. Prof. Saulius Kaciulis, ISMN, Rome, Italy; e-mail: saulius.kaciulis@ismn.cnr.it

A-15b. Reviewer 2: 2. Prof. Marjorie A. Langell, Nebraska University, USA; e-mail: mlangell@unlserve.unl.edu

A-15c. Reviewer 3: 3. Prof. A.R. Chourasia, Texas University; e-mail: chouras@boisdarc.tamu-commerce.edu

Keywords: iron oxide, platinum, nanocomposites, PE-CVD, Sputtering, X-ray Photoelectron Spectroscopy

Major Elements in Spectra: C, O, Fe, Pt

Minor Elements in Spectra:

SECTION A - REFERENCES

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SECTION B - SPECIMEN DESCRIPTION

Specimen #: 1

B-1. Host Material: Pt/Fe_2O_3 (1)

B-2. Chemical Abstract Service (CAS) Registry #: unknown

B-3a. Material Designation Code:

B-3b. Material Designating Organization:

B-4. Host Composition: Fe, Pt, O

B-5. Chemical Name: iron(III) oxide - platinum

B-6. Specimen Manufacturer/Supplier:

B-7. Specimen Form: supported nanocomposite

B-8. Lot Number:

B-9. Structural Formula: Besides strong signals attributable to the FTO substrate, X-ray Diffraction (XRD, using Cu Kalpha radiation, lambda = 1.5418 Å) pattern revealed the presence of the rhombohedral alpha-Fe_2O_3 phase, as indicated by peaks at 24.1{deg}, 33.2{deg}, 35.6{deg}, 40.9{deg} and 49.5{deg} corresponding to the (012), (104), (110), (113), and (024) reflections, respectively (Refs. 8, 15). Conversely, no peaks related to Pt-containing species could be clearly observed. In line with previous literature works, this phenomenon could be attributed to the low Pt amount and/or the reduced size of Pt-based particles (Ref. 10). Secondary Ion Mass Spectrometry (SIMS) indicated a remarkable in-depth penetration of Pt throughout the Fe_2O_3 deposit. Field Emission-Scanning Electron Microscopy (FE-SEM) (see inset to Spectrum #1) showed that the hematite nanodeposit had a very rough and porous surface. Such features, along with the high penetration power of the RF-sputtering technique, are likely responsible for the efficient Pt dispersion within Fe_2O_3.

B-10. Homogeneity: Homogeneous

B-11. Phase: Solid

B-12. Crystallinity: Polycrystalline

B-13. Electrical Characteristics: Semiconductor

B-14. Material Family: Composite

B-15. Special Material Classes: Thin Film

B-16. History and Significance: alpha-Fe_2O_3 was deposited using a custom-built PE-CVD apparatus equipped with a RF (frequency = 13.56 MHz) generator (Refs. 12, 16). Experiments were performed using Ar/O_2 plasmas for a total duration of 1 h (RF-power = 10 W, total pressure = 1.0 mbar). The iron precursor Fe(hfa)_2TMEDA, synthesized according to a previously reported procedure (Ref. 17), was placed in an external vessel heated to 65 {deg}C and transported into the reaction chamber by means of electronic grade Ar [purity = 5.0; flow rate = 60 standard cubic centimeters per minute (sccm)]. Two further auxiliary gas-lines were used to introduce Ar (flow rate = 15 sccm) and electronic grade O_2 (flow rate = 20 sccm) directly into the reactor chamber. Fe_2O_3 growth was performed at a temperature of 300 {deg}C on FTO substrates (size = 20 mm x 10 mm x 3.2 mm). Prior to deposition, the substrates were suitably cleaned by iterative dipping in acetone, sulphonic detergent, distilled water, and finally dried under an air flow.
Subsequently, the as-prepared alpha-Fe_2O_3 sample was annealed in air at 650 {deg}C for 1 h using a Carbolite HST 12/200 tubular oven and a heating rate of 20 {deg}C/min.
Finally, platinum sputtering was performed on the above air-annealed iron oxide matrix in the same reactor adopted for PE-CVD experiments. To this aim, a Pt target (0.3 mm thick; Alfa Aesar^{Reg}, 99%) was fixed on the RF electrode, and the FTO-supported alpha-Fe_2O_3 matrix was mounted on a second grounded electrode. Sputtering was carried out using electronic grade Ar (purity = 5.0) as a plasma source under the following conditions: substrate temperature = 60 {deg}C; RF-power = 5 W; total pressure = 0.30 mbar; Ar flow rate = 10 sccm. Experiment duration was set at 50 min.

B-17. As Received Condition: as-grown

B-18. Analyzed Region: same as host material

B-19. Ex Situ Preparation and Mounting: Specimen mounted as received with a metallic clip on a grounded sample holder and introduced into the analysis chamber through a fast entry lock system

B-20. In Situ Preparation: None

B-21. Specimen Temperature During Analysis (Kelvin): 298

B-22. Maximum Chamber Pressure During Analysi (in Pa): 10^{-7} Pa

B-23. Pre-Analysis Beam Exposures: The analyzed region was exposed to X-ray irradiation for alignment for a period no longer than 5 min.

B-24. Charge Control Conditions and Procedures: No flood gun was used. For further details, see Data Analysis Methods, Energy Scale Correction.

Specimen #: 2

B-1. Host Material: Pt/Fe_2O_3 (2)

B-2. Chemical Abstract Service (CAS) Registry #: unknown

B-3a. Material Designation Code:

B-3b. Material Designating Organization:

B-4. Host Composition: Fe, Pt, O

B-5. Chemical Name: iron(III) oxide - platinum

B-6. Specimen Manufacturer/Supplier:

B-7. Specimen Form: supported nanocomposite

B-8. Lot Number:

B-9. Structural Formula: Similarly to the specimen #B1, the XRD (using Cu Kalpha radiation, lambda = 1.5418 Å) pattern of the sample #B2 was characterized by hematite reflections only, with very close angular values, and no peaks attributable to Pt or its oxides could be detected. Even in this case, SIMS depth profiling indicated an even Pt distribution throughout the Fe_2O_3 deposit. Furthermore, besides the presence of Pt particles, FE-SEM analyses (see inset to Spectrum #6) evidenced a more pronounced faceting for the Fe_2O_3 matrix, likely arising from a decreased grain boundary content produced by annealing.

B-10. Homogeneity: Homogeneous

B-11. Phase: Solid

B-12. Crystallinity: Polycrystalline

B-13. Electrical Characteristics: Semiconductor

B-14. Material Family: Composite

B-15. Special Material Classes: Thin Film

B-16. History and Significance: The sample was prepared following exactly the same procedure already described for the specimen #B1. The only difference was that thermal treatment in air was carried out after (and not before) Pt sputtering.

B-17. As Received Condition: as grown

B-18. Analyzed Region: same as host material

B-19. Ex Situ Preparation and Mounting: Specimen mounted as received with a metallic clip on a grounded sample holder and introduced into the analysis chamber through a fast entry lock system.

