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Fundamentals of X-Ray Photoelectron Spectroscopy (XPS)

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X-Ray Photoelectron Spectroscopy (XPS)

Fundamental

Author: Shihui Zou

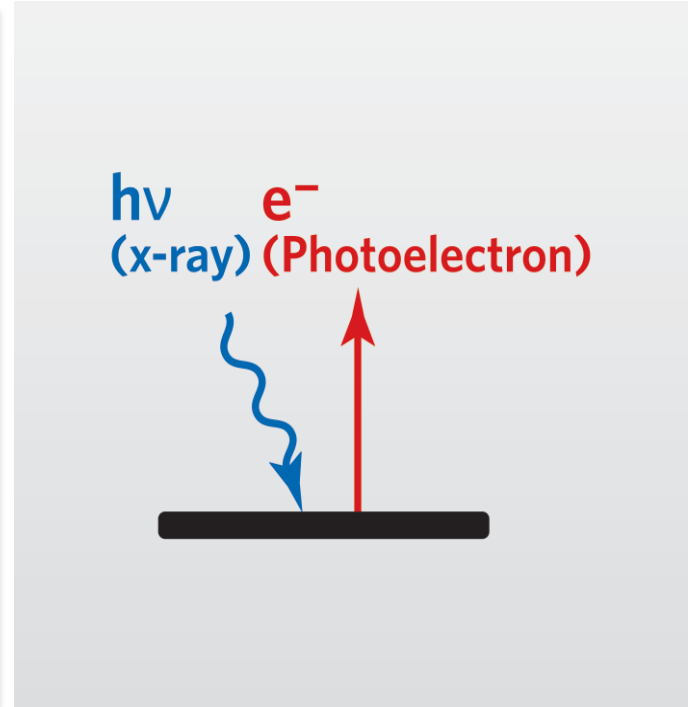
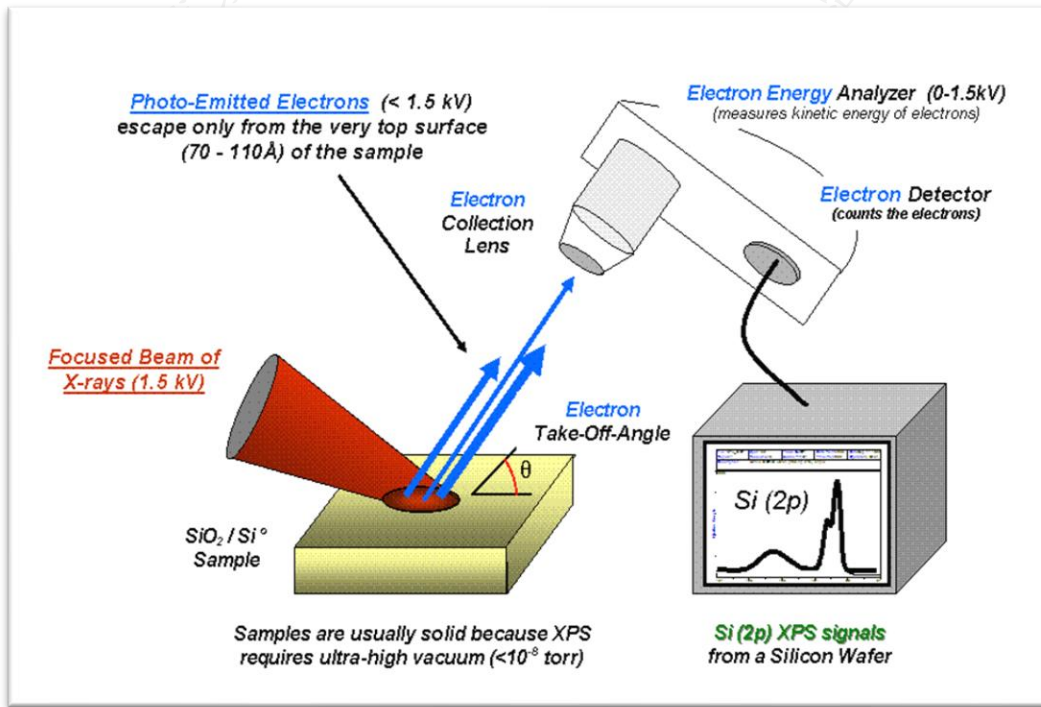
Translator: Tianyu Liu



I. What is XPS?



A spectroscopic technique gauging the energy distribution of photoelectrons generated by irradiating sample surfaces with X-ray.



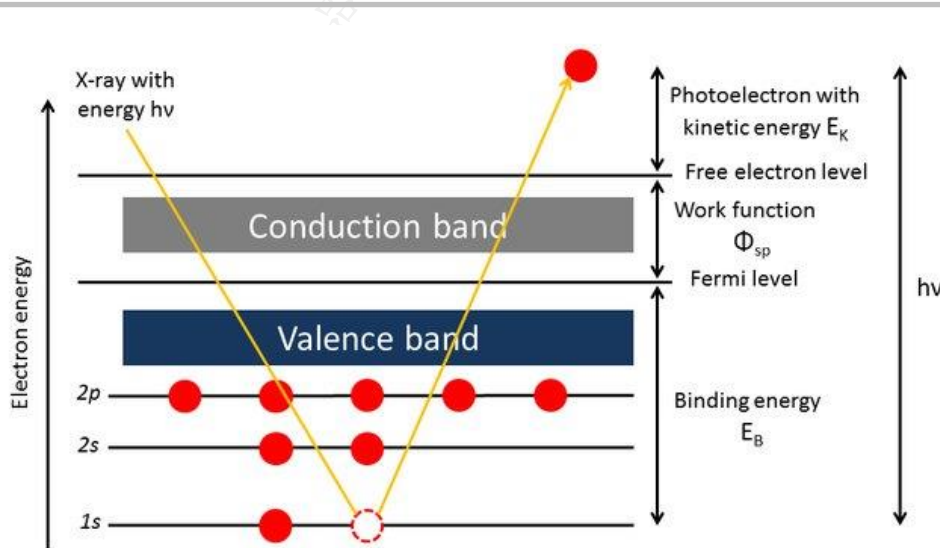
XPS is a **qualitative and semi-quantitative** analysis technique.

- **Peak position and shape**: surface composition, elemental valence, molecular structure, etc.
- **Peak intensity**: content of element on surface

I. What is XPS?



➤ Photoelectric effect (photoionization)



Einstein's Photoelectric Equation

$$E_k = h\nu - E_B - \varphi_{sp}$$

E_k : kinetic energy of photoelectron;

$h\nu$: X-ray energy;

E_B : binding energy of photoelectron;

φ_{sp} : work function of XPS spectrometer (a constant with an average value between 3 and 5 eV)

XPS Mechanism: When a beam of X-ray hits the surface of a sample, the electrons in the surface can absorb the photon energy and be excited. In some cases, these electrons can escape the host material (ionization). By measuring the kinetic energy of the escaping electrons, one can determine the binding energy (E_B) of the electrons using the Einstein's photoelectric equation. E_B reflects the type and valence of the elements in the tested sample.

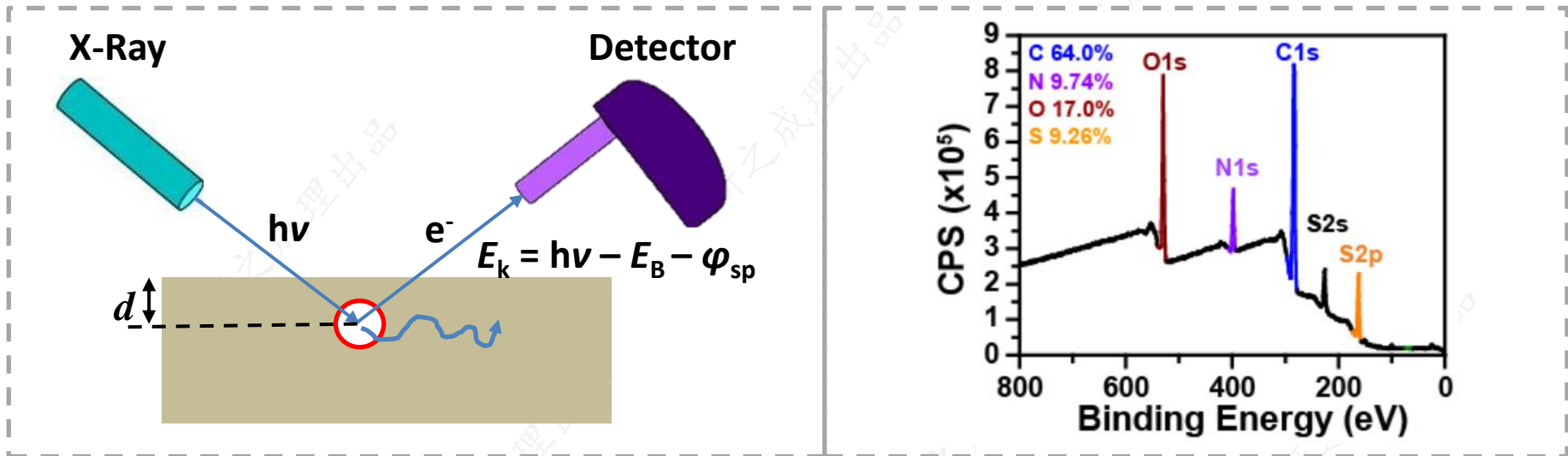
I. What is XPS?



➤ Why only surfaces?

Although X-ray can easily penetrate samples, only photoelectrons close to the sample surface (~10 nm thickness) can escape without significantly losing energy.

XPS signal (shallow surface): without significant energy loss; characteristic of elements. Escaping electrons with energy partially lost — baseline.

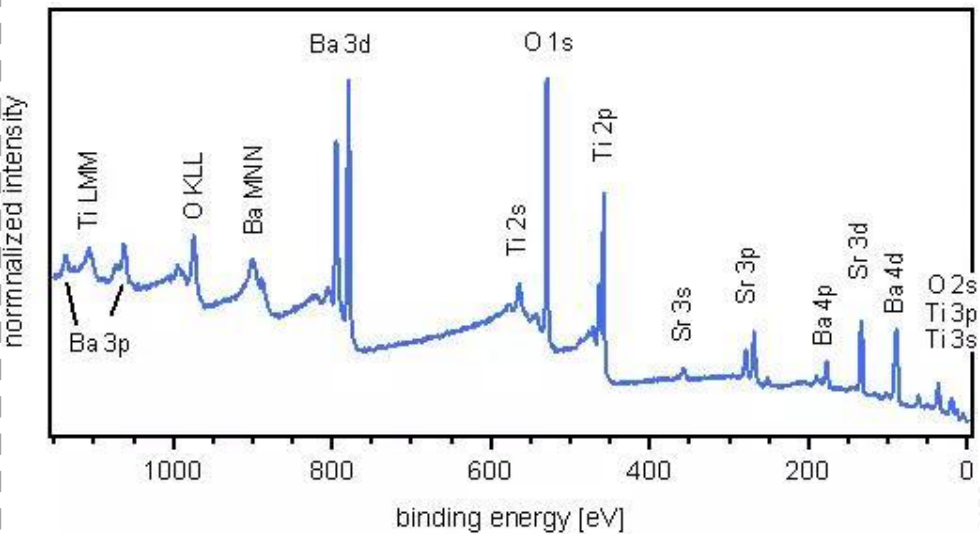


Detection depth (d) depends on the escape depth of photoelectrons (λ , a function of X-ray wavelength and sample composition).

