

过渡元素XPS分析II--数据处理

XPS analysis for transition-metal elements (II): Data processing

吴正龙

北京师范大学分析测试中心

XPS分析方法通则及XPS 标准术语的介绍

Introduction to General rules for XPS analysis method, and XPS Vocabulary

基本理论

- 本底扣除
 - Shirley
 - Tougaard (Seah REELS)

基本理论

- 过渡元素XPS中光电子激发
 - 自旋轨道分离
 - CK跃迁
 - 多电子相互作用
 - 终态效应
 - 第3周期过渡元素 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^n 4s^2$
 -
 - 带间跃迁、带内跃迁

基本理论

- 过渡元素XPS谱特征
 - 不对称、拖尾
 - 多峰
 - 多价态*
 - $\text{Ti}^{2+}, 3+, 4+$; $\text{Fe}^{2+, 3+}$; $\text{Cr}^{2+, 3+, 6+}$; $\text{Mn}^{2+, 3+, 4+}$;
 $\text{V}^{3+, 4+, 5+}$; $\text{Co}^{2+, 3+}$; $\text{Ni}^{2+, 3+}$
 - $\text{Cu}^{1+, 2+}$; $\text{Zn}^{1+, 2+}$
 - $\text{Sb}^{2+, 5+}$; $\text{Sn}^{2+, 4+}$
- 如何谱峰指认和价态分析、定量分析？

探究谱峰结构及分析方法、建立谱图库应用于指认价态、定量分析

- 过渡元素化学性质活泼；
 - 多价态，与不同元素化合-谱峰结构变化
- 化学环境、物理环境影响谱峰
- XPS多峰结构以及终态、Shake-up等

背景扣除：分峰前先扣除背景

- 对于HAS的CAE，响应函数(IERF)校正

$$j(E) = j_0(E) * E^{0.7} \quad j_0(E) \text{ 测量谱}; j(E) \text{ 校正谱}$$

*IERF $\sim E^\alpha$, 这里 $\alpha = 0 \sim -1$, 随 E 增加 α 负增加, 即
KE 高能 IERF = E^{-1} ;
约 KE = 500eV IERF = $E^{-0.5}$;
在 Avantage 中 取 IERF = $E^{-0.6}$;*

E_{\min} (最低) 处为 $J(E)$ 零, 常数扣除背景

背景扣除：分峰前先扣除背景

- Shirley Background

$$F_{k+1}(E) = j(E) - j(E_{\min}) \frac{\int_E^{E_{\max}} F_k(T) dT}{\int_{E_{\min}}^{E_{\max}} F_k(T) dT}$$

优点：计算方便，……；
缺点：物理意义不明确。

*k*为迭代次数，取 $F_1(E)=j(E)=j_0(E)$ ， $F_{k+1}(E_{\min})=0$ ，
 $F_{k+1}(E_{\max})=j(E_{\max})$ ，确定 $j(E_{\min})$ 实际使用中取3点或多点平均值；
背景与高KE侧的峰面积成正比；
为避免出现负值采用smart方法

背景扣除：分峰前先扣除背景

优点：物理意义明确；

缺点：计算困难，实验数据量大，……

• Tougaard Background

$$F(E) = j(E) - \lambda_i \int_E^{+\infty} j(E') K(E' - E) dE'$$

$$\lambda_i K(T) = \frac{BT^2}{(C + T^2)^2}$$

或者

$$\lambda_i K(T) = \frac{BT^2}{(C - T^2)^2 + DT^2}$$

损失能量T的非弹性散射微分截面K(T)

为避免Plasmon和Shake-up特征峰采用3参数(B C D)的微分截面函数

推荐尝试使用

1) Tougaard 普适参数, B=3250 eV², C=1643 eV²

2) Seah-Tougaard 普适参数, B=1430 eV², C=756 eV²

峰拟合

- Voigt (GL)

- GLP

$$GLP = \exp[-\ln 2 * (1 - m) \frac{(E - E_0)^2}{\beta^2}] / [1 + \frac{m(E - E_0)^2}{\beta^2}]$$

- GLS

$$GLS = (1 - m) \exp[-\ln 2 * \frac{(E - E_0)^2}{\beta^2}] + m / [1 + \frac{m(E - E_0)^2}{\beta^2}]$$

$$\beta = 0.5 * FWHM$$

- 尾部函数T

$$T = TM * CT + (1 - TM) \exp(-D * ET)$$

$$D = (E_0 - E) / \beta, \quad \beta = 0.5 F(WHM), \quad E < E_0$$

- 谱峰的表达

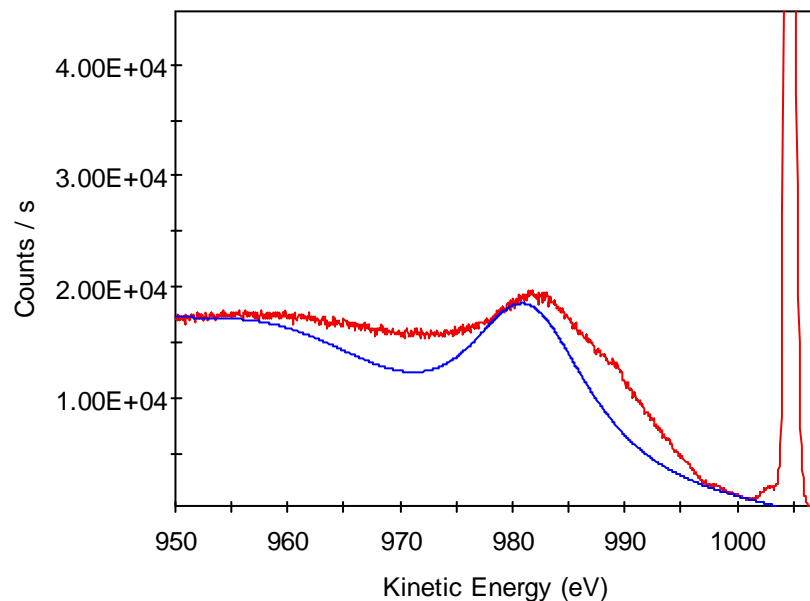
$$Y = H * [GL + (1 - GL) * T] \quad (E < E_0)$$

$$Y = H * GL \quad (E \geq E_0)$$

背景扣除实例

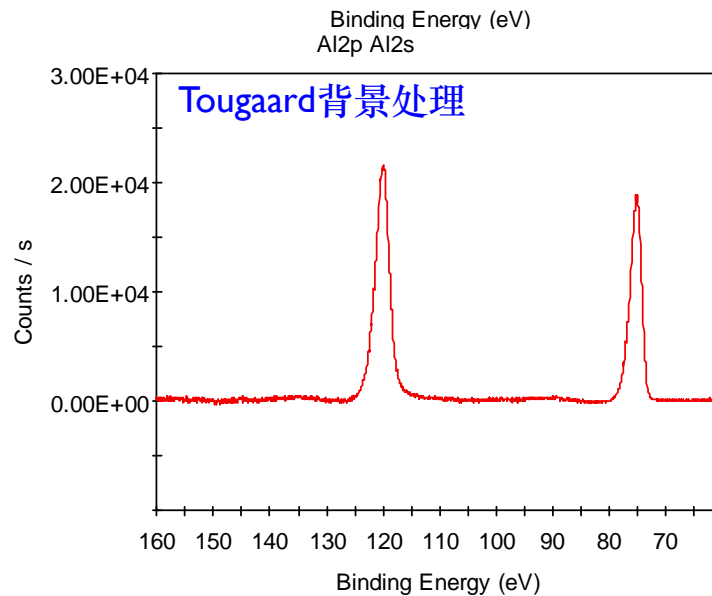
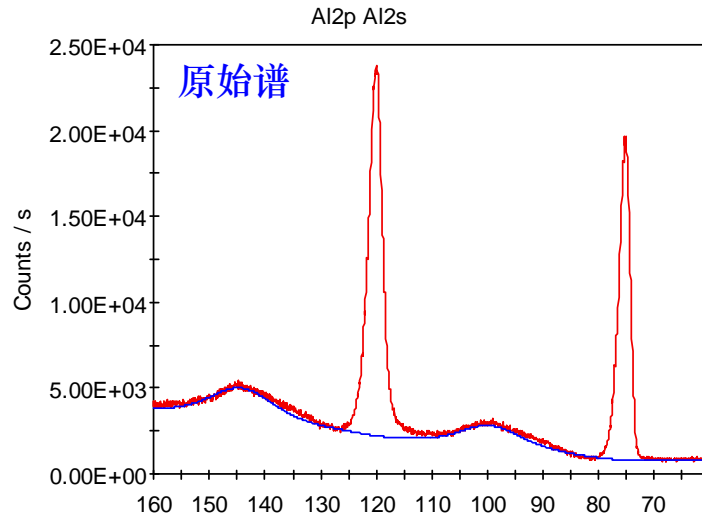
Al₂O₃/Al的 REELS

Scan 979eV



- * 样品性质差异，背景存在差异；
- * **思路**：利用REELS找出Tougaard中的B，C，D等参数，用于XPS扣除背景；

纯Al₂O₃的XPS (Al2p、Al2s)

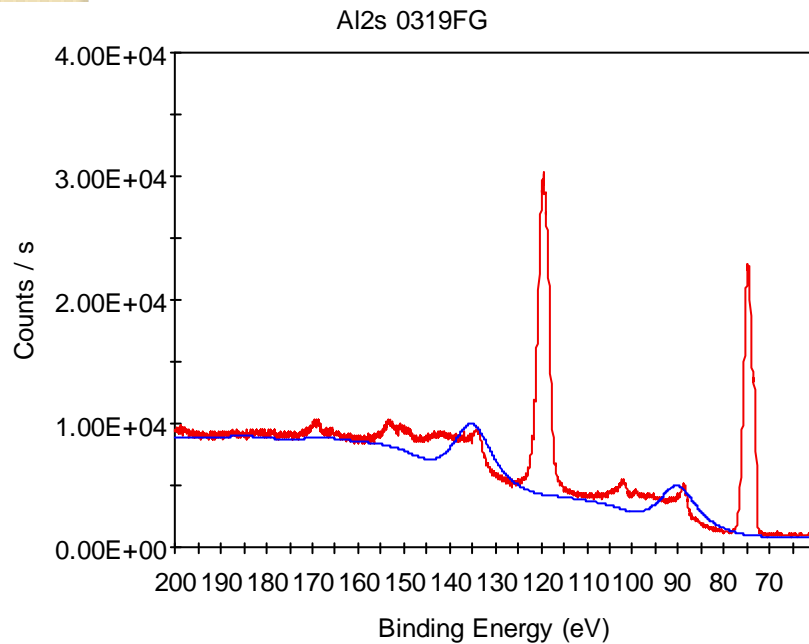


Tougaard中
B=295、C=657、D=295 eV²

等离子激元峰可以通过Tougaard
扣除

Al2p和Al2s峰

- Al₂O₃/Al, 无终态效应等
- 非弹性散射和明显的等离子激元

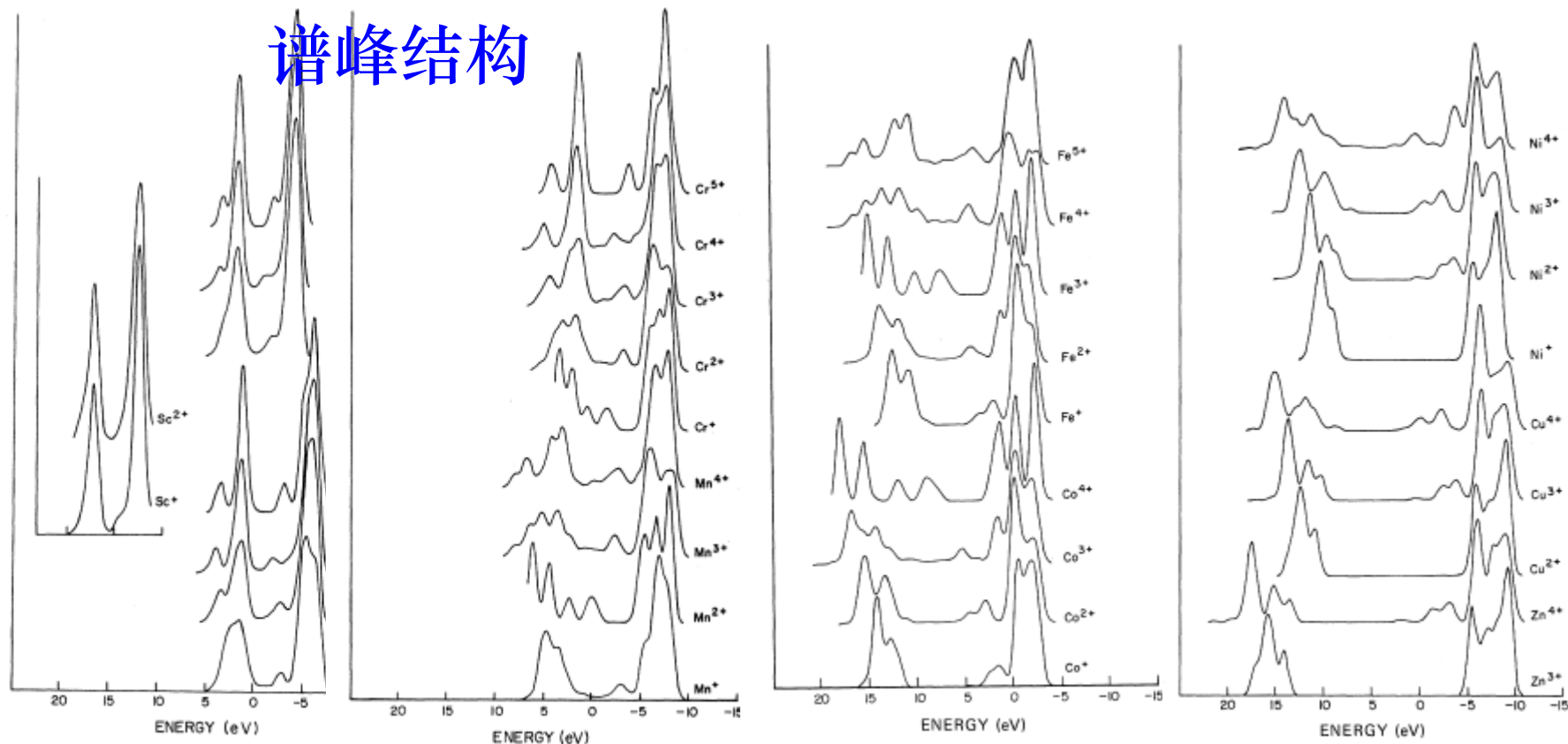


需要完善，谱中出现Al₂O₃和Al的等离子激元峰；需要更复杂的计算，剥离等离子激元峰

影响谱峰结构

- 原子外部 (Extrinsic) : Plasmon, 多电子, 带间跃迁,
- 原子内部 (Intrinsic) : Shake-up satellite, 终态效应峰,
 - 对于低自旋态化合物元素, 终态效应不明显
 - 如 Ti, V, Cu, Zn
 - 对于高自旋态化合物元素, 终态效应明显
 - 如 Cr, Mn, Fe, Co, Ni

谱峰结构



终态 $2p^53d^n$ ($n=1\sim 10$)

自由离子模型的理论计算XPS谱，希望能用于过渡元素XPS谱峰拟合。

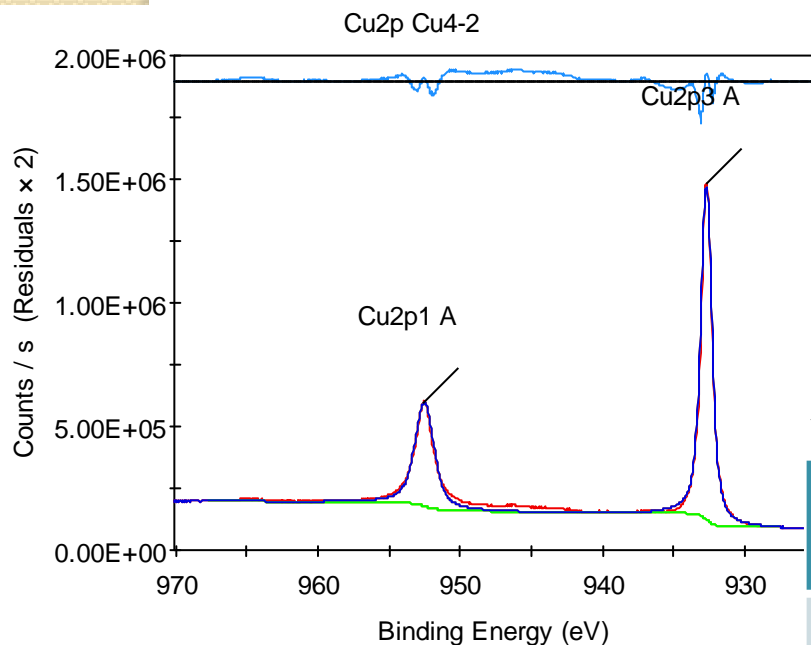
[PRB 12 (1975) 15-19]

结论：同一元素不同价态(外层未成对电子数不同)，其XPS峰形存在差异。

XPS计算谱与实际测试谱

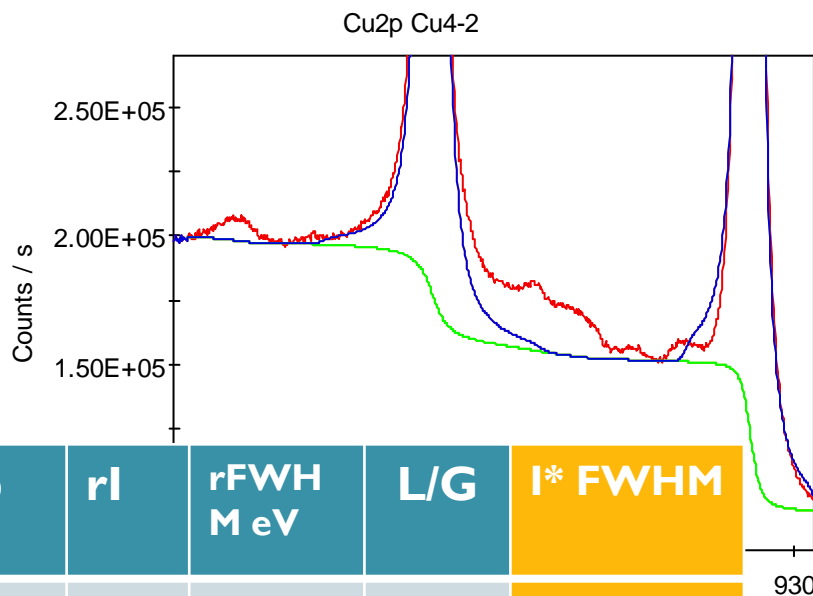
分峰处理方法：参考物质XPS谱拟合得到峰形参数(拟合参数)。
 比较NNLSF。信号电子在不同材料中的散射（背景）、损失等不同