B-20. In Situ Preparation: none

B-21. Specimen Temperature During Analysis (Kelvin): 298

B-22. Maximum Chamber Pressure During Analysi (in Pa): 10^{-7} Pa

B-23. Pre-Analysis Beam Exposures: The analyzed region was exposed to X-ray irradiation for alignment for a period no longer than 5 min.

B-24. Charge Control Conditions and Procedures: No flood gun was used. For further details, see Data Analysis Methods, Energy Scale Correction.

Specimen #: 3

B-1. Host Material: gold

B-2. Chemical Abstract Service (CAS) Registry #: 7440-57-5

B-3a. Material Designation Code:

B-3b. Material Designating Organization:

B-4. Host Composition: Au

B-5. Chemical Name: gold

B-6. Specimen Manufacturer/Supplier: BAL-TEC AG, Liechtenstein

B-7. Specimen Form: thin sheet

B-8. Lot Number:

B-9. Structural Formula:

B-10. Homogeneity: Homogeneous

B-11. Phase: Solid

B-12. Crystallinity: Polycrystalline

B-13. Electrical Characteristics: Conductor

B-14. Material Family: Metal

B-15. Special Material Classes: Other

B-16. History and Significance:

B-17. As Received Condition: thin sheet

B-18. Analyzed Region: same as host material

B-19. Ex Situ Preparation and Mounting: specimen rinsed in 2-propanol, mounted with a metallic clip on a grounded sample holder and introduced into the analysis chamber though a fast entry lock system

B-20. In Situ Preparation: Ar^{+} ion sputter cleaning for 5 min (3 keV, 2x2 mm^2 raster size)

B-21. Specimen Temperature During Analysis (Kelvin): 298

B-22. Maximum Chamber Pressure During Analysi (in Pa): 10^{-7}

B-23. Pre-Analysis Beam Exposures: The analysed region was exposed to X-ray irradiation for alignment for a period no longer than 5 min.

B-24. Charge Control Conditions and Procedures: none (sample used for BE calibration)

Specimen #: 4

B-1. Host Material: copper

B-2. Chemical Abstract Service (CAS) Registry #: 7440-50-8

B-3a. Material Designation Code:

B-3b. Material Designating Organization:

B-4. Host Composition: Cu

B-5. Chemical Name: copper

B-6. Specimen Manufacturer/Supplier: BAL-TEC AG, Liechtenstein

B-7. Specimen Form: thin sheet

B-8. Lot Number:

B-9. Structural Formula:

B-10. Homogeneity: Homogeneous

B-11. Phase: Solid

B-12. Crystallinity: Polycrystalline

B-13. Electrical Characteristics: Conductor

B-14. Material Family: Metal

B-15. Special Material Classes: Other

B-16. History and Significance:

B-17. As Received Condition: thin sheet

B-18. Analyzed Region: same as host material

B-19. Ex Situ Preparation and Mounting: specimen rinsed in 2-propanol, mounted with a metallic clip on a grounded sample holder an introduced into the analysis chamber through a fast entry lock system.

B-20. In Situ Preparation: Ar^{+} ion sputter cleaning for 5 min (3 keV, 2x2 mm^2 raster size)

B-21. Specimen Temperature During Analysis (Kelvin): 298

B-22. Maximum Chamber Pressure During Analysi (in Pa): 10^{-7}

B-23. Pre-Analysis Beam Exposures: The analysed region was exposed to X-ray irradiation for allignment for a period no longer than 5 min.

B-24. Charge Control Conditions and Procedures: None (sample used for BE calibration).

SECTION C - INSTRUMENT DESCRIPTION

C-1. Spectrometer Manufacturer: Perkin-Elmer Physical Electronics, Inc.

C-2. Manufacturer Model #: 5600ci

C-2a. Short identifying name for instrument: PHI 5600 at the University of Padova

C-3. Analyzer Type: SSA

C-4. Non-Standard Analyzer or Lens: N/A

C-5. Acceptance Angle from Analyzer Axis (degrees): 0

C-6. Analyzer Mode: constant pass energy

C-7. Instrument Throughput Function: 1

C-8. Instrument Throughput Function Comment: N/A

C-10. Excitation Source Window or Filter: 1.5 micron Al window

C-11. Detector Description: multi-channel detector, part number 619103

C-12. Number of Detector Elements: 16

C-12a. Was an Ion Gun Used? yes

C-13a. Ion Gun Manufacturer: PHI

C-13b. Ion Gun Model #: 04-303A

C-14. Sputtering Current Measurement Method: Faraday Cup

Ion Gun Operating Parameters

C-15a. Energy (in eV): 3000

C-15b. Current Value: 0.4

C-15c. Current Units: mA/cm2

C-15d. Sputter Species: Ar

C-15e. Sputter Charge: +1

C-16. Ion Gun Spot Size (um): 250

Ion Gun Raster Parameters (normal to source):

C-17a. Was Ion Gun rastered? Yes

C-17b. X-Raster (um): 2000

C-17c. Y-Raster (um): 2000

C-18. Sputtering Comments: differentially pumped ion gun

C-19a. Emission Angle (Θ e): 45

C-19b. Incident Angle (Ψ i): 9

C-19c. Source-to-Analyzer Angle (Θ s): 53.8

C-19d. Specimen Azimuthal Angle (Φ sp): 0

C-19e. Sputter Source Incident Angle (Ψ ig): 40

C-19f. Sputter Source Polar Angle (Θ ig): 45

C-19g. Sputter Source Azimuthul Angle (Φ ig): 111

C-20. Angular Geometry Comments: N/A

SECTION D - CALIBRATION INFORMATION

Analyzer Calibration Table

Seq #	Spec trum #	Ele- ment	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensi- tivity Factor	Concen -tration	Peak Assign- ment	Peak Assignment Comment
11		Au	4f_{7/2}	84.0	1.4	186403			Au(0)	The signal was acquired after Ar^+ erosion.
12		Cu	2p_{3/2}	932.7	1.6	86973			Cu(0)	The signal was acquired after Ar^+ erosion.

