

XPS测试样品准备及谱图处理

前言

- 电子能谱测量固体样品表面，原样分析，不消解样品；
- 电子能谱制样简单，但并不等于无需制样
- 样品准备是电子能谱实验重要的环节，影响谱图质量，甚至决定实验的成败
 - 了解样品
 - 了解仪器
 - 需要一定经验方法的积累
 -

前言

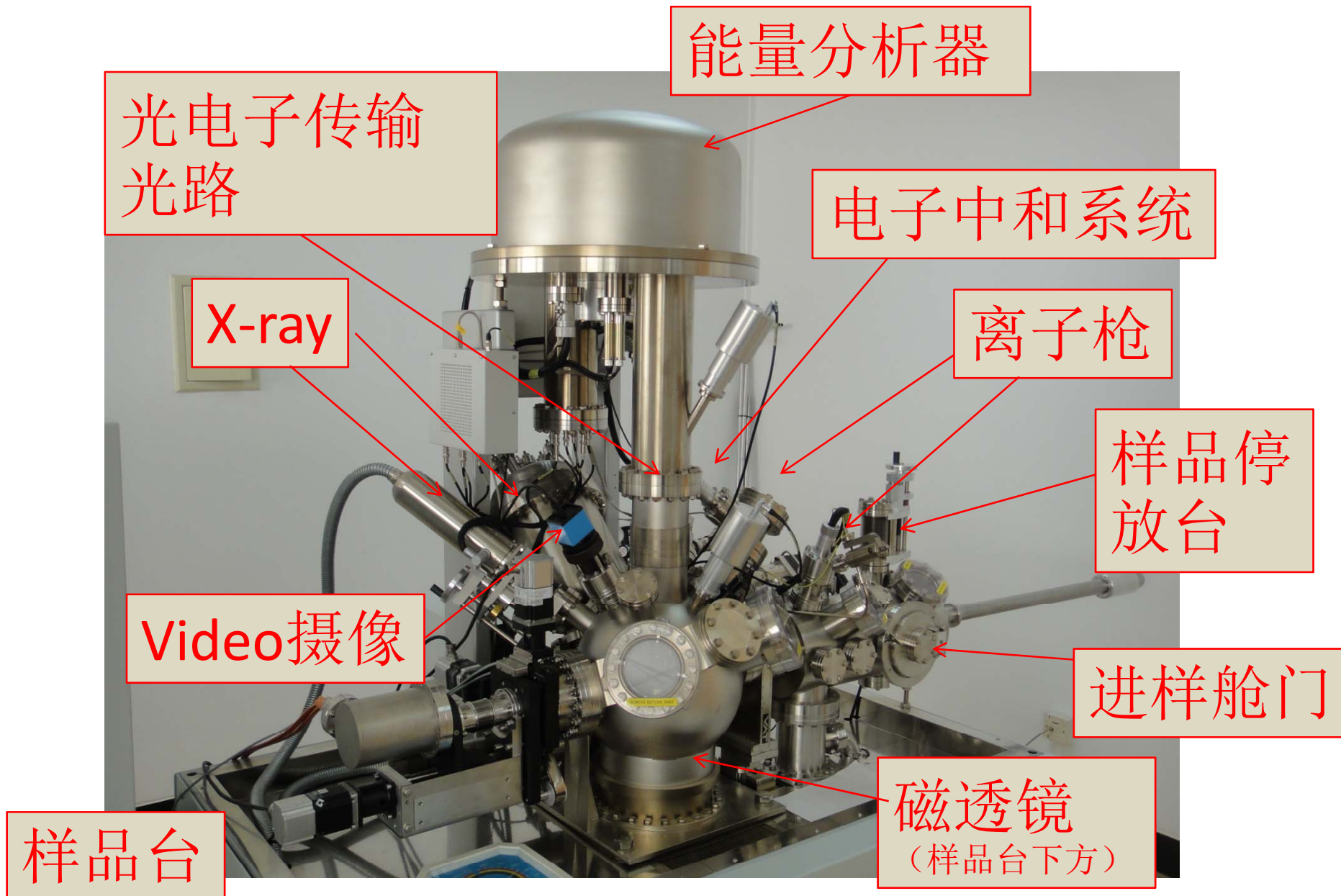
- 谱图处理
 - 根据实验结果、实验目的进行
 - 结合样品、仪器实验目的给出合理的谱图处理结果
 - 需要了解基础理论和方法，了解样品和仪器
- Avtange具有强大的谱图处理功能
 -

实验流程

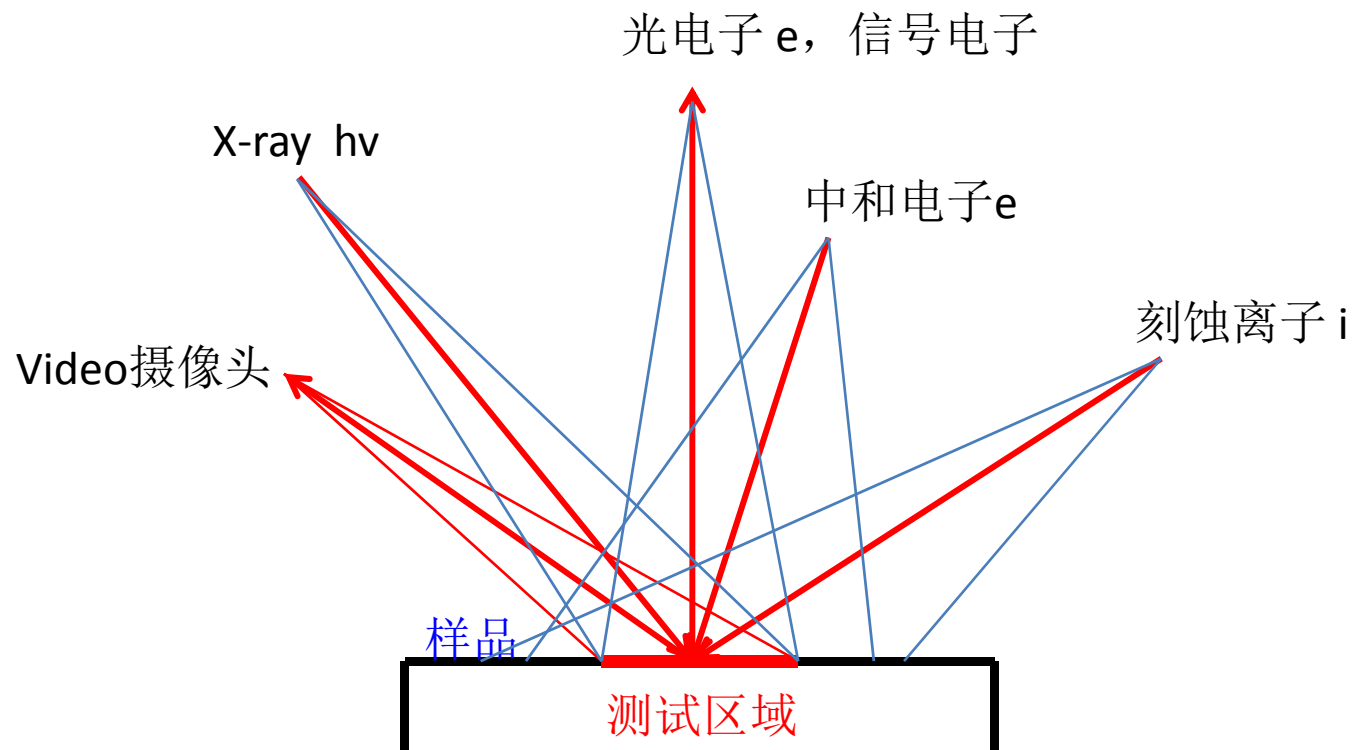
- 实验
 - 硬件条件：仪器功能和结构
 - 制样、装样、进样
 - 实验方案制定
 - 实验测量参数设置
 - 实验操作
- 实验结果
 - 数据处理
 - 优化实验
 - 实验结果报告

电子能谱仪器功能和结构

- 了解所用仪器的功能和结构，发挥仪器的功效
- 了解实验过程



ESCALAB 250Xi 电子能谱仪器



所有射线束光路要求共点、共焦于测试区域!

图 一般XPS分析中光电子激发和光电子采集示意图

了解各部件的位置, 几何方位

与样品制备有关部件

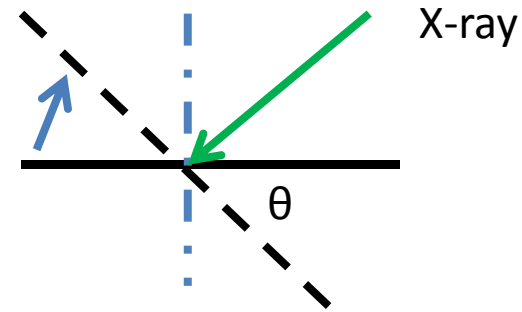
- 样品台及配件
- 加热台、冷冻台、蒸发器、高压反应池
- 断裂台、刮削器
- 手套箱
- 原位制样
-

样品制备方法标准

- ASTM
 - Surf. & Interf. Anal. 1991, 17(13), 965-971
 -
- ISO及GB/T

样品台结构

- X, Y, Z行程范围和倾角 (θ) 范围
 - X: 50mm, Y: 20mm, Z: 12mm / 1 μ m
 - θ : $-90\text{deg} \sim 60\text{deg}$, 分辨1deg
- 样品大小:
 - 高度: ≤ 2 (大台子), $\leq 3\text{mm}$ (小台子)
 - X, Y
 - 倾角: $\theta < 60\text{deg}$



一般XPS实验过程

1. 保持分析室超高真空，气压 $P \leq 1e-7$ Pa
 2. 通过Video摄像装置选择样品上分析位置
 3. X射线激发样品分析位置，收集光电子
 4. 同时电子中和系统喷射慢电子中和分析位置剩余电荷
 5. 如果需要，打开氦离子枪原位刻蚀样品
- 注意：如果2-4项不能对中分析位置，谱图可能出现异常，不能给出正确结果

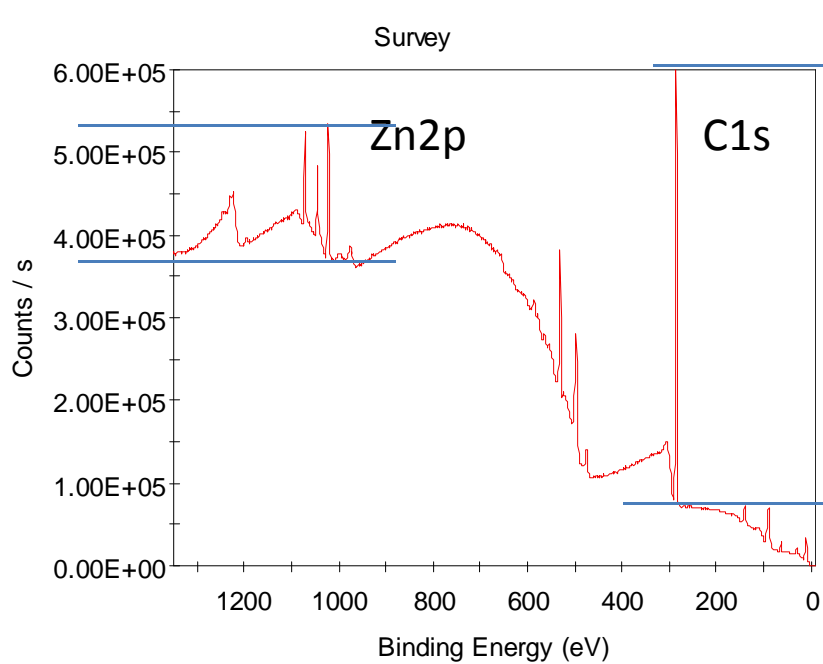
XPS样品要求

- XPS分析固体样品表面
- 样品表面平整、干净
- 样品放气气压低
- 不受污染、不分解退变
- 便于安装固定在仪器中
- 控制样品荷电
-

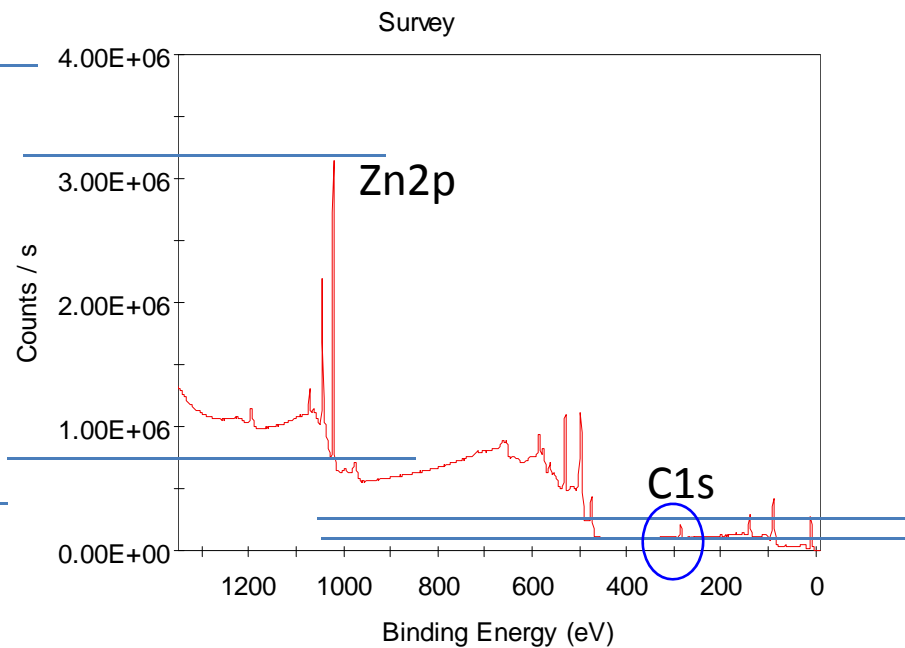
样品表面污染

- 样品存放在环境中不可避免地存在表面污染；
- 环境气氛污染元素一般：
 - C、O、Na、Cl、S、Si、Ca等
- 例如：在空气存放的ZnO样品表面

氧化锌薄膜：长久暴露在空气中表面被污染



放置约半年



新制备

样品表面污染

- 样品表面污染不可避免，样品在真空中污染慢、程度小；
- 为减少污染，样品制备后应尽早送入样品真空室测试
- 清洁样品表面方法
 - 干氮气吹；
 - 有机溶剂（酒精）、水等直接物理清洗，用干氮气吹干；
 - 离子（ Ar^+ ）刻蚀清洁；
 - 机械清洁，刮削、打磨、断裂等；
 - 预抽、加热脱附等；
 - 化学清洁；
 -