例如，Cu metal



参数

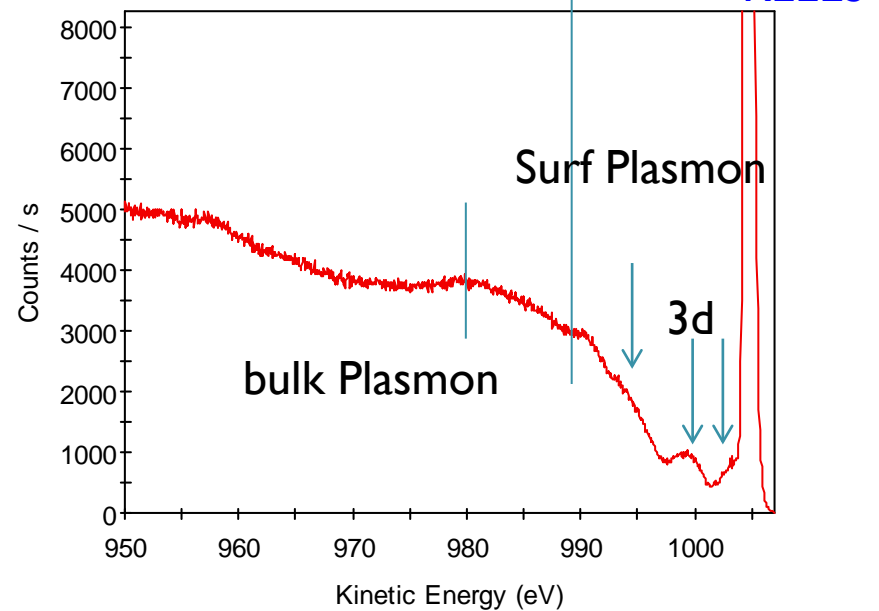
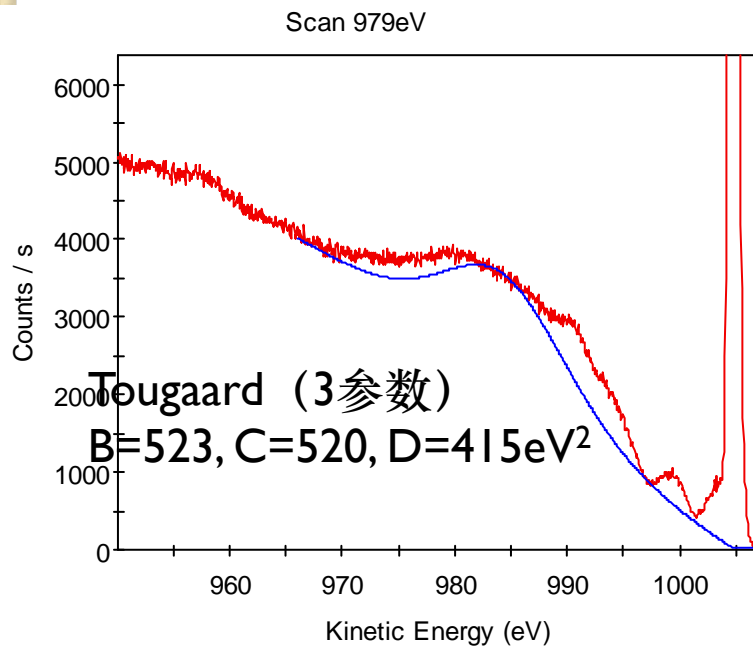
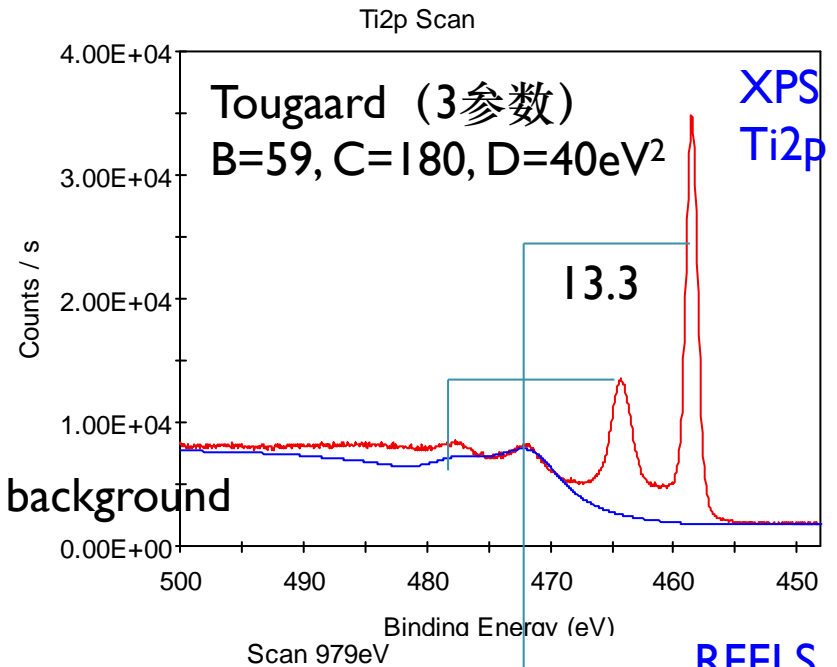
dEb eV	rl	rFWH MeV	L/G	I* FWHM
19.81	0.31	1.69	45%	0.532



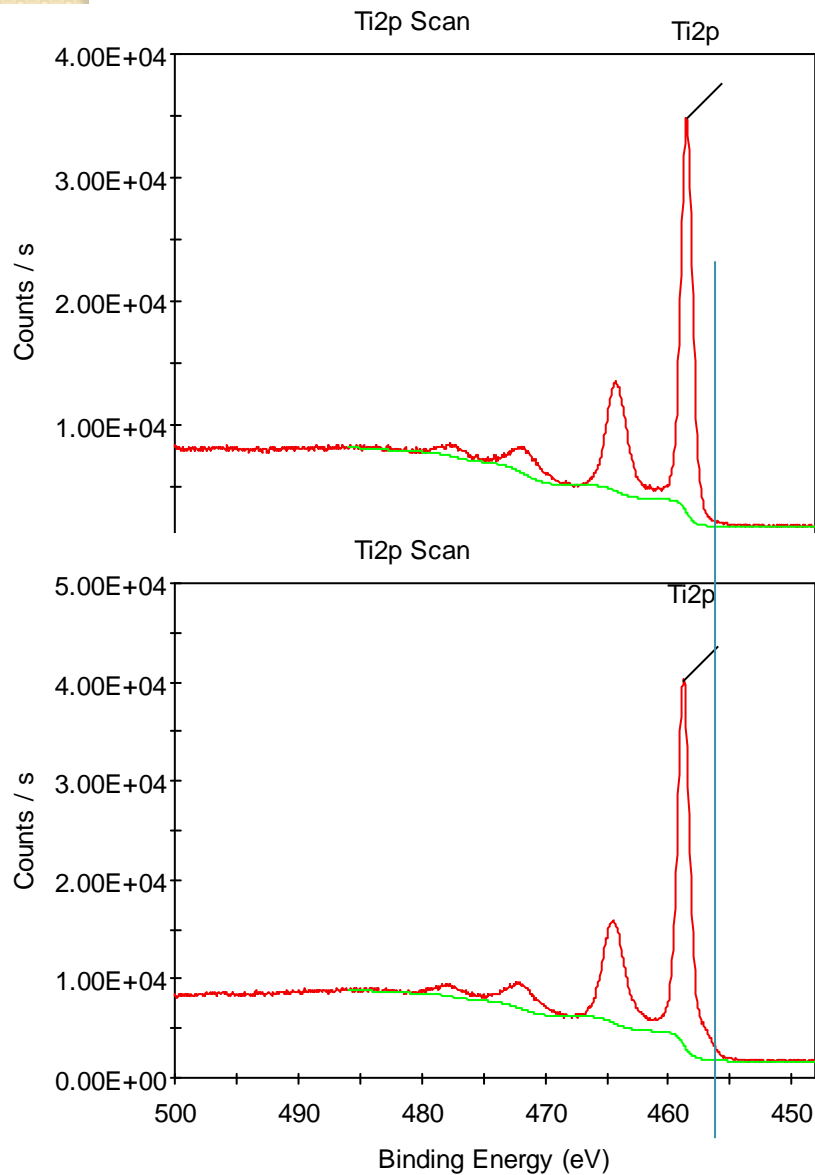
BE	Orbit	Ratio	Orbit (eV)	Ratio	param (eV)	Converge	Mix (%)	Height (%)	Exponent

TiO₂

- 2p1与2p3
- Tougaard(3参数)
考虑plasmon。



Ti2p分析:TiO2

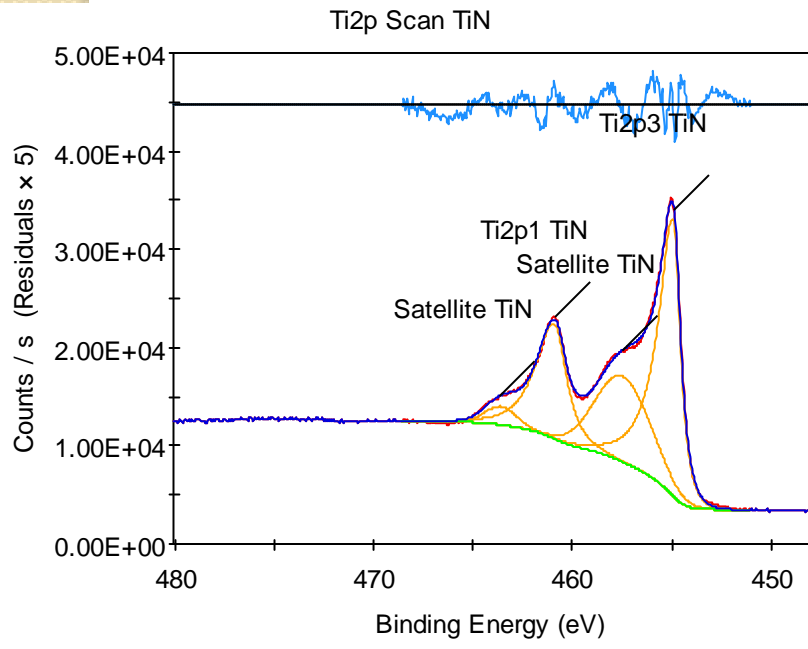


TiO2 XPS谱

- 1: Ar⁺刻蚀诱导还原态Ti^{x+};
- 2: 4:1>2:1, 2p1展宽, CK跃迁;
- 3: plasmon;

过渡金属元素拟合方法探索

- 过渡金属元素XPS谱峰结构复杂，尝试先分析参考样品，获得谱峰峰形参数（拟合参数），再用于实测样品的谱峰分析拟合，……



参考样品TiN 参数

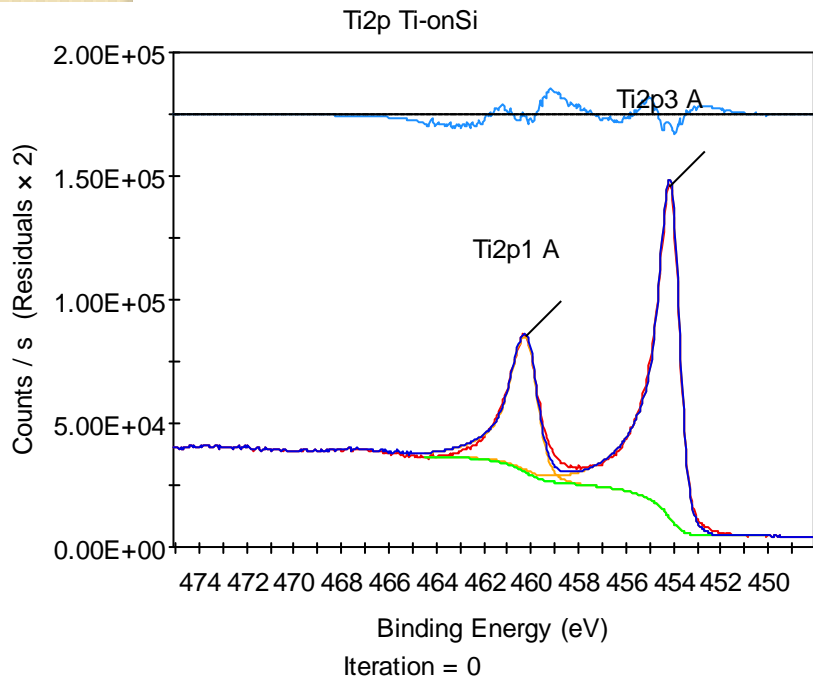
From Avantage

BE (eV)	Ratio	BE (eV)	Ratio	Product	Mix (%)	Height (%)	Exponent

BE (eV)	Ratio	BE (eV)	Ratio	param (eV)	Convolve	Mix (%)	Height (%)	Exponent

- Ref
- Ti 453.8-454.1
- TiC ~454.3
- TiN 454.9
- TiO2 458.5

Pure Ti



参考样品Ti 参数

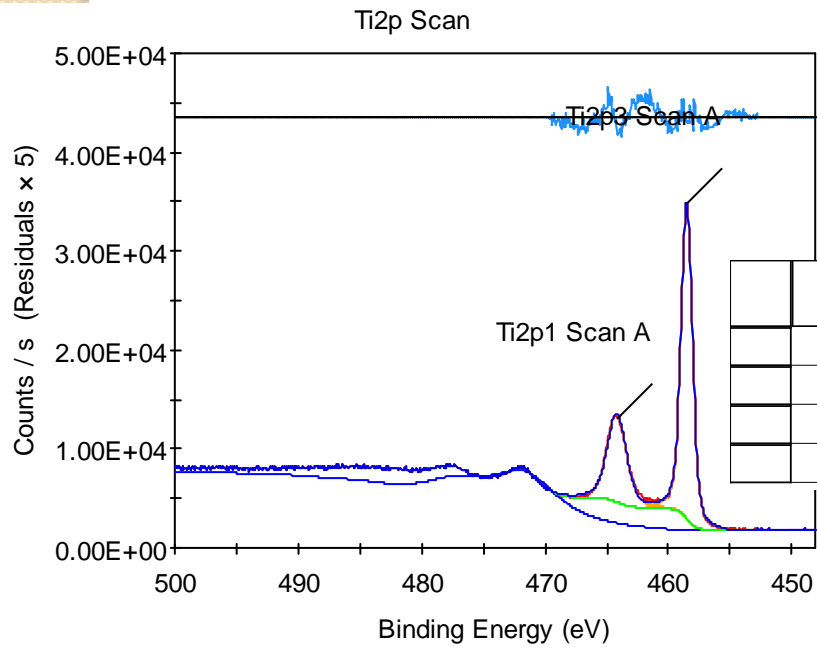
BE	Ratio	Orbital	Ratio	Component	Area (%)	Height (%)	Exponent

拟合参数不同

TiO₂ Ti2p 对称

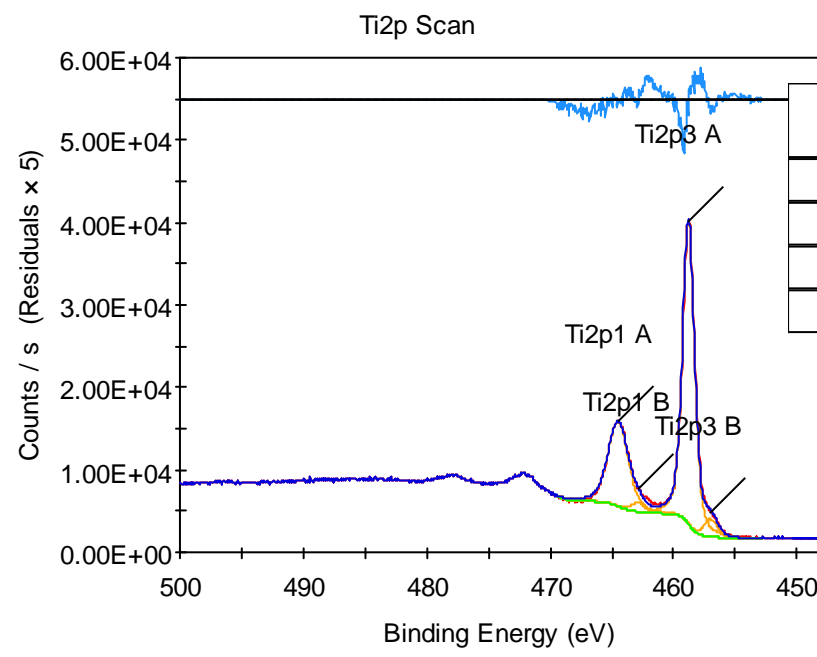
金属Ti Ti2p 不对称, 源于终态效应、多电子激发等

- Ref
- Ti 453.8-454.1
- TiC ~454.3
- TiN 454.9
- TiO₂ 458.5



参考样品TiO₂ 参数
 $\Delta=5.7\text{eV}$, $I3/I1=1/0.28$, $W3/W1=1/1.7$

关键常数: Smart backg, BE, FWHM, 对称



大量TiO₂的XPS测试表明, TiO₂中Ti2p峰形为对称峰, 但存在CK跃迁效应。可以解释Ti⁴⁺为抗磁(自旋为0), 无终态效应-谱峰分裂。

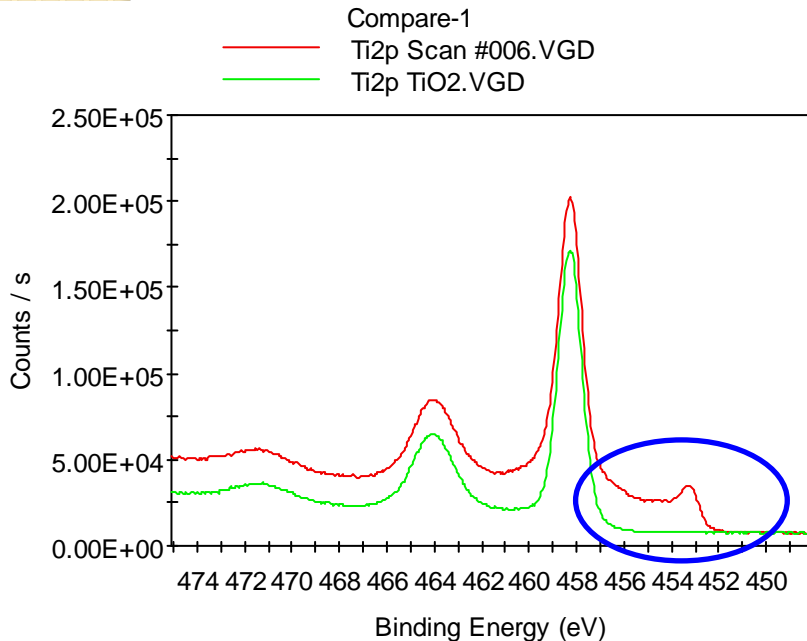
Ti2p谱

- 总结有关Ti的2p峰参数

	峰位eV	背景	峰形	2p峰高比	2p峰宽比	2p ΔE_b eV
TiO ₂	458.7	Shirley	对称	0.3	1.75	5.7
TiO _x	457.0	Shirley	对称	0.4	1	5.7
TiC	453.7	Shirley	非对称 (0.02/2.53/0.034)	0.31	1.6	5.8
TiN	454.9	Shirley	非对称 (0/10.7/.0465) Sat 2.6	0.4	1.68	6
Ti	454.1		非对称 (40.5/0/.0358)	0.4	1.3	6.1