SECTION E - VARIABLE INSTRUMENT PARAMETERS

E-1. Param Set #: 1

E-1a. Technique: XPS

E-1b. Describe Technique if you selected 'other' above:

Excitation Source Parameters

ES-1. Source Label: Al Ka

ES-2. Describe Source if you selected 'other' above:

E-2. Source Energy (eV): 1486.6

E-3a. Strength: 200

E-3b. Strength Unit: watts

Excitation Source Beam

E-4a. Source Beam Size, X Value (um): > 25000

E-4b. Source Beam Size, Y Value (um): > 25000

E-5. Was the Source rastered? No

Excitation Source Beam Size at Specimen Surface

E-6a. Source Size at Specimen Surface, X (um): > 25000

E-6b. Source Size at Specimen Surface, Y (um): > 25000

E-7. Raster Frame Rate (Hz):

E-8. Analyzer Resolution: 1.9

E-8a. Analyzer Resolution Unit: eV (constant pass energy)

E-9 Analyzer Constants: 187.85

E-9a. Choose eV for pass energy, otherwise blank: eV

Analyzer Widths

E-10a. Analyzer Widths, X Value (um): 800

E-10b. Analyzer Widths, Y Value (um): 800

E-10c. Was the Analyzer Width constant with energy? yes

E-10d. Analyzer Widths, at Energy (eV):

Analyzer Angular Acceptance Widths

E-11a. Analyzer Angular Acceptance Width, X Angle (degrees): 14

E-11b. Analyzer Acceptance Width, Y Angle (degrees): 14

E-11c. Was the Analyzer Angular Acceptance Width constant with energy? yes

E-11d. Analyzer Angular Acceptance Width, at Energy (eV):

E-1. Param Set #: 2

E-1a. Technique: XPS

E-1b. Describe Technique if you selected 'other' above:

Excitation Source Parameters

ES-1. Source Label: Al Ka

ES-2. Describe Source if you selected 'other' above:

E-2. Source Energy (eV): 1486.6

E-3a. Strength: 200

E-3b. Strength Unit: watts

Excitation Source Beam

E-4a. Source Beam Size, X Value (um): > 25000

E-4b. Source Beam Size, Y Value (um): > 25000

E-5. Was the Source rastered? No

Excitation Source Beam Size at Specimen Surface

E-6a. Source Size at Specimen Surface, X (um): > 25000

E-6b. Source Size at Specimen Surface, Y (um): > 25000

E-7. Raster Frame Rate (Hz):

E-8. Analyzer Resolution: 0.6

E-8a. Analyzer Resolution Unit: eV (constant pass energy)

E-9 Analyzer Constants: 58.70

E-9a. Choose eV for pass energy, otherwise blank: eV

Analyzer Widths

E-10a. Analyzer Widths, X Value (um): 800

E-10b. Analyzer Widths, Y Value (um): 800

E-10c. Was the Analyzer Width constant with energy? yes

E-10d. Analyzer Widths, at Energy (eV):

Analyzer Angular Acceptance Widths

E-11a. Analyzer Angular Acceptance Width, X Angle (degrees): 14

E-11b. Analyzer Acceptance Width, Y Angle (degrees): 14

E-11c. Was the Analyzer Angular Acceptance Width constant with energy? yes

E-11d. Analyzer Angular Acceptance Width, at Energy (eV):

E-1. Param Set #: 3

E-1a. Technique: XPS

E-1b. Describe Technique if you selected 'other' above:

Excitation Source Parameters

ES-1. Source Label: Al Ka

ES-2. Describe Source if you selected 'other' above:

E-2. Source Energy (eV): 1486.6

E-3a. Strength: 200

E-3b. Strength Unit: watts

Excitation Source Beam

E-4a. Source Beam Size, X Value (um): > 25000

E-4b. Source Beam Size, Y Value (um): > 25000

E-5. Was the Source rastered? No

Excitation Source Beam Size at Specimen Surface

E-6a. Source Size at Specimen Surface, X (um): > 25000

E-6b. Source Size at Specimen Surface, Y (um): > 25000

E-7. Raster Frame Rate (Hz):

E-8. Analyzer Resolution: 0.3

E-8a. Analyzer Resolution Unit: eV (constant pass energy)

E-9 Analyzer Constants: 29.35

E-9a. Choose eV for pass energy, otherwise blank: eV

Analyzer Widths

E-10a. Analyzer Widths, X Value (um): 800

E-10b. Analyzer Widths, Y Value (um): 800

E-10c. Was the Analyzer Width constant with energy? yes

E-10d. Analyzer Widths, at Energy (eV):

Analyzer Angular Acceptance Widths

E-11a. Analyzer Angular Acceptance Width, X Angle (degrees): 14

E-11b. Analyzer Acceptance Width, Y Angle (degrees): 14

E-11c. Was the Analyzer Angular Acceptance Width constant with energy? yes

E-11d. Analyzer Angular Acceptance Width, at Energy (eV):

SECTION F - SPECTRA

Field Name	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
Spectrum #	1	2	3	4
This spectrum is from which Part B Specimen?	1 - Pt/Fe_2O_3 (1)	1 - Pt/Fe_2O_3 (1)	1 - Pt/Fe_2O_3 (1)	1 - Pt/Fe_2O_3 (1)
Suggested Publication Status:	Print in SSS	Print in SSS	Print in SSS	Print in SSS
Spectrum Data File Name	PtFeO_1.txt	PtFeO_2.txt	PtFeO_3.txt	PtFeO_4.txt
Data File Comment:			The attached data file contains 8 different blocks: 1) binding energy for raw spectrum 2) raw spectrum 3) binding energy for fitted spectrum 4) fitted spectrum 5) background 6) first fit component 7) second fit component 8) third fit component	
Spectrum Figure Image File Name	PtFeO_1.pdf	PtFeO_2.pdf	PtFeO_3.pdf	PtFeO_4.pdf
Specimen or Calibration Spectrum:	specimen	specimen	specimen	specimen
Parameter Set # Used	1 - Al Ka	2 - Al Ka	2 - Al Ka	2 - Al Ka
Spectrum Date	2014-06-06	2014-06-06	2014-06-06	2014-06-06
Species/ Transitions:	survey	C 1s	O 1s	Fe, Pt 2p, 4s

Field Name	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
Spectral Region Comment:		The C 1s peak, centered at Binding Energy (BE) = 284.8 eV, was assigned to adventitious carbon contamination due to sample manipulation. The slight tailing on the high BE side could be attributed to traces of carbonate species arising from atmospheric exposure (Refs. 13, 18).	The O 1s peak appeared rather broad, suggesting in the co-presence of oxygen species in different chemical environments. The signal could be deconvoluted by three different contributing bands. The one centered at BE = 530.0 eV (17.4 % of the total oxygen) was assigned to lattice oxygen in Fe_2O_3 (Ref. 13). The peak located at 531.4 eV [62.8 % of the total oxygen] could be related to the presence of to platinum oxides [PtO_x (x = 1,2)], as well as to absorbed -OH and carbonate groups (Refs. 10, 13, 18). Finally, the signal located at BE = 533.0 eV was attributed to adsorbed water (Refs. 18, 19).	The Fe 2p region was characterized by the presence of two spin-orbit distinct spectral features. As concerns the Fe 2p_{3/2} one, its BE of 711.2 was in agreement with that expected for Fe_2O_3 (Refs. 10, 13). As reported in the literature, the Fe 2p_{1/2} component was heavily overlapped with the Pt 4s peak (Refs. 10, 13). For this reason, quantitative analyses reported in the Spectral Features Table have been carried out considering only the Fe 2p_{3/2} band.
Abscissa Label	binding energy	binding energy	binding energy	binding energy
Abcissa Starting Value (eV):	1350	295	540.0	750
Abcissa Increment Value:	-0.8	-0,125	-0.125	-0.125
Ordinate Label:	Intensity	Intensity	Intensity	Intensity
Ordinate Units:	counts/s	counts/s	counts/s	counts/s
Number of Data Channels:	1688	161	161	401
Number of Scans:	5	12	12	45
Signal Mode:	multichannel pulse	multichannel pulse	multichannel pulse	multichannel pulse
Detector Width (eV):	1.9	0.6	0.6	0.6
Total Signal Accumulation Time (sec):	168.8	96.6	96.6	902.4
Total Elapsed Time (sec):	185.7	106.3	106.3	992.6