General d values: 0.5-3 nm (metal); 2-4 nm (inorganic); 4-10 nm (organic)



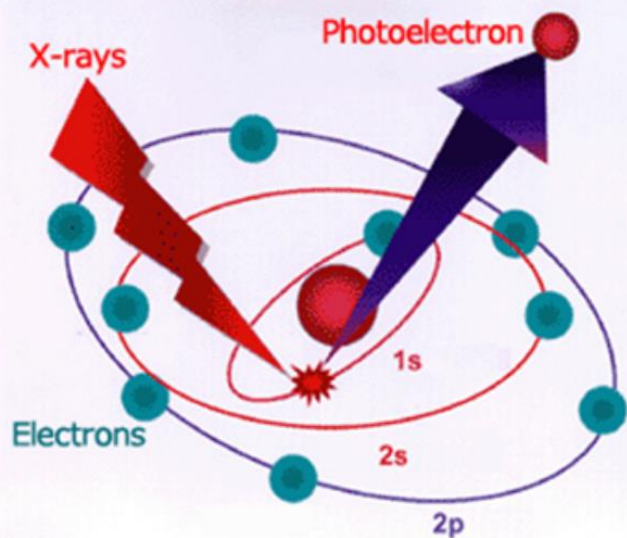
2. What Can XPS Do?



Name	Position (eV)	FWHM (eV)	Atomic % conc.
Au 4f _{7/2}	84.7	0.9	0.3
Au 4f _{5/2}	88.4	0.8	
Si 2p _{3/2} (SiO ₂)	103.6	1.6	22.2
Si 2p _{1/2} (SiO ₂)	104.2	1.6	
Ag 3d _{5/2}	368.6	1.1	0.2
Ag 3d _{3/2}	374.5	0.7	
O 1s (SiO ₂)	532.9	1.5	33.6
O 1s (C-O-C)	534.6	2.3	
C 1s (CC-CH)	285.0	1.5	43.7
C 1s (C-O)	286.5	2.9	

- 1) [Peak position] Qualitative info: **elemental composition, valence, and bonding environment**
- 2) [Peak intensity] Semi-quantitative info: **relative contents of different elements**

2. What Can XPS Do?



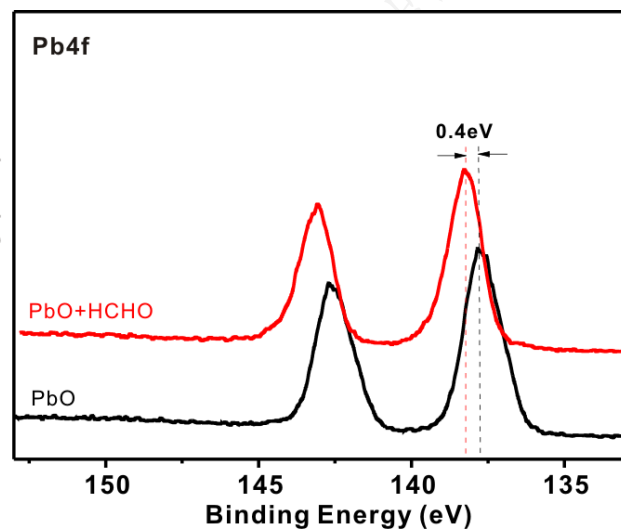
➤ Elemental Composition

For a specific pair of monochromatic excitation source and electron orbital, the kinetic energy of photoelectrons is a constant. **This kinetic energy is a fingerprint of the electrons on a specific electronic subshell of a certain element.**

➤ Valence & Bonding Environment

Any variations in the type and number of neighboring nuclei or different valences of the excited nuclei can alter the E_B . This alteration is displayed as peak shift in XPS spectroscopy

Oxidation increases E_B and reduction decreases E_B . The shifts in all the peaks belonging to one element are equal.





2. What Can XPS Do?

➤ What elements can XPS detect?

XPS usually uses Al $K\alpha$ or Mg $K\alpha$ X-ray as the excitation source. Theoretically, XPS detect **any elements other than H and He**. Detection limit: **0.1 atom%**.

Most Intense/Most Used XPS Core Lines
(Al $K\alpha$ source at 1486.7 eV)

Element		Most Intense/Most Used Core Line		Nominal Binding Energy in eV	
⁷ Li	1s	56	112	¹¹ B	1s
⁴ Be	1s	112	112	⁶ C	1s
¹¹ Na	1s	1072	50	¹⁴ N	1s
¹² Mg	2p	50	50	⁸ O	1s
¹⁹ K	2p _{3/2}	294	294	⁹ F	1s
²⁰ Ca	2p _{3/2}	347	347	¹⁸ Ar	2p _{3/2}
²¹ Sc	2p _{3/2}	399	399	¹⁵ P	2p _{3/2}
²² Ti	2p _{3/2}	454	454	¹⁶ S	2p _{3/2}
²³ V	2p _{3/2}	512	512	¹⁷ Cl	2p _{3/2}
²⁴ Cr	2p _{3/2}	574	574	³⁶ Kr	3d _{5/2}
²⁵ Mn	2p _{3/2}	639	639	³⁷ Rb	3d _{5/2}
²⁶ Fe	2p _{3/2}	707	707	³⁸ Sr	3d _{5/2}
²⁷ Co	2p _{3/2}	778	778	³⁹ Y	3d _{5/2}
²⁸ Ni	2p _{3/2}	853	853	⁴⁰ Zr	3d _{5/2}
²⁹ Cu	2p _{3/2}	933	933	⁴¹ Nb	3d _{5/2}
³⁰ Zn	2p _{3/2}	1022	1022	⁴² Mo	3d _{5/2}
³¹ Ga	2p _{3/2}	1117	1117	⁴³ Tc	3d _{5/2}
³² Ge	3d	29	29	⁴⁴ Ru	3d _{5/2}
³³ As	3d _{5/2}	42	42	⁴⁵ Rh	3d _{5/2}
³⁴ Se	3d _{5/2}	57	57	⁴⁶ Pd	3d _{5/2}
³⁵ Br	3d _{5/2}	69	69	⁴⁷ Ag	3d _{5/2}
³⁶ Kr	3d _{5/2}	87	87	⁴⁸ Cd	3d _{5/2}
³⁷ Rb	3d _{5/2}	111	111	⁴⁹ In	3d _{5/2}
³⁸ Sr	3d _{5/2}	134	134	⁵⁰ Sn	3d _{5/2}
³⁹ Y	3d _{5/2}	158	158	⁵¹ Sb	3d _{5/2}
⁴⁰ Zr	3d _{5/2}	179	179	⁵² Te	3d _{5/2}
⁴¹ Nb	3d _{5/2}	202	202	⁵³ I	3d _{5/2}
⁴² Mo	3d _{5/2}	228	228	⁵⁴ Xe	3d _{5/2}
⁴³ Tc	3d _{5/2}	280	280	⁵⁵ Cs	3d _{5/2}
⁴⁴ Ru	3d _{5/2}	307	307	⁵⁶ Ba	3d _{5/2}
⁴⁵ Rh	3d _{5/2}	355	355	⁵⁷ La	4f _{7/2}
⁴⁶ Pd	3d _{5/2}	368	368	⁵⁸ Ce	4f _{7/2}
⁴⁷ Ag	3d _{5/2}	384	384	⁵⁹ Pr	4f _{7/2}
⁴⁸ Cd	3d _{5/2}	405	405	⁶⁰ Nd	4f _{7/2}
⁴⁹ In	3d _{5/2}	444	444	⁶¹ Pm	4f _{7/2}
⁵⁰ Sn	3d _{5/2}	485	485	⁶² Sm	4f _{7/2}
⁵¹ Sb	3d _{5/2}	528	528	⁶³ Eu	4f _{7/2}
⁵² Te	3d _{5/2}	573	573	⁶⁴ Gd	4f _{7/2}
⁵³ I	3d _{5/2}	619	619	⁶⁵ Tb	4f _{7/2}
⁵⁴ Xe	3d _{5/2}	670	670	⁶⁶ Dy	4f _{7/2}
⁵⁵ Cs	3d _{5/2}	726	726	⁶⁷ Ho	4f _{7/2}
⁵⁶ Ba	3d _{5/2}	781	781	⁶⁸ Er	4f _{7/2}
⁵⁷ La	4f _{7/2}	14	14	⁶⁹ Tm	4f _{7/2}
⁵⁸ Ce	4f _{7/2}	22	22	⁷⁰ Yb	4f _{7/2}
⁵⁹ Pr	4f _{7/2}	31	31	⁷¹ Lu	4f _{7/2}
⁶⁰ Nd	4f _{7/2}	40	40	⁷² Ac	4f _{7/2}
⁶¹ Pm	4f _{7/2}	51	51	⁷³ Th	4f _{7/2}
⁶² Sm	4f _{7/2}	61	61	⁷⁴ Pa	4f _{7/2}
⁶³ Eu	4f _{7/2}	71	71	⁷⁵ U	4f _{7/2}
⁶⁴ Gd	4f _{7/2}	84	84	⁷⁶ Np	4f _{7/2}
⁶⁵ Tb	4f _{7/2}	101	101	⁷⁷ Pu	4f _{7/2}
⁶⁶ Dy	4f _{7/2}	118	118	⁷⁸ Am	4f _{7/2}
⁶⁷ Ho	4f _{7/2}	137	137	⁷⁹ Cm	4f _{7/2}
⁶⁸ Er	4f _{7/2}	157	157	⁸⁰ Bk	4f _{7/2}
⁶⁹ Tm	4f _{7/2}	182	182	⁸¹ Cf	4f _{7/2}
⁷⁰ Yb	4f _{7/2}	182	182	⁸² Es	4f _{7/2}
⁷¹ Lu	4f _{7/2}	7	7	⁸³ Fm	4f _{7/2}
⁷² Ac	4f _{7/2}	307	307	⁸⁴ Md	4f _{7/2}
⁷³ Th	4f _{7/2}	333	333	⁸⁵ No	4f _{7/2}
⁷⁴ Pa	4f _{7/2}	358	358	⁸⁶ Lr	4f _{7/2}
⁷⁵ U	4f _{7/2}	377	377		
⁷⁶ Np	4f _{7/2}	403	403		
⁷⁷ Pu	4f _{7/2}	425	425		
⁷⁸ Am	4f _{7/2}	448	448		
⁷⁹ Cm	4f _{7/2}	472	472		
⁸⁰ Bk	4f _{7/2}	499	499		
⁸¹ Cf	4f _{7/2}	523	523		
⁸² Es	4f _{7/2}	550	550		

Legend:

- Non metals (Green)
- Alkaline Earth (Red)
- Alkali Metals (Yellow)
- Transition Metals (Light Blue)
- Rare Earth (Light Purple)
- Lanthanides (Pink)
- Metalloids (Dark Blue)
- Main Group Metals (Orange)
- Actinides (Magenta)
- Halogens (Dark Green)
- Noble Gases (Light Blue)

Also Used:

- 3d 19 eV
- 4d 128 eV
- 3d_{5/2} 1186 eV
- 3d_{5/2} 1241 eV
- 3d_{5/2} 1296 eV

Why no H and He?