样品表面污染

- 样品表面污染不仅降低原始信号的强度，还出现污染物的干扰峰和背景的提升

信号电子逃逸深度与表面分析

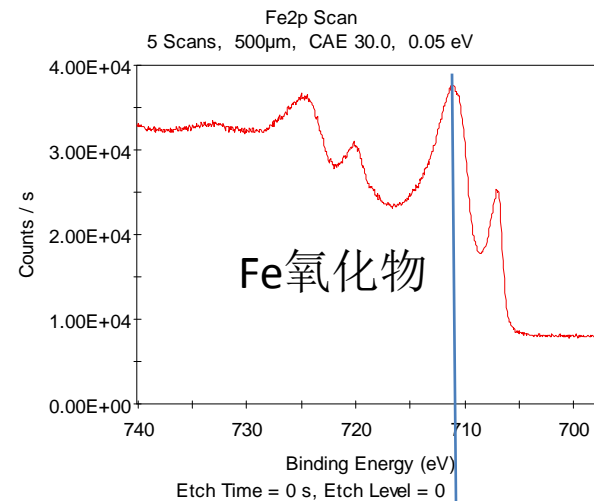
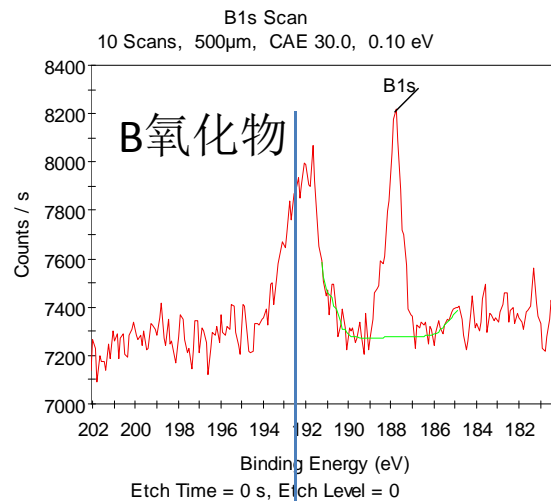
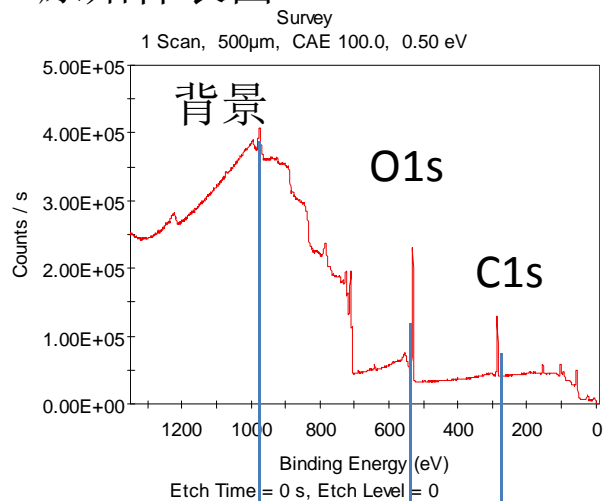
- XPS属于表面分析，分析深度取决于信号电子逃逸深度，取决于电子在固体中散射平均自由程 λ ，其典型分析深度 $3\lambda = 6\text{nm}$ 。
- 覆盖层厚度 t 对信号电子强度的影响

$$I = I_m \exp(-t/\lambda_{tm})$$

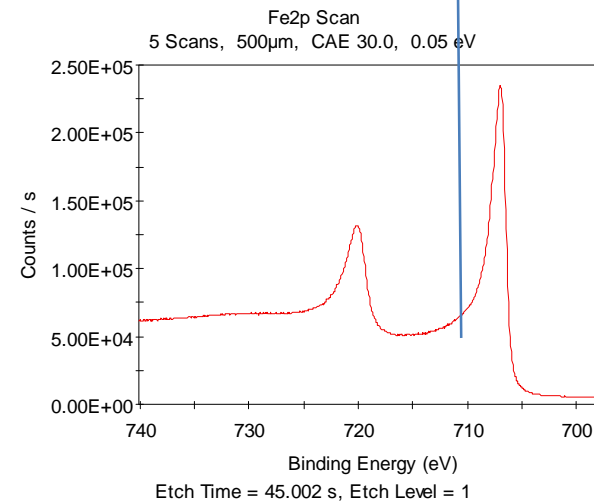
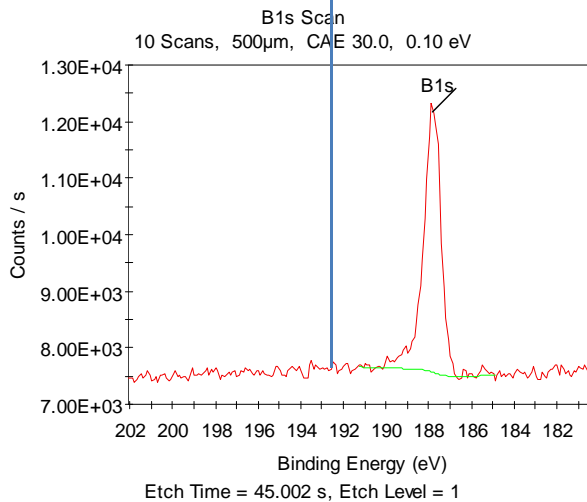
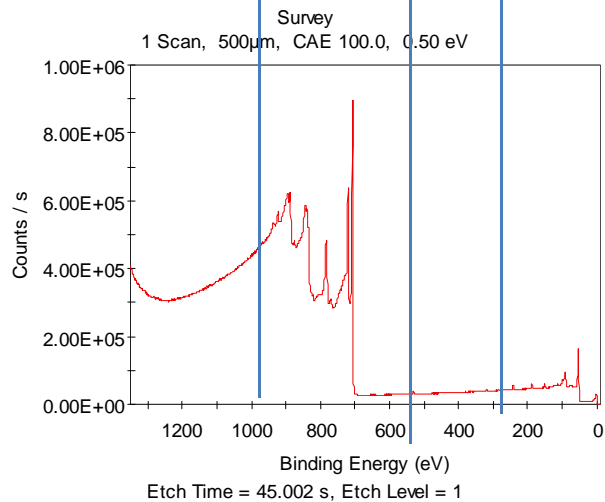
如果样品表面存在 $t=2\text{nm}$ 污染覆盖层，则信号 I_m 衰减(I_m/I)= $\exp(2/2)=2.7$ 倍，这里取 $\lambda_{tm}=2\text{nm}$ 。