Field Name	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
Is 'raw data' signal intensity corrected? (Yes/No):	No	No	No	No
Signal Intensity Correction Comment:				
Signal Modulation Method:	none	none	none	none
Peak-to-peak amplitude of Modulation (eV):				
Modulation Frequency of Reference Signal (Hz):				
Time Constant of Lock-in Amplifier Used (sec):				

Field Name	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
Spectrum #	5	6	7	8
This spectrum is from which Part B Specimen?	1 - Pt/Fe_2O_3 (1)	2 - Pt/Fe_2O_3 (2)	2 - Pt/Fe_2O_3 (2)	2 - Pt/Fe_2O_3 (2)
Suggested Publication Status:	Print in SSS	Print in SSS	Print in SSS	Print in SSS
Spectrum Data File Name	PtFeO_5.txt	PtFeO_6.txt	PtFeO_7.txt	PtFeO_8.txt
Data File Comment:	The attached data file contains 7 different blocks: 1) binding energy for raw spectrum 2) raw spectrum 3) binding energy for fitted spectrum 4) fitted spectrum 5) background 6) first fit component 7) second fit component			The attached data file contains 8 different blocks: 1) binding energy for raw spectrum 2) raw spectrum 3) binding energy for fitted spectrum 4) fitted spectrum 5) background 6) first fit component 7) second fit component 8) third fit component
Spectrum Figure Image File Name	PtFeO_5.pdf	PtFeO_6.pdf	PtFeO_7.pdf	PtFeO_8.pdf
Specimen or Calibration Spectrum:	specimen	specimen	specimen	specimen
Parameter Set # Used	2 - Al Ka	1 - Al Ka	2 - Al Ka	2 - Al Ka
Spectrum Date	2014-06-06	2014-06-06	2014-06-06	2014-06-06
Species/ Transitions:	Pt 4f	survey	C 1s	O 1s

Field Name	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
Spectral Region Comment:	The Pt 4f peak presented a marked tailing on the low BE side, suggesting the co-presence of different Pt-containing species. In fact, the signal could be fitted by two separate doublets, each with a spin-orbit separation of 3.3 eV (Ref. 18). The main contribution, with Pt 4f_{7/2} BE = 74.8 eV (72.3% of total Pt signal), was attributed to Pt(IV) in PtO_2. The second doublet (Pt 4f_{7/2} BE = 72.6 eV) was assigned to Pt(II) in PtO (Refs. 18, 20-22). A detailed analysis revealed the absence of metallic Pt signals, suggesting that, unlike the case of Pt-beta-Fe_2O_3 nanocomposites (Refs. 10, 13), the present hematite matrix played an active role in promoting platinum oxidation.		The C1s peak (BE 284.8 eV) was due to adventitious contamination. The tailing towards higher BE was attributed to carbonate species arising from atmospheric exposure (Refs. 13, 18).	Similarly to the previous specimen (sample #B1, spectrum #3), the oxygen signal could be deconvoluted by three distinct contributing peaks. The one centered at BE = 530.0 eV (54.9 % of the total oxygen) was assigned to the lattice oxygen in Fe_2O_3 (Ref. 13). The peak at BE = 531.4 eV (37.7 % of the total oxygen) arose from the concurrent contributions of platinum oxides [PtO_x (x = 1,2)], as well as to absorbed -OH and carbonate moieties (Refs. 10, 13, 18). The peak at BE = 533.2 eV was attributed to adsorbed water (Refs. 18, 19).
Abscissa Label	binding energy	binding energy	binding energy	binding energy
Abcissa Starting Value (eV):	88.0	1350	295.0	540.0
Abcissa Increment Value:	-0.125	-0.8	-0.125	-0.125
Ordinate Label:	Intensity	Intensity	Intensity	Intensity
Ordinate Units:	counts/s	counts/s	counts/s	counts/s
Number of Data Channels:	192	1688	161	161
Number of Scans:	9	5	12	15
Signal Mode:	multichannel pulse	multichannel pulse	multichannel pulse	multichannel pulse
Detector Width (eV):	0.6	1.9	0.6	0.6
Total Signal Accumulation Time (sec):	86.4	168.6	96.6	120.6

Field Name	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
Total Elapsed Time (sec):	95.04	185.7	106.3	132.7
Is 'raw data' signal intensity corrected? (Yes/No):	No	No	No	No
Signal Intensity Correction Comment:				
Signal Modulation Method:	none	none	none	none
Peak-to-peak amplitude of Modulation (eV):				
Modulation Frequency of Reference Signal (Hz):				
Time Constant of Lock-in Amplifier Used (sec):				

Field Name	Spectrum 9	Spectrum 10	Spectrum 11	Spectrum 12
Spectrum #	9	10	11	12
This spectrum is from which Part B Specimen?	2 - Pt/Fe_2O_3 (2)	2 - Pt/Fe_2O_3 (2)	3 - gold	4 - copper
Suggested Publication Status:	Print in SSS	Print in SSS	Database Only	Database Only
Spectrum Data File Name	PtFeO_9.txt	PtFeO_10.txt	Au1.txt	Cu1.txt
Data File Comment:		The attached data file contains 8 different blocks: 1) binding energy for raw spectrum 2) raw spectrum 3) binding energy for fitted spectrum 4) fitted spectrum 5) background 6) first fit component 7) second fit component 8) third fit component		
Spectrum Figure Image File Name	PtFeO_9.pdf	PtFeO_10.pdf	Au1.pdf	Cu1.pdf
Specimen or Calibration Spectrum:	specimen	specimen	calibration	calibration
Parameter Set # Used	2 - Al Ka	2 - Al Ka	3 - Al Ka	3 - Al Ka
Spectrum Date	2014-06-06	2014-06-06	2014-05-28	2014-05-28
Species/ Transitions:	Fe, Pt 2p, 4s	Pt 4f	Au 4f	Cu 2p_3/2