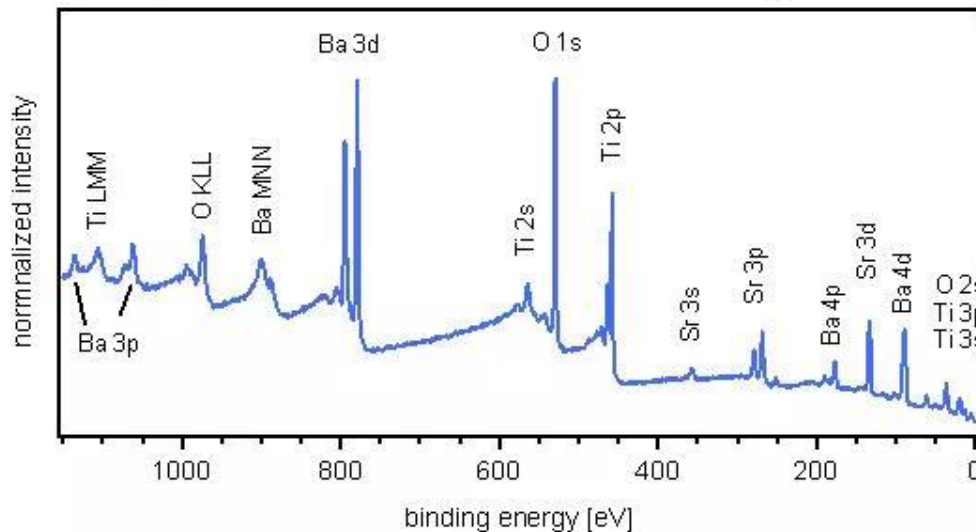
- 1) Ionization of H and He are unlikely;
- 2) H 1s electron is too diffusive. Its E_B varies;
- 3) Lack of inner electrons and all-paired outer electrons make H and He resistant to ionization.

2. What Can XPS Do?



➤ Survey Spectrum — What elements?

Identifying elements using the binding energies of photoelectrons and auger electrons, with reference to standard values in refs, handbooks, and databases.



E_B range: 0-1200 eV

Steps for Peak Identification:

1. Elements always present due to contamination, e.g., C
2. Main elements exhibiting strong, well-resolved peaks;
3. Other elements with less prominent peaks.

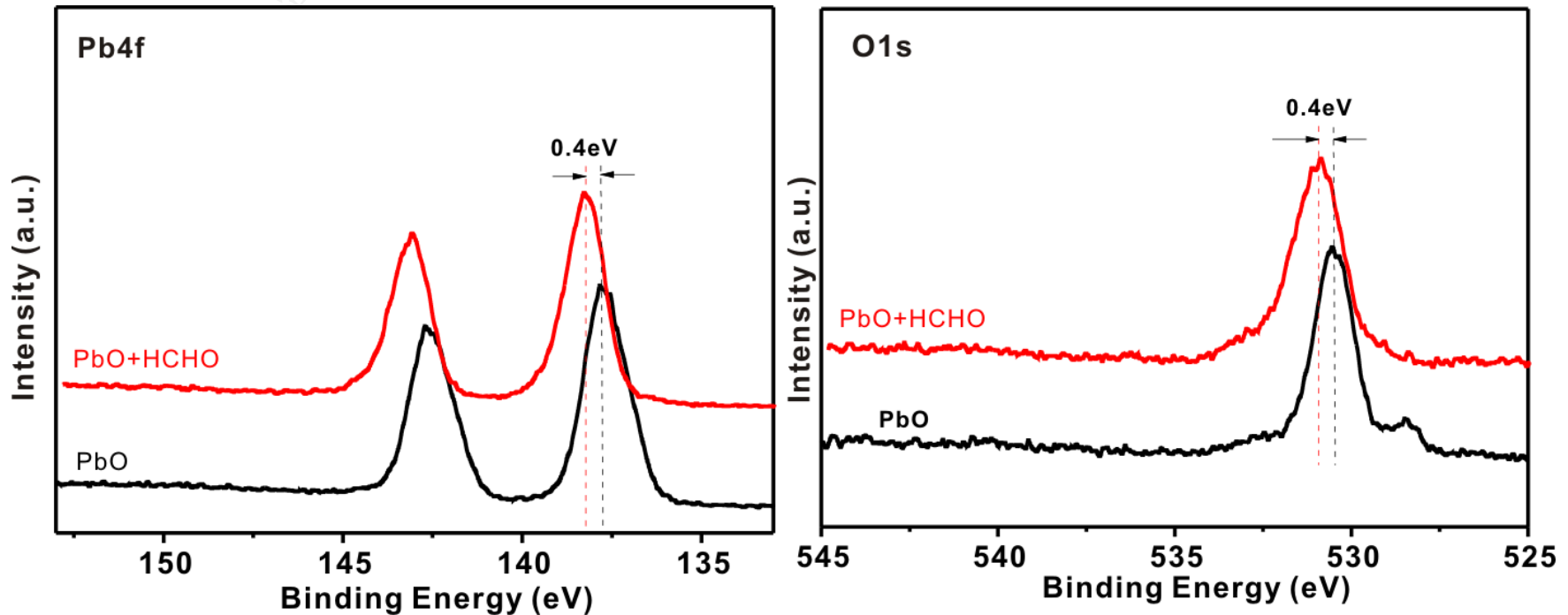
XPS handbook: Moulder, John F. *et al.* Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data.

NIST XPS database: <http://srdata.nist.gov/xps/ElmSpectralSrch.aspx?selEnergy=PE>

2. What Can XPS Do?



➤ High-Resolution Spectroscopy — Valence and Structure



- **Peak position:** **element** and **valence**
- **Peak intensity:** **content** (depends on sensitivity)
- **Full width at half maximum (FWHM):** the intrinsic properties of the detected element, X-ray source, spectrometer, and sample.

2. What Can XPS Do?



➤ Why semi-quantitative?

The intensity of the photoelectrons (I , peak area) scales linearly with the content of the element (n).

$$n = I / S \qquad \frac{n_i}{n_j} = \frac{I_i / S_i}{I_j / S_j}$$

S – sensitivity factor (empirical value, may need calibration)

Attention:

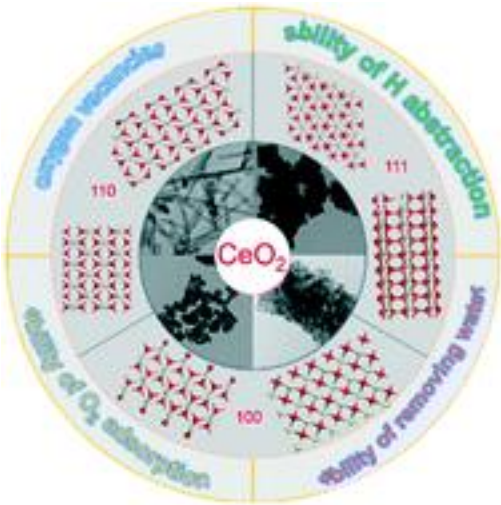
- Peaks of one element can differ in the intensity and S . Selecting peaks with high intensity and large S improves sensitivity.
- Sensitivity of one element can vary due to its presence in different compounds, e.g., mixtures.



2. What Can XPS Do?

➤ Why semi-quantitative?

Peak area also depends on the mean free path of photoelectrons, cleanness of sample surface, valence, X-ray intensity, and spectrometer condition. Therefore, XPS can give relative contents but not absolute values.



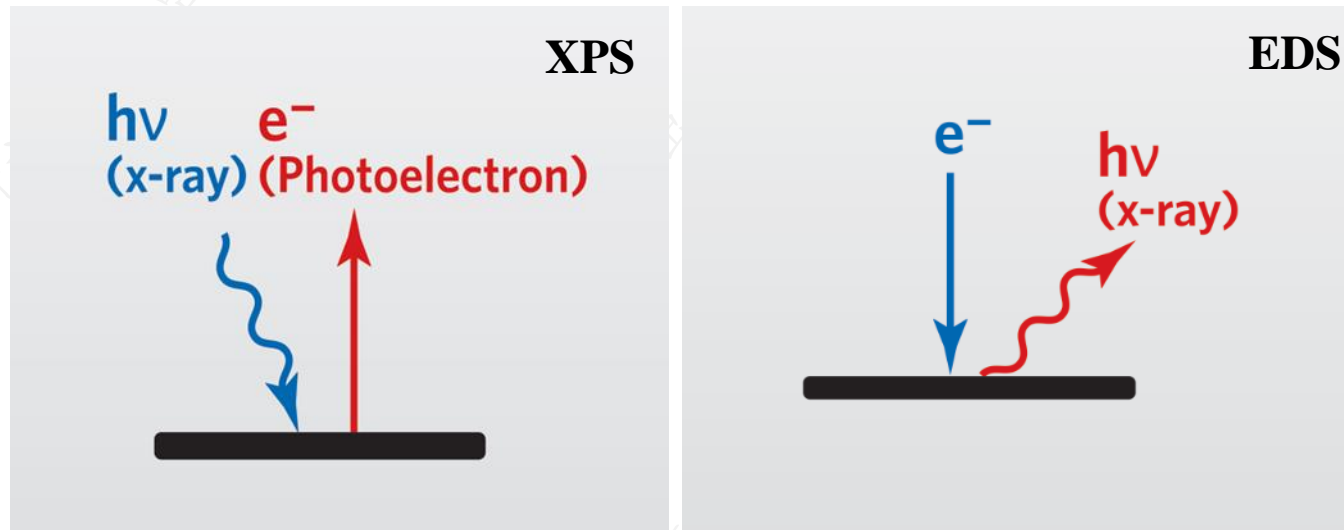
Catal. Sci. Technol.,
2019, 9, 2960-2967

catalysts	average size (nm)	S_{BET} (m^2/g)	surface plane	Ce^{3+} fraction (%) ^a	Surface oxygen Fraction (%) ^b		
					O _s	O _H	total
rods	8.4 × 149	99.9	(110) (100)	21	37	19	56
octahedra	57	12.2	(111)	17	32	13	45
cubes	36	32.5	(100)	19	32	17	49
particles	4.3	99.3	(111) (110) (100)	12	22	5	27

3. XPS & EDS (Energy Dispersive Spectroscopy)



a. EDS & XPS both are techniques for elemental analysis.



b. Differences between EDS and XPS:

- 1) XPS uses X-ray, detects electrons; EDS uses electrons, detects X-ray;
- 2) EDS can only detect composition and content, not valence; detection limit is high (>2 atom%);
- 3) EDS is usually coupled with electron microscopy; XPS is typically used independently.