- 覆盖层以下的信号电子进入探测器前，在覆盖层中散射，导致背景抬起。

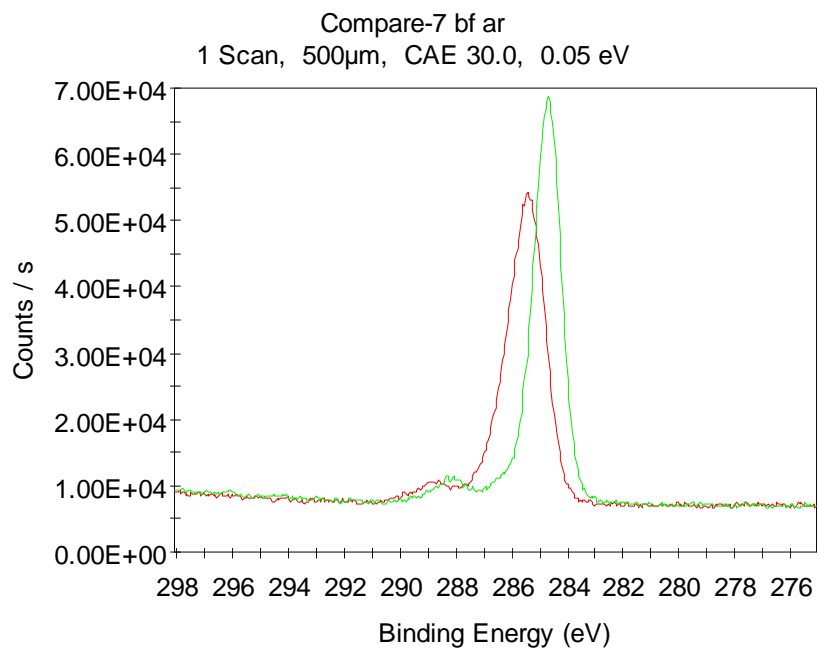
原始样表面



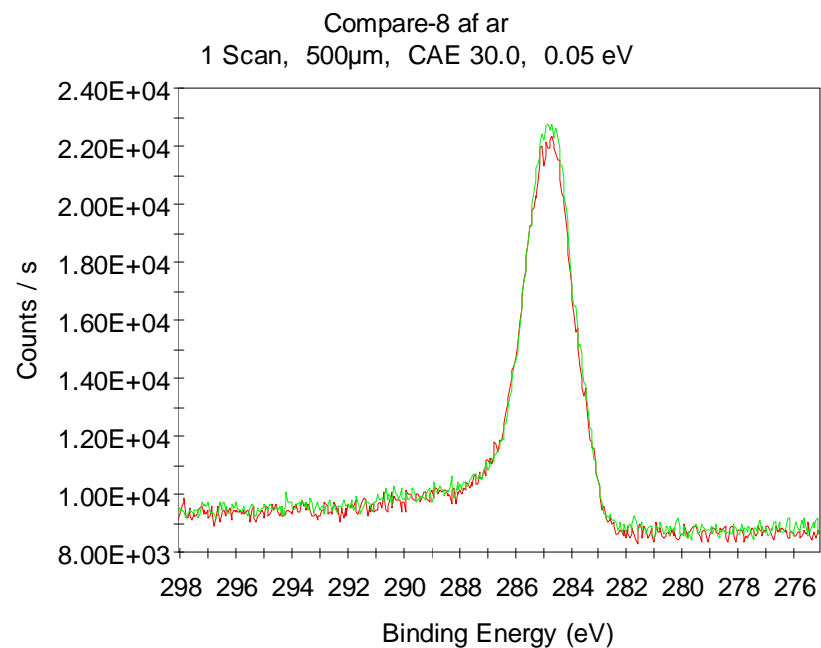
经过Ar+刻蚀45s后



有污染金属(Ni)表面打开中和枪前后的XPS

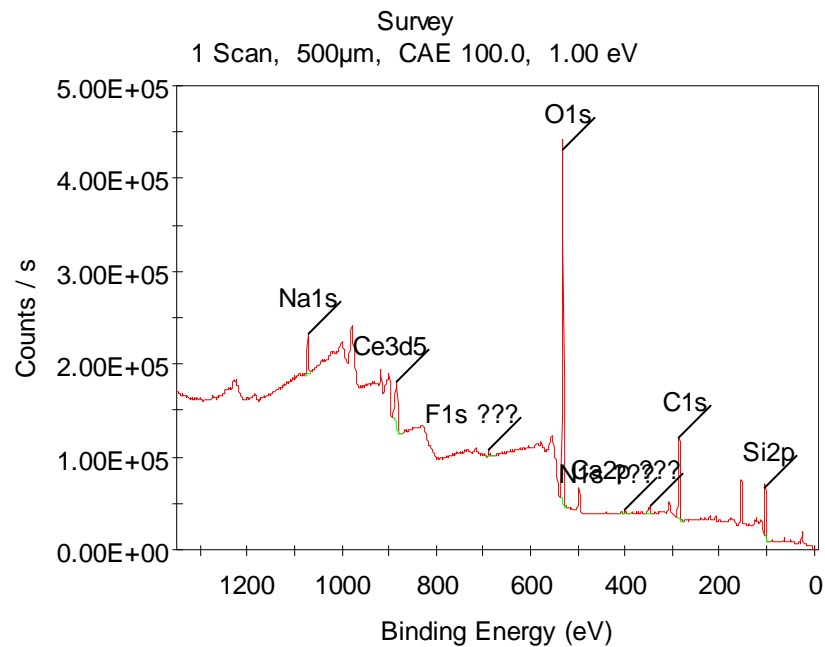
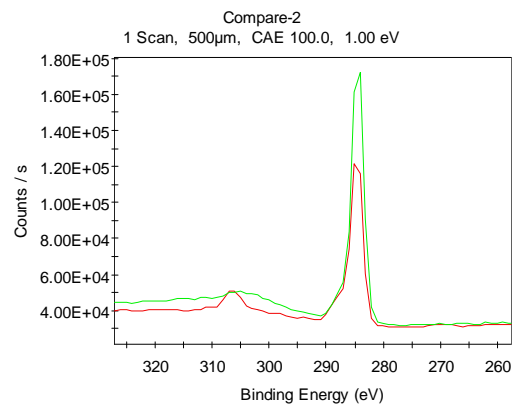
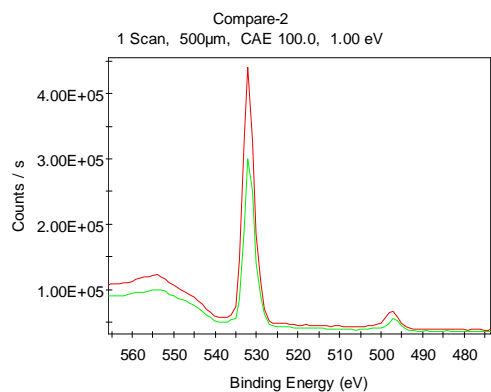
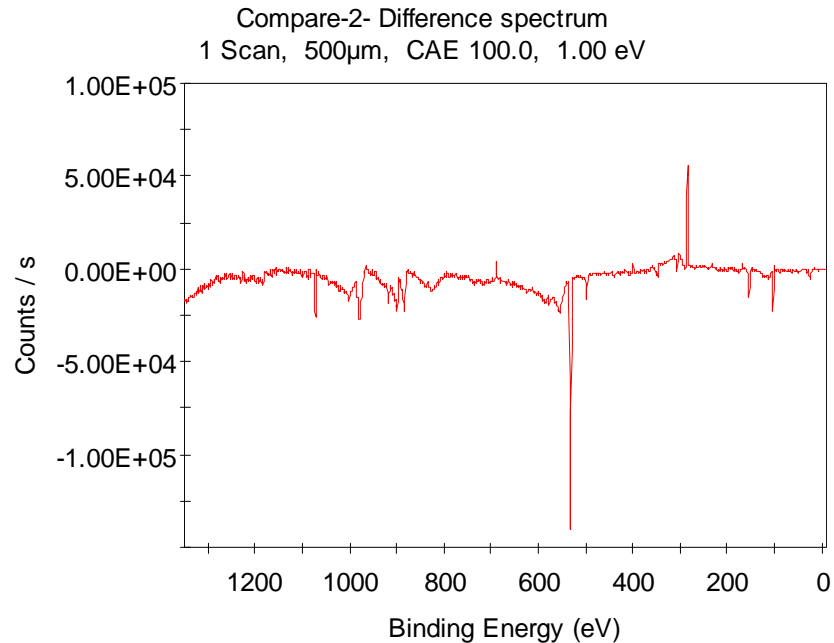
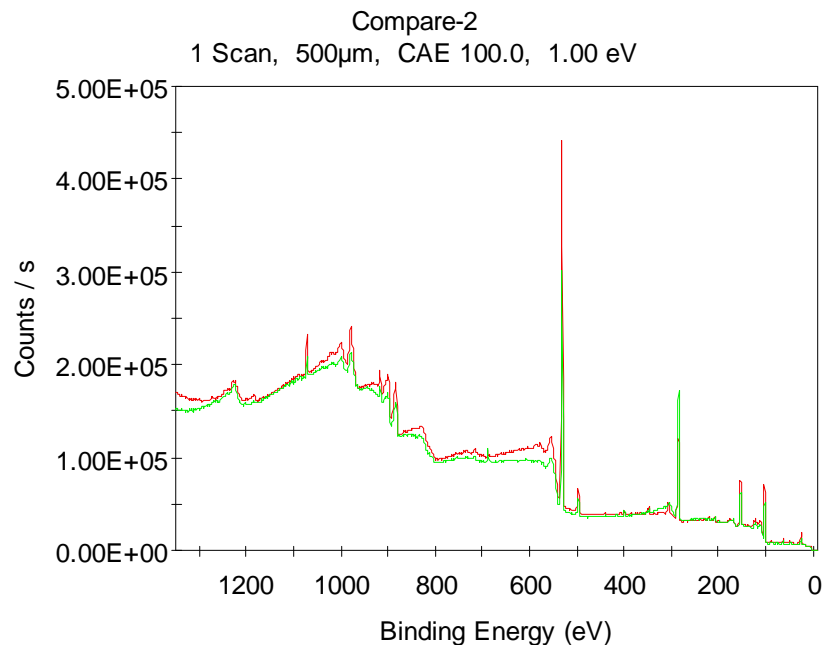


经Ar+清洁后打开中和枪前后的XPS



表面污染不同程度地影响样品表面荷电，深度剖析时常出现。

样品表面受污染, C1s 285增加,其它峰减小.

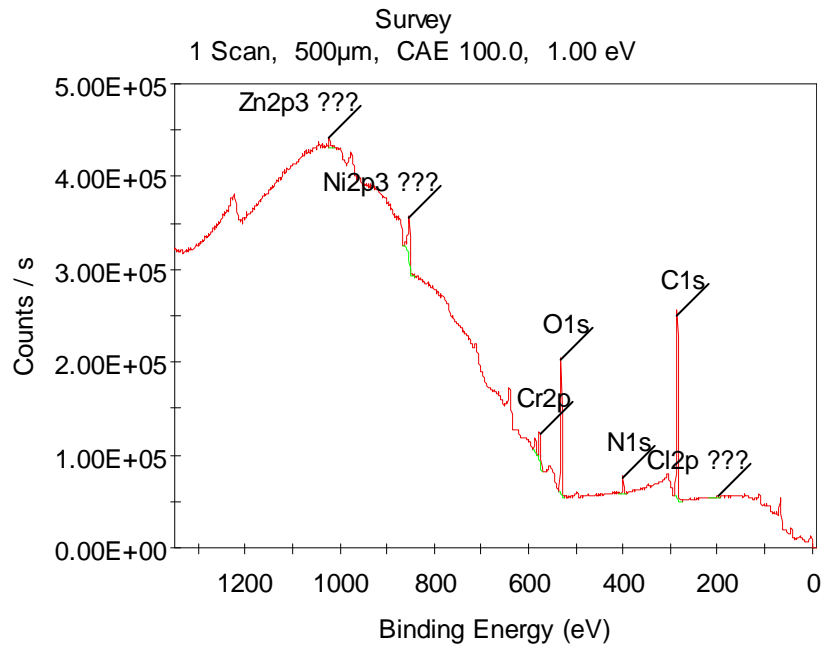


比较样品放置时间长（绿）与短（红）XPS谱比较

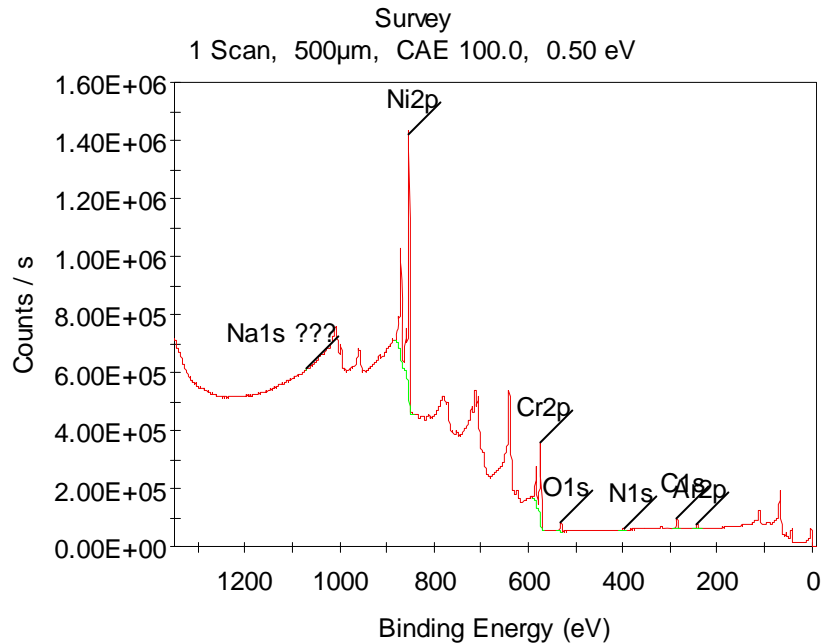
减少样品表面污染

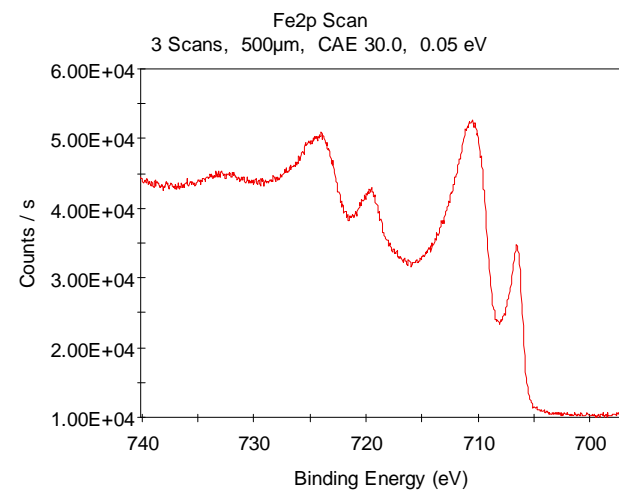
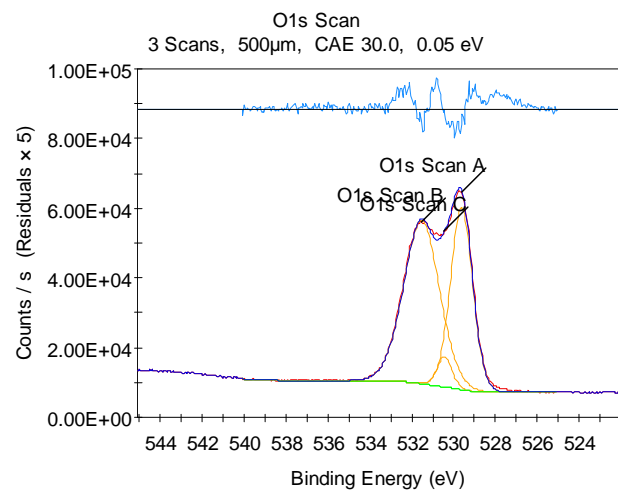
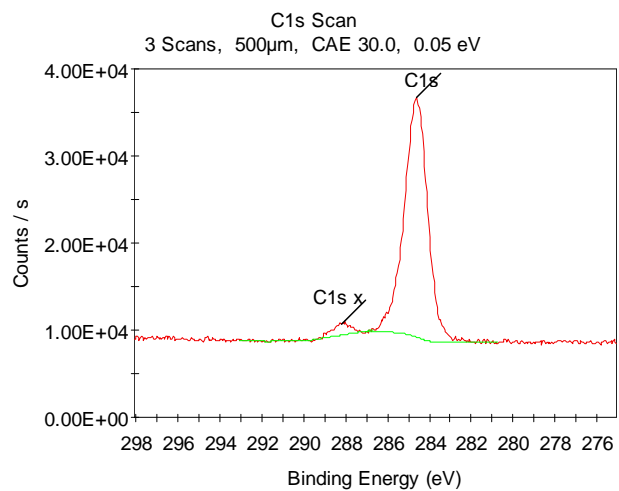
- 减少污损样品方法

- 注意保存样品，尽量存放时间短、环境干净、妥善保存；
- *沉积Ta、Pt等盖帽层，防止表面氧化污染；*
- 实验中尽量少用 或 不用胶带，而使用卡子或螺丝簧片安装样品，减少样品在真空中的污染；
- 对于已经出现的污染，采用适当清洁方法：如刮削、打磨、水或有机溶剂清洗；可用温和 Ar^+ 离子轻轻刻蚀样品表面，如有条件可以采用团簇离子枪；
- 样品受污染后能用 Ar^+ 刻蚀？粉末样品能 Ar^+ 刻蚀？

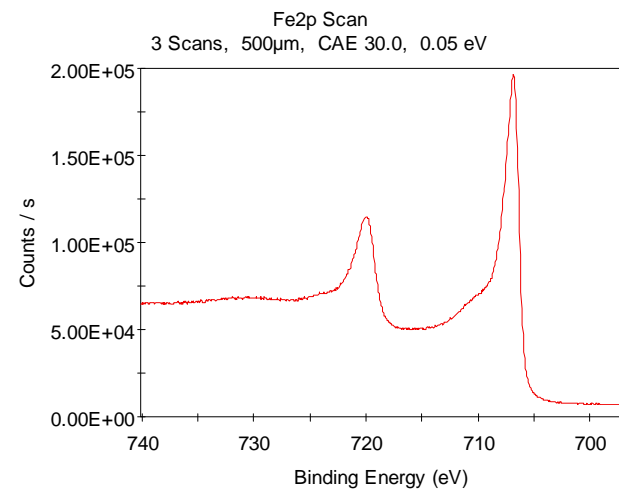
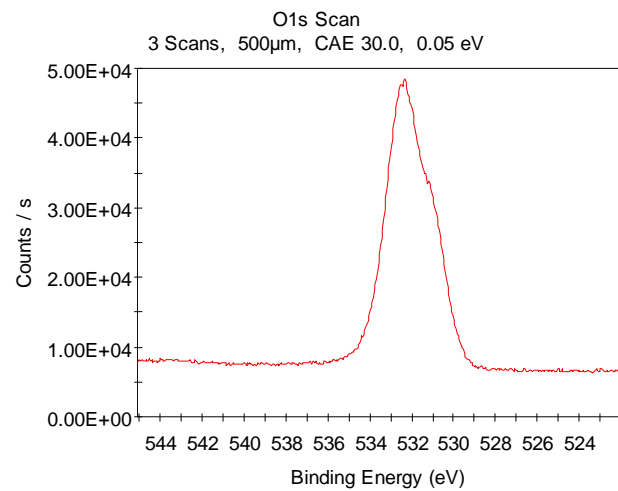
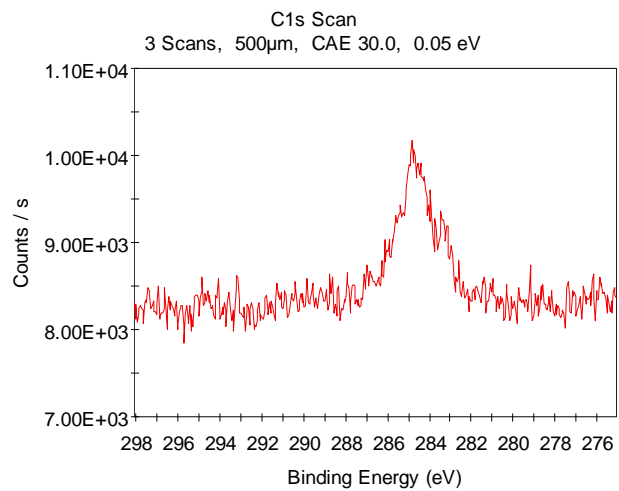