Field Name	Spectrum 9	Spectrum 10	Spectrum 11	Spectrum 12
Spectral Region Comment:	As previously observed (see comment to the sample #B1, spectrum #4), the Fe 2p region showed two different spectral features. The Fe 2p_{3/2} position (BE = 711.1) was in agreement with that expected for Fe_2O_3 (Refs. 10, 13). As discussed above, the Fe 2p_{1/2} component was heavily overlapped with the Pt 4s peak. For this reason, quantitative analyses reported in the Spectral Features Table have been carried out considering only the Fe 2p_{3/2} signal.	The Pt4f spectrum showed a complex peak shape and could be deconvoluted by three doublets (with spin-orbit separation of 3.3 eV), corresponding to three diverse Pt chemical environments [Ref. 18]. The lower BE contribution [Pt4f_{7/2} BE = 71.2 eV,37.4 % of total Pt] was attributed to Pt(0) (Refs. 10, 13). The second doublet, with a Pt4f_{7/2} BE = 72.6 eV (29.3 % of total Pt content), corresponded to Pt(II) in PtO (Refs. 18, 20-22). Finally, the last doublet (Pt4f_{7/2} BE = 74.4 eV) was assigned to Pt(IV) in PtO_2 (Refs. 18, 20-22). Compared to sample #B1, the presence of Pt(0) and the concomitant decrease of the Pt(IV) content in the present specimen were traced back to the partial decomposition of PtO_2 to metallic platinum upon thermal treatment at 650 {deg}C (Refs. 22, 23).		
Abscissa Label	binding energy	binding energy	binding energy	binding energy
Abcissa Starting Value (eV):	750	84	86	935.5
Abcissa Increment Value:	-0.125	-0.125	-0.125	-0.125
Ordinate Label:	Intensity	Intensity	Intensity	Intensity
Ordinate Units:	counts/s	counts/s	counts	counts
Number of Data Channels:	401	161	32	40
Number of Scans:	30	12	51	28
Signal Mode:	multichannel pulse	multichannel pulse	multichannel pulse	multichannel pulse
Detector Width (eV):	0.6	0.6	0.3	0.3

Field Name	Spectrum 9	Spectrum 10	Spectrum 11	Spectrum 12
Total Signal Accumulation Time (sec):	601.8	96.6	49	33.6
Total Elapsed Time (sec):	662.0	106.3	53	37.0
Is 'raw data' signal intensity corrected? (Yes/No):	No	No	No	No
Signal Intensity Correction Comment:				
Signal Modulation Method:	none	none	none	none
Peak-to-peak amplitude of Modulation (eV):				
Modulation Frequency of Reference Signal (Hz):				
Time Constant of Lock-in Amplifier Used (sec):				

SECTION H - ANALYSIS METHODS

H-1. Energy Scale Correction: The reported BEs were corrected for charging phenomena by assigning a BE of 284.8 eV to the adventitious C 1s signal (Ref. 24).

H-2. Recommended Energy-Scale Shift: -0.4 eV for sample #B1; -0.8 eV for sample #B2

H-3. Intensity Scale Correction: N/A

H-4. Peak Shape and Background Methods: After a Shirley-type background subtraction (Ref. 25), peak position and widths were determined from a least-square fitting procedure, using Gaussian/Lorentzian functions.
For the fitting of Pt 4f peaks, the following parameters were used: spin-orbit separation between 4f_7/2 and 4f_5/2 components = 3.3 eV; FWHM for Pt(0) = 1.7 ± 0.2 eV; FWHM for Pt(II) = 2 ± 0.2 eV; FWHM for Pt(IV) = 2.3 ± 0.2 eV (Ref. 22).

H-5. Quantitation Method: The atomic concentrations were calculated by using sensitivity factors taken from standard PHI

V5.4A software (Ref. 26). The peak areas were measured above an integrated background.

SECTION I - Units for Spectral Features Quantitative fields

I-1. Peak Amplitude Method: peak area

I-2. Peak Amplitude Units: eV x counts/sec

I-3. Concentration Units: atomic percent

I-4. Comments to Spectral Features Table:

Table of Spectral Features

Seq #	Spectrum #	Element	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensitivity Factor	Concentration	Peak Assignment	Peak Assignment Comment
2	2427	C	1s	284.8	2.5	70246	0.296	51.8	Adventitious surface contamination	
3	2428	O	1s	530.0	2.0	19564	0.711	6.0	Lattice oxygen in Fe_2O_3	The sensitivity factor refers to the whole O1s signal.
4	2428	O	1s	531.4	2.1	70506	0.711	21.6	Oxygen in platinum oxides [PtO_x (x = 1,2)]; Adsorbed -OH groups/carbonates	The sensitivity factor refers to the whole O1s signal.
5	2428	O	1s	533.0	2.2	22120	0.711	6.8	Adsorbed water	The sensitivity factor refers to the whole O1s signal.
6	2429	Fe	2p_{3/2}	711.2	3.7	8543	1.971	0.9	Fe(III) in Fe_2O_3	The sensitivity factor, peak amplitude and concentration refer to the sole Fe2p_{3/2} component, due to an overlap of the Fe 2p_(1/2) one with Pt4s (see the comment to the corresponding spectral region).

Seq #	Spectrum #	Element	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensitivity Factor	Concentration	Peak Assignment	Peak Assignment Comment
7	2430	Pt	4f			238405	5.575	9.3	Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
8	2430	Pt	4f_{7/2}	74.8	2.5				Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
9	2430	Pt	4f_{5/2}	78.1	2.5				Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
10	2430	Pt	4f			91230	5.575	3.6	Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
11	2430	Pt	4f_{7/2}	72.6	2.2				Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
12	2430	Pt	4f_{5/2}	75.9	2.2				Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
13	2432	C	1s	284.8	2.5	52436	0.296	42.9	Adventitious surface contamination	
14	2433	O	1s	530.0	2.0	52870	0.711	18.0	Lattice oxygen in Fe_2O_3	The sensitivity factor refers to the whole O1s signal.
15	2433	O	1s	531.4	2.0	36228	0.711	12.4	Oxygen in platinum oxides [PtO_x (x = 1,2)]; Adsorbed -OH groups/carbonates	The sensitivity factor refers to the whole O1s signal.
16	2433	O	1s	533.2	2.4	7125	0.711	2.4	Adsorbed water	The sensitivity factor refers to the whole O1s signal.