TiO₂/Ti

• 分析



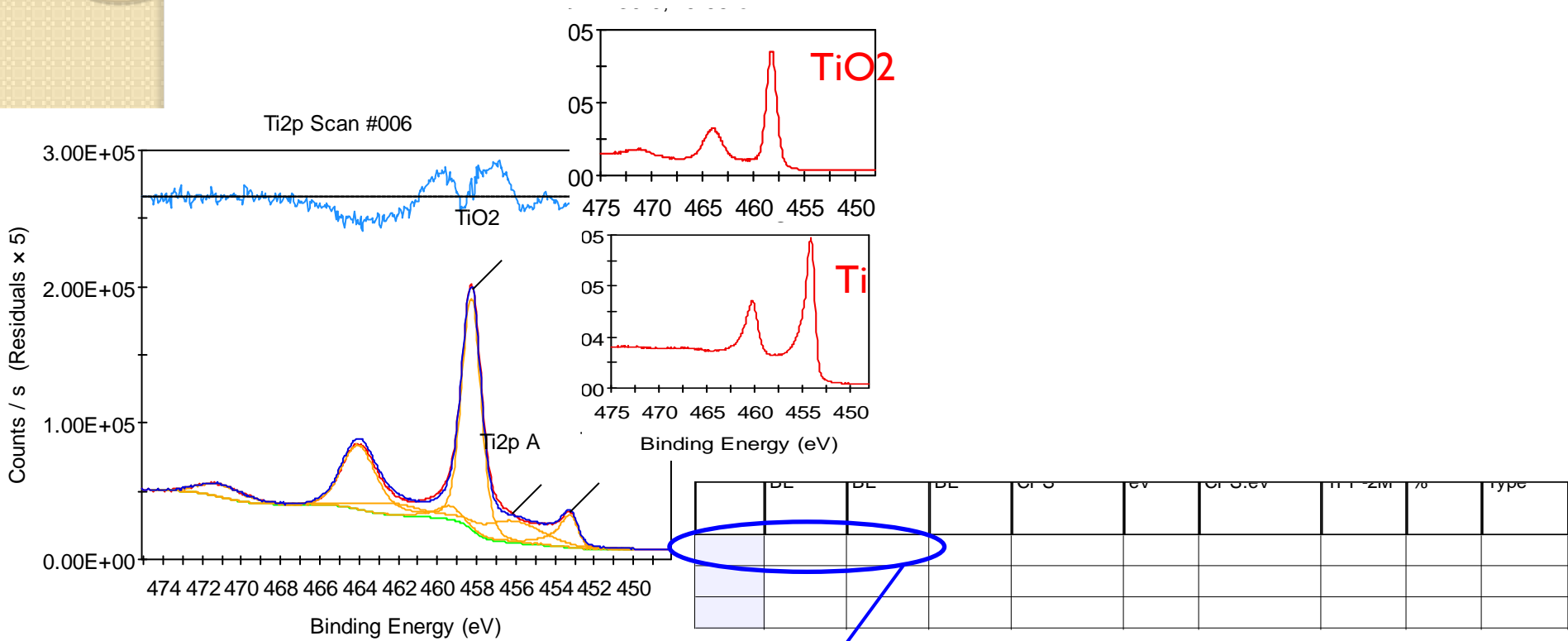
出现纯Ti峰Ti2p_{3/2} 543.1eV同时背景提升，是纯Ti本身出现背景提升还是覆盖层出现的提升？对照Ti-onSi，发现是由于本身背景提升，源于金属Ti的多电子损失或非弹性散射。如何处理该背景，尤其在TiO₂+Ti（混相）中处理数据。

表明纯Ti被覆盖在TiO₂薄膜下。出射信号光电子Ti2p_{3/2}受到TiO₂薄膜散射。通常采用两种技术处理此类问题。

- 1) 在Ti2p峰低动能侧增加拖尾；
- 2) （非均匀物质）覆盖层薄膜/基底背景提升；

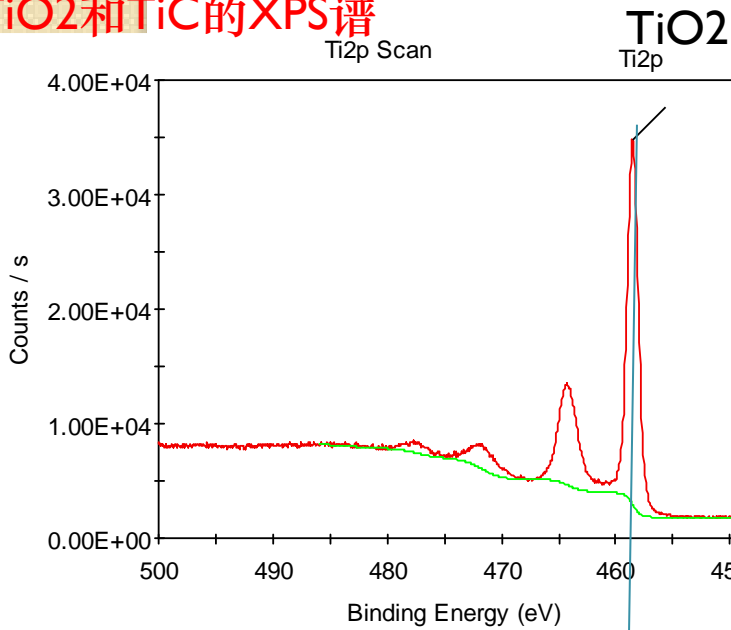
TiO₂/Ti

- 参考峰模板拟合(非线性最小二乘法拟合)

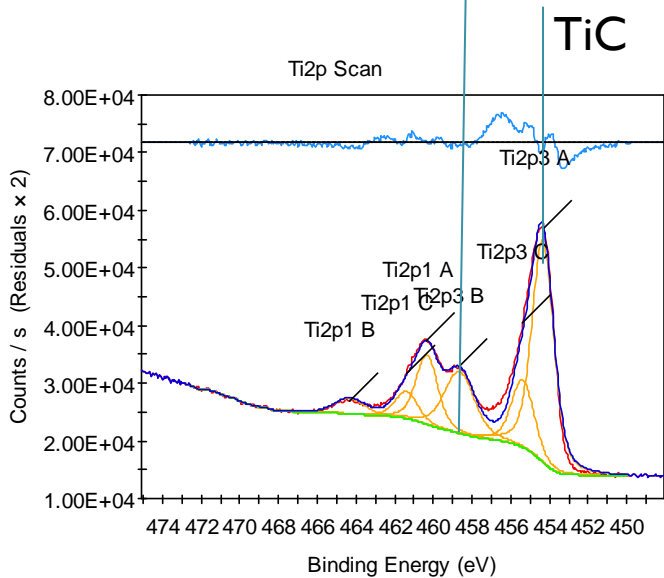


~456eV处添加TiO_x峰, 参考TiO₂和纯Ti峰综合进行拟合。
北京师范大学分析测试中心 电子能谱

TiO₂和TiC的XPS谱



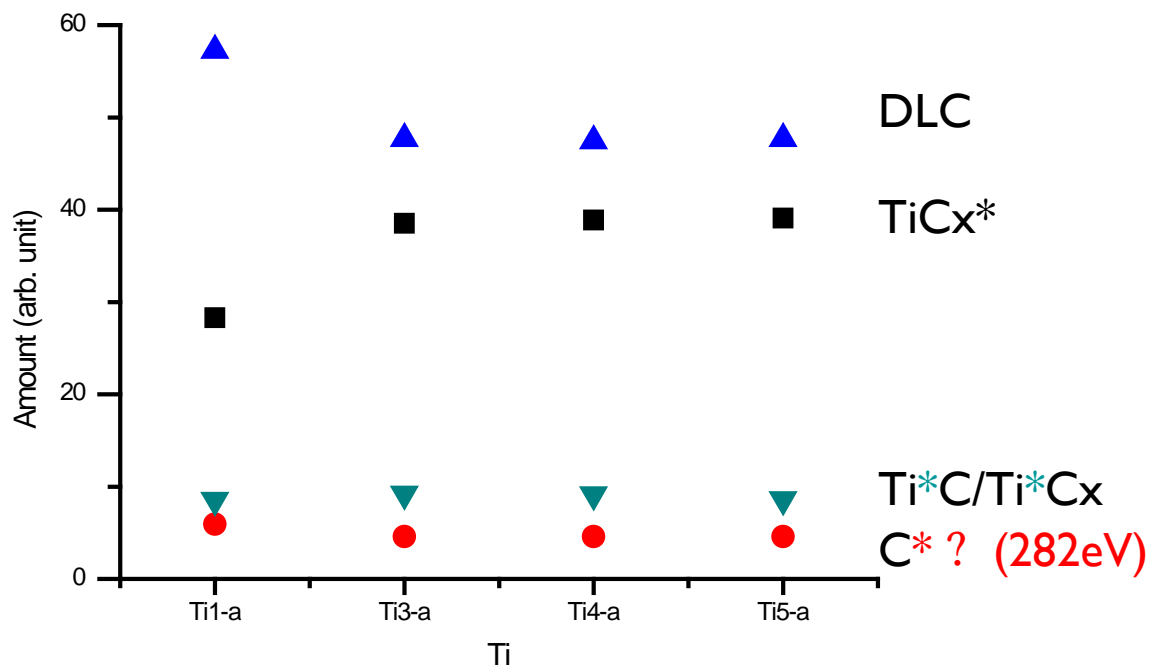
	BE	Orbit	Ratio	Orbit (eV)	Ratio	param (eV)



不同化学态的Ti2p有不同的参数。

TiO₂参数:
 $\Delta=5.7\text{eV}$, $I_3/I_1=1/0.25$, $W_3/W_1=1/2$;

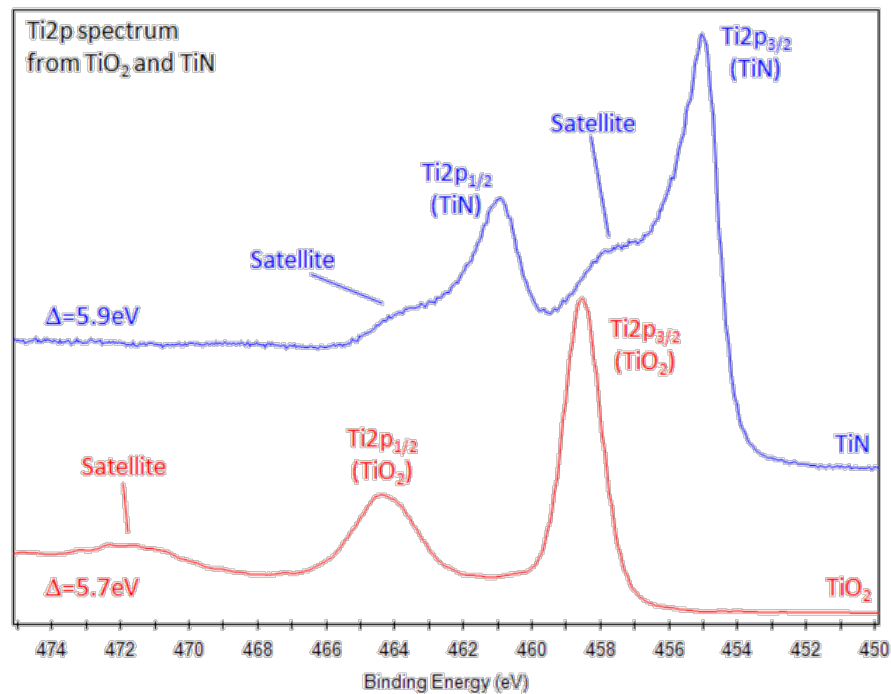
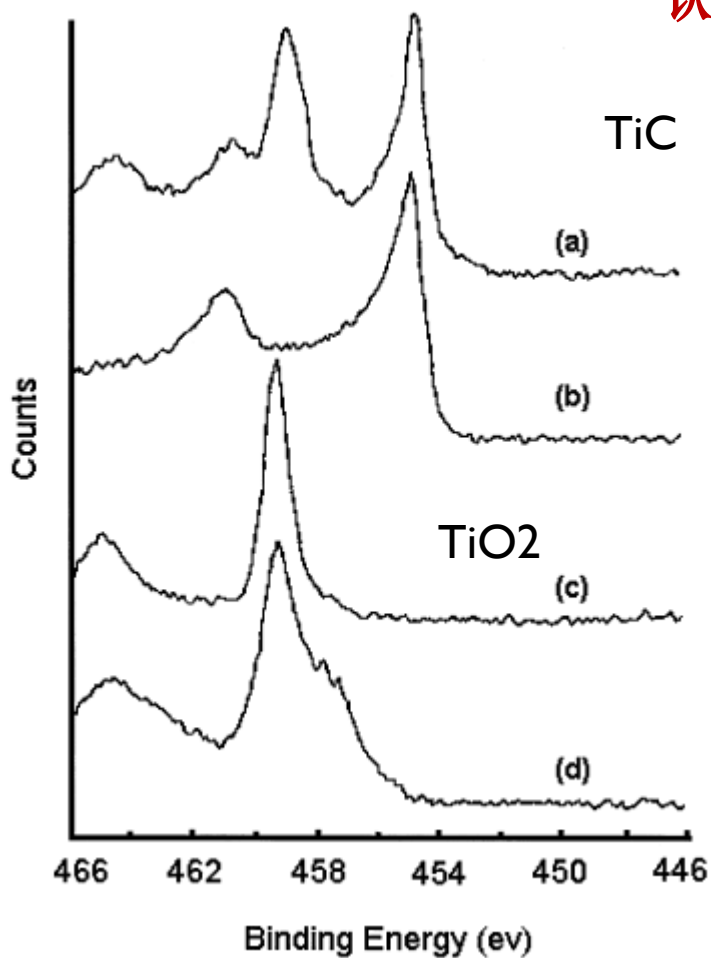
TiC/TiC_x or n-TiC 参数:
 $\Delta=6\text{eV}$, $I_3/I_1=1/0.3$, $W_3/W_1=1/1.7$
 $\Delta=6\text{eV}$, $I_3/I_1=1/0.4$, $W_3/W_1=1/1.3$



TiC/TiC_x 中 Ti与C的比值?

测量DLC薄膜中TiC含量

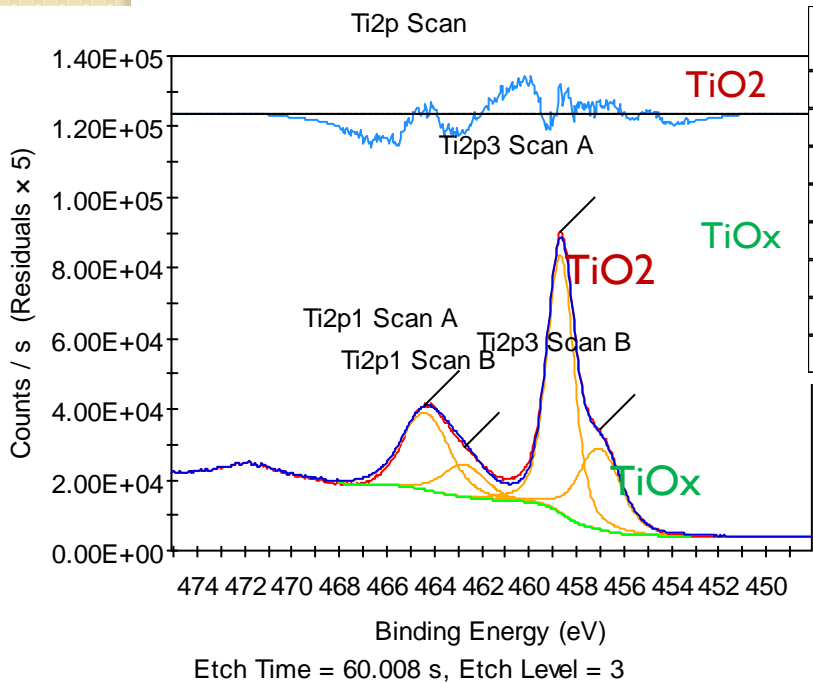
认识TiC/TiO₂/TiN的Ti2p谱峰



Ti(IV)O₂ 抗磁， Ti(IV)C 抗磁， 非对称拖尾来源于多电子带间内激发

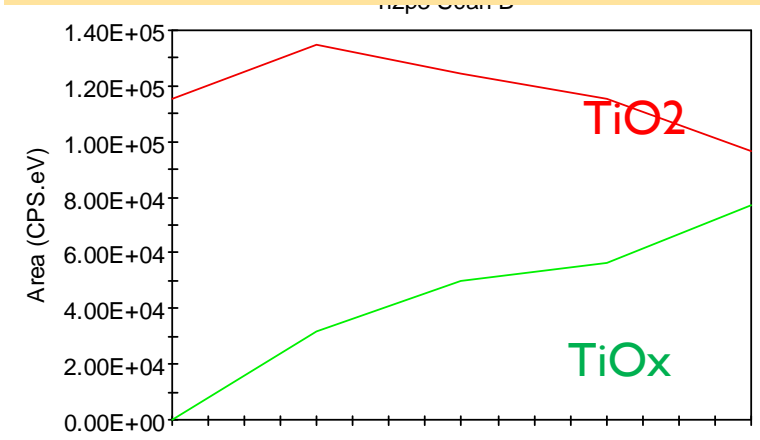
在空气气氛中很难找到
纯TiC参考谱
纯TiN参考谱

TiO₂表面分峰分析



		BE	Orb	Ratio	Orb (eV)	Ratio	param (eV)

Ar⁺刻蚀TiO₂表面化合物还原深度剖析

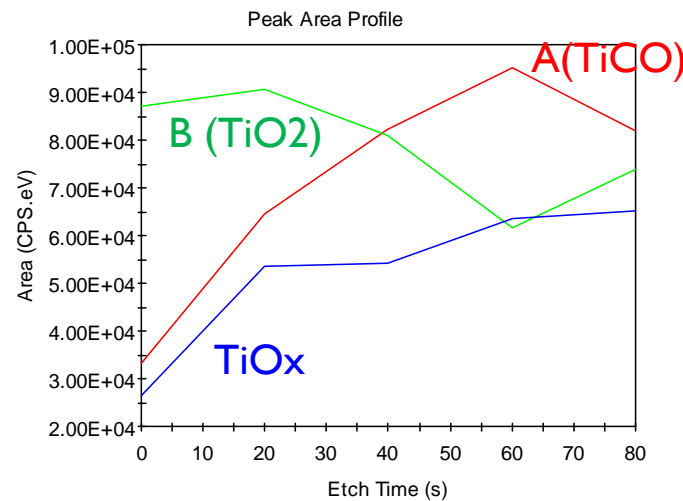
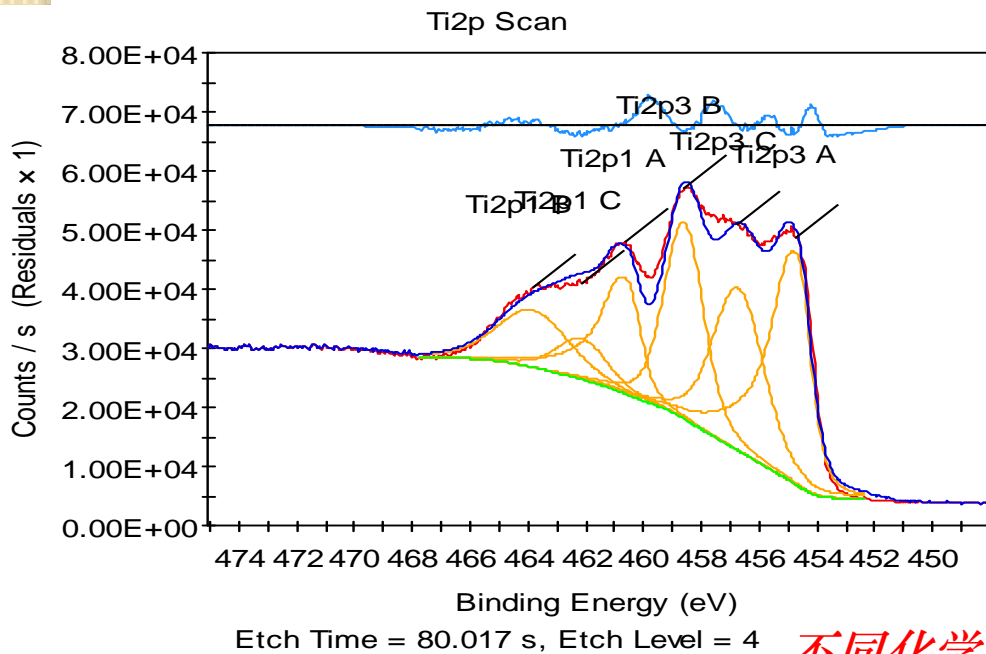