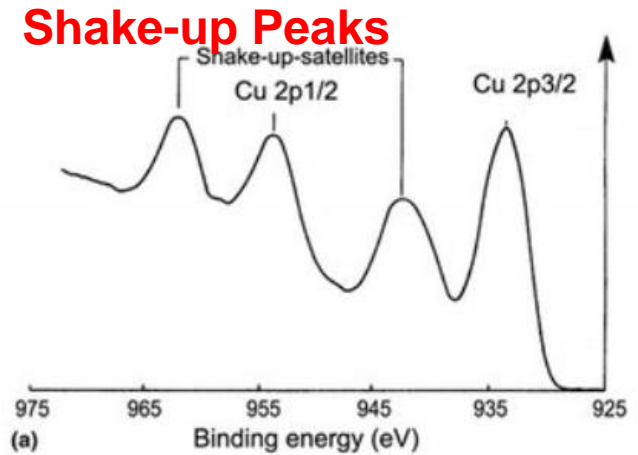
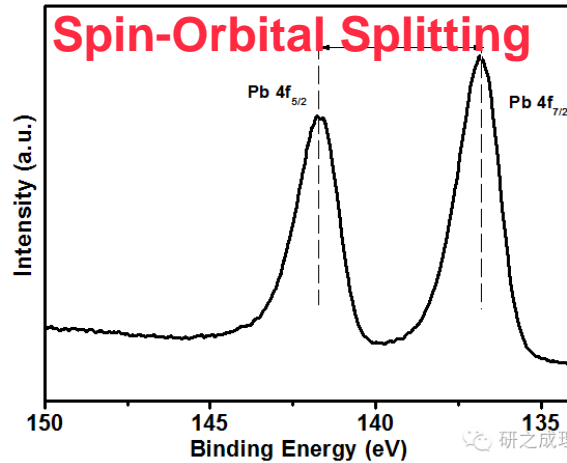
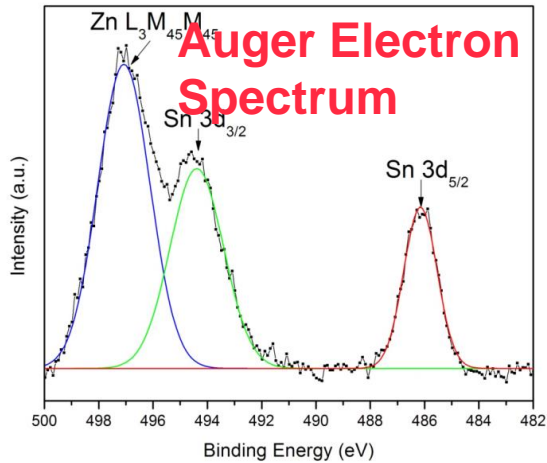
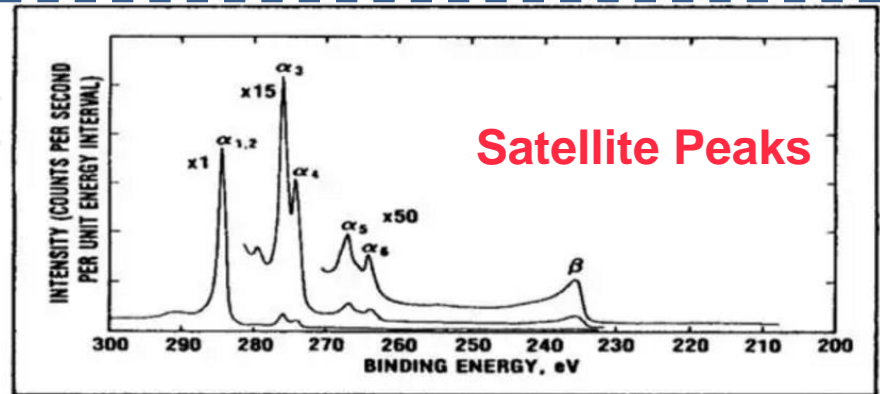
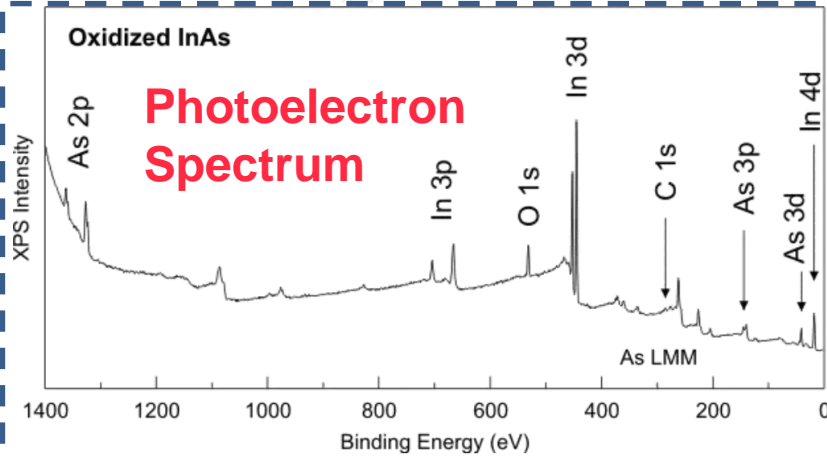
X-Ray Photoelectron Spectroscopy (XPS) Spectrum

Author: Shihui Zou

Translator: Tianyu Liu



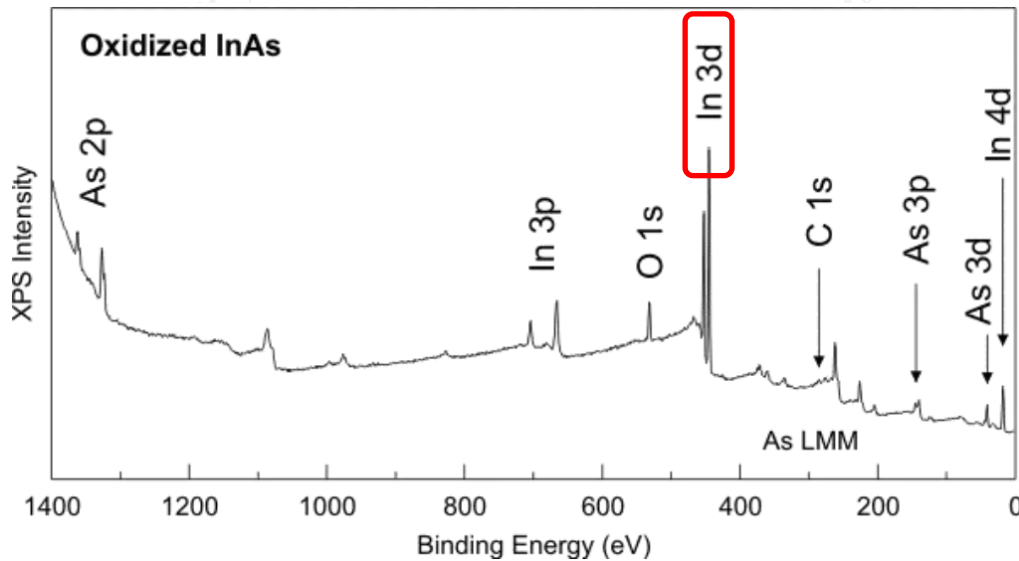
Important Features



I. Photoelectron Spectroscopy



- Every element has its characteristic spectrum — the **basis for elemental analysis**. The strongest, sharpest, and most symmetric peak is the main XPS peak.



Probability of photoelectrical effect: The number of photoelectrons generated is associated with a factor called **photoionization cross section (σ)**.



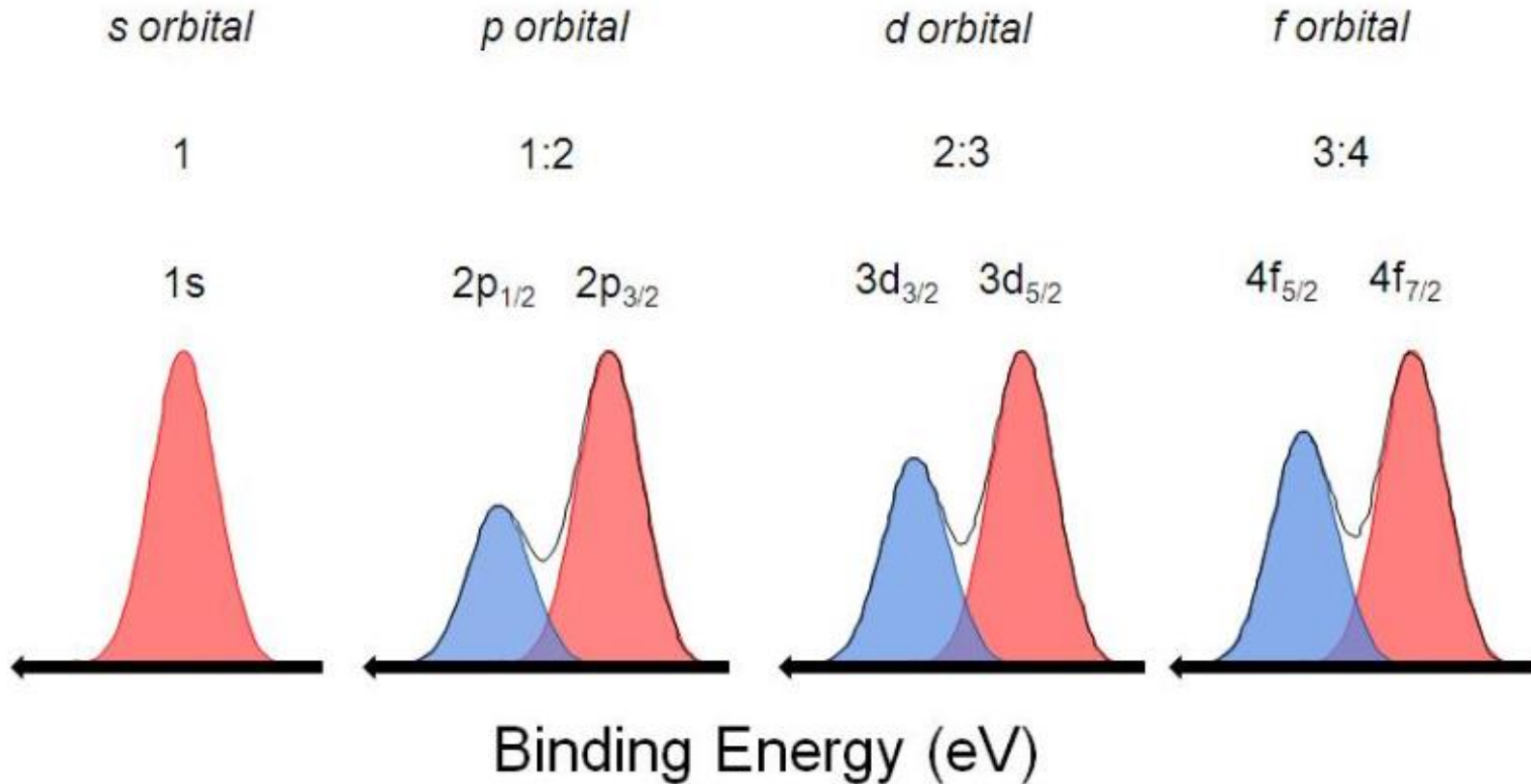
main peak

The main peak of In is its 3d peak. Besides, there are In 4d and In 3p peaks due to the multiple inner electrons of In.



2. Spin-Orbital Coupling

- The coupling of electron movements in orbitals and self-spin leads to peak separation.