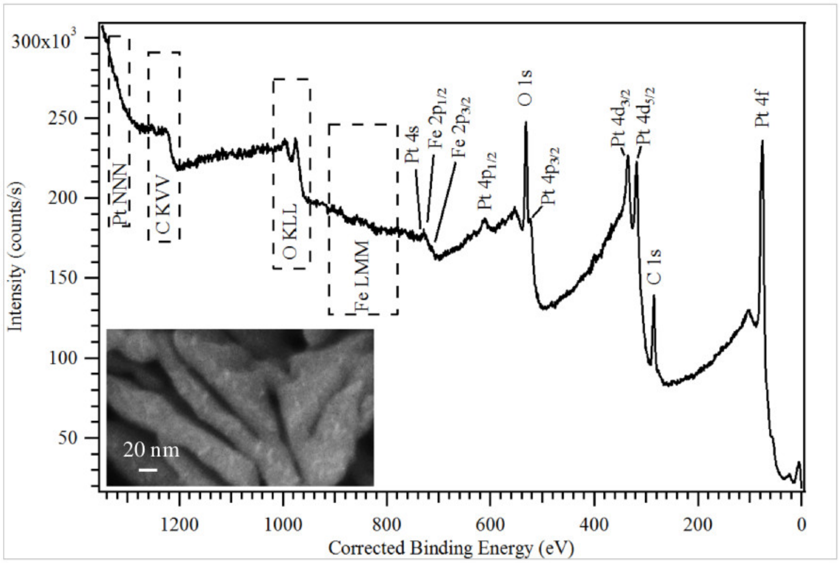
Seq #	Spec trum #	Ele-ment	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensi-tivity Factor	Concen-tration	Peak Assign-ment	Peak Assignment Comment
17	2434	Fe	2p_{3/2}	711.1	3.7	52407	1.971	6.4	Fe(III) in Fe_2O_3	The sensitivity factor, peak amplitude and concentration refer to the sole Fe 2p_{3/2} component, due to an overlap of the Fe2p_(1/2) one with Pt4s (see the comment to the corresponding spectral region).
18	2435	Pt	4f			137595	5.575	6.0	Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
19	2435	Pt	4f_{7/2}	74.4	2.5				Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
20	2435	Pt	4f_{5/2}	77.7	2.5				Pt(IV) in PtO_2	The sensitivity factor refers to the whole Pt4f signal.
21	2435	Pt	4f			120775	5.575	5.2	Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
22	2435	Pt	4f_{7/2}	72.6	2.0				Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
23	2435	Pt	4f_{5/2}	75.9	2.0				Pt(II) in PtO	The sensitivity factor refers to the whole Pt4f signal.
24	2435	Pt	4f			154119	5.575	6.7	Pt(0)	The sensitivity factor refers to the whole Pt4f signal.
25	2435	Pt	4f_{7/2}	71.2	1.9				Pt(0)	The sensitivity factor refers to the whole Pt4f signal.
26	2435	Pt	4f_{5/2}	74.5	1.9				Pt(0)	The sensitivity factor refers to the whole Pt4f signal.

FIGURE IMAGE FILES

This submission has 12 spectrum records with associated image files.

Spectrum No 1: *PtFeO_1.pdf*
Spectrum No 2: *PtFeO_2.pdf*
Spectrum No 3: *PtFeO_3.pdf*
Spectrum No 4: *PtFeO_4.pdf*
Spectrum No 5: *PtFeO_5.pdf*
Spectrum No 6: *PtFeO_6.pdf*
Spectrum No 7: *PtFeO_7.pdf*
Spectrum No 8: *PtFeO_8.pdf*
Spectrum No 9: *PtFeO_9.pdf*
Spectrum No 10: *PtFeO_10.pdf*
Spectrum No 11: *Au1.pdf*
Spectrum No 12: *Cu1.pdf*