	峰位eV	背景	峰形	2p峰高比	2p峰宽比	2p ΔEb eV
TiO ₂	458.7	Shirley	对称	0.3	1.75	5.7
TiO _x	457.0	Shirley	对称	0.4	1	5.7

REF ΔEb (纯Ti 2p) = 6.15eV

XPS分析TiCO

参考TiO₂、TiO_x及TiC分峰参数分析TiCO



不同化学态有不同的谱峰参数

BE	CPS	Ratio	CPS.eV	Ratio	param (eV)	Convolve	mix (%)	Height (%)	Exponent

TiCO
TiO₂
TiO_x

不同化学态有不同的谱峰参数

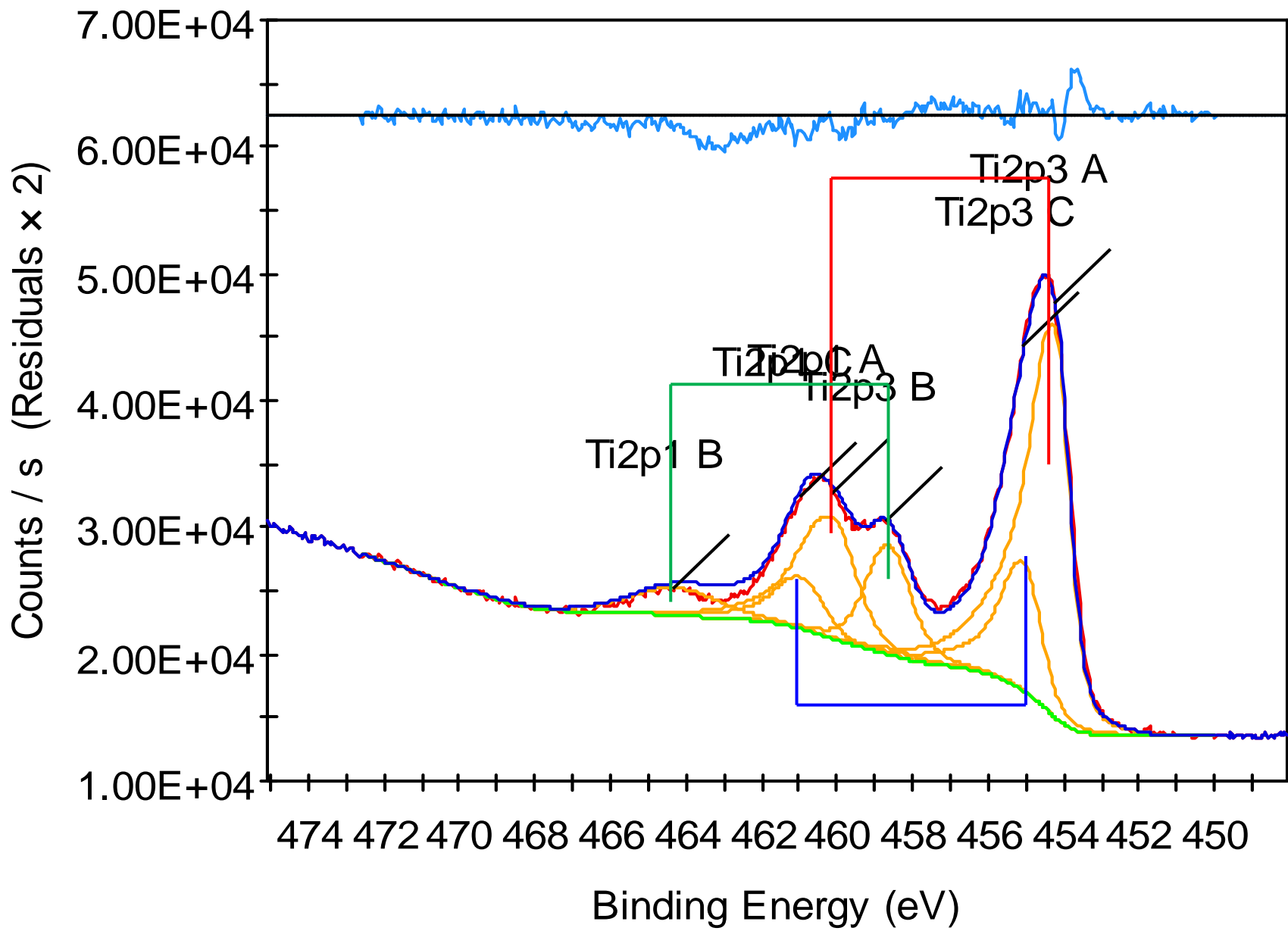
- 对于化合物或多相谱峰采用不同的谱峰参数拟合

	峰位eV	背景	峰形	2p峰高比	2p峰宽比	2p ΔE_b eV
TiO ₂	458.6	Shirley	对称	0.29	1.8	5.2
TiO _x	456.7	Shirley	对称	0.25 *	1 *	5.4
TiC	454.7	Shirley	非对称 (4.43/0.9/0.04) #	0.5	1	5.9

(尾参数)

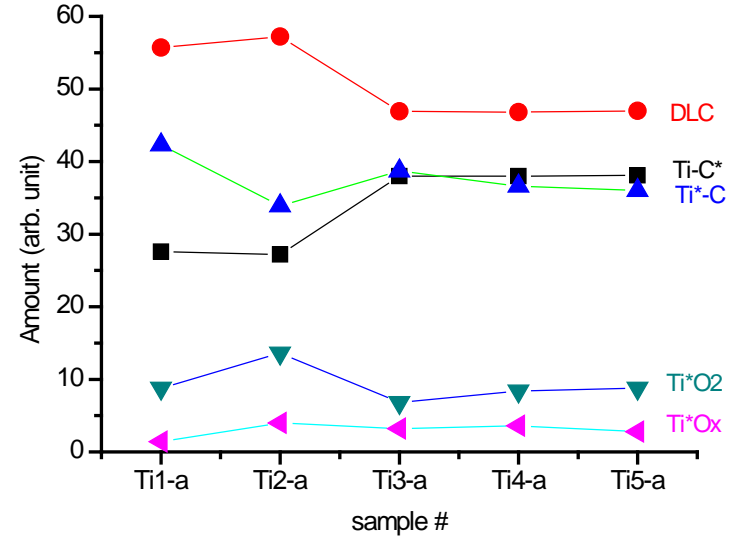
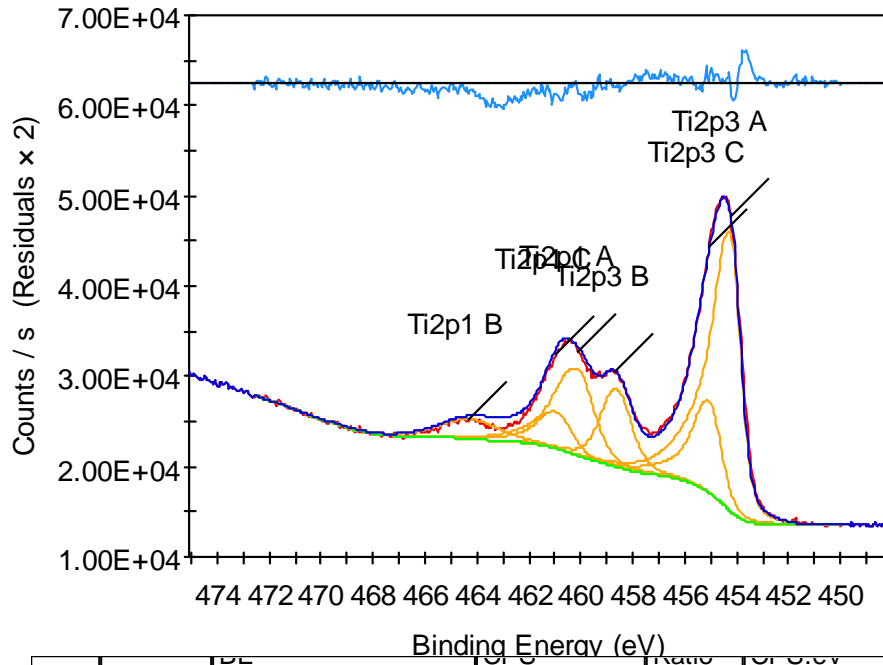
(考量背景影响?)

Ti2p Scan



Ti5-a

Ti2p Scan



	BE	Area	Ratio	Or 0.5eV	Ratio	param (eV)	Convolve	mix (%)	Height (%)	Exponent

分析TiCNO/DLC复杂化合物薄膜

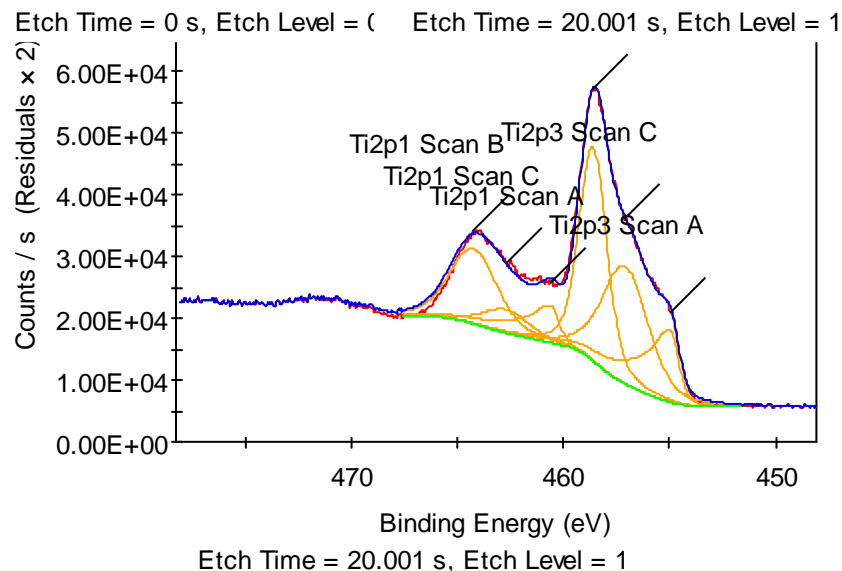
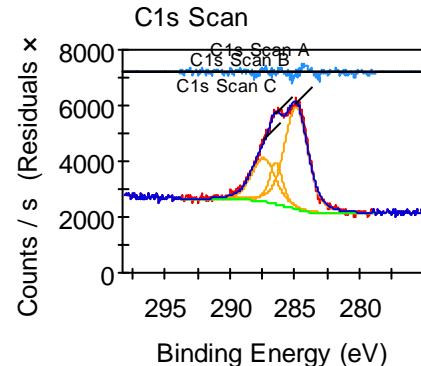
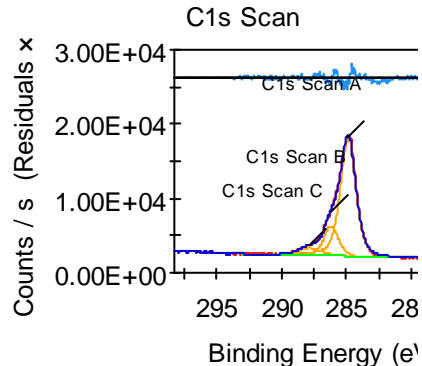
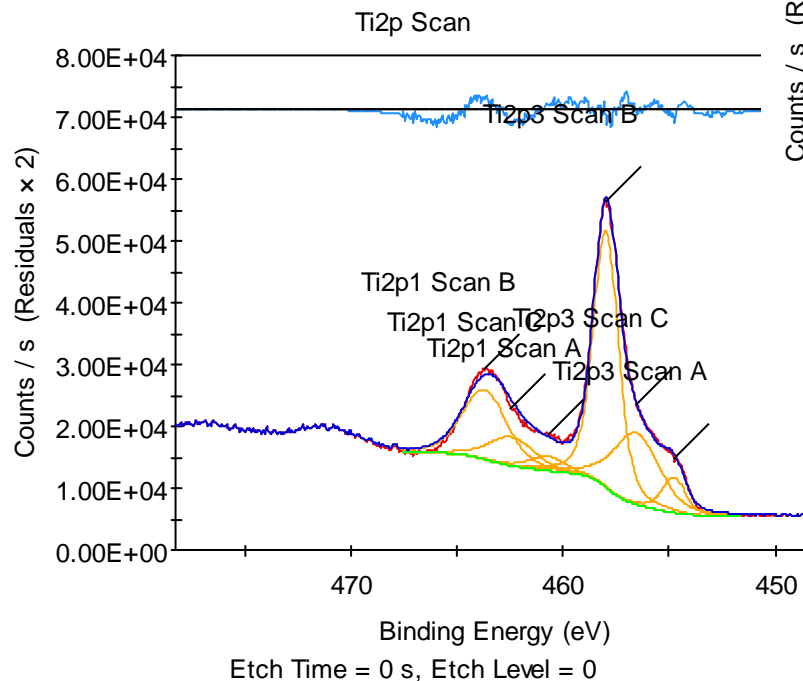
- 根据TiO₂等样品的分析得到Ti2p谱参数

	峰位eV	背景	峰形	2p峰高比	2p峰宽比	2p ΔEb eV
TiO ₂	458.7	Shirley	对称	0.3	1.75	5.7
TiO _x	457.0	Shirley	对称	0.4	1	5.7
TiC	453.7	Shirley	非对称 (0.02/2.53/0.034)	0.31	1.6	5.8
TiN	454.9	Shirley	非对称(0/10.7/0.0465) Sat 2.6	0.4	1.68	6
Ti	454.1	Shirley	非对称(40.5/0/0.0358)	0.4	1.3	6.1

分析 TiNCO

TiNO

物相: TiO₂ TiN (DLC)
C1s中无TiC, 出现DLC



TiN

TiO₂

TiN sat + TiO_x

Ref

Ti 453.8-454.1

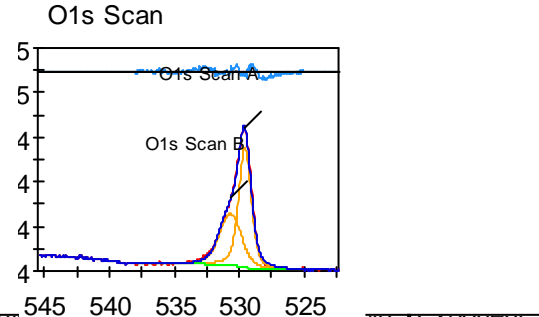
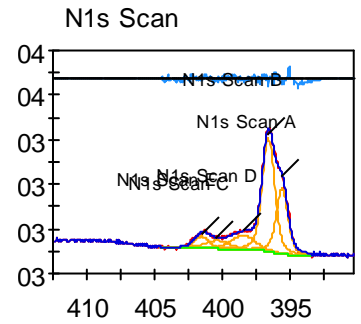
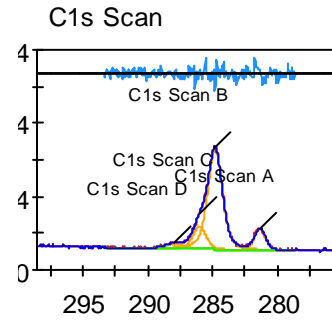
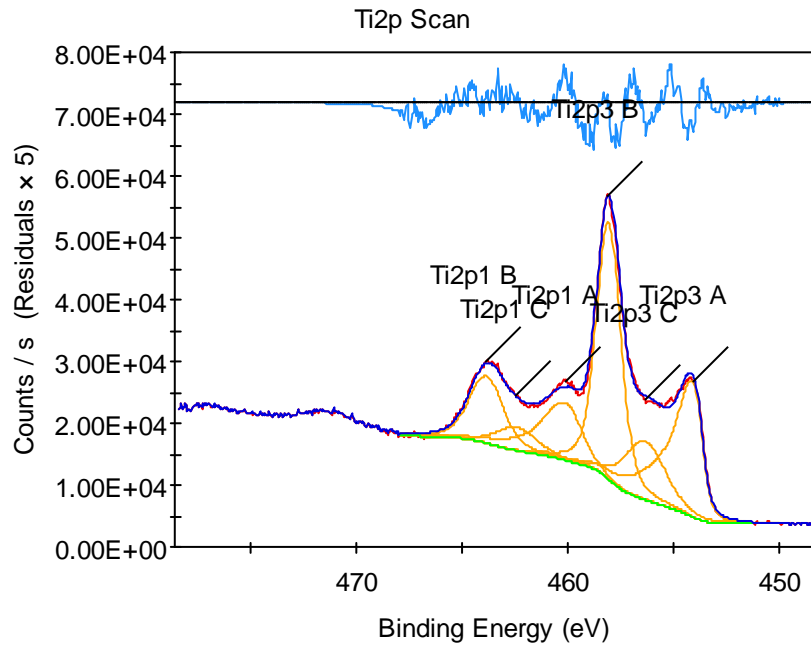
TiC ~454.3/282

TiN 454.9/396.9

TiO₂ 458.5/530

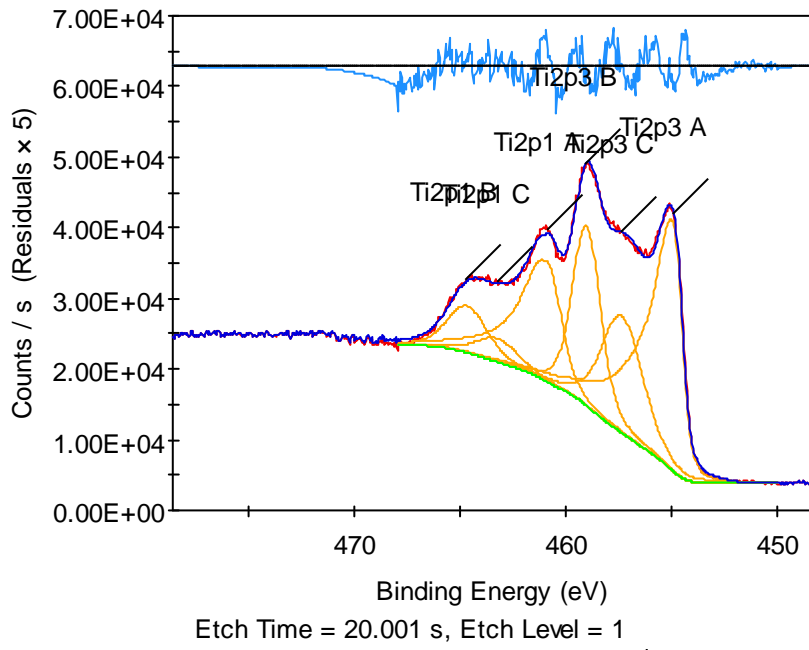
	BE	Or	Ratio	Or	Ratio	param (eV)	Convolve	Area (%)	Height (%)	Exponent
TiN										
TiO ₂										
TiN sat + TiO _x										

TiCON

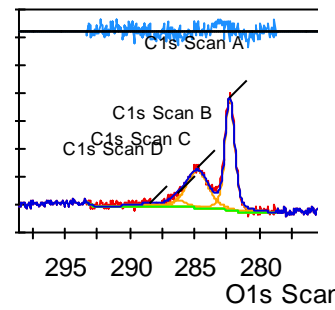


	param (eV)	Comp	Area (%)	Exponent
TiC+TiN				
TiO ₂				
TiO _x				

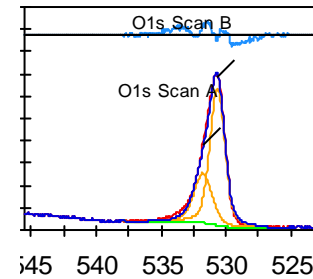
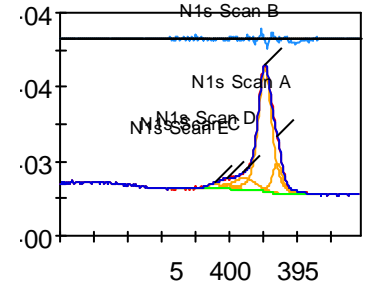
TiCON