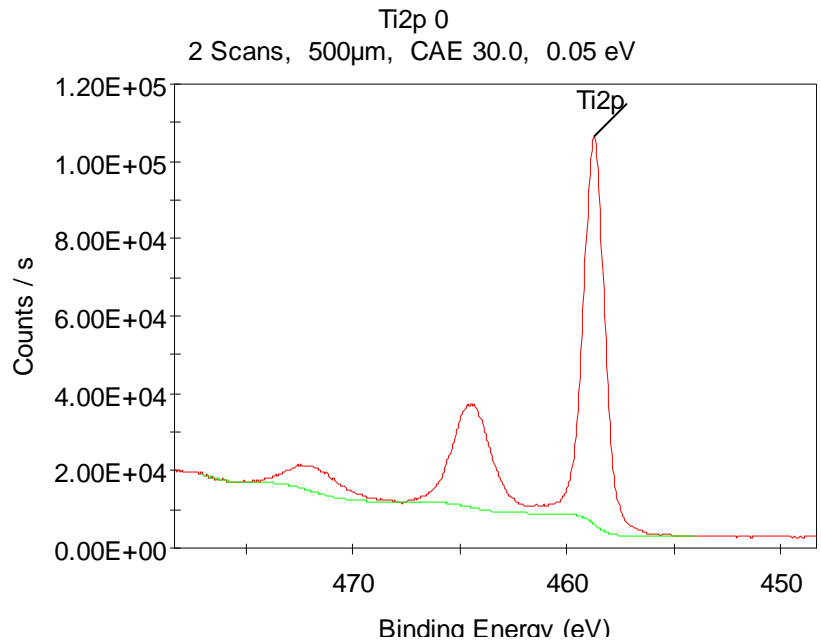
Ar⁺清洁样品NiCr合金表面，刻蚀60s





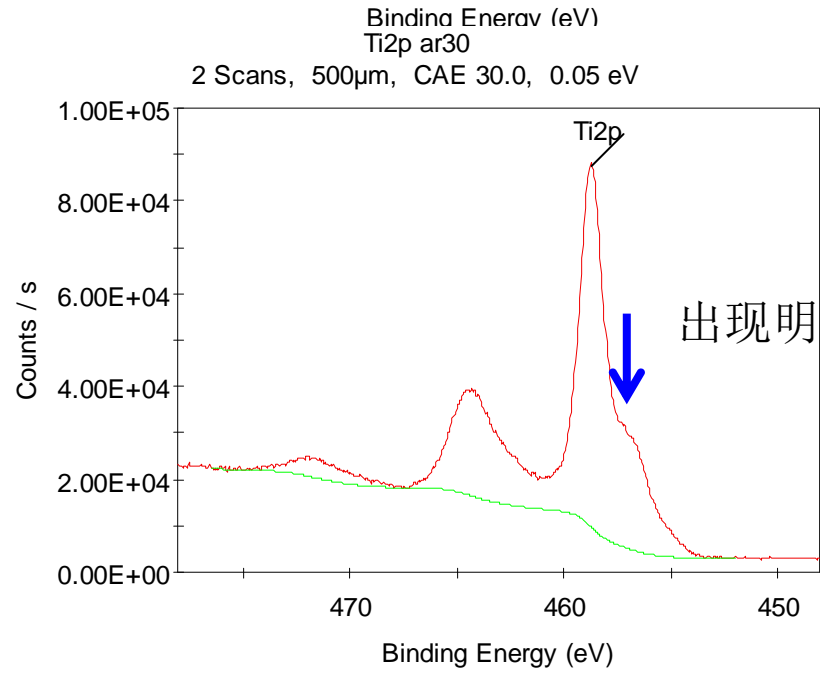
含Fe样品表面Ar离子清洁前后，XPS对比





原始样

但是对于TiO₂, Ar离子刻蚀诱导还原反应发生。不是所有的样品均可以随意进行Ar+清洁刻蚀。

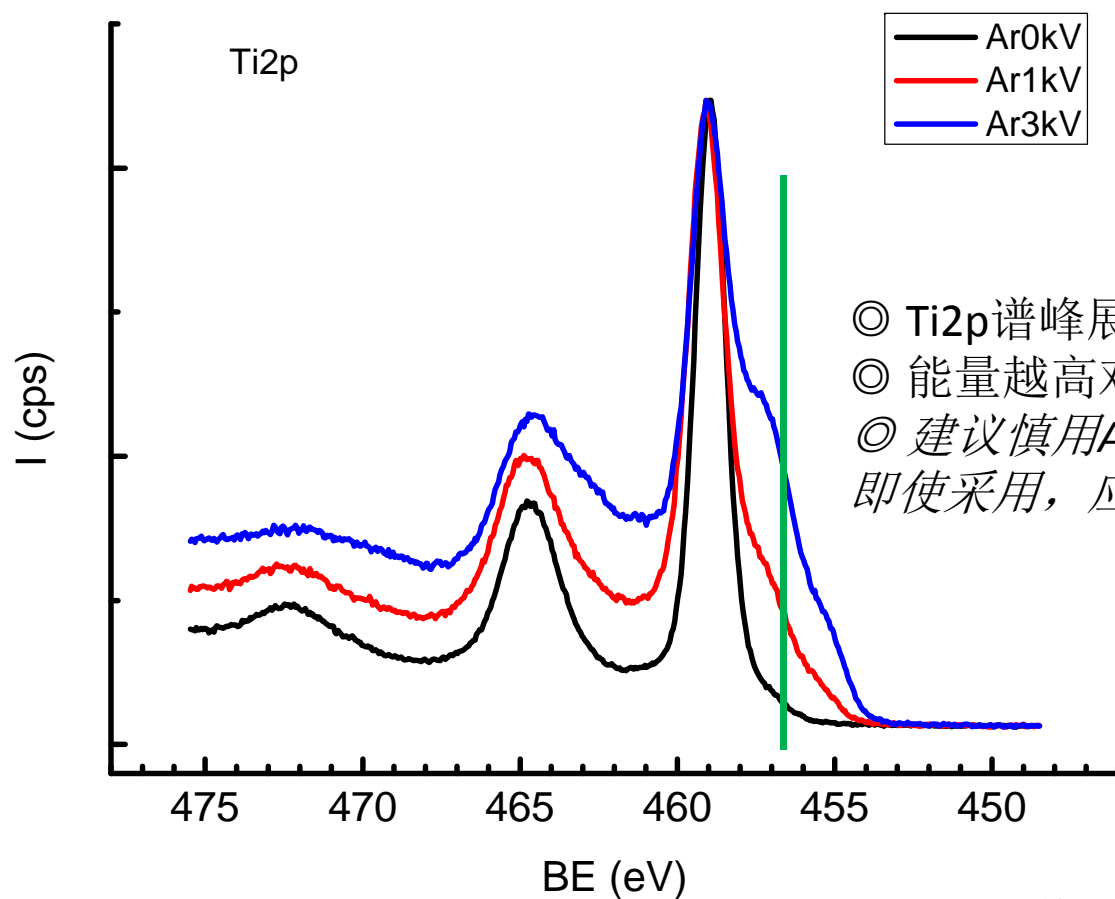


Ar⁺刻蚀30s后

出现明显的Ar⁺损伤, Ti被部分还原

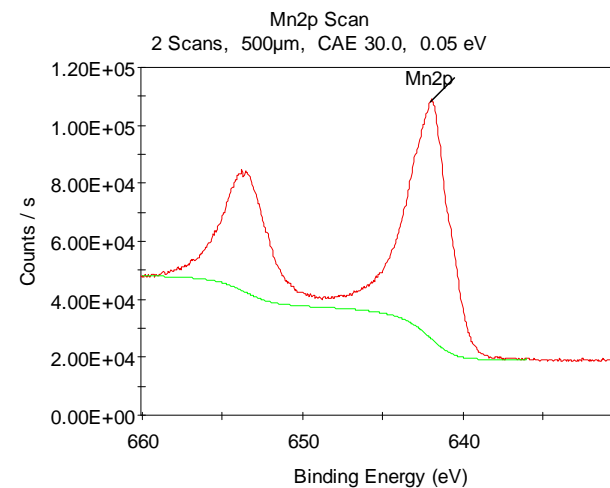
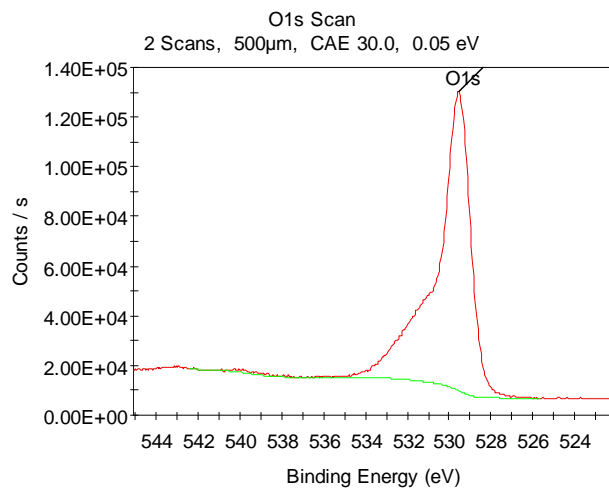
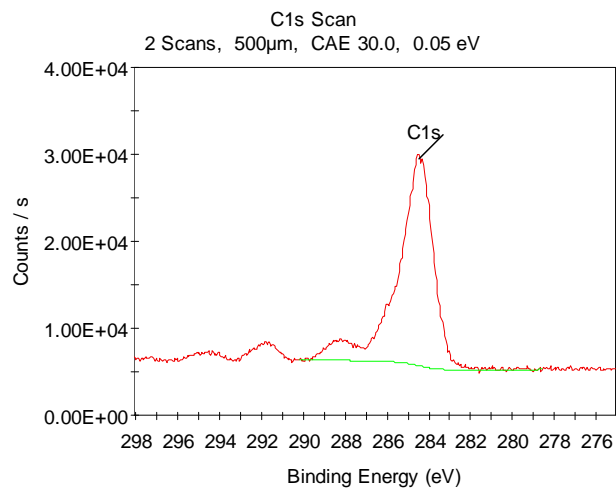
Ar⁺刻蚀前后对比, 刻蚀条件1keV, 50uAcm⁻², 30s

Ar⁺刻蚀TiO₂诱导损伤



- ◎ Ti2p谱峰展宽。
- ◎ 能量越高对TiO₂的损伤越大，即Ti⁴⁺还原反应。
- ◎ 建议慎用Ar⁺刻蚀TiO₂；均衡考虑污染和损伤，即使采用，应采用低能Ar⁺，并控制好剂量。

其它条件相同：
Ar⁺刻蚀60s；
~50uA/cm²



C信号减小



Mn₃O₄粉末样品，采用温和条件 500eV， 50uAcm-2, 30s
对样品损伤、诱导反应可忽略！

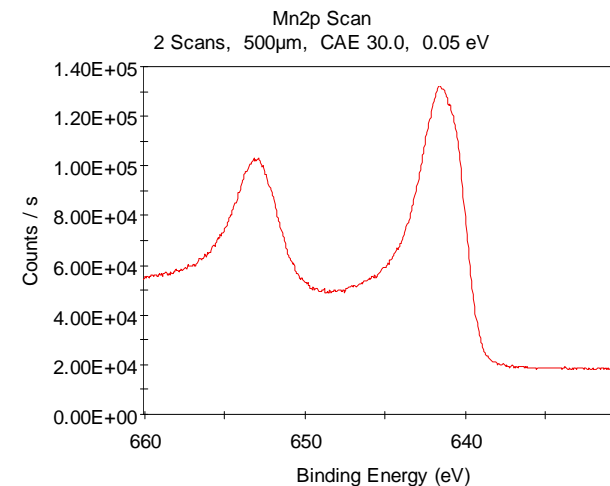
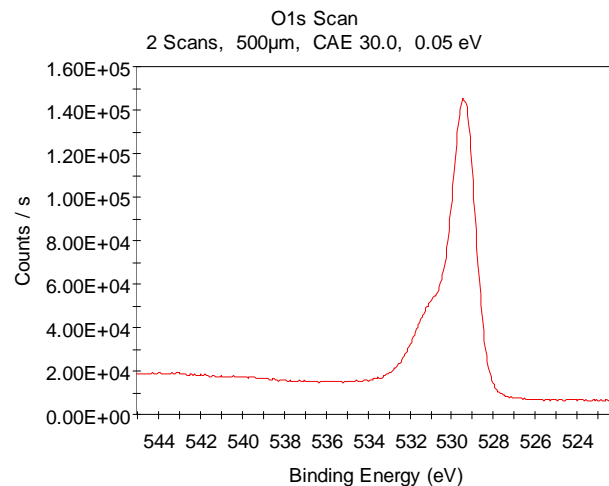
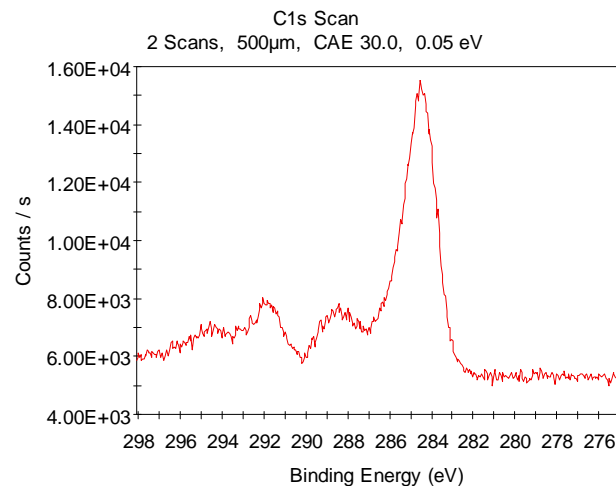