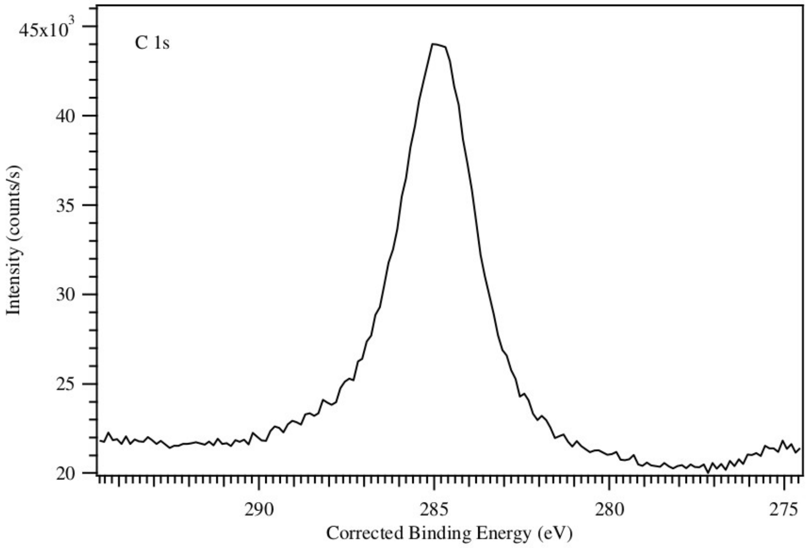
PtFeO_1.pdf



Survey - Spectrum #1

File Name: PtFeO_1

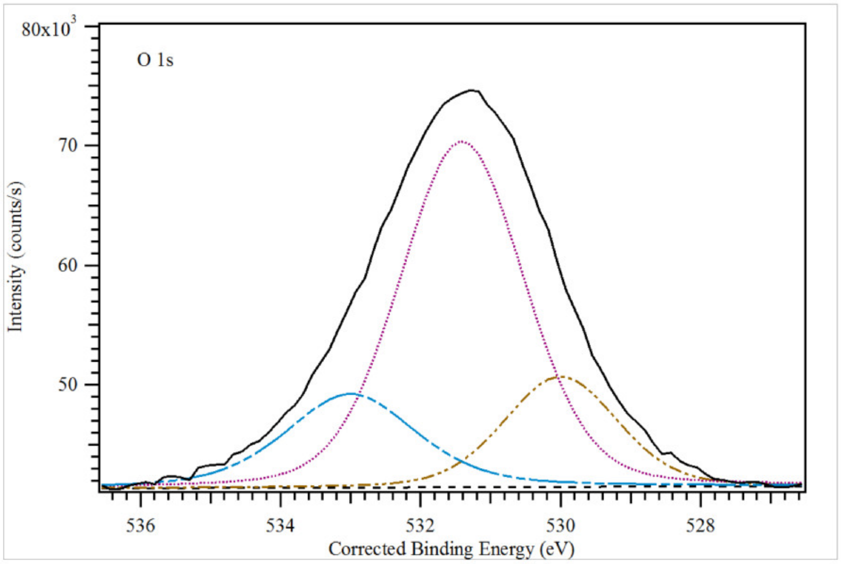
PtFeO_2.pdf



C 1s – Spectrum #2

File Name: PtFeO_2

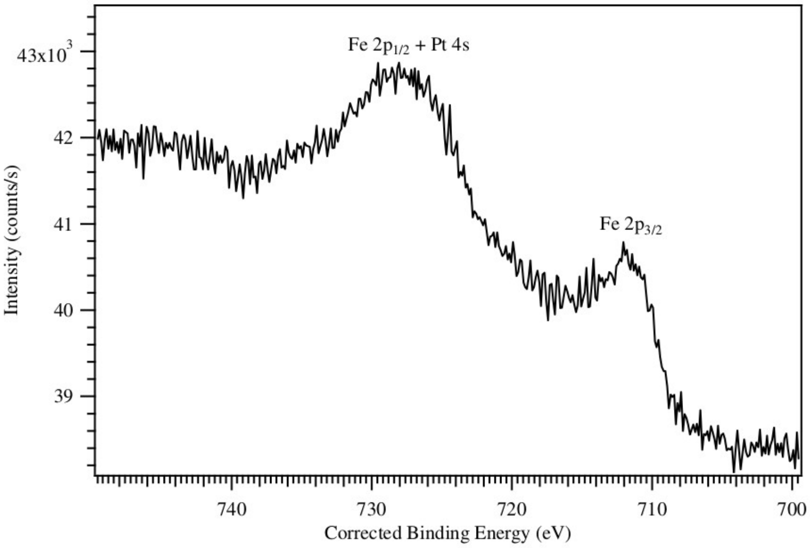
PtFeO_3.pdf



O 1s – Spectrum #3

File Name PtFeO_3

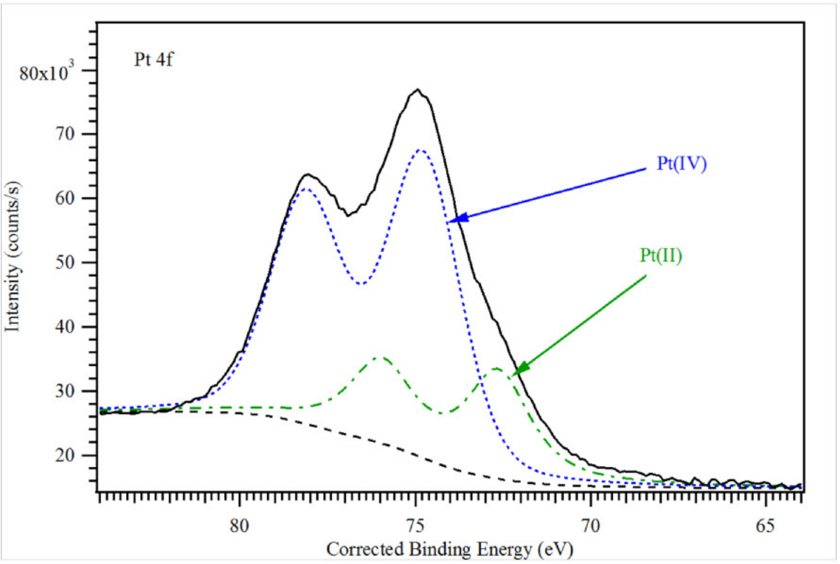
PtFeO_4.pdf



Fe 2p – Spectrum #4

File Name: PtFeO_4

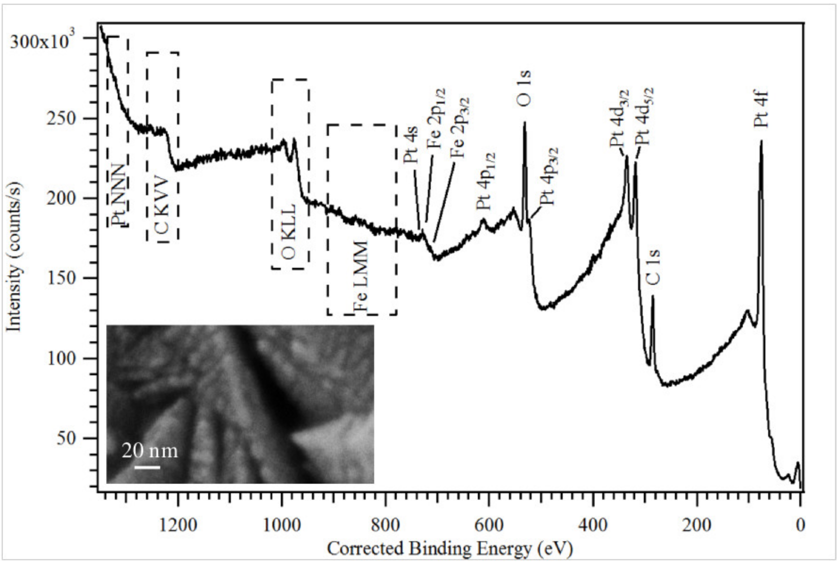
PtFeO_5.pdf



Pt 4f – Spectrum #5

File Name: PtFeO_5

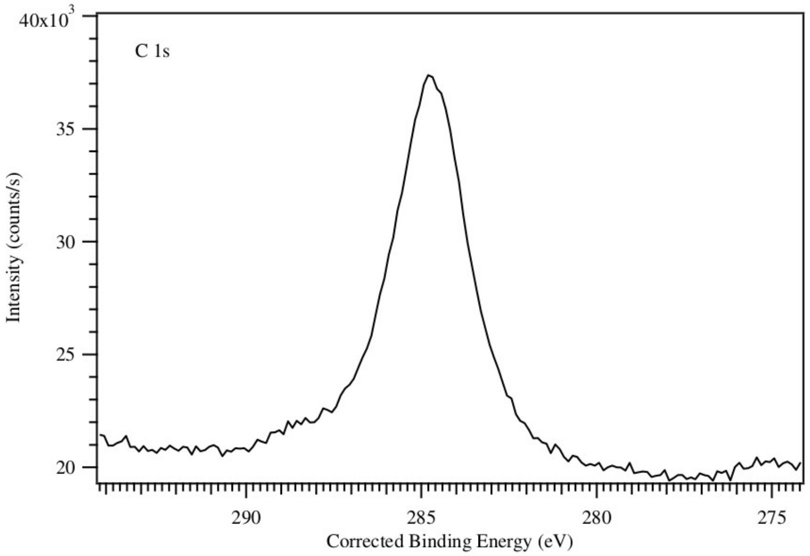
PtFeO_6.pdf



Survey – Spectrum #6