C1s Scan

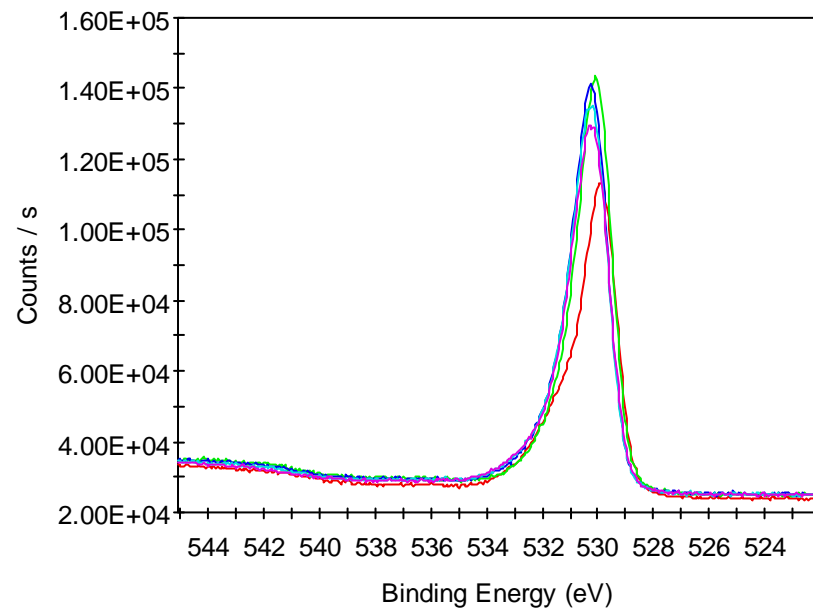
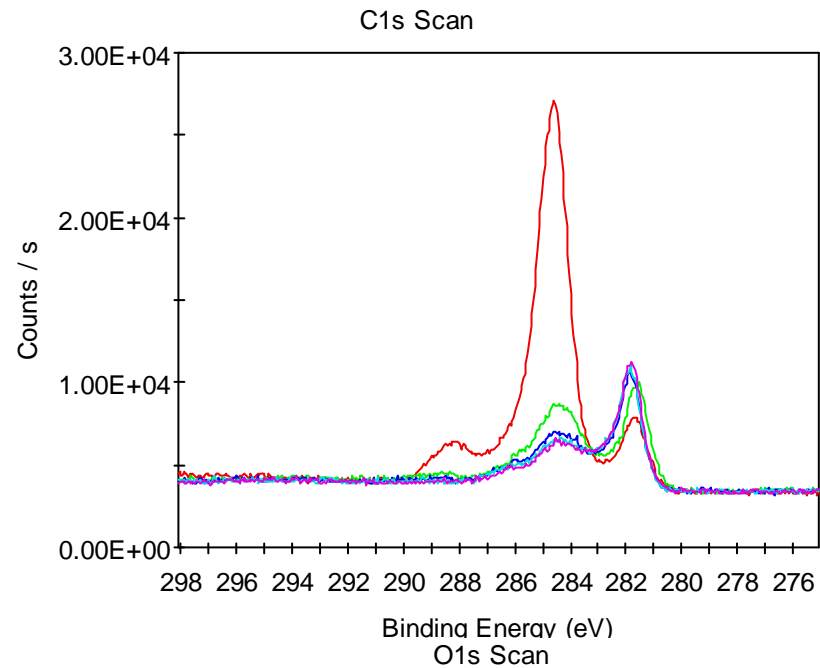
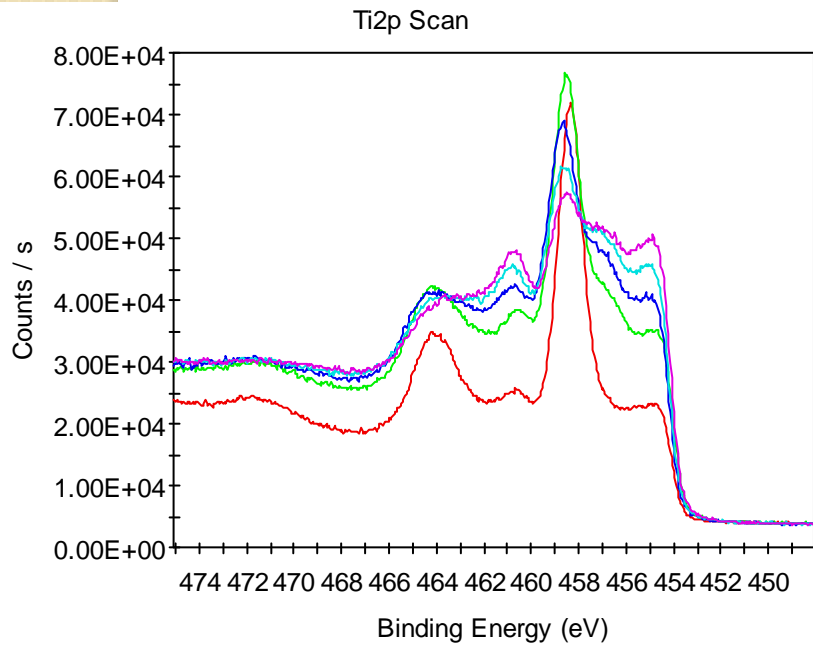


N1s Scan



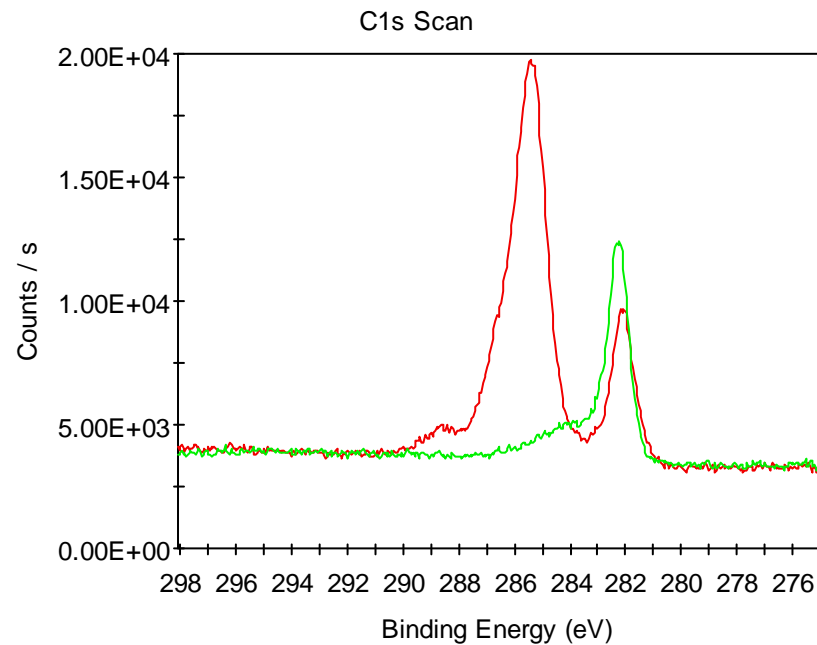
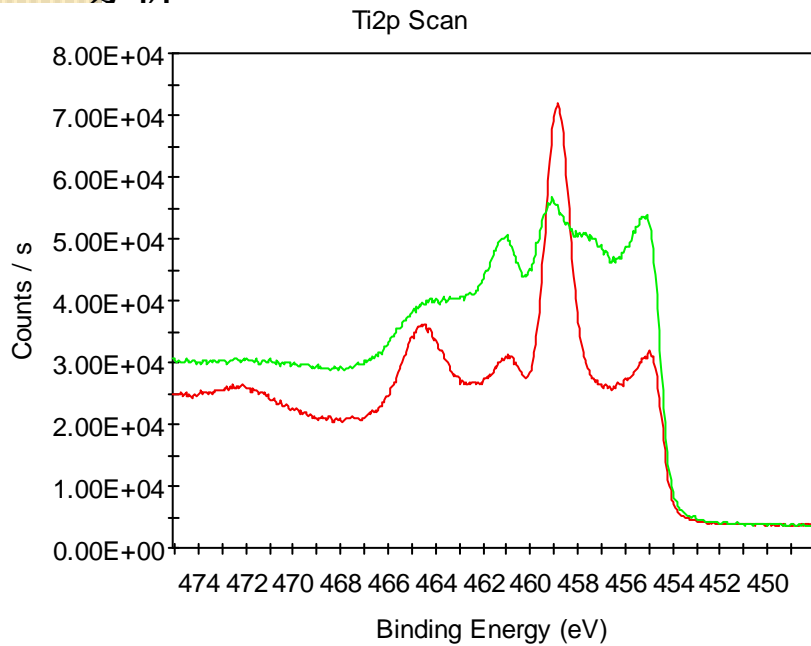
	BE	Orb	Ratio	Orb (eV)	Ratio	param (eV)	Convolve	Mix (%)	Height (%)	Exponent
TiN+TiC										
TiO2										
TiOx										

结论： 包覆TiN-TiC/TiO2-DLC

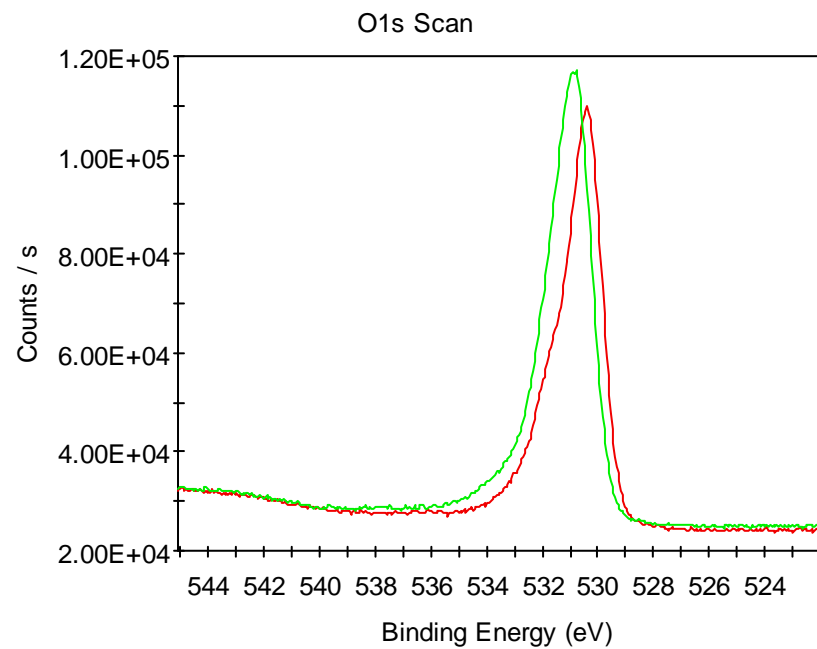


140318-1#

分析



TiCO (I404I6-7)



Ti2p峰对称: extrinsic (plasmon) , intrinsic (shake-up 等损失峰)
总结不同价态Ti的Ti2p峰参数

Ti, TiO₂ , TiO_x TiC, TiOC, TiN, TiCN等参数

$\Delta E_b(2p_{1-2} / 2p_3)$

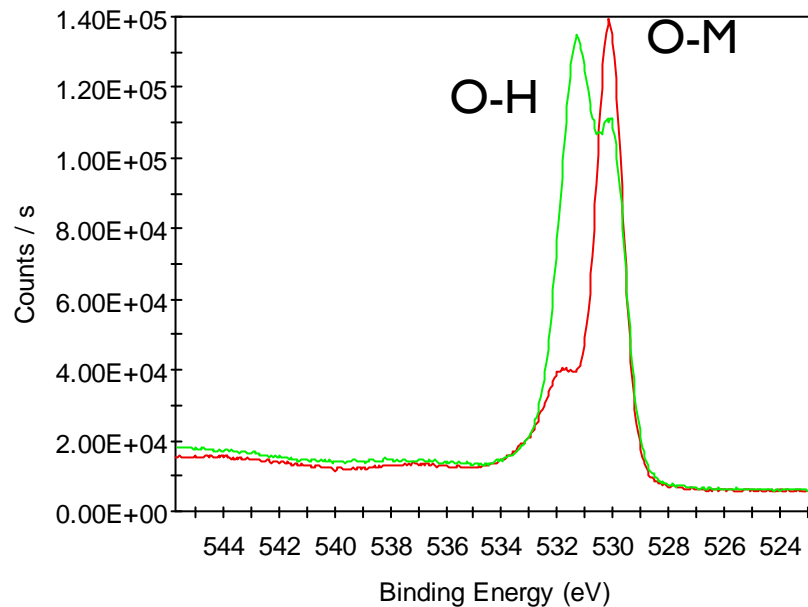
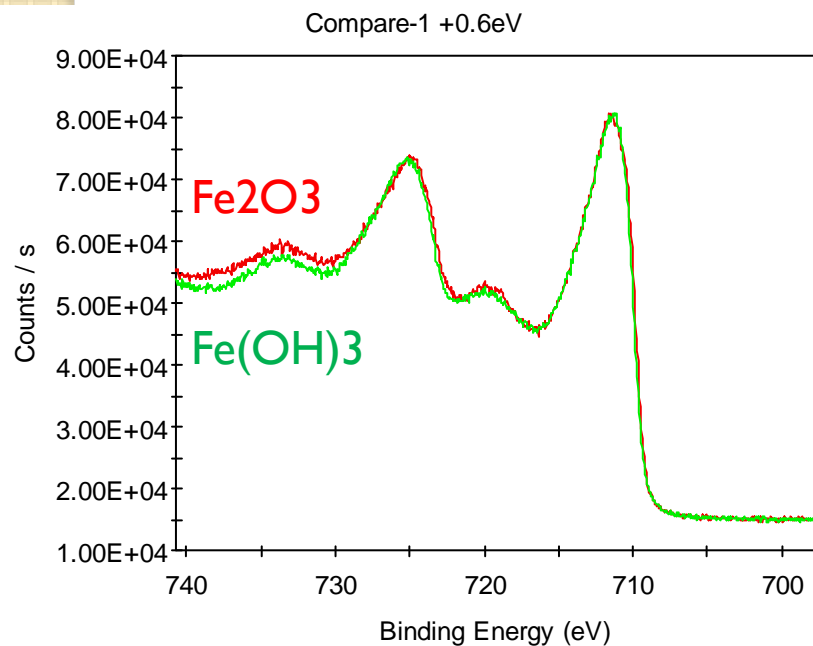
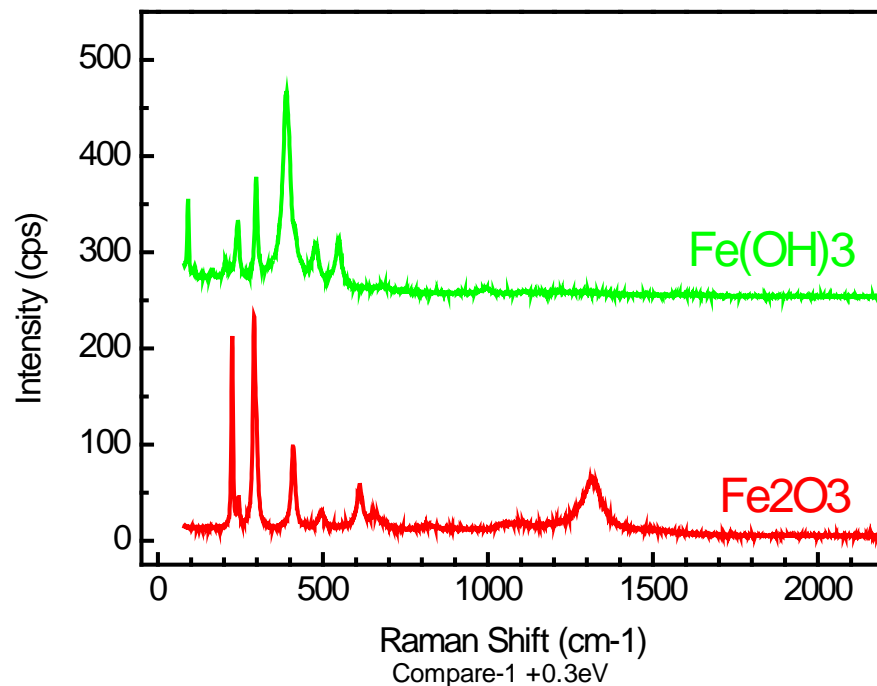
$I_{ratio}(2p_{1-2} / 2p_3)$

$W(2p_{1-2} / 2p_3)$

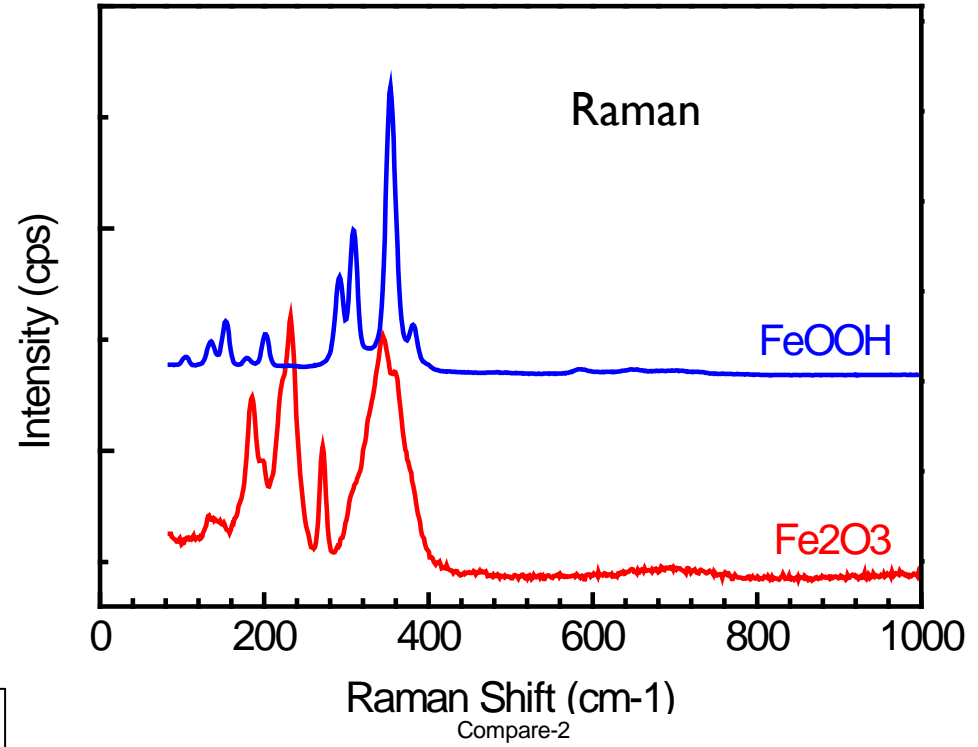
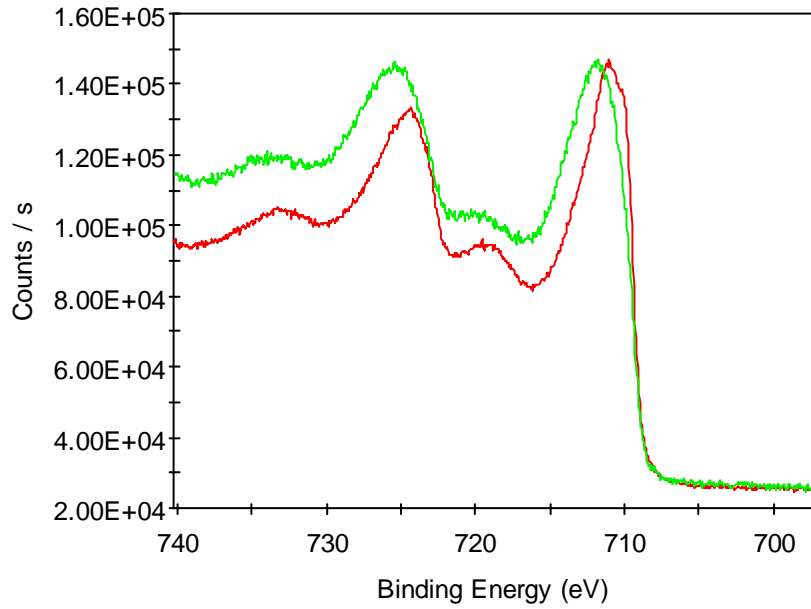
参考样品Ti/ TiO₂等XPS谱图及参数积累。