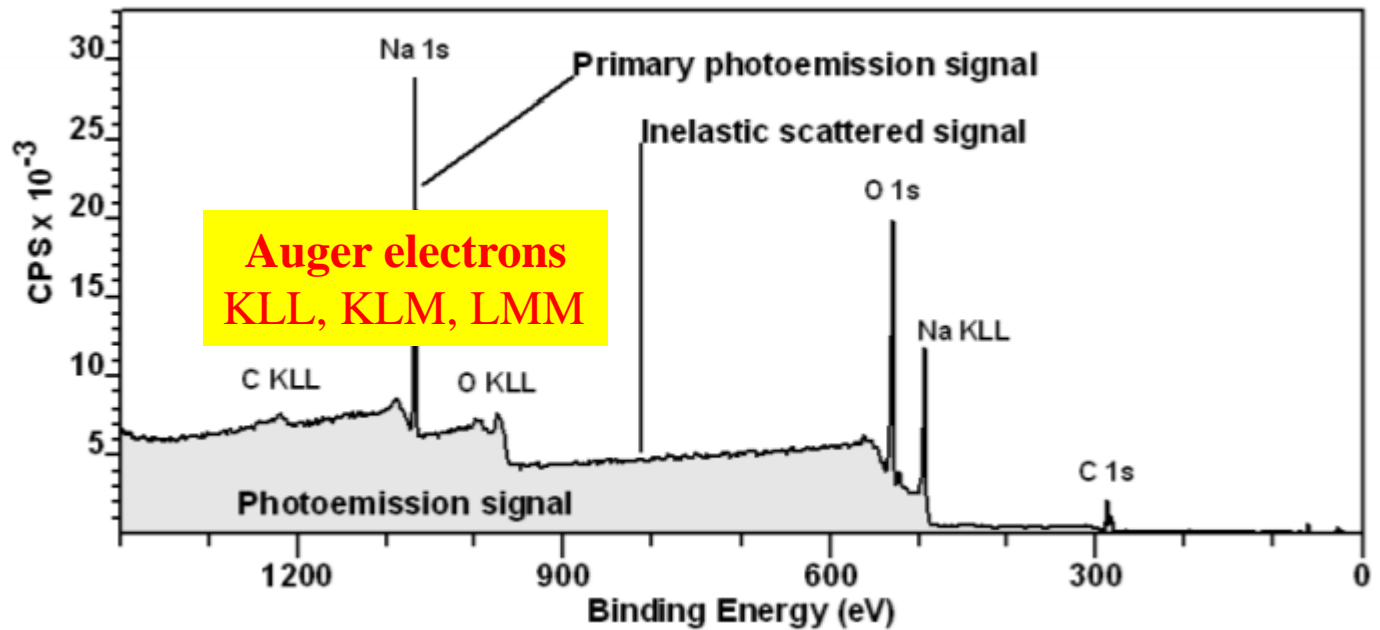
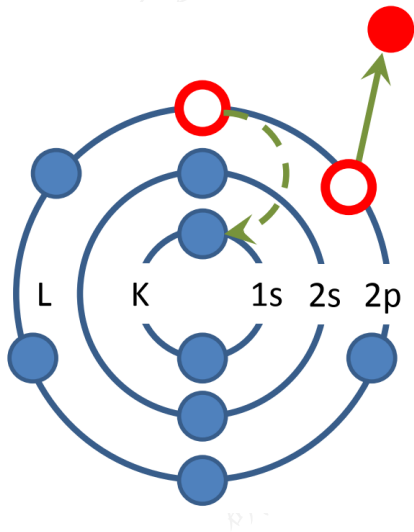


- Why usually two peaks? spin quantum number: $\pm 1/2$
- For a specific element, its p, d, and f doublets typically exhibit fixed peak separation and peak intensity ratio.



3. Auger Electron Spectroscopy

- When a core electron is ionized and left a vacancy, an electron from a higher energy level may fall into the vacancy and release energy. The released energy is transferred to another electron, which is ejected from the atom. This second ejected electron is an **Auger electron**.



C KLL, O KLL, Na KLL are Auger electron peaks from C, O, Na, respectively. O KLL has three peaks: vacancy level (left), re-filling electron level (middle), and Auger electron level (right).



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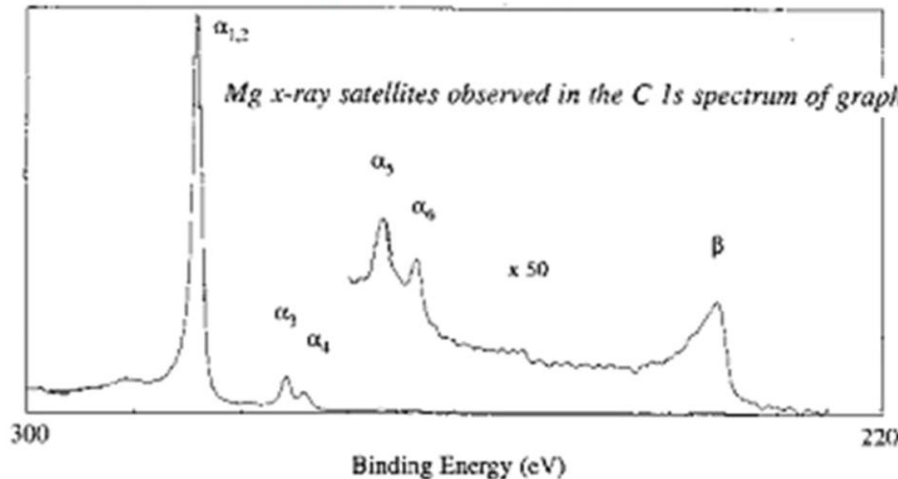
4. Satellite Peaks (Shoulder Peaks)

➤ “Impurities” of the energy in the X-ray source (non-monochromaticity):

e.g., Al/Mg $K\alpha_{1,2}$ include $K\alpha_{3,4,5}$ and $K\beta$

	$\alpha_{1,2}$	α_3	α_4	α_5	α_6	β
Mg displacement, eV	0	8.4	10.1	17.6	20.6	48.7
relative height	100	8.0	4.1	0.6	0.5	0.5
Al displacement, eV	0	9.8	11.8	20.1	23.4	69.7
relative height	100	6.4	3.2	0.4	0.3	0.6

Emission from non-monochromatic x-ray sources produces satellite peaks in XPS spectrum at lower BE.



C 1s main peak ($\alpha_{1,2}$) and shoulder peaks ($\alpha_{3,4,5}$ and β). The intensity of the main peak is much stronger than those of the shoulder peaks.

X-Ray Photoelectron Spectroscopy (XPS)

Example

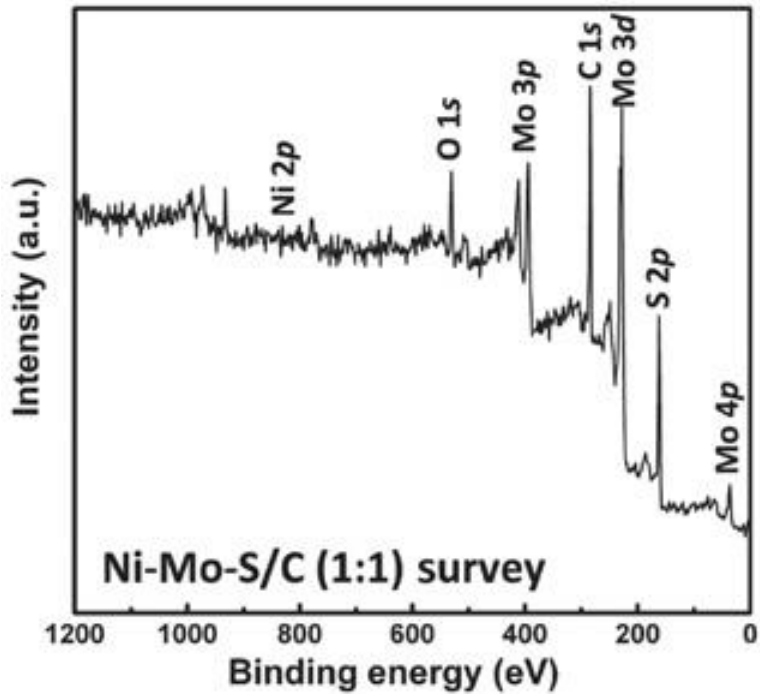
Author: Shihui Zou

Translator: Tianyu Liu

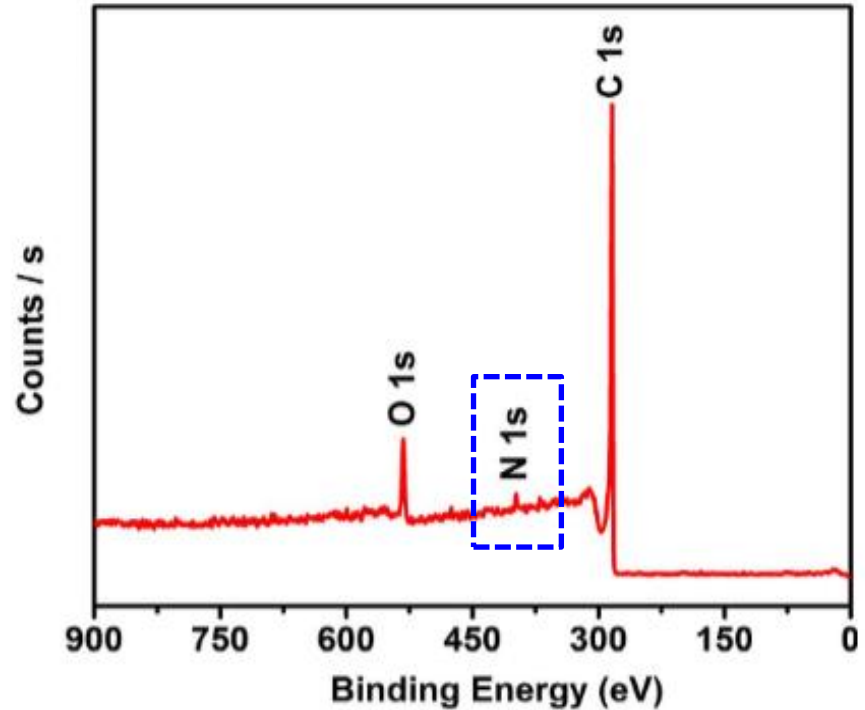




I. Survey Spectrum – Element Identification



Sci. Adv. **2015**, 1, e1500259

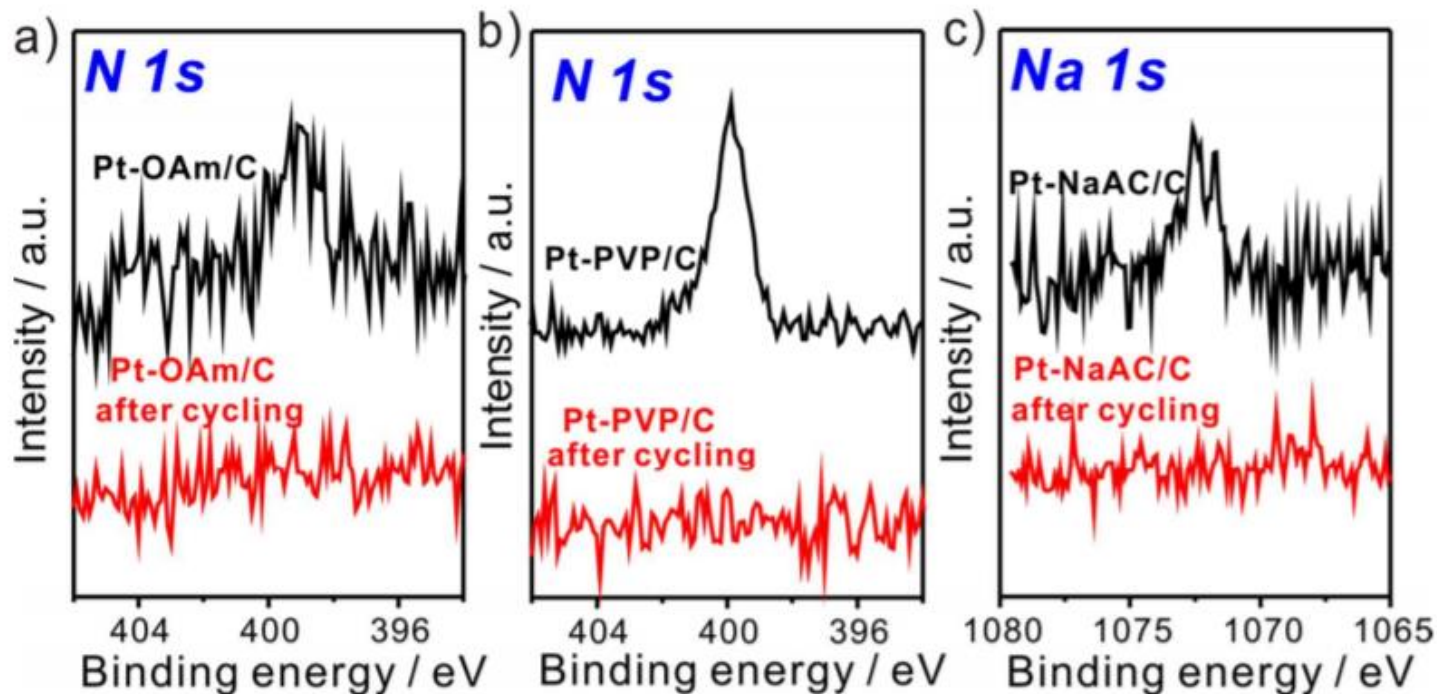


Sci. Rep. **2016**, 6, 26146

Example 1:

- [Left] What elements? **Ni, Mo, O, S**
- [Right] Is the N-doping successful? **Yes.**

2. Presence of Peak

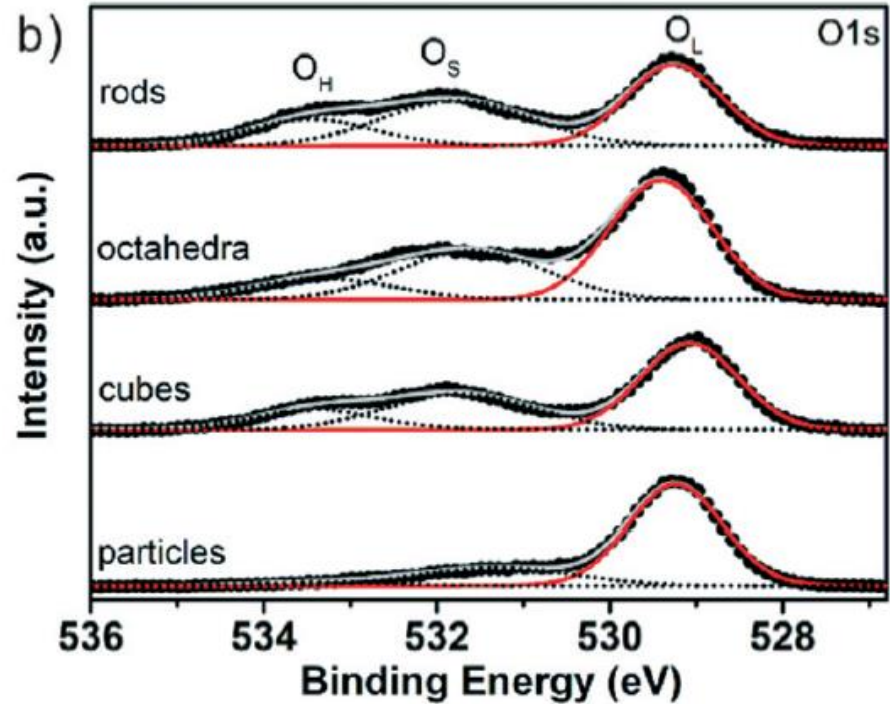
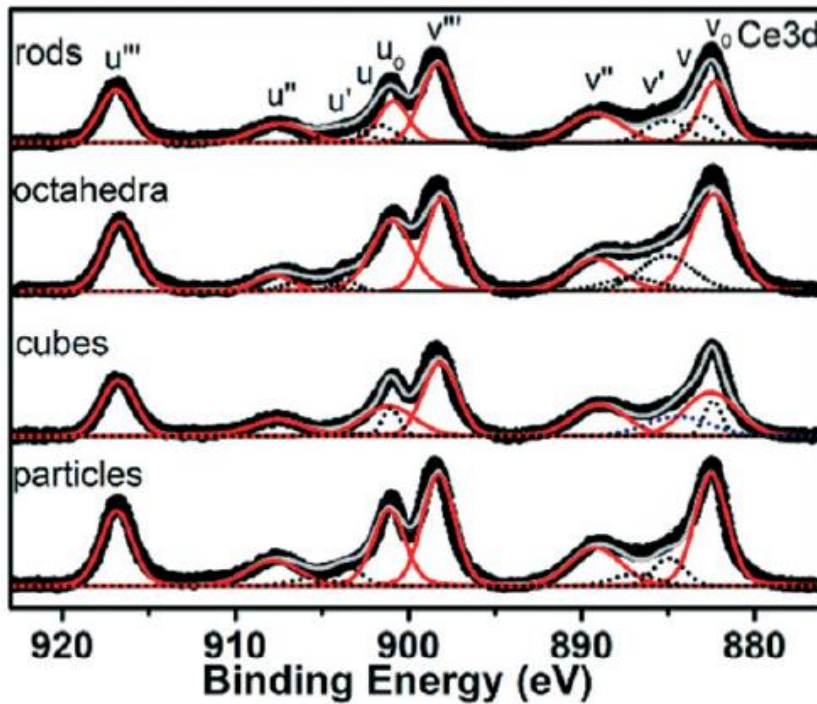


ACS Catal. **2018**, 8, 8484–8492

Example 2:

- After cycling, the N element in the compounds was lost or significantly reduced
- Reasons for peak absence: no element or content below 0.1 atom%

2. Peak Position



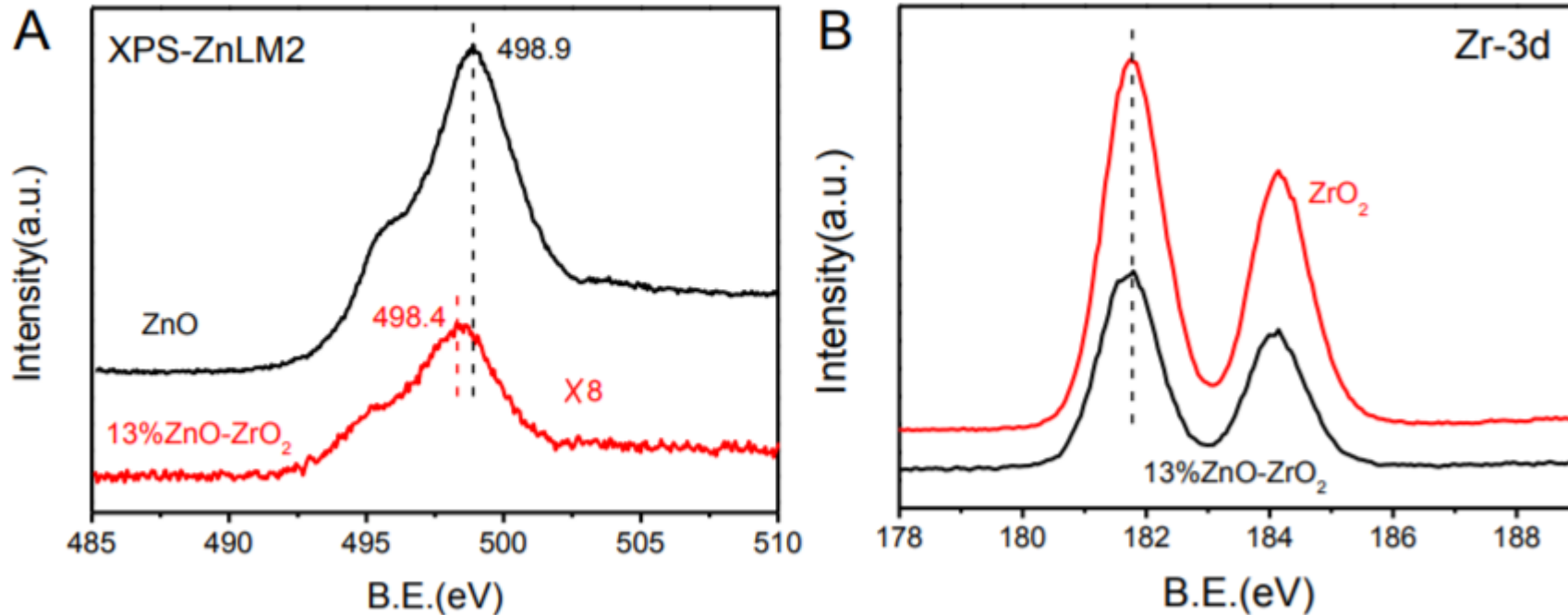
Catal. Sci. Technol., 2019, 9, 2960

Example 3:

➤ What elements should these peaks be assigned to?

Look up in references, databases, or handbooks.

3. Peak Shift



Sci.Adv. **2017**, 3, e1701290

Example 4:

- The Zn 2p peak of 13%ZnO-ZrO₂ shifts 0.5 eV compared to that of ZnO.
- Which direction? Toward lower binding energy – Zn gets electrons (from ZrO₂).



4. Peak Intensity or Area

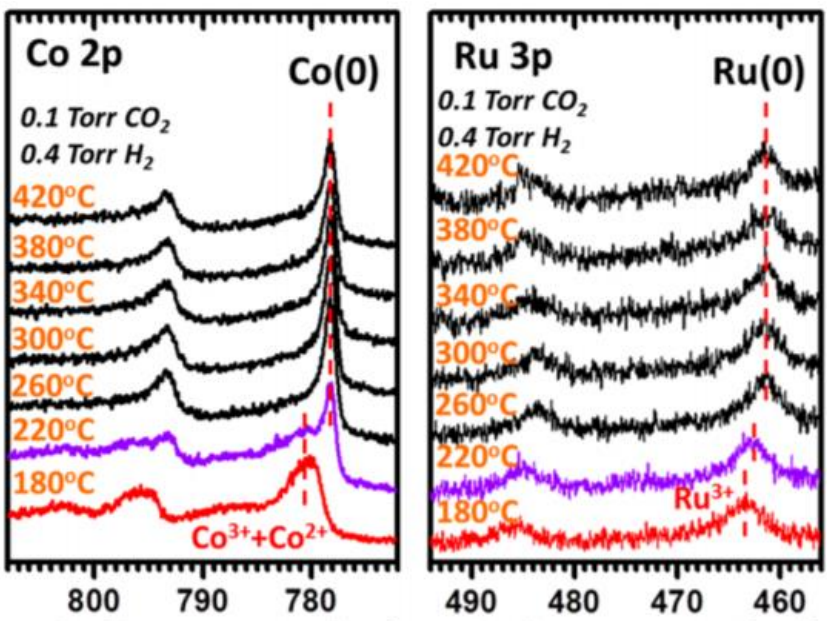


Table 1. Fraction of Ru in the Total of Ru and Co in the Surface Region of $(\text{Co}_{0.95}\text{Ru}_{0.05})_3\text{O}_4$ Catalyst and the Corresponding Conversion and Selectivity

temp (°C)	Ru/(Ru + Co) ratio (%)	conversion of CO ₂ (%)	selectivity to CH ₄ (%)
180	9.3	0.0	0.0
220	10.6	2.5	92.6
260	11.9	13.2	98.0
300	13.6	24.8	98.7
340	14.2	30.4	98.7
380	14.1	33.5	98.4
420	14.8	34.2	97.4

ACS Catal. 2012, 2, 2403–2408

Example 5:

➤ peak area → relative content → surface composition

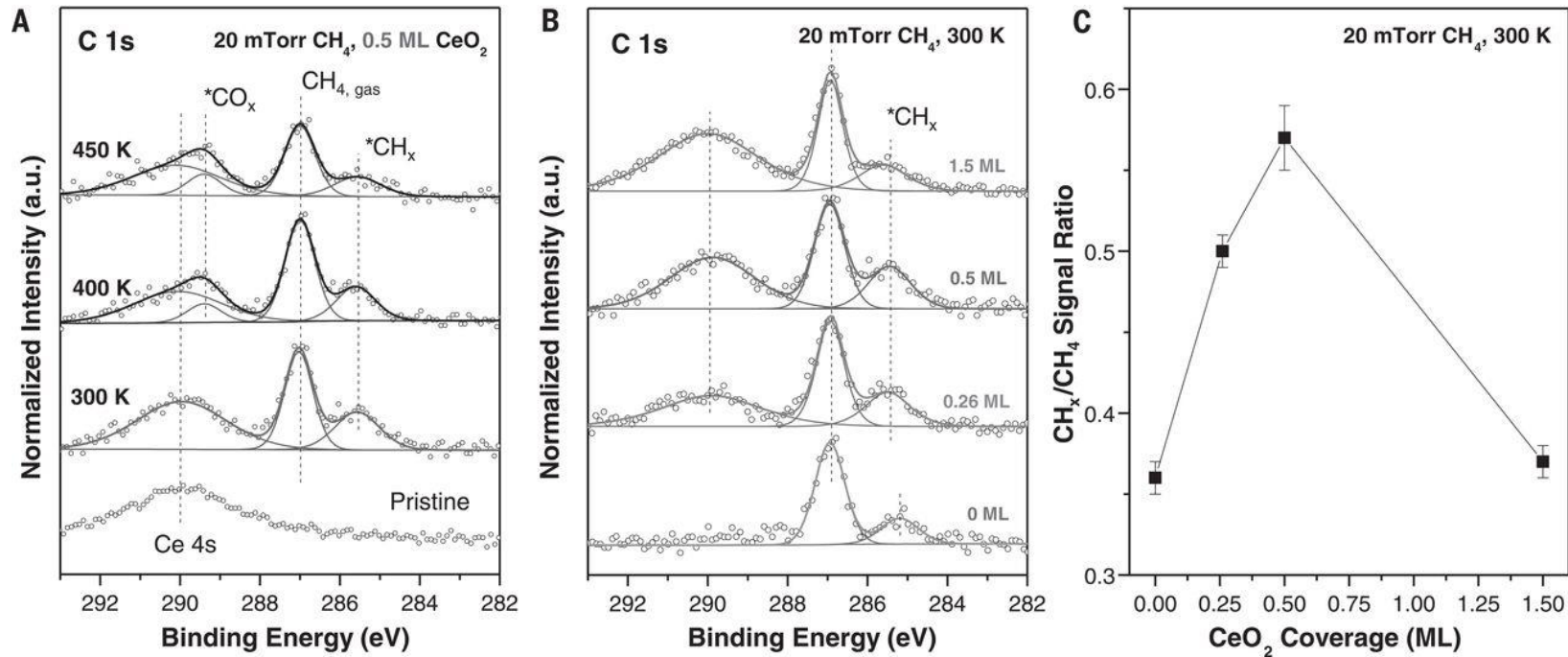
In this example, temperature ↑, Ru ↑ (determine from peak intensity)



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4. Peak Intensity or Area



Science 2020, 368, 513-517

Example 6:

➤ peak area → relative content → surface composition

CH_x/CH₄ ratio changes with CeO₂ coverage and reaches the highest when the coverage is around 0.5 ML.

X-Ray Photoelectron Spectroscopy (XPS)

Data Analysis

Author: Shihui Zou

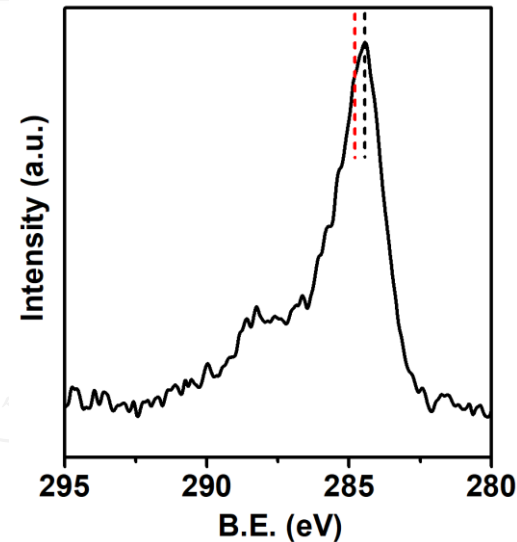
Translator: Tianyu Liu



Steps of XPS Data Analysis



1. Survey Spectroscopy
2. **Charge Correction**
3. Baseline Subtraction
4. **Peak Deconvolution and Fitting**
5. Semi-Quantitative Analysis



Charging Effect: The surfaces of insulators and semiconductors can build up positive charges due to continuous escape of electrons without replenishment. The generation of positive charges due to loss of surface electrons is termed charging effect.

Charging effect creates a steady, positive potential. This potential restrains electrons from escaping. Therefore, charging effect deviates the binding energy and reduces accuracy. **Charge correction** is performed to eliminate the charge-effect-induced deviation.

I. Four Methods for Charge Correction



1. Adventitious C 1s — easy, widely used, but might introduce large errors. **C-C, C-H: 284.6-284.8 eV** *Angew. Chem. Int. Ed.* 2020, 59, 5002-5006
2. Peaks from the **stable** component of the sample, e.g., Si 2p of SiO₂
3. Sputter Au islands **Au 4f_{7/2} = 84.0 eV**
4. Inject trace amount of Ar and use Ar 2p as an internal standard

Not a single method ensures 100% accuracy.

Select the one that is most applicable and feasible for you.

2. Principles for Peak Deconvolution

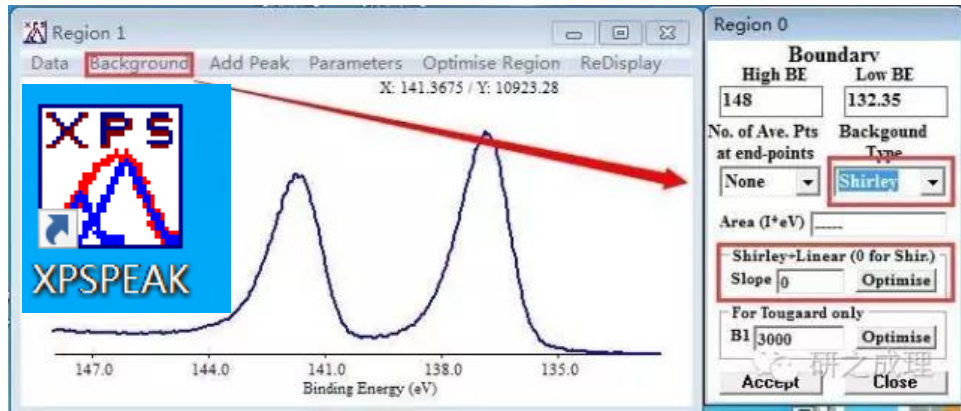


Key parameters:

peak position, FWHM, peak intensity or area, peak symmetry, peak number, etc.

- When fitting peaks, one needs to consider the assignment of each deconvoluted peaks. Arbitrarily adding deconvoluted peaks is prohibited.
- When fitting doublets induced by spin-orbital coupling, one needs to check that the peak separation, intensity ratio, and FWHW are reasonable. For example, intensity ratio:
 $2p_{1/2}:2p_{3/2} = 1:2$ (except TiO_2 and V_2O_5 . Their 4p electrons do not follow)
 $3d_{3/2}:2d_{5/2} = 2:3$
 $4f_{5/2}:4f_{7/2} = 3:4$
Coster-Kronig transition
- **Pay extra attention to overlapped peaks**
- The asymmetry of 2p peaks of transition metal elements.

2. Software for XPS Peak Analysis



AVANTAGE 5.52
Surface Chemical Analysis

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SCIENTIFIC

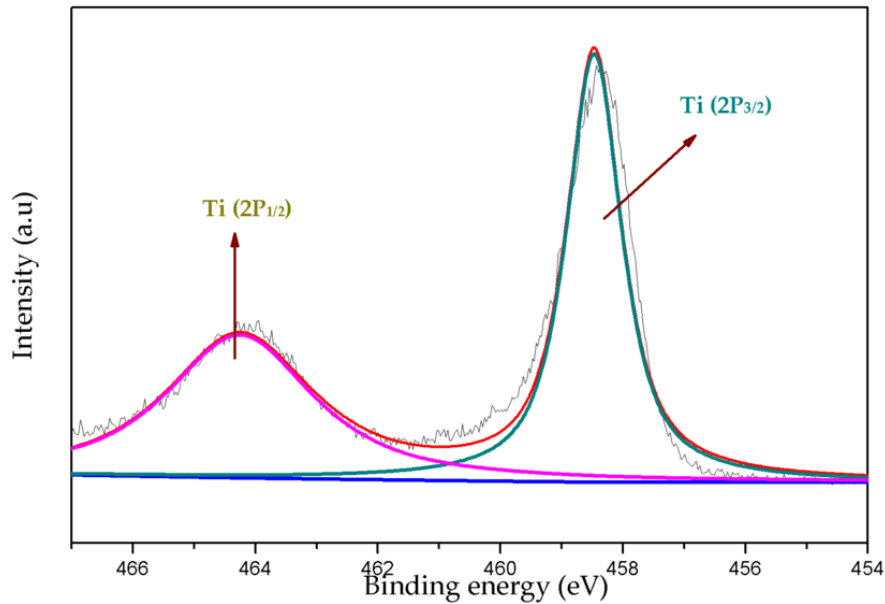
Peak Fitting with CasaXPS

a Casa Pocket Book

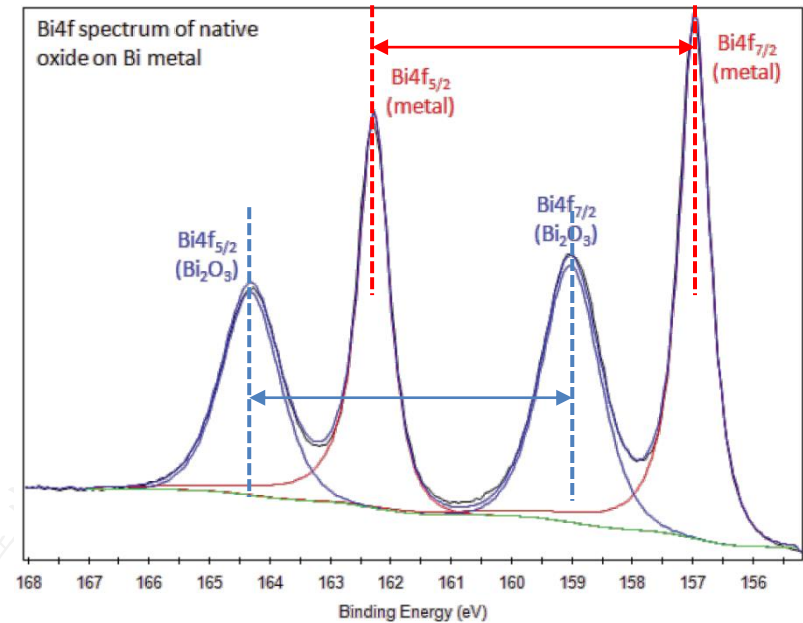
John Walton
Paul Wincott
Neal Fairley
and Alan Carrick

Acolyte Science

3. Requirements for XPS Peak Analysis



$$2p_{1/2}:2p_{3/2} \neq 1:2$$



$$4f_{5/2}:4f_{7/2} = 3:4$$

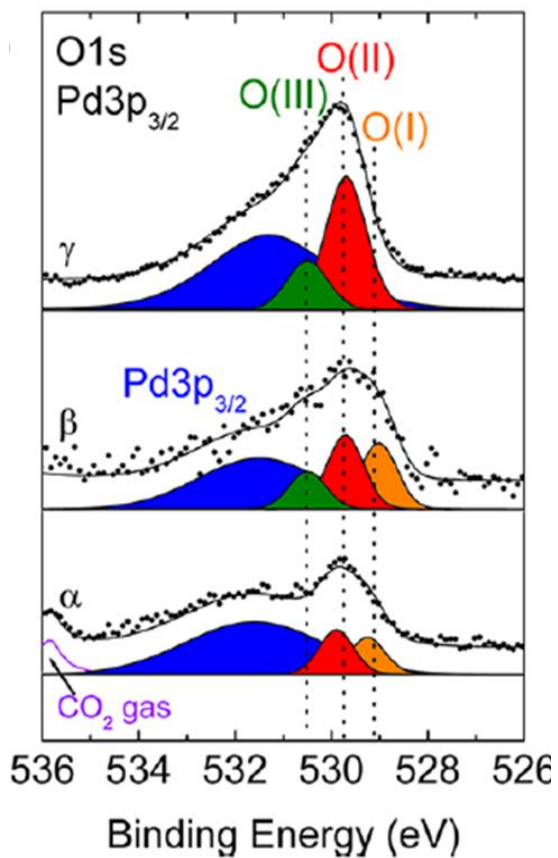
1. Separation of a set of satellite peaks shall remain the same [Right]
2. Special peak area ratio
3. FWHMs of different valences might differ, but those of the same valence of an identical element should remain the same.