图 粉末Mn₃O₄在温和条件Ar+刻蚀前后的XPS结果对比

样品准备

- 样品准备是XPS分析中的重要环节，必须结合结合实验目的、实验条件等，有很强的技巧性，需要经验积累。
- 本报告主要涉及已有样品在分析前的准备，不涉及样品的加工、生长等

样品准备

- XPS几乎能分析所有固体样品，且现代XPS仪器样品的用量很小。但是要得到理想的XPS结果，还需要掌握必要的制样技术，认真制样。
- 根据样品的特性和分析目的合适制备样品。需遵循：不损伤仪器（如污染真空）；不损毁样品待测信息；引入杂质不影响分析结果；降低分析中荷电效应等对谱峰的影响；

样品准备

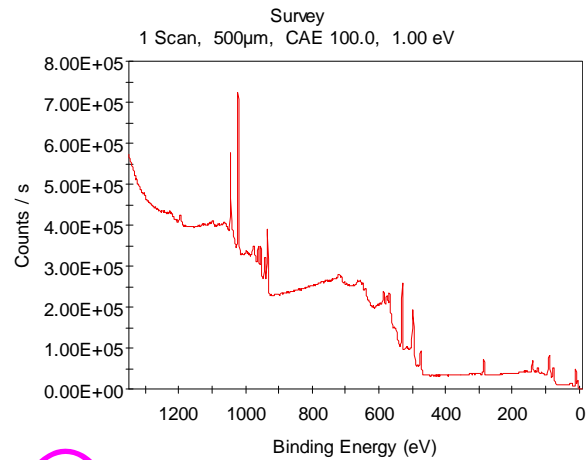
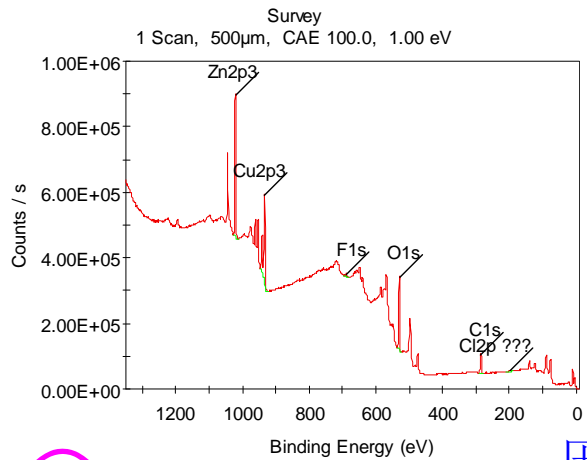
- 一般制样要求，表面干净、平整、不含挥发性物质
 - 片状样
 - 粉体样
 - 纤维细丝（网）样品
 - 液体、离子液体、膏状、明胶样品
 - 避免基底干扰峰

样品准备

- 粉体制样
 - 压片
 - 粘到双面胶带上
 - 分散到水火挥发性有机溶剂中，形成悬浊液滴到硅片等固体基片、金属箔或滤膜、海绵等基底上

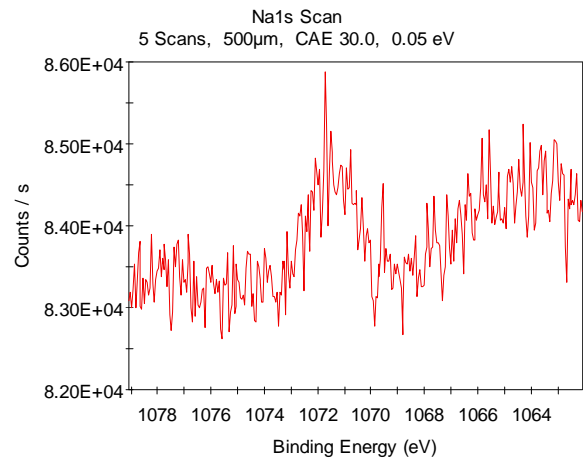
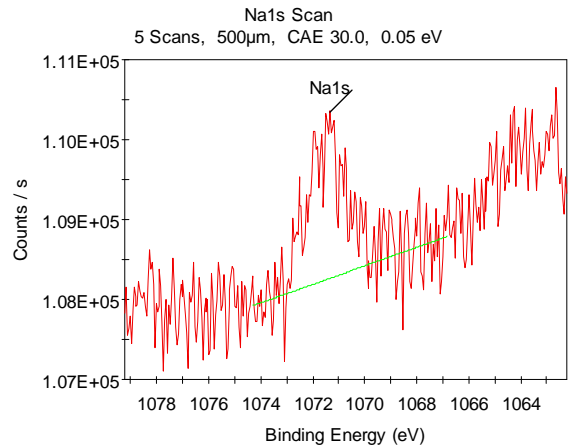
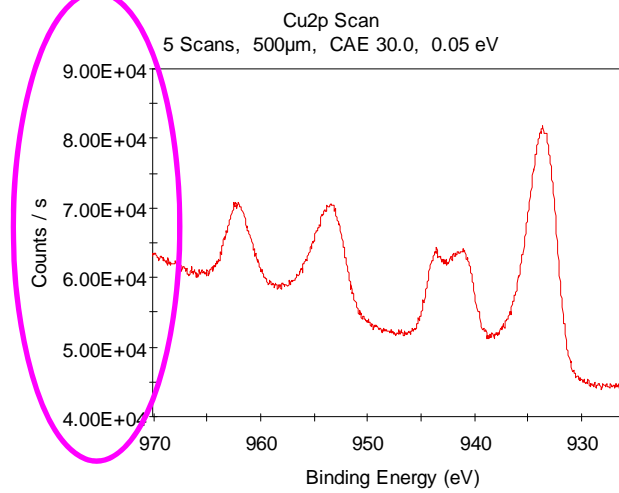
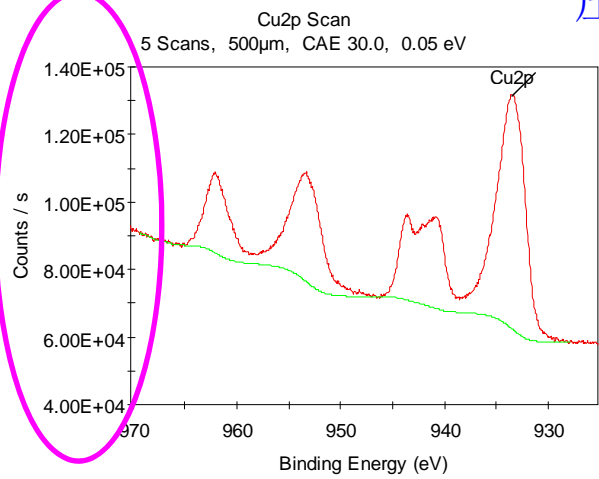
粉末颗粒细、样品表面平整

- 颗粒细（一般小于0.2mm）且均匀
- 尽量选用平整测试区域

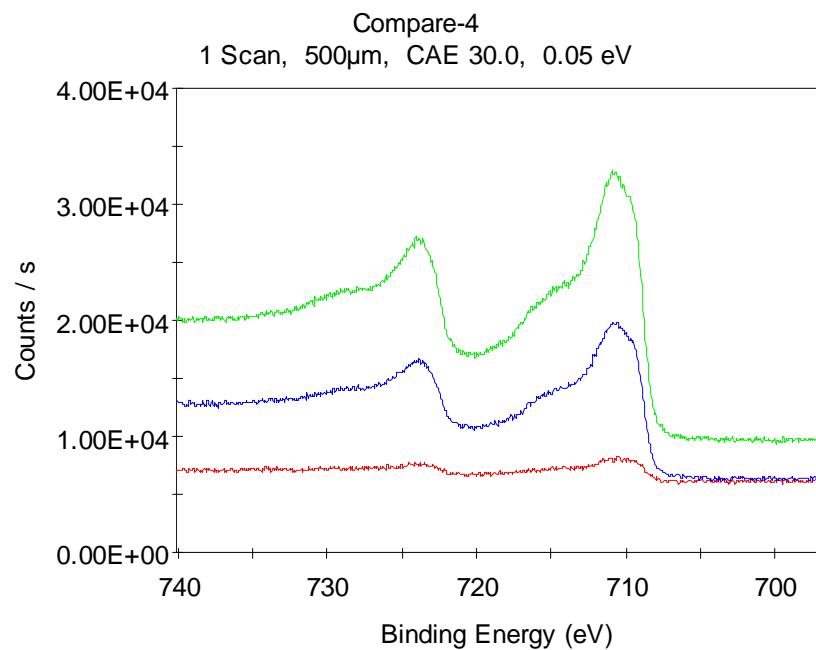
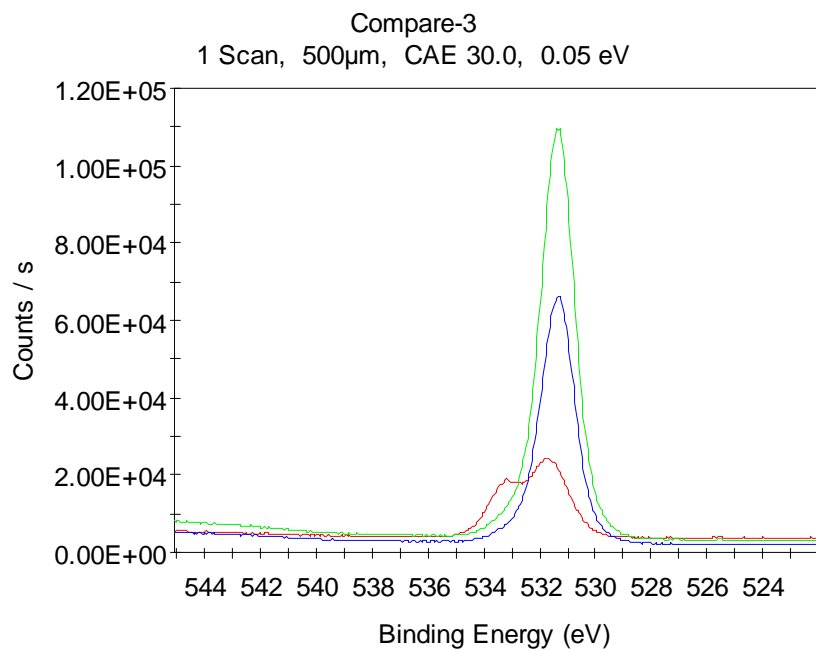
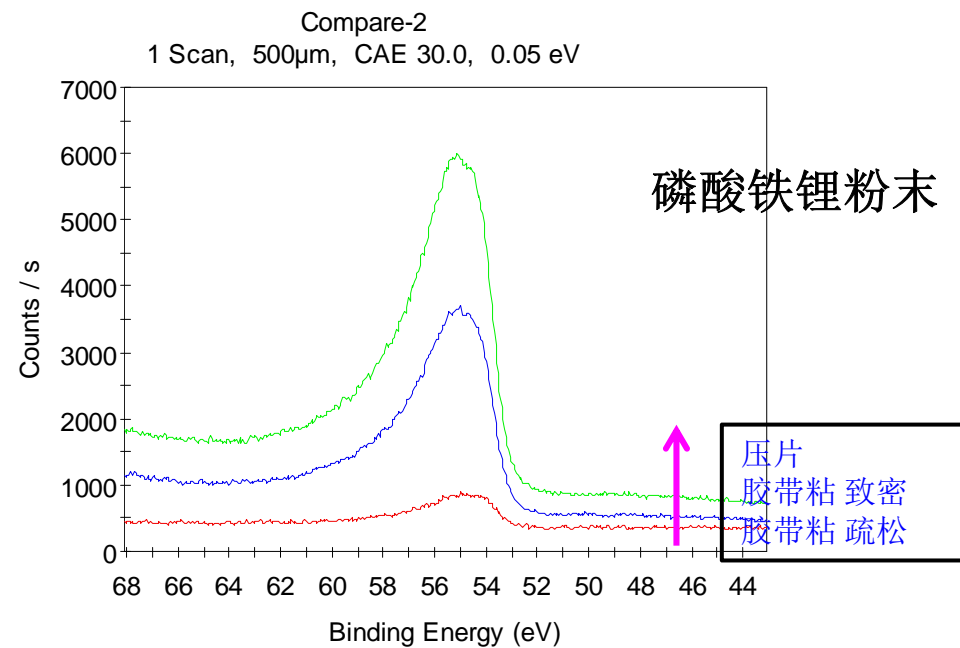
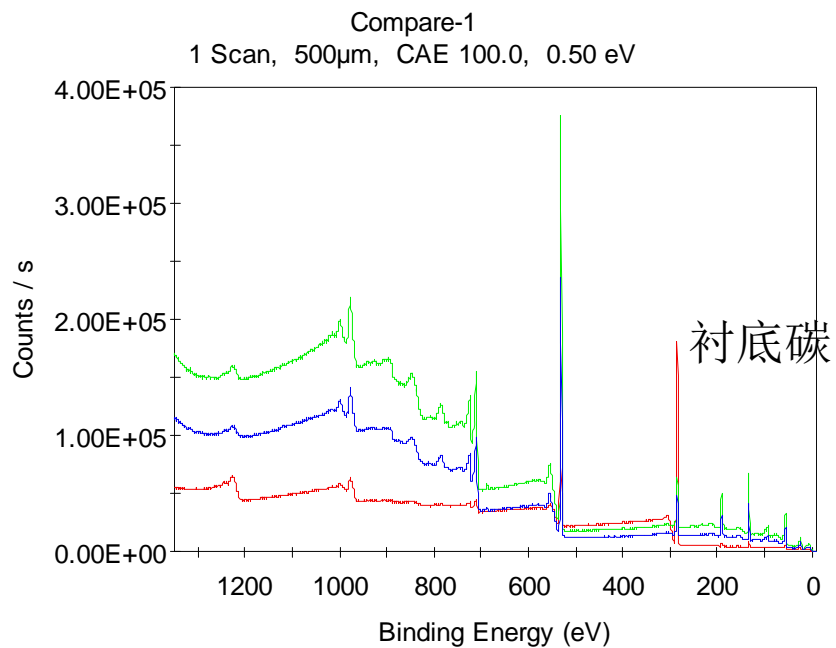