Fe2谱 XPS分析

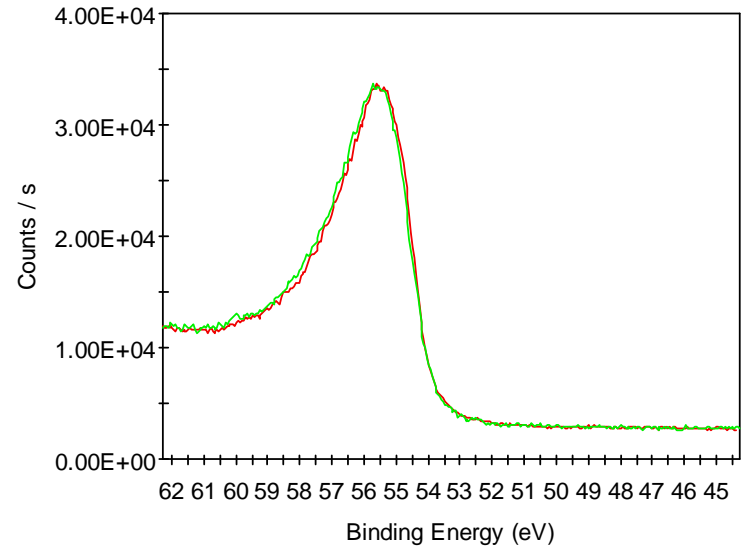
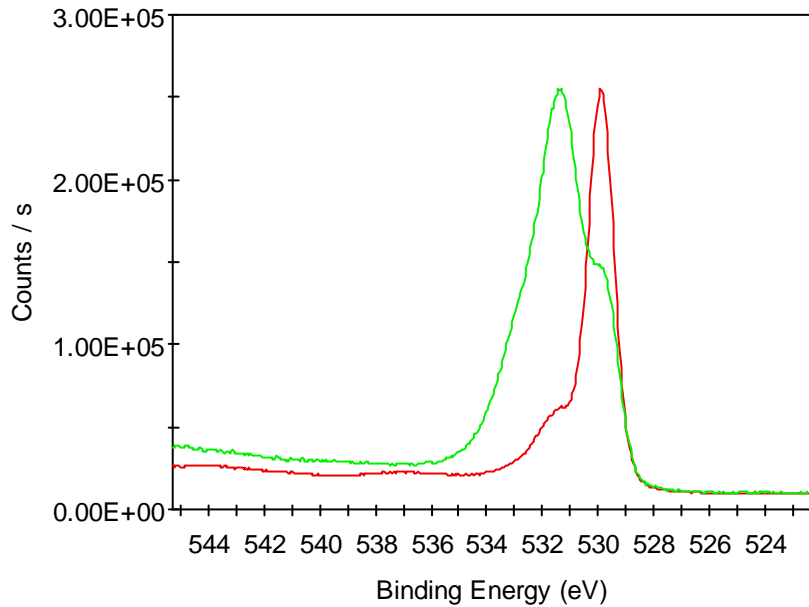
- Fe³⁺



Compare-3



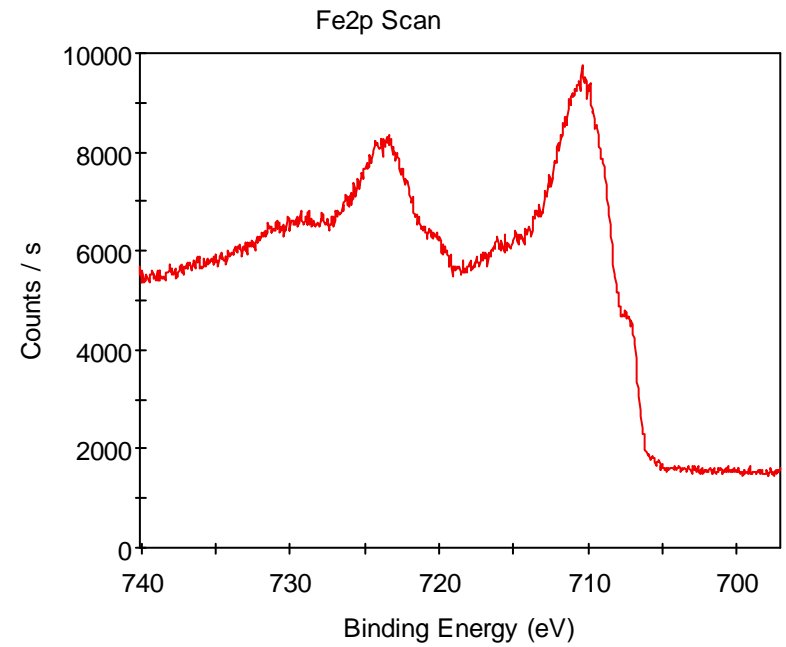
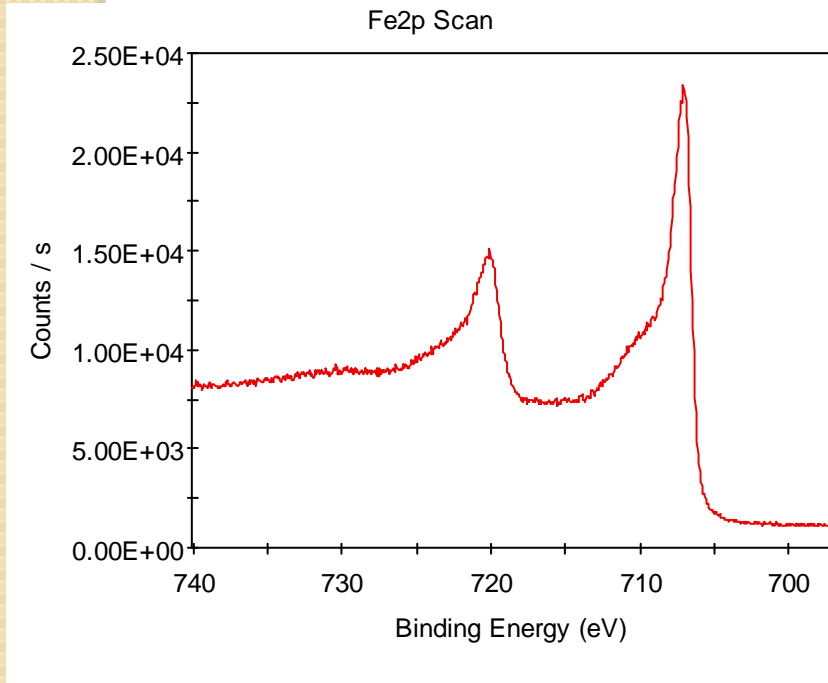
Compare-4



Fe XPS

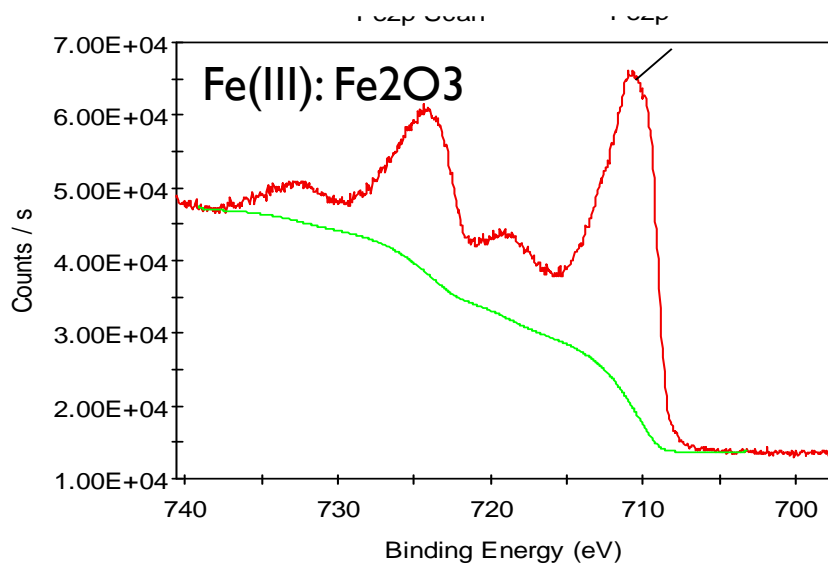
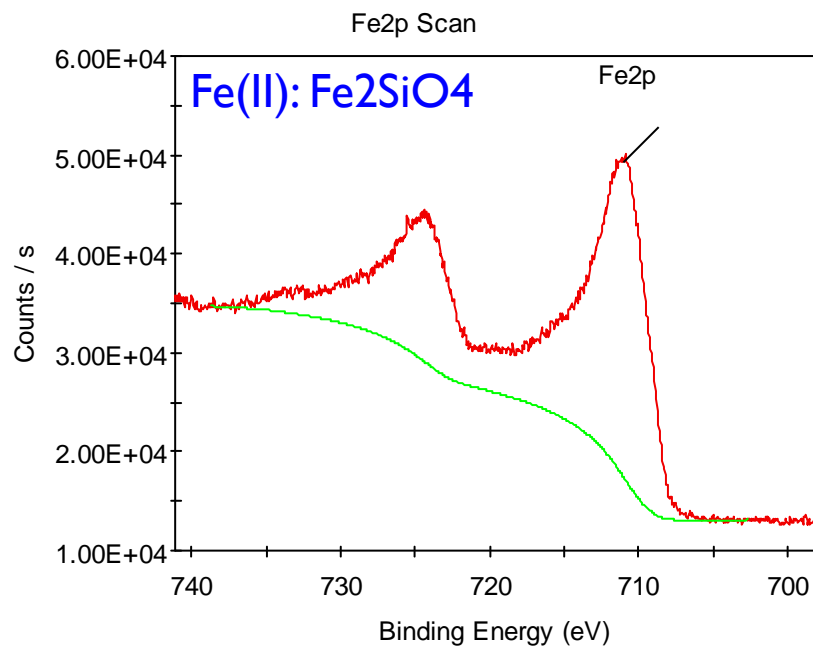
REF	Fe	FeO	Fe ₂ O ₃	FeOH ₃	FeOOH
Eb eV	706.7	709.4	710.8	711.7	711.8

- Fe 0+ Fe n+(自然氧化)

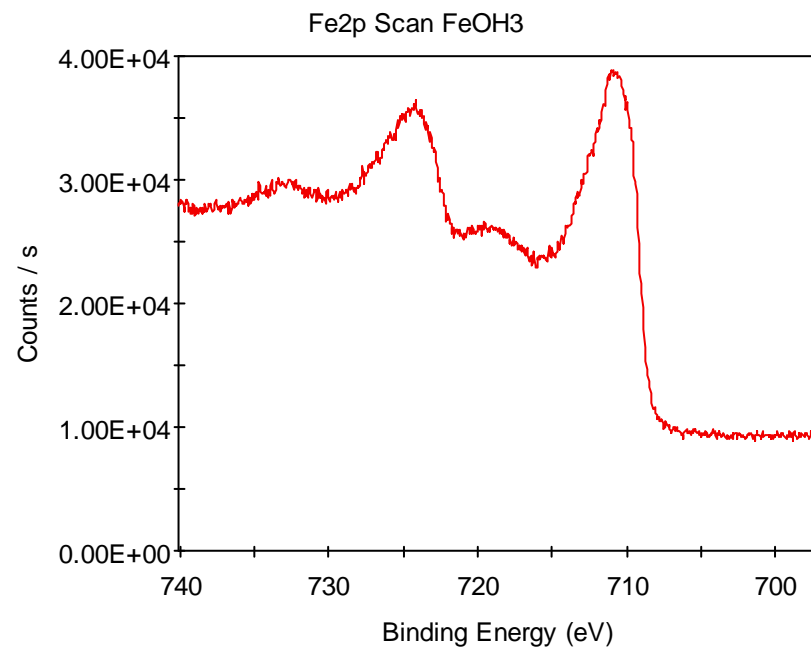
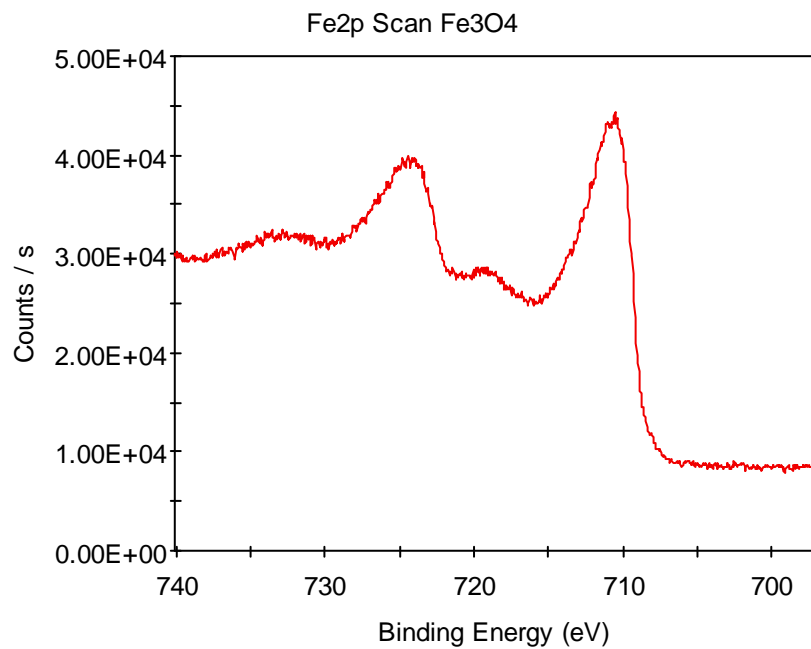
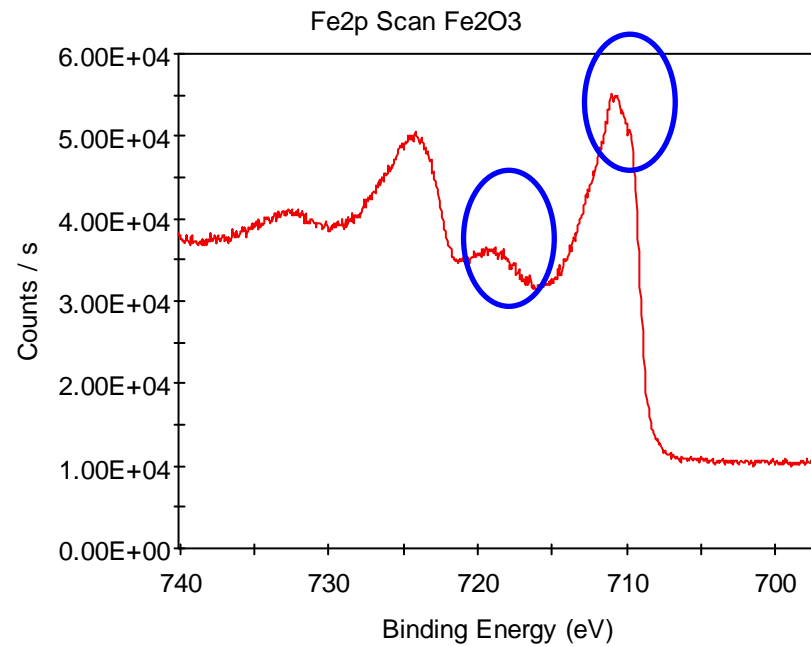
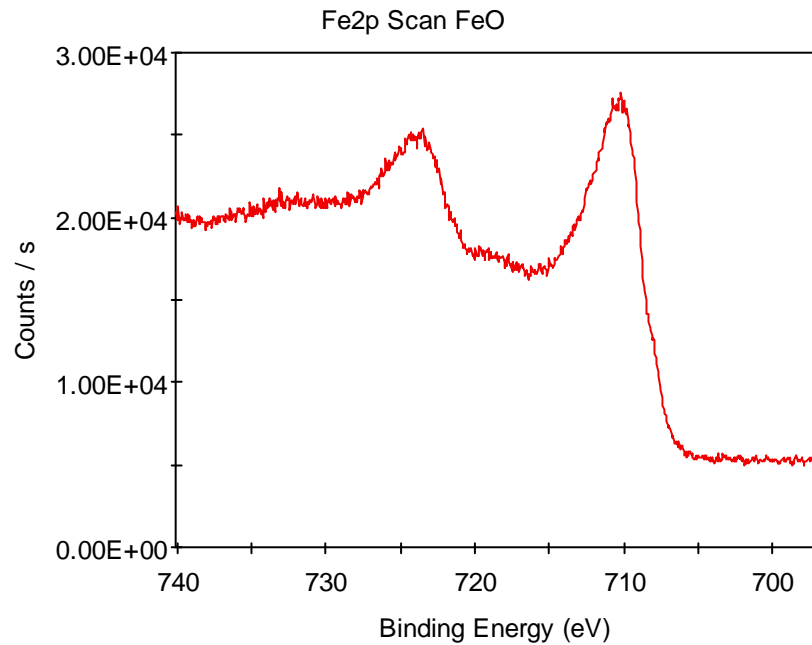