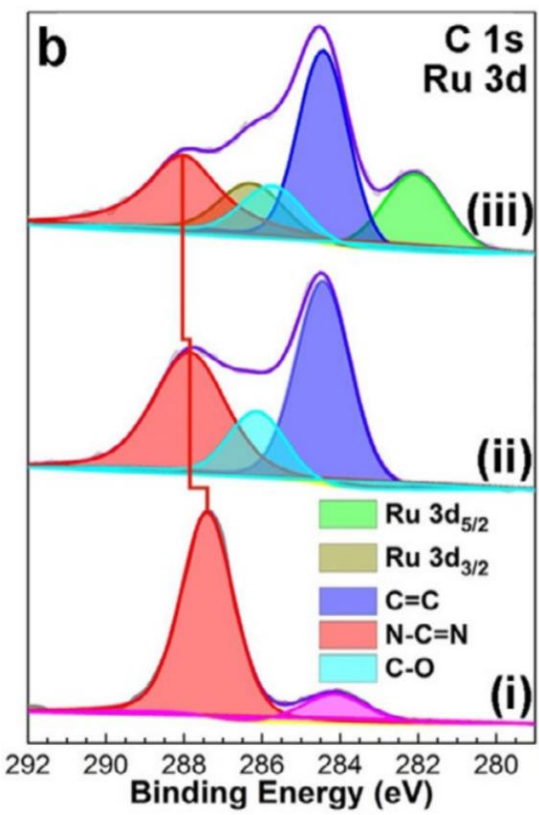
3. Requirements for XPS Peak Analysis

➤ Pay attention to **peak overlapping**

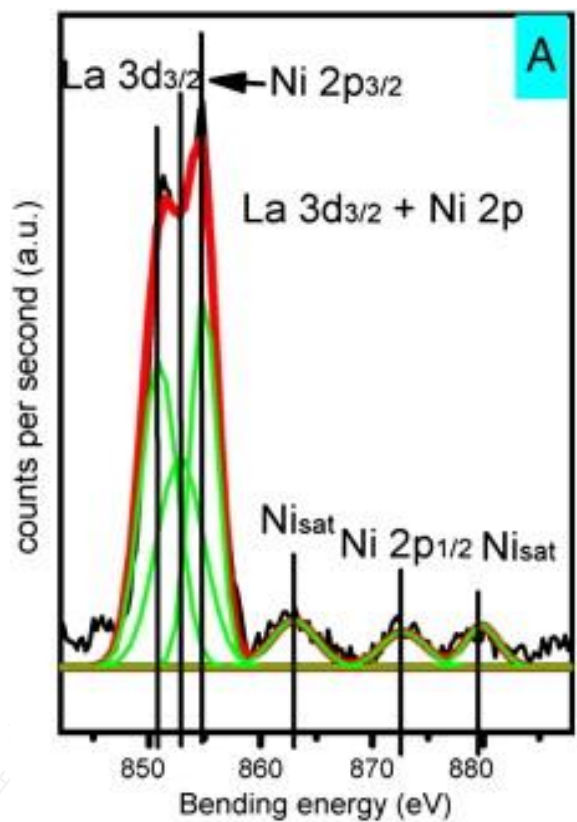
(different peaks displaying the same or nearly identical binding energy)



O 1s & Pd 3p



C 1s & Ru 3d



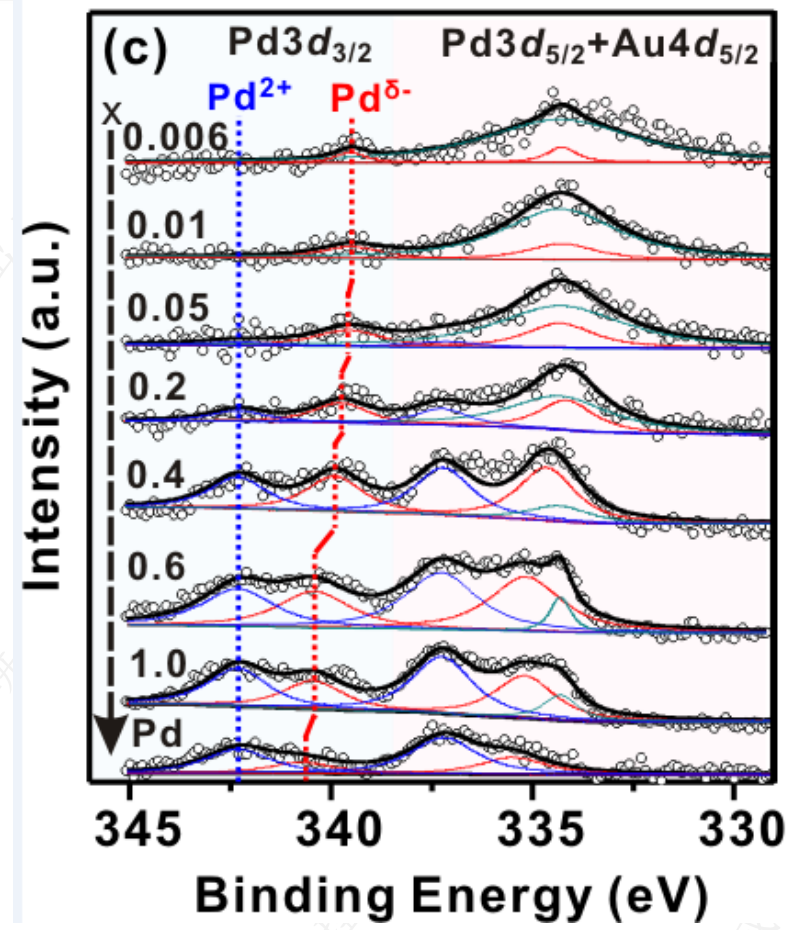
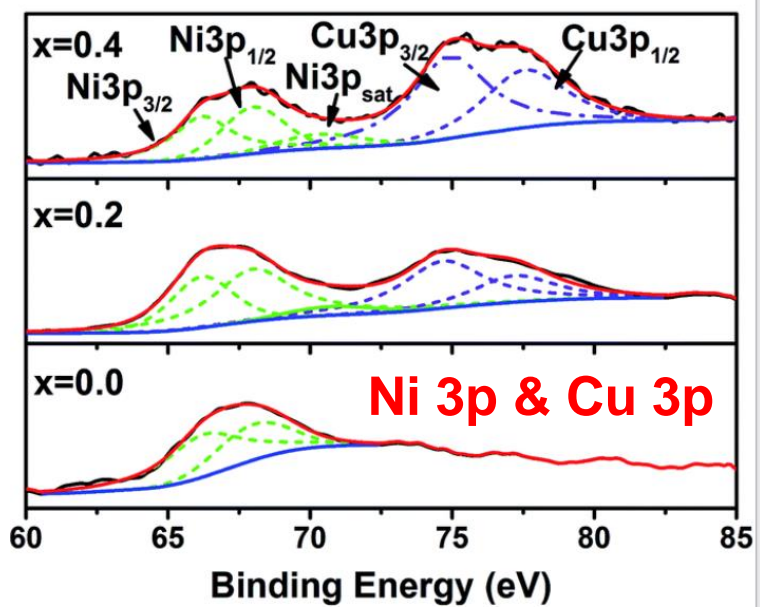
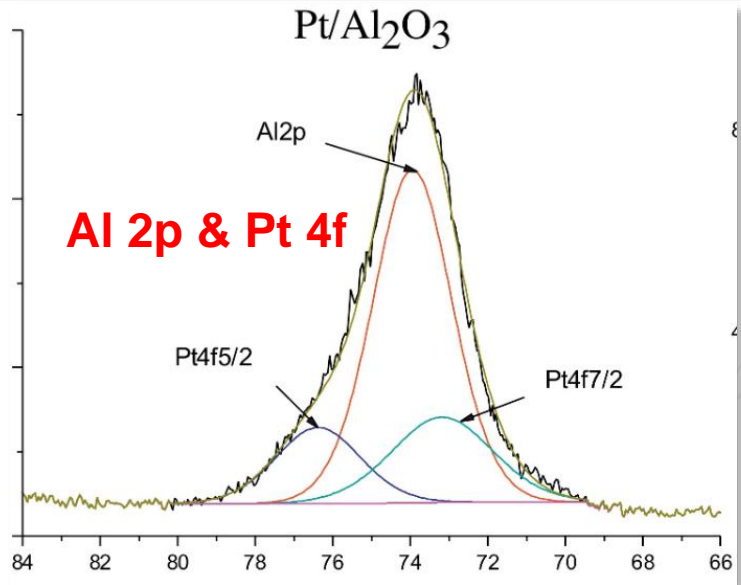
Ni 2p & La 3d

J. Phys. Chem. C **2012**, 116, 18691–18697; *ChemSusChem* **2018**, 11, 130 – 136; *Catal. Commun.* **2011**, 12, 817-821

3. Requirements for XPS Peak Analysis



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Pd 3d & Au 4d

Ref.: *Appl. Catal. B* **2016**, 185, 77-87; *RSC Adv.*, **2017**, 7, 41847-41854; *Chin. J. Catal.* **2020**, 41 (8), 1240-1247

Summary of Overlapped Peaks



Mg K α

N KVV & Ce 3d

O KVV & Co 2p, Ba 3d

F KLL & Mn 2p

Na KLL & C 1s, K 2p, Ca 2p

Ti LMM & La 3d, Ni 2p

V LMM & Co 2p, Ba 3d

Mn LMM & Mn 2p, Fe 2p

Co LMM & Sn 3d

Ni LMM & Sn 3d

Cu LMM & Pd 3d, Cd 3d

Al K α

F KLL & La 3d

Na KLL & Sn 3d

Mg KLL & Ca 2p, Rh 3d

Fe LMM & Co 2p

Co LMM & Co 2p, Fe 2p

Ni LMM & Mn 2p

Zn LMM & Sn 3d

Ce M₄₅N₄₅N₄₅ & La 3d_{5/2}

O KVV & Nd 3d