压片

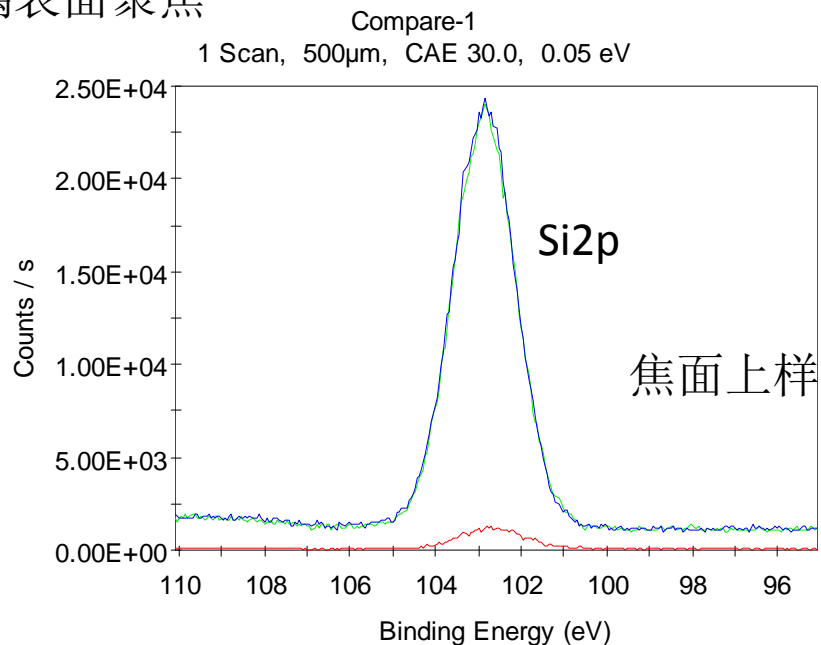
粘在双面胶带上



两种制样比较：
粉末样品压片与
粘在双面胶带上。
强度和信噪比明显改善



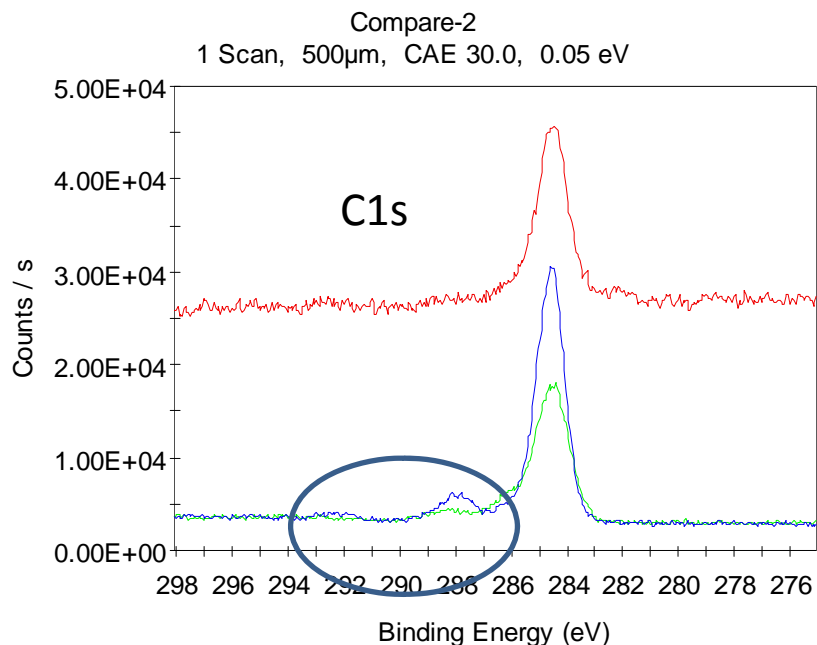
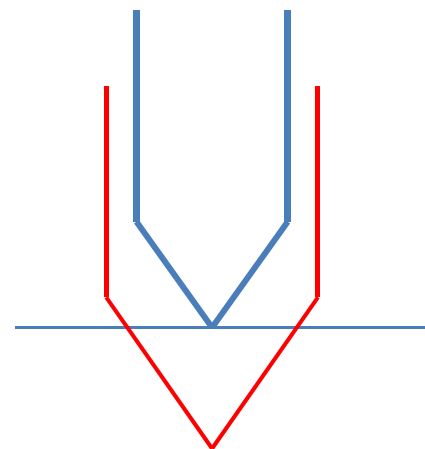
玻璃表面聚焦



焦面上样品信号

过焦300um

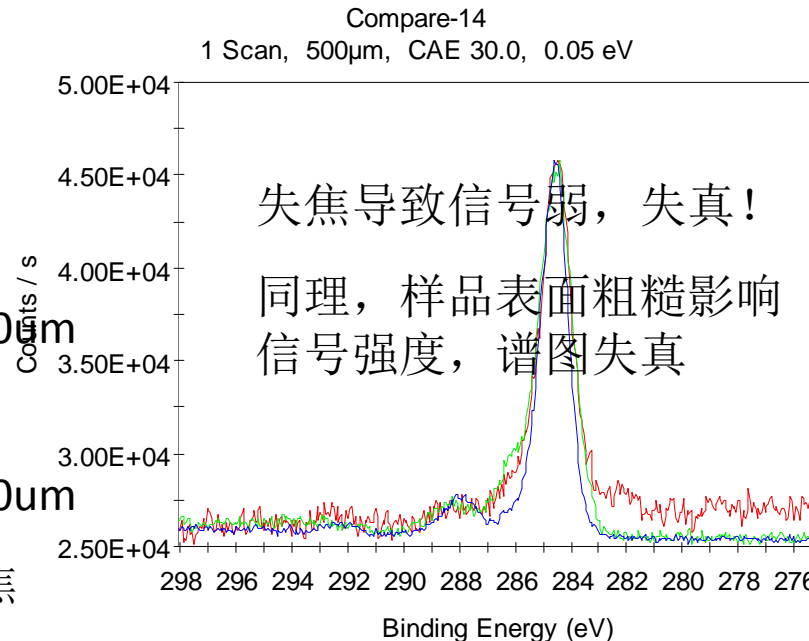
失焦对采集信号的影响



欠600um

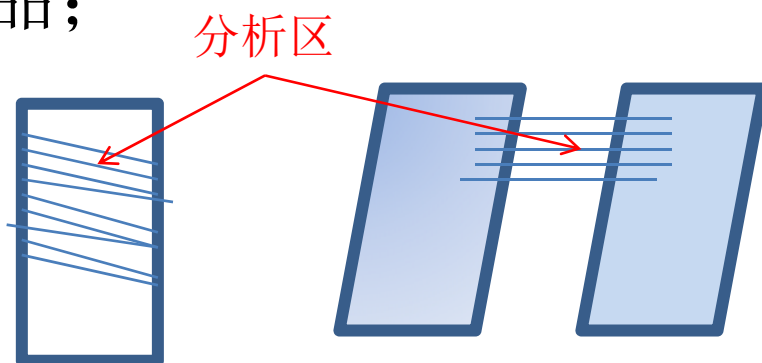
欠300um

正焦

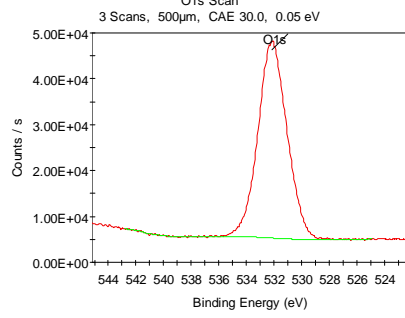
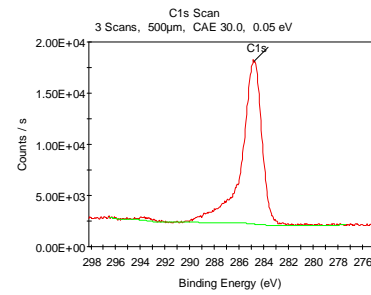
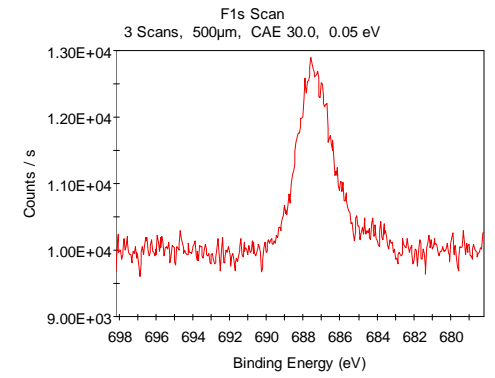
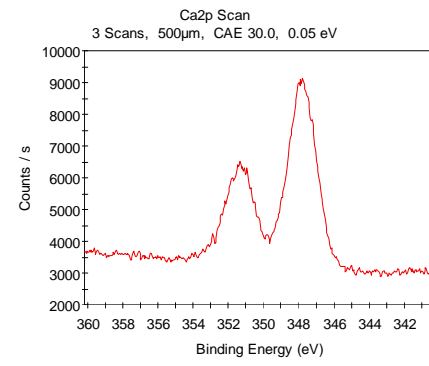
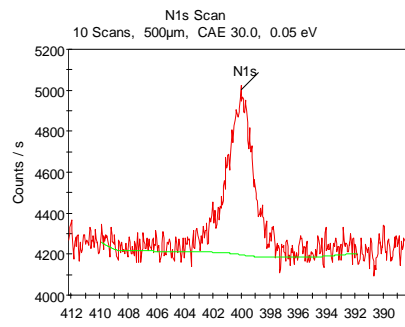
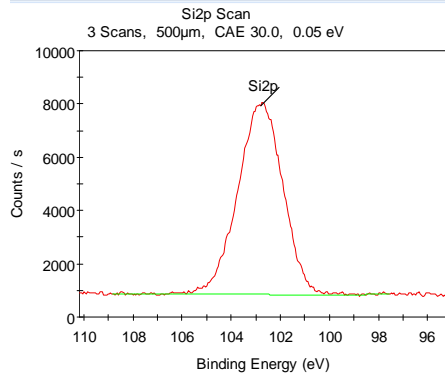
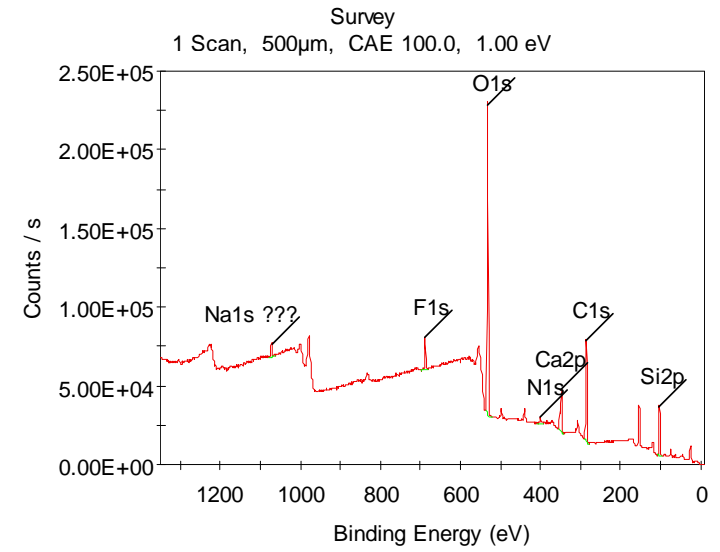
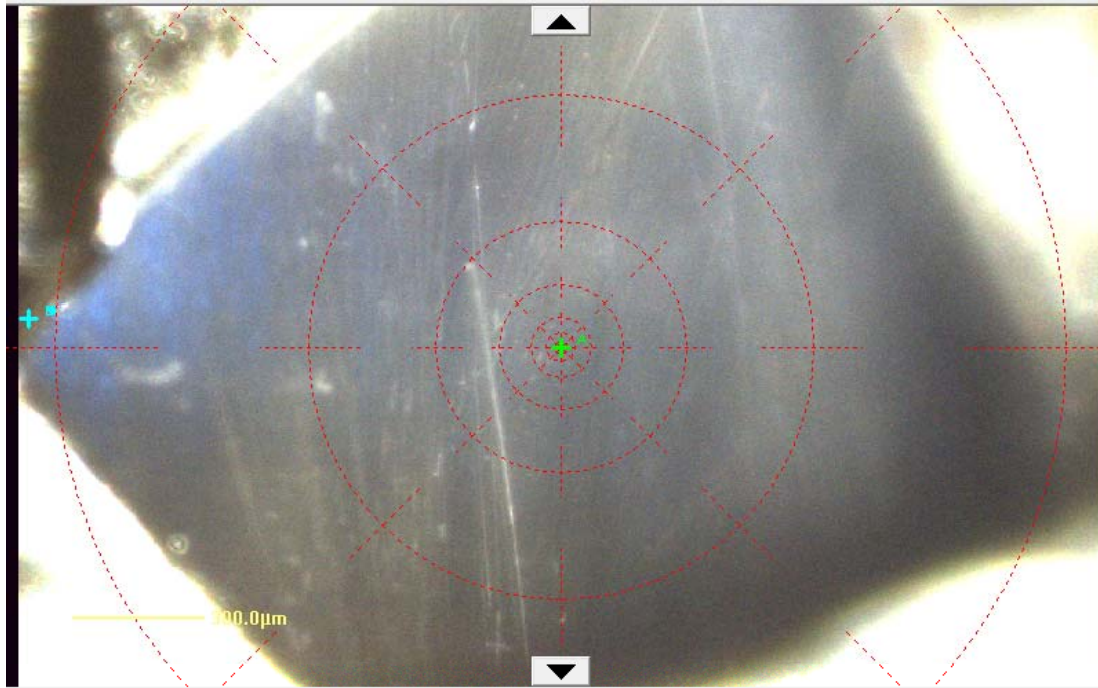