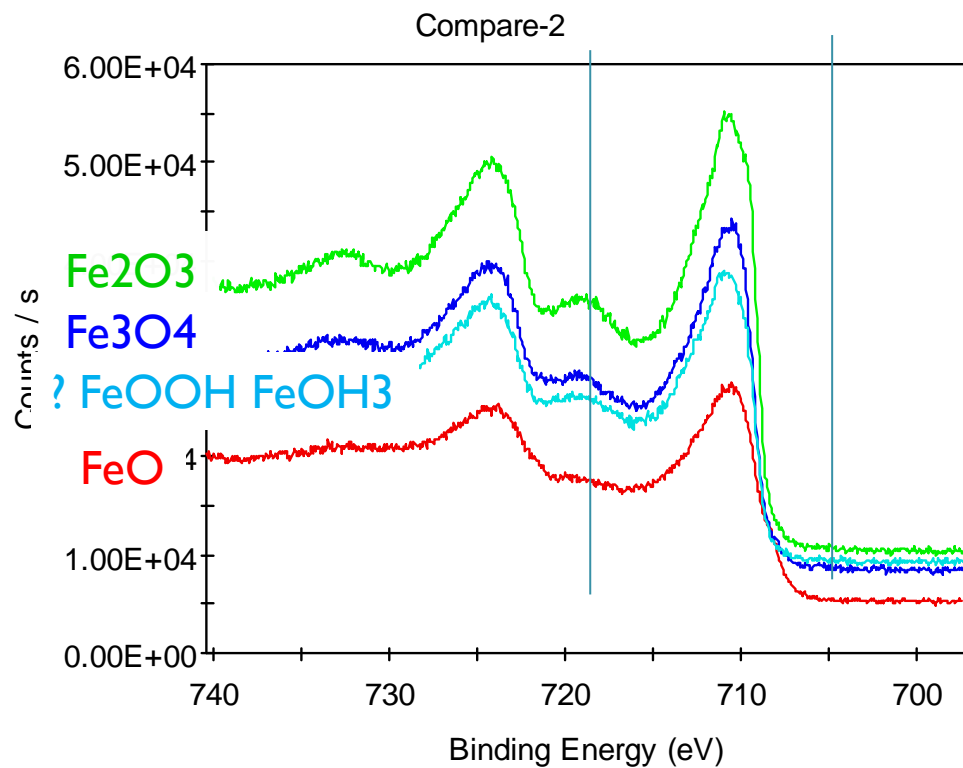
Fe XPS

- Fe_2^+ 、 Fe_3^+



- Fe_2O_3 、 Fe_3O_4 、 FeO 等比较

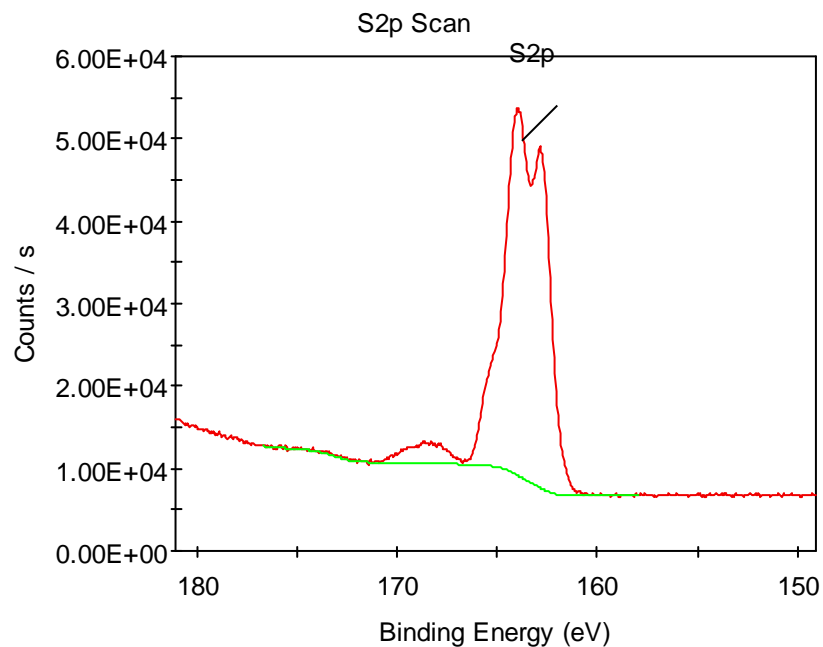
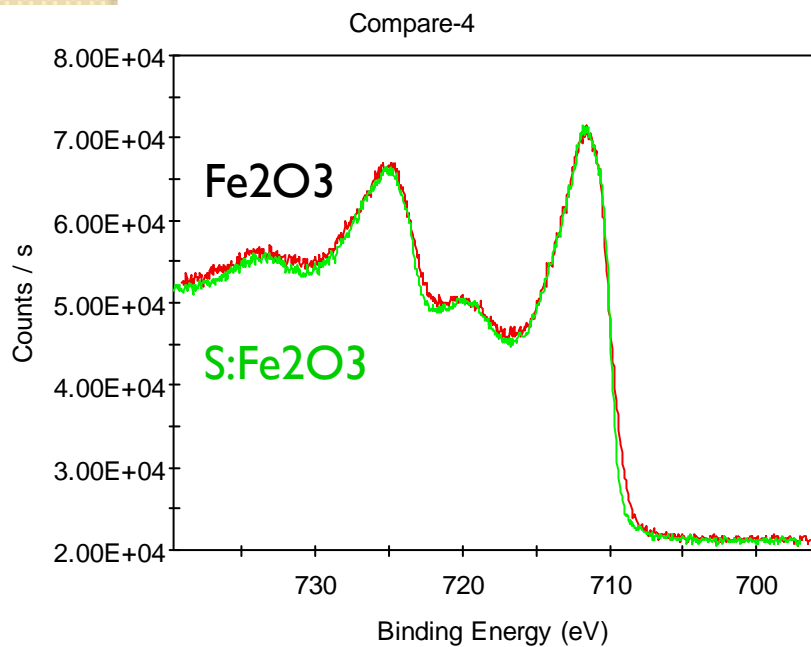




REF	Fe	FeO	Fe ₂ O ₃	FeOH ₃	FeOOH
Eb eV	706.7	709.4	710.8	?	711.8

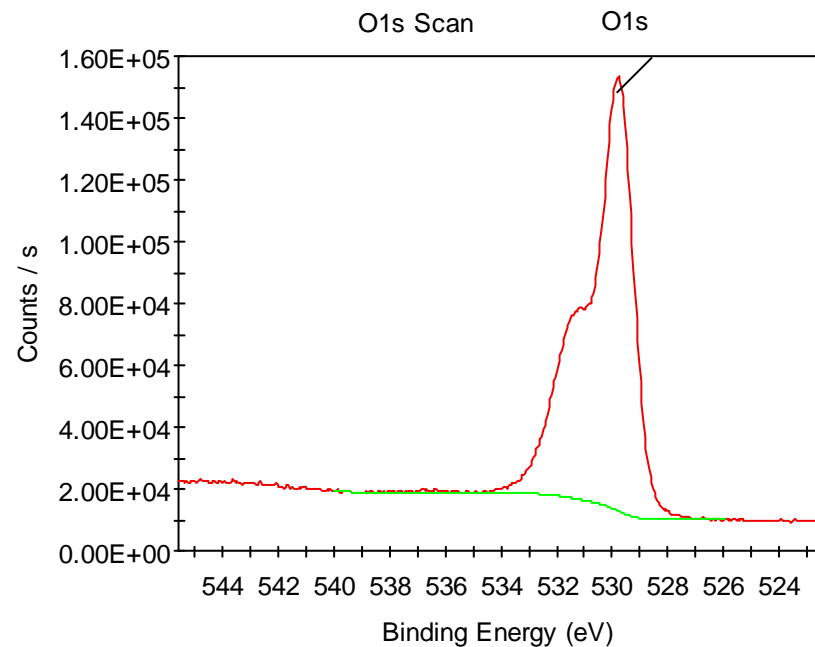
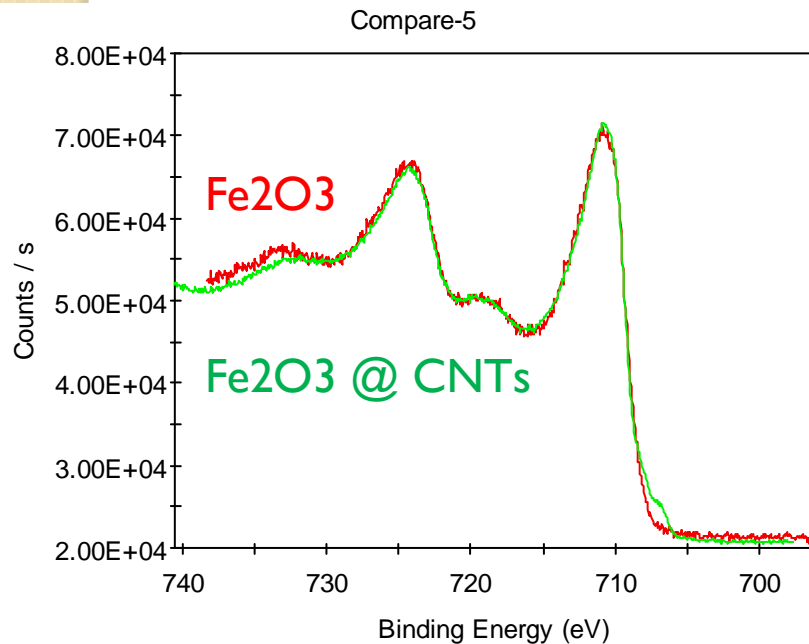
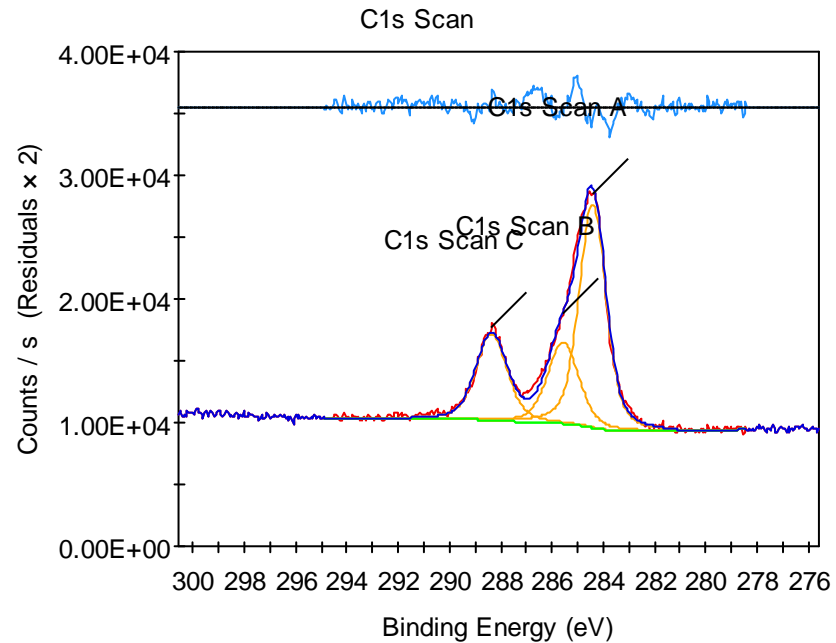
Fe₂O₃硫化

- Fe价态



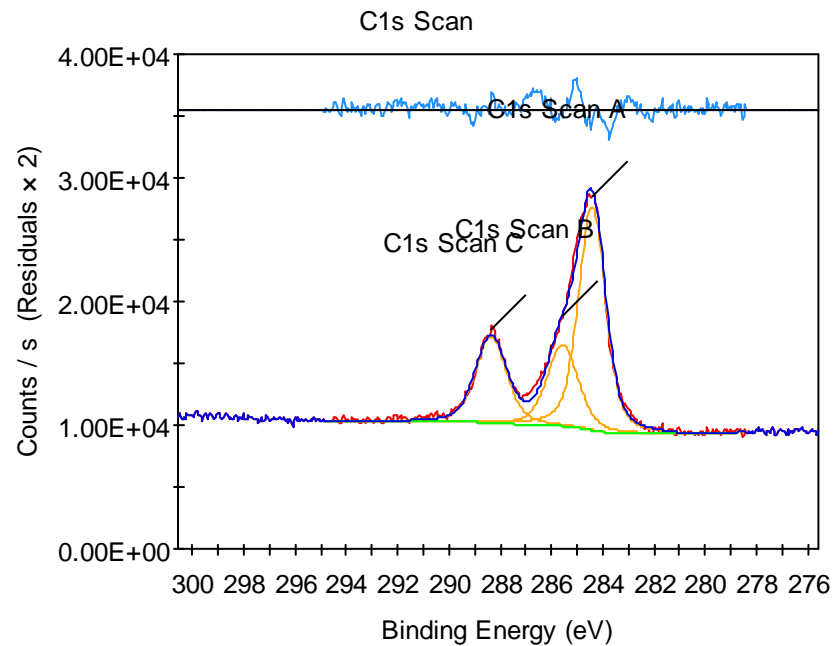
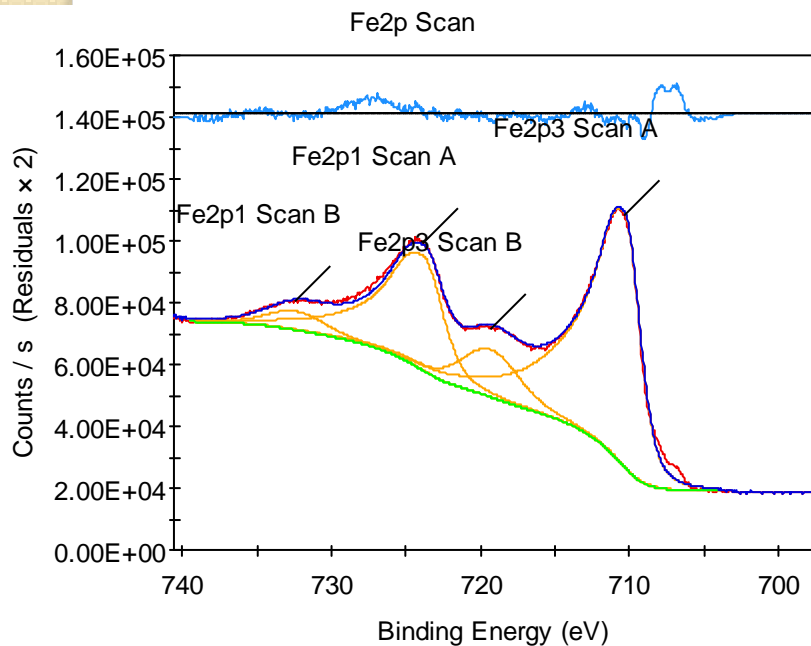
Fe-O负载 CNTs

- Fe2p峰形



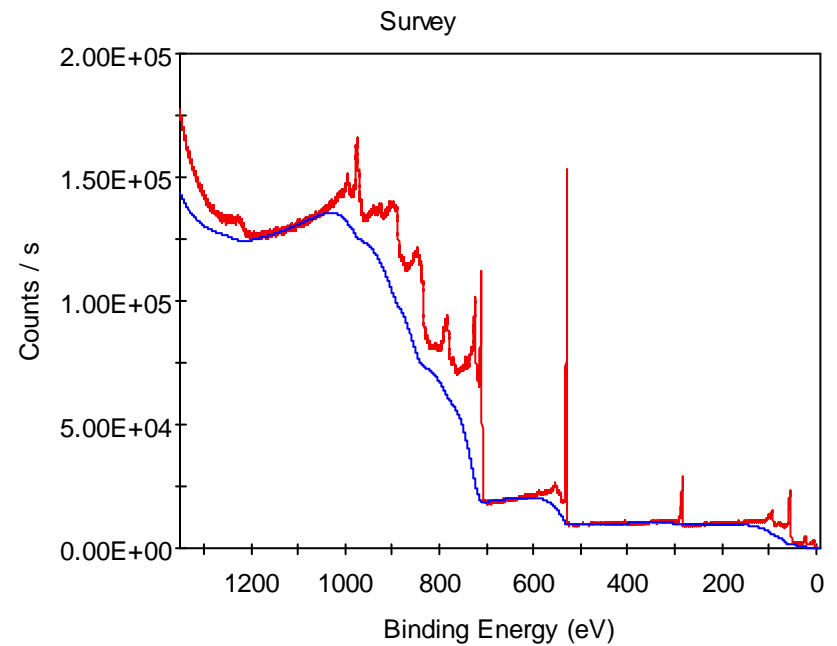
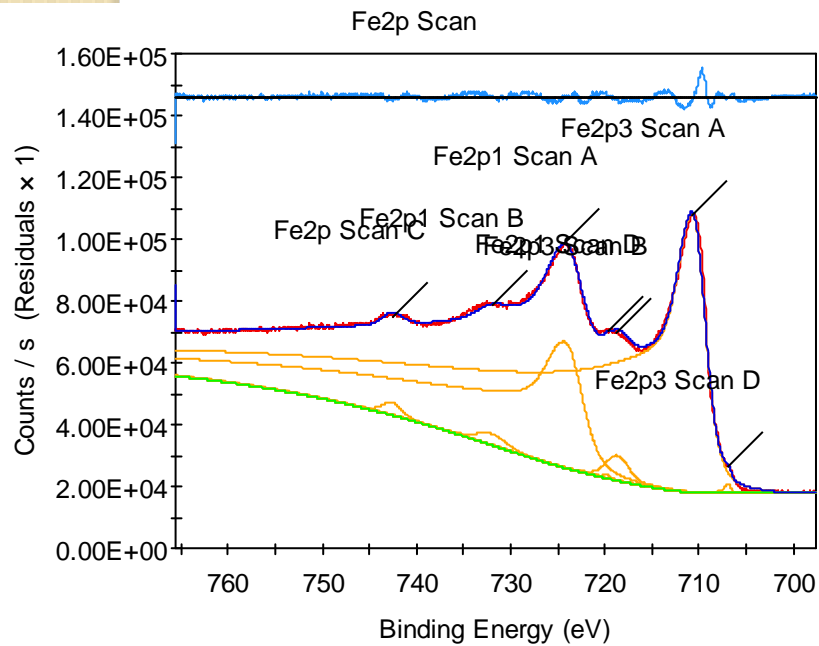
Fe-CNTS Fe2p分析