File Name: PtFeO_6

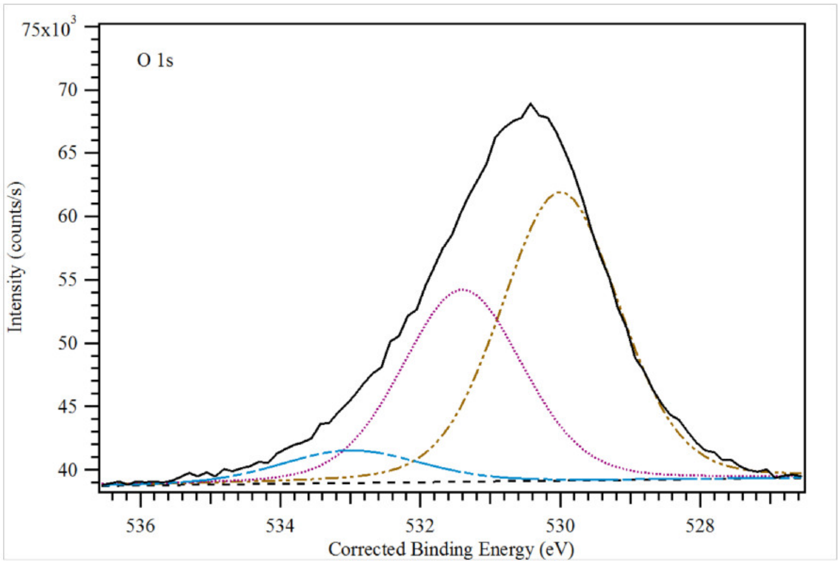
PtFeO_7.pdf



C 1s – Spectrum #7

File Name: PtFeO_7

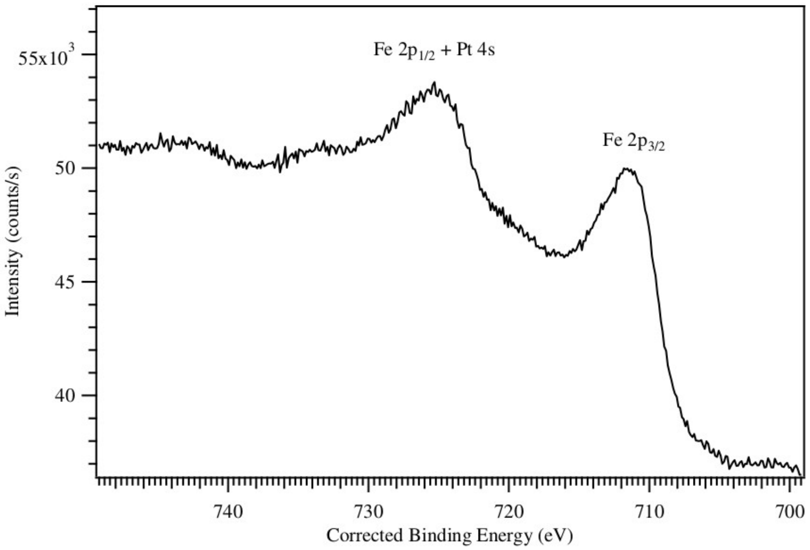
PtFeO_8.pdf



O 1s – Spectrum #8

File Name: PtFeO_8

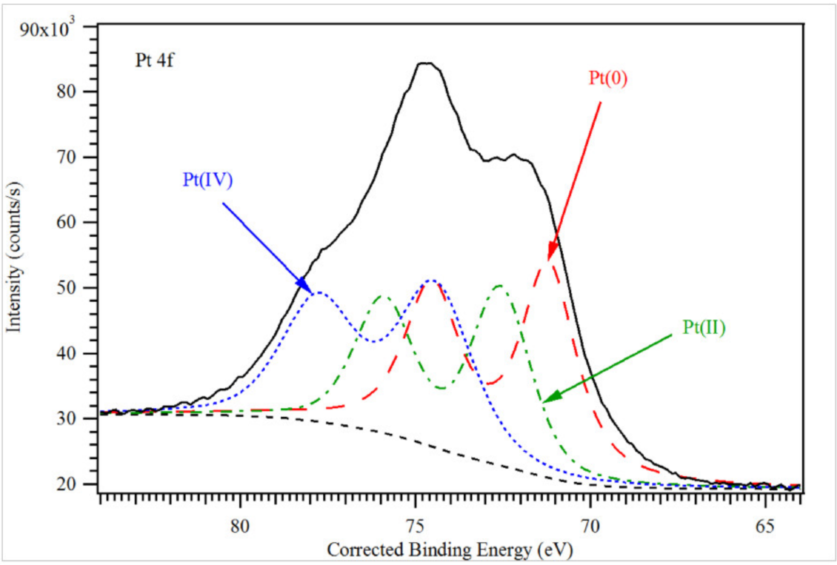
PtFeO_9.pdf



Fe 2p – Spectrum #9

File Name: PtFeO_9

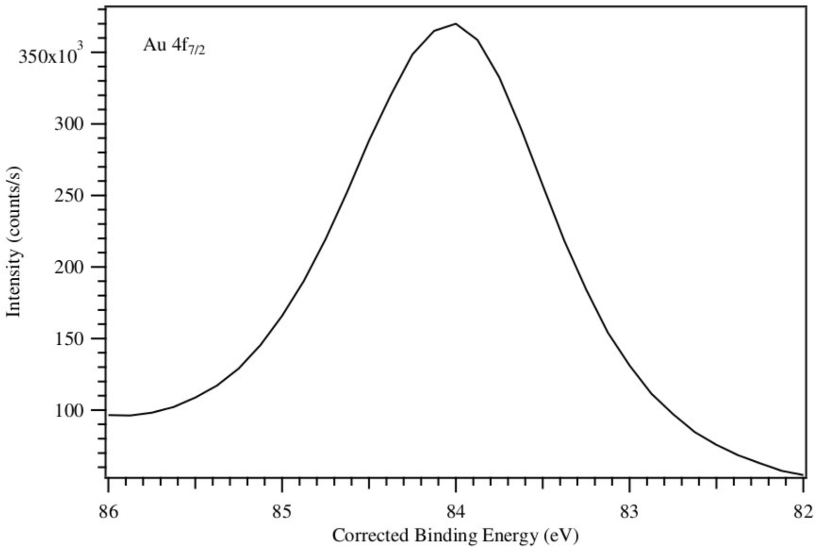
PtFeO_10.pdf



Pt 4f – Spectrum #10

File Name:PtFeO_10

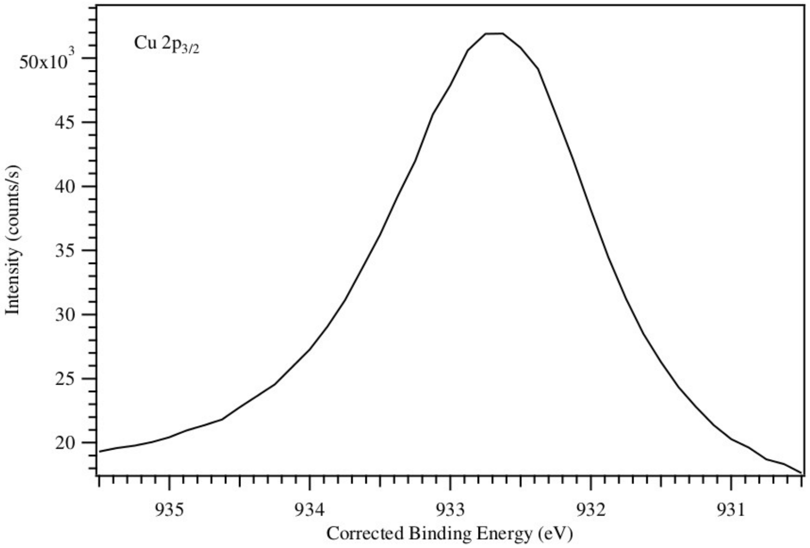
Au1.pdf



Au 4f$_{7/2}$ – Spectrum #11

File Name:Au1

Cu1.pdf



Cu $2p_{3/2}$ – Spectrum #12

File Name:Cu1