样品准备

- 纤维细丝（网）样品
 - 缠绕或压在架子或回形针上，或样品台的孔中央，分析区域内纤维丝悬空，避免基底元素干扰分析结果；
 - 包裹在有孔的铝箔中，用小束斑XPS分析孔内样品；

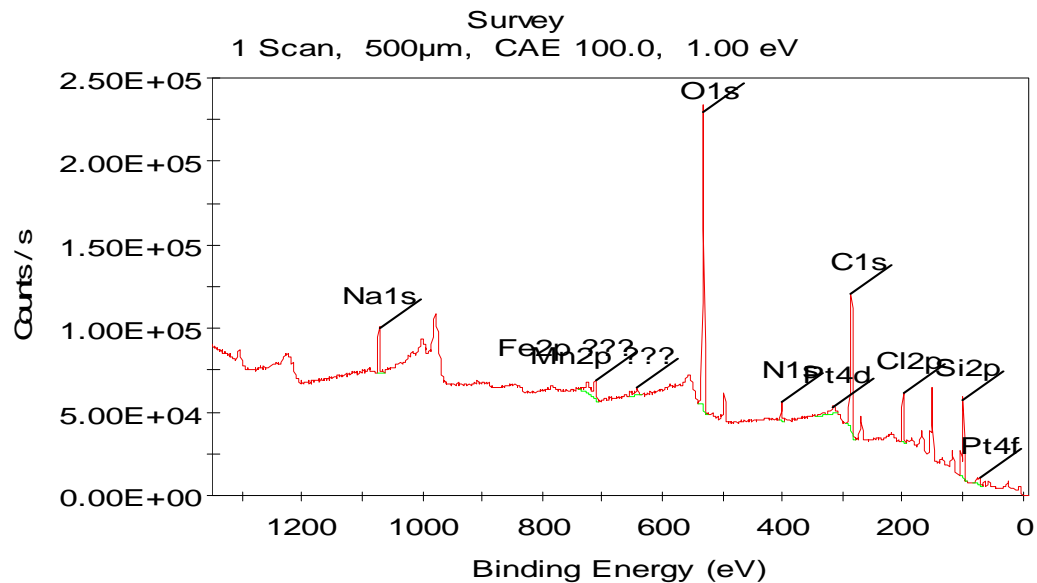


小束斑XPS分析孔内的玻璃纤维丝

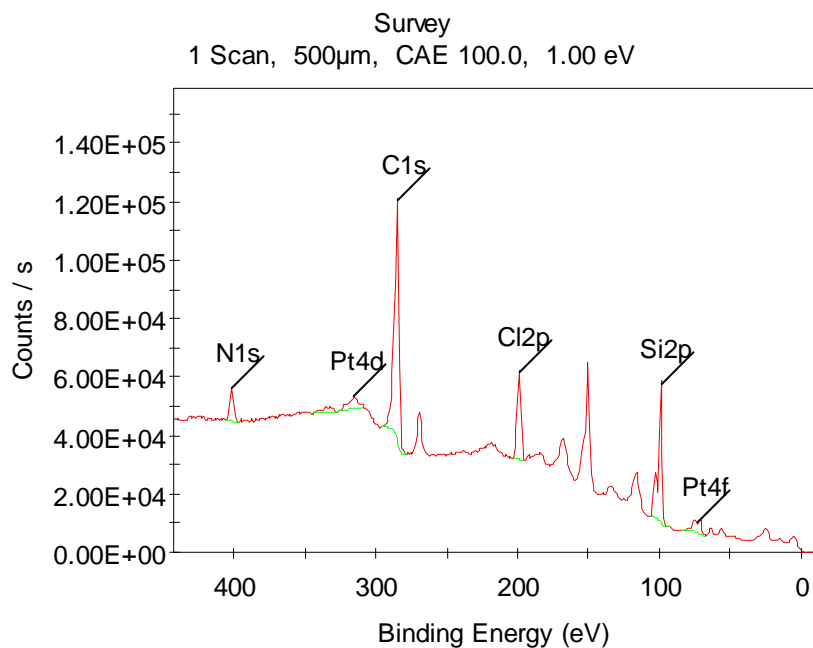


样品准备

- (悬浊) 液体、离子液体、膏状、明胶样品制样
 - 滴到Si片、聚乙烯/聚丙烯、金属片、滤膜、树脂、海绵等固体基片上晾干或冷冻干燥后上机测试
 - 注意基底干扰，预测空白，正确选择基底



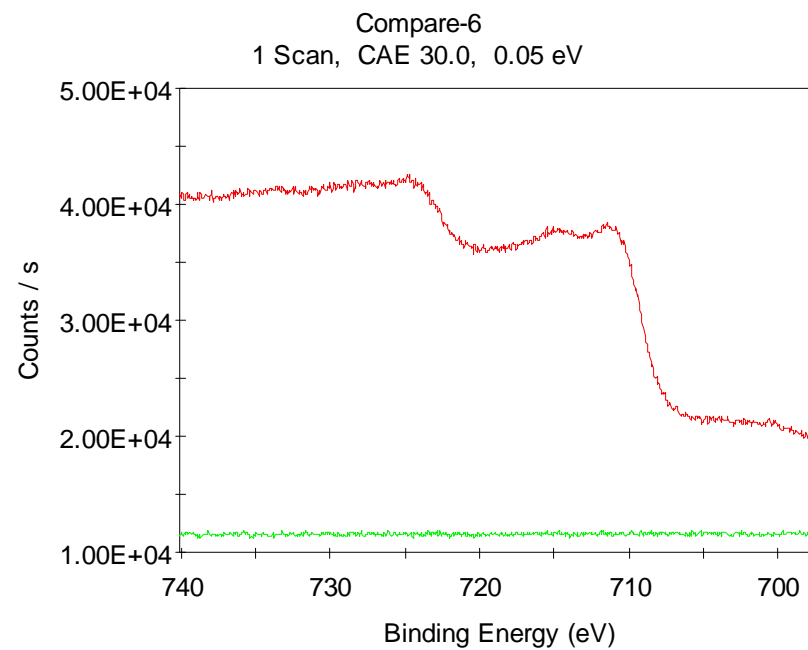
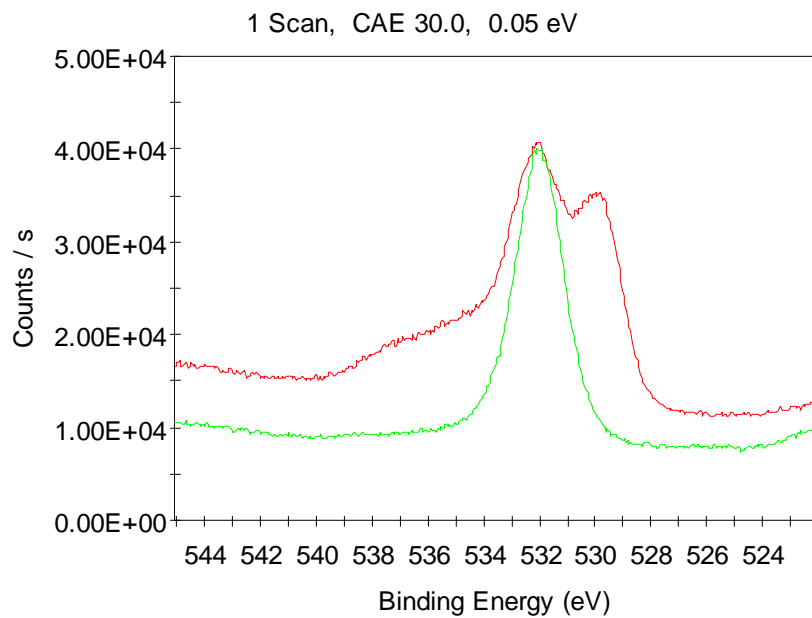
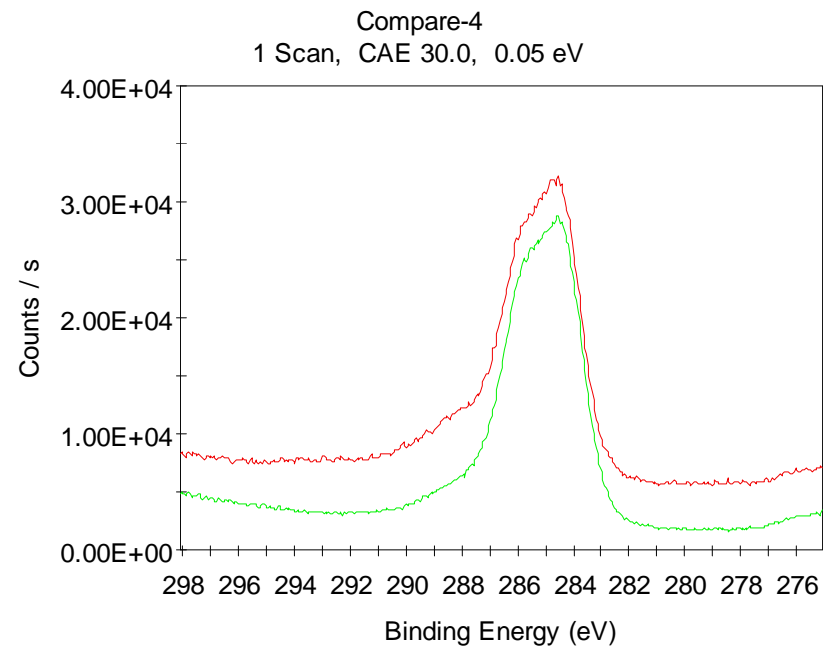
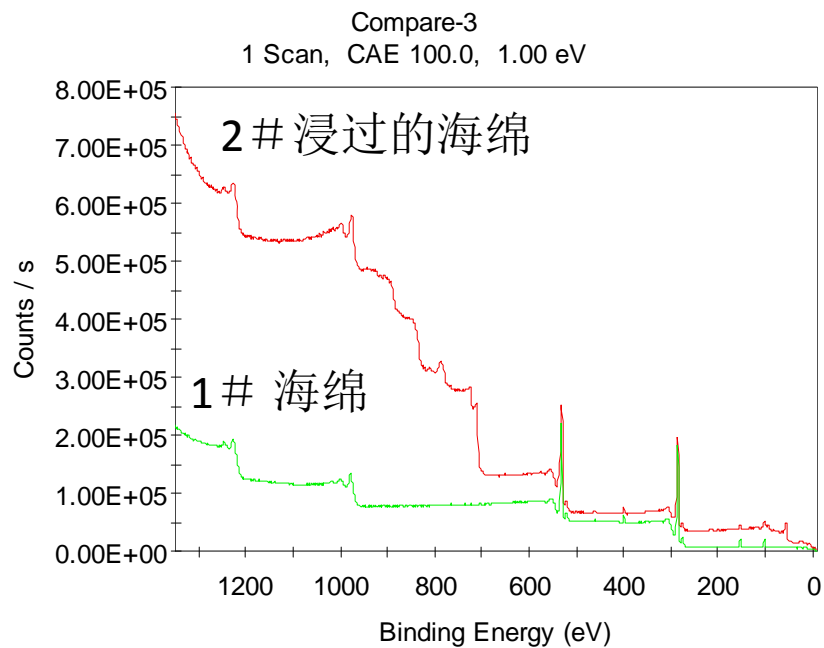
比较基片在负载样品前后的
XPS峰，注意存在等离子激元峰