- Shirley

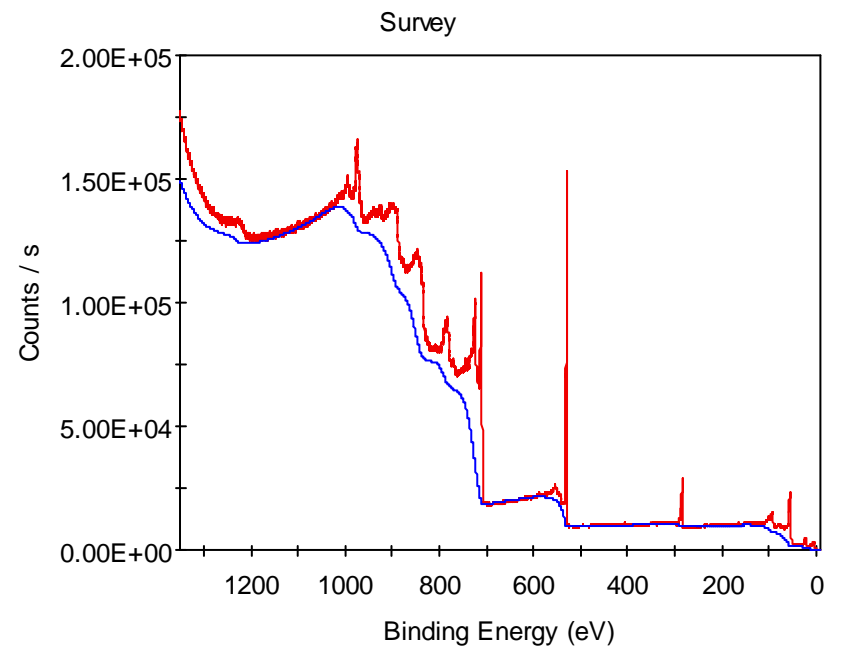


Fe-CNTS Fe2p分析

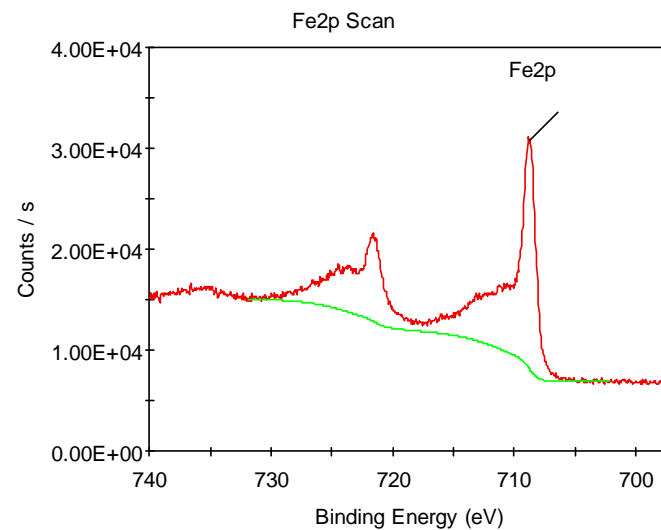
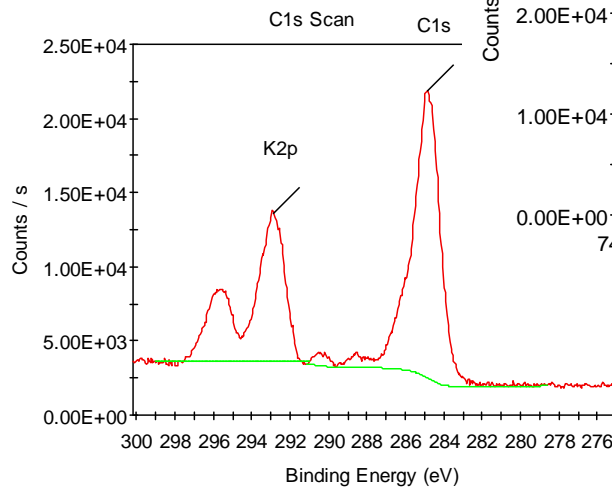
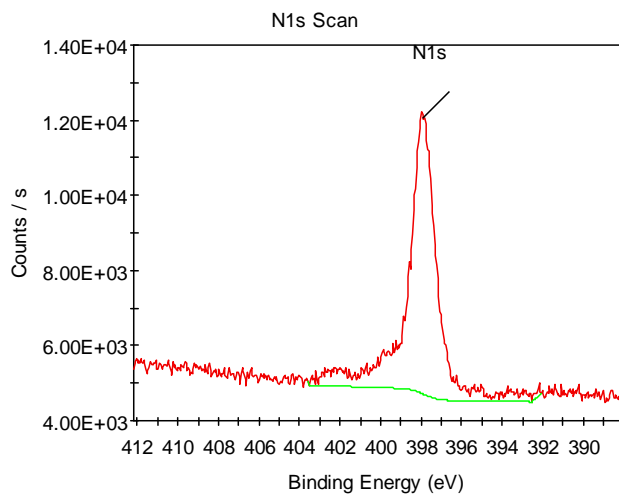
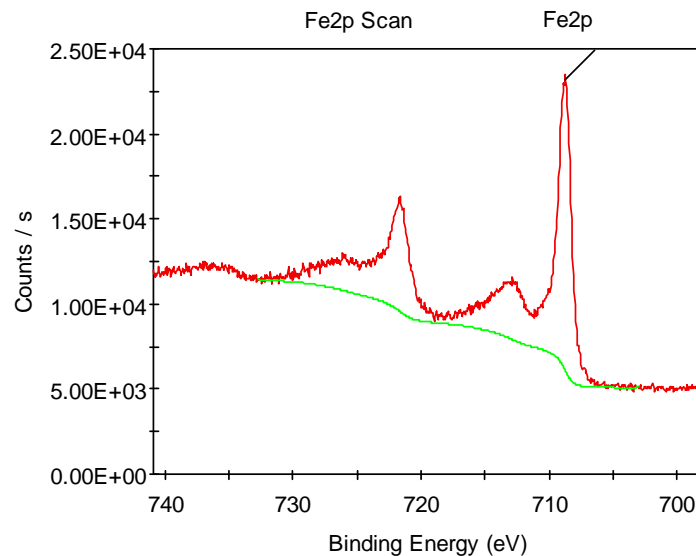
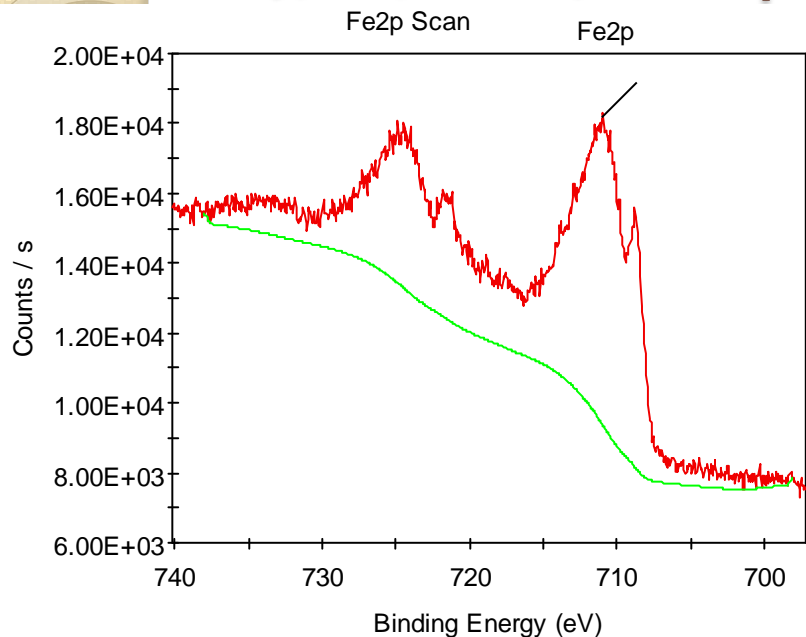
- Tougaard



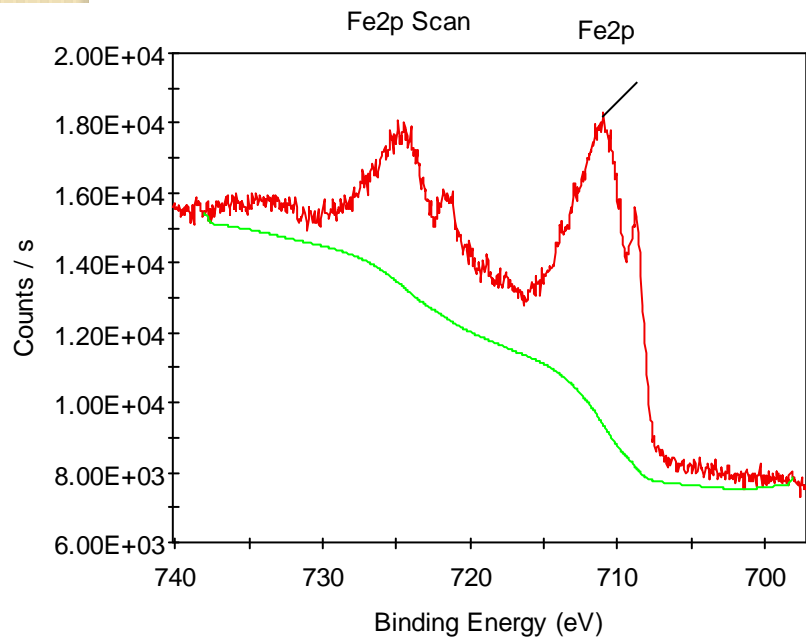
Fe-CNTS Fe2p分析



催化剂 $K_4Fe(CN)$



分析使用过的亚铁氰化铁



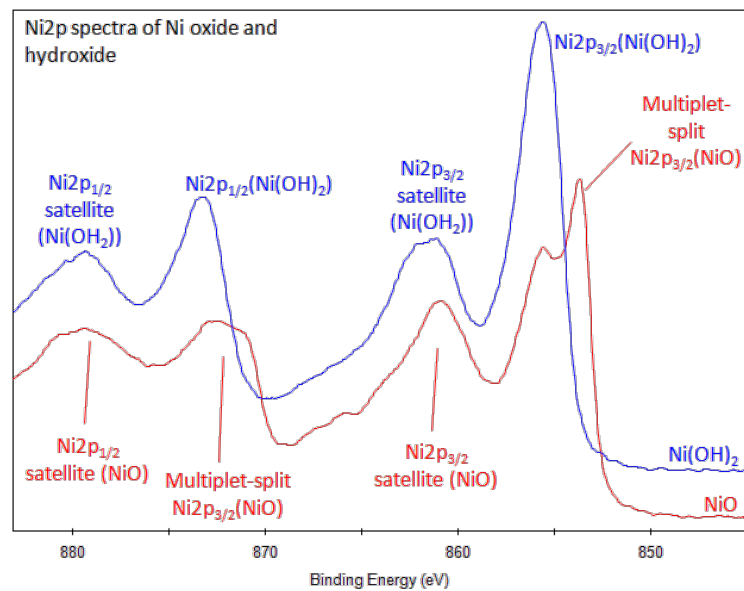
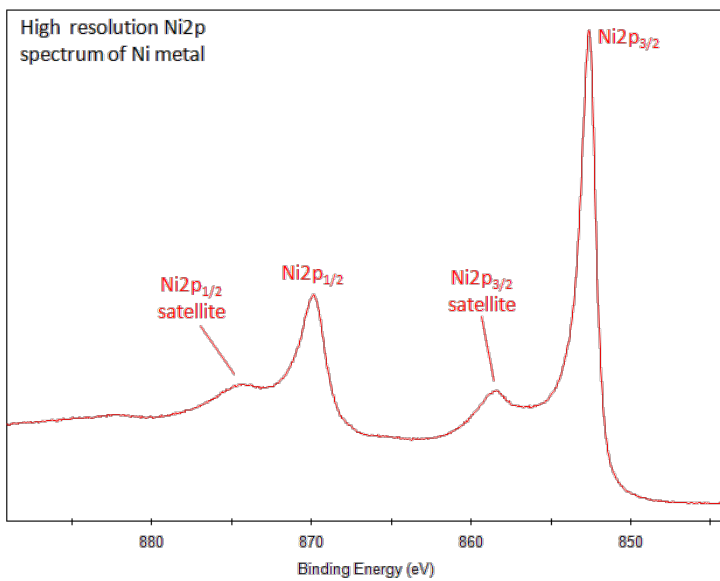
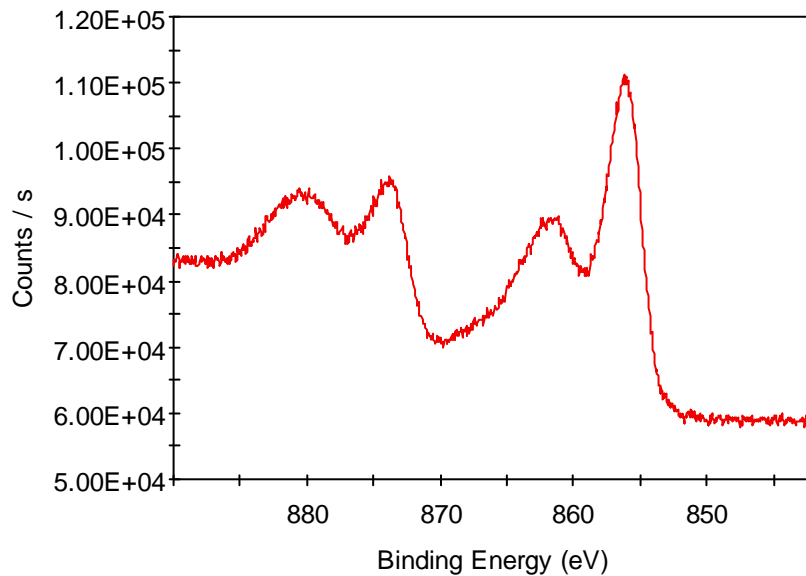
用Tougaard和Seah Tougaard扣除背景

Ni2p谱XPS分析

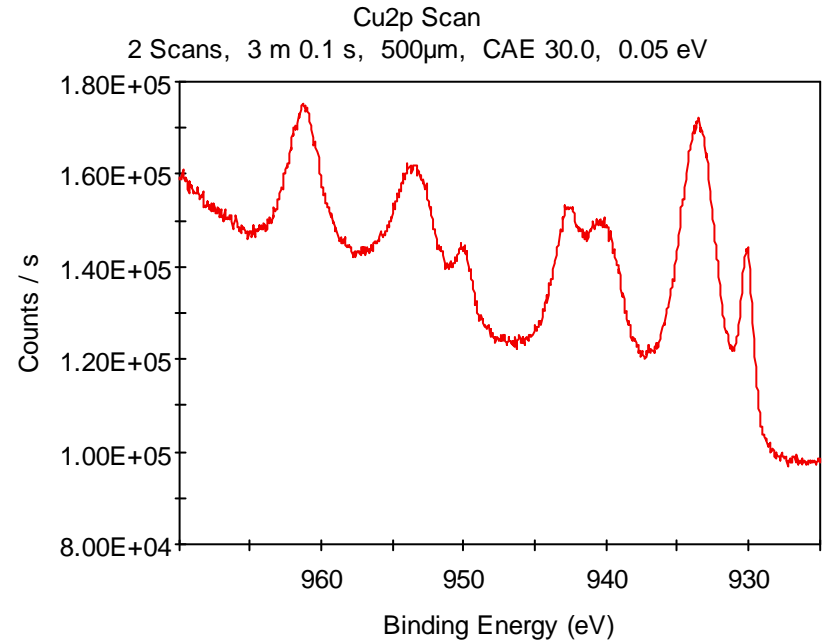
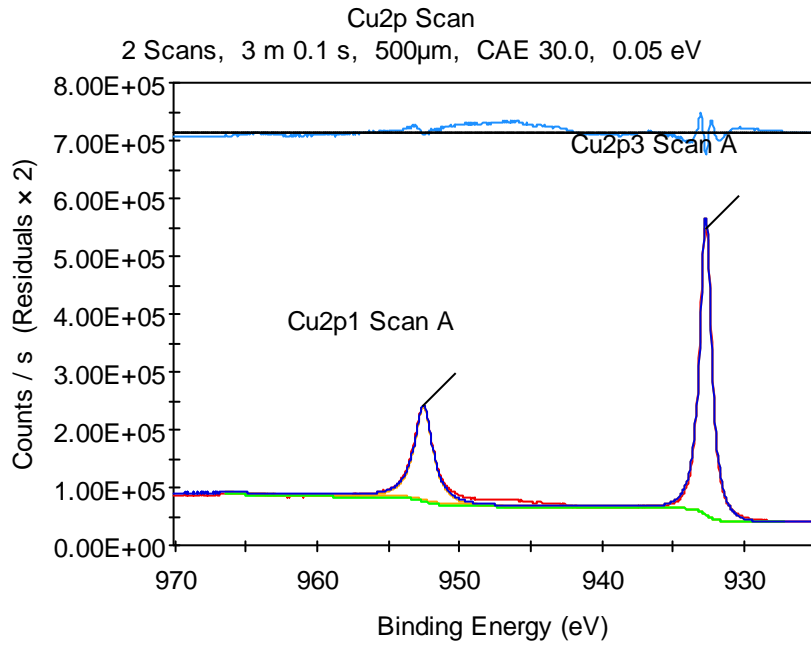
- Ni2p 出现
 - 多电子激发，终态分裂，CK跃迁等现象，谱峰非对称性
 - 多价态，不同价态等出现不同的谱峰结构，相互叠加、展宽
 -

Ni2p Scan

2 Scans, 3 m 12.1 s, 500 μ m, CAE 30.0, 0.05 eV

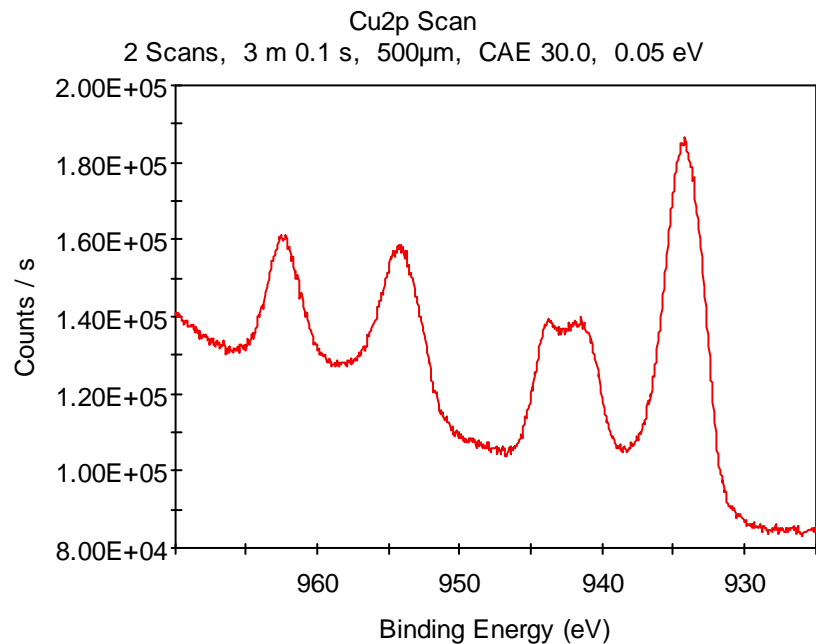
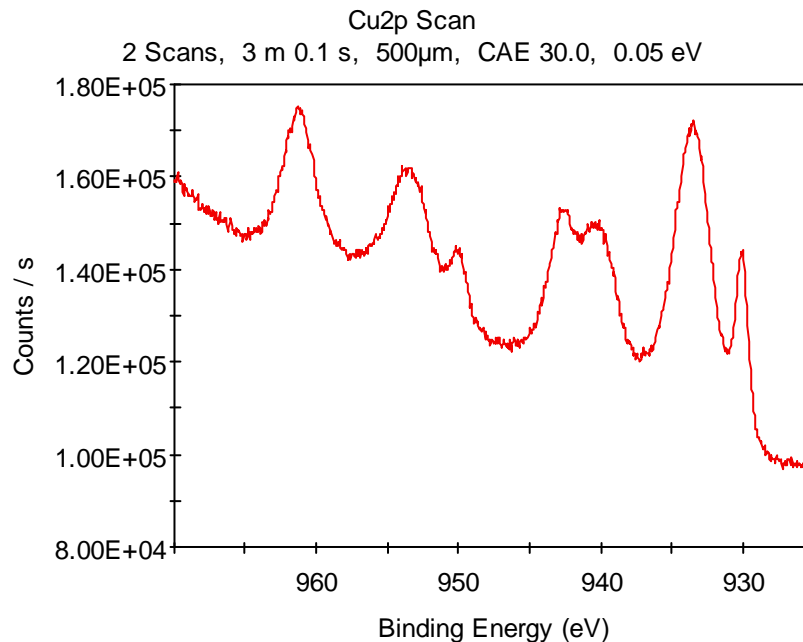
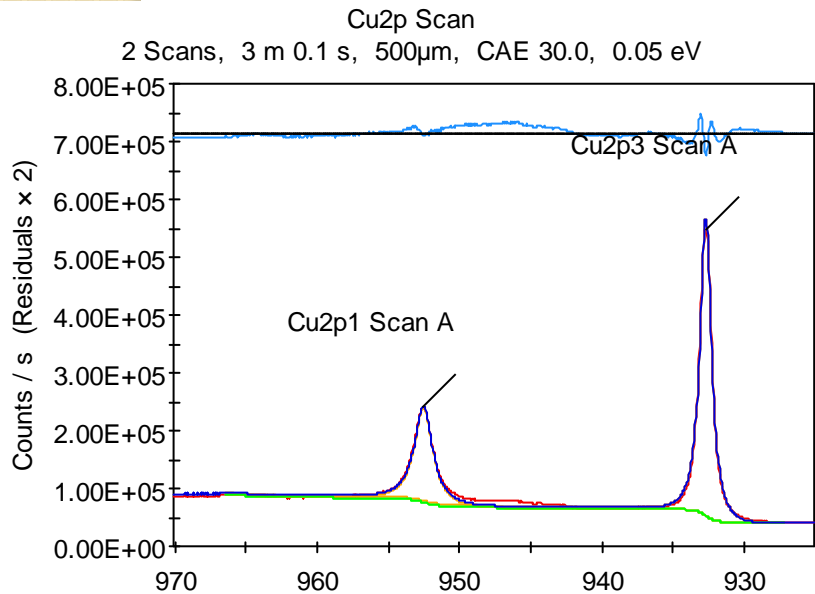


Cu2p谱峰分析



BE	CF	Ratio	CF	Ratio	param (eV)	Product	Mix (%)	Height (%)	Exponent

Cu2p谱峰分析



Ratio	param (eV)	Height	Mix (%)	Height (%)	Exponent

非线性拟合NLLSF

- 元素在不同的化学态的化合物中，
 - 峰形变化，如改变通过能
 - 背景变化，
 -
- 在NLLSF中无法调节参数

谢谢关注

- 联系方式:
- 北京师范大学分析测试中心 吴正龙
- wuzl@bnu.edu.cn