Si片基底，在Si2p和Si2s高结合能
方向上出现一系列的等离子激元
损失峰，应充分估计这些峰对负载
样品的干扰。同样Al箔也有类似的
损失峰。

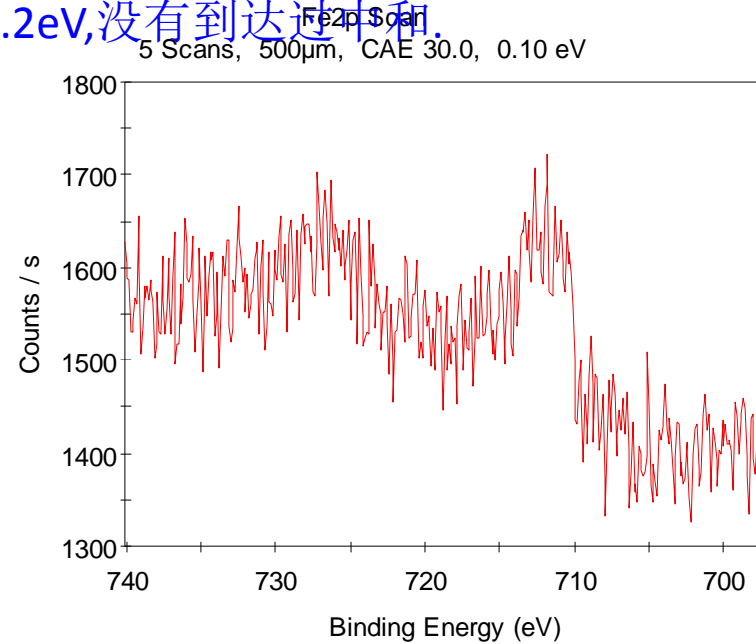
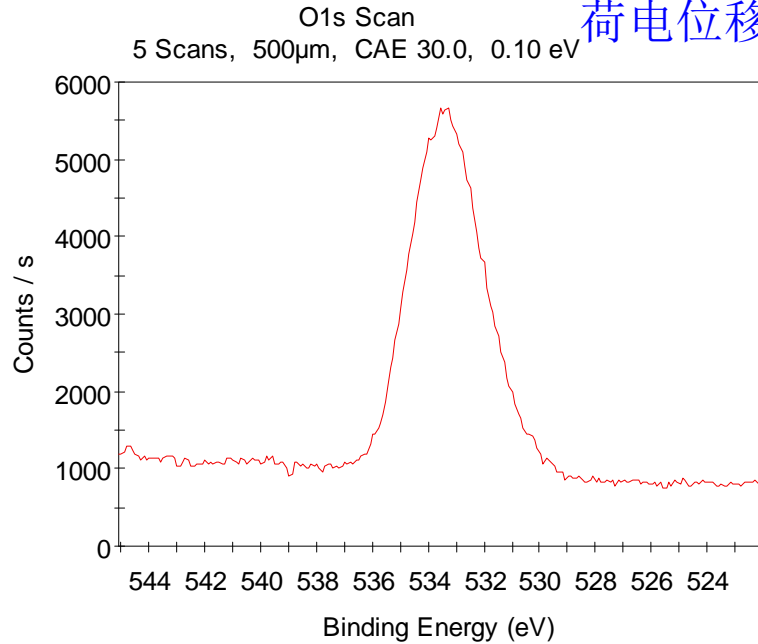
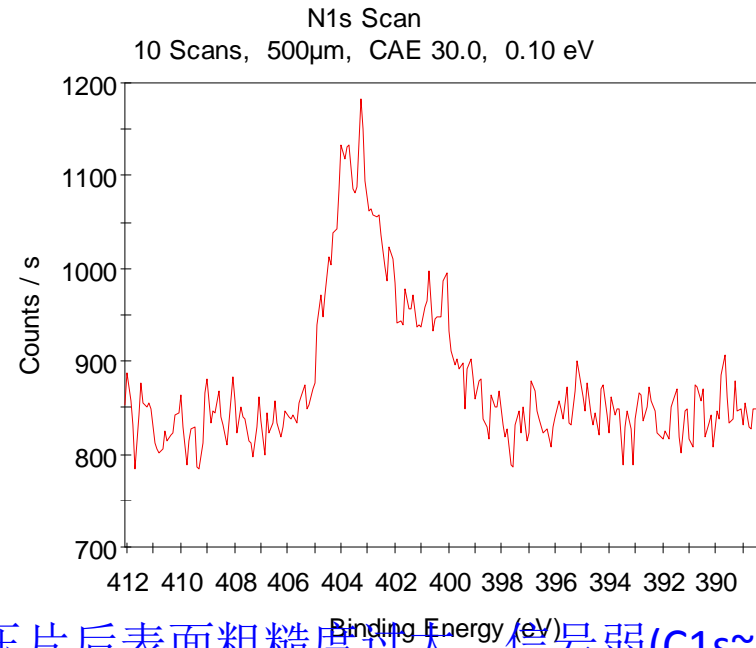
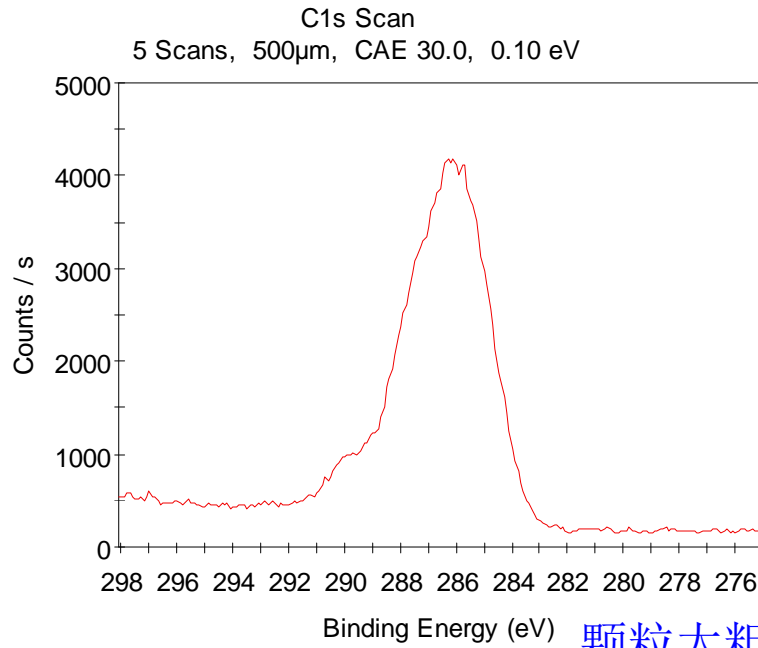
样品准备：悬浊液浸入海绵

- 案例：测量某废液中Fe等元素；
- 制样方法：用液体样品浸泡海绵，晾干后直接XPS测试

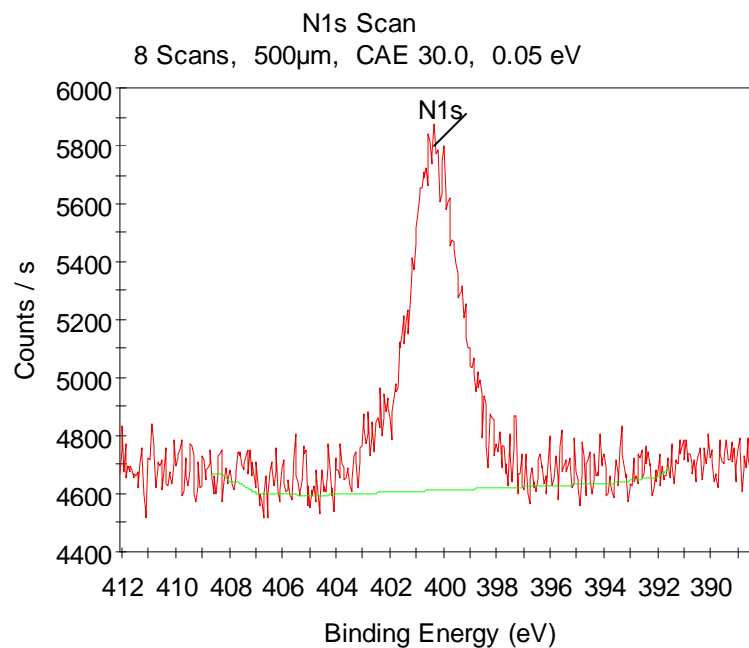
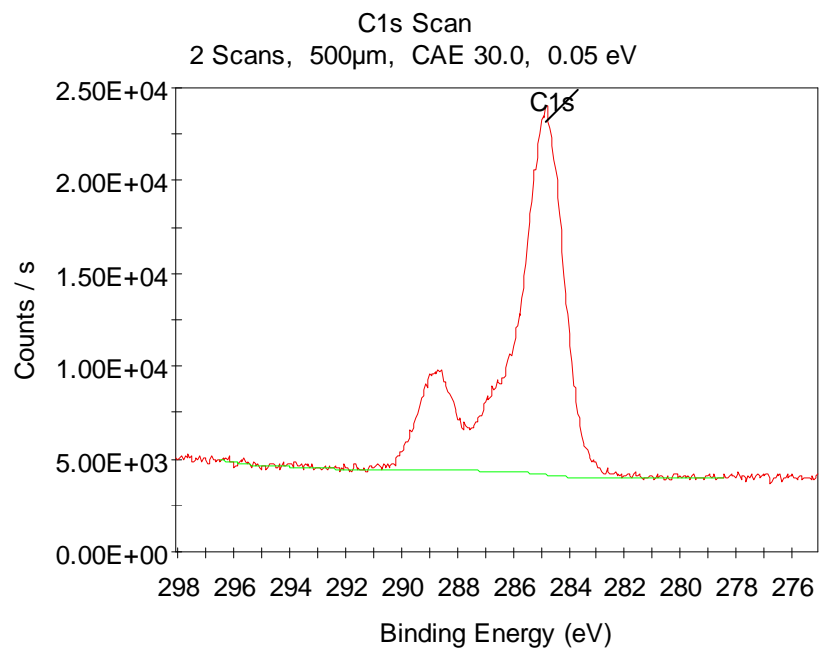


样品准备

- 小束斑Mono XPS（常规分析）的样品
 - 片样、小颗粒样品等直接粘在胶带上；
 - 粉末压片。要求表面平整，否则出现谱峰的荷电加宽、畸变；
 - 纤维细丝样品如前所述
 -
 - 如果样品制备合适，荷电位移小， $\sim 0.X \text{ eV}$

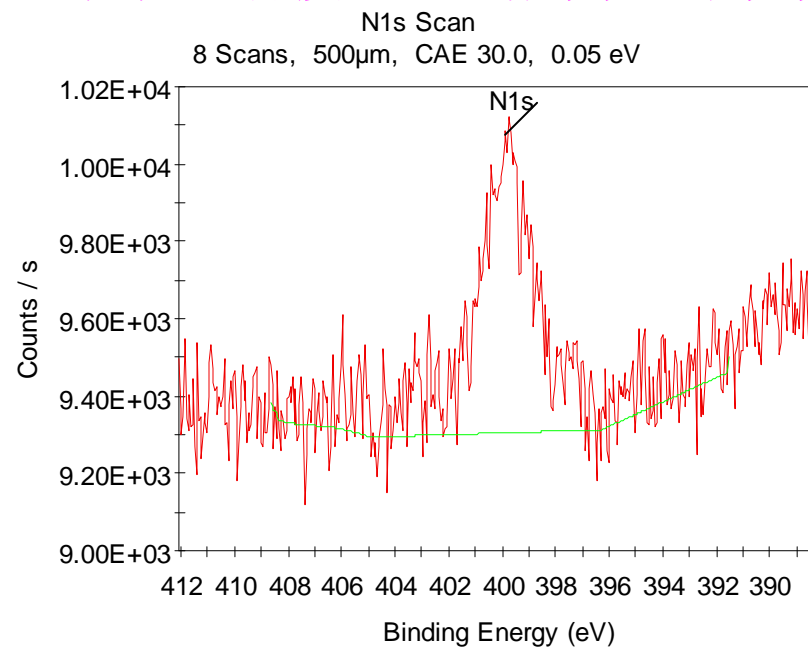
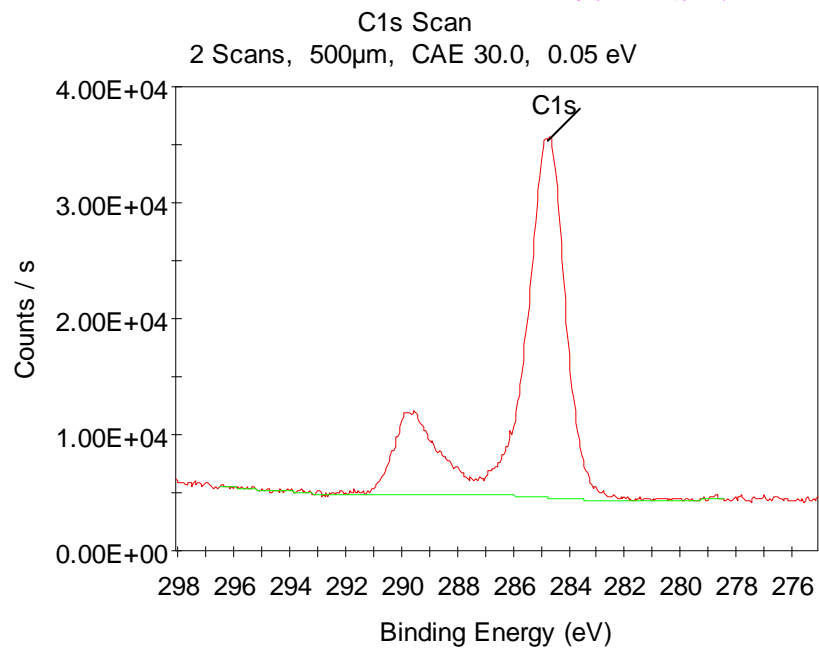


颗粒太粗，压片后表面粗糙度过大，信号弱(C1s $\sim 10^3$ 计数率)
荷电位移+1.2eV,没有到达过中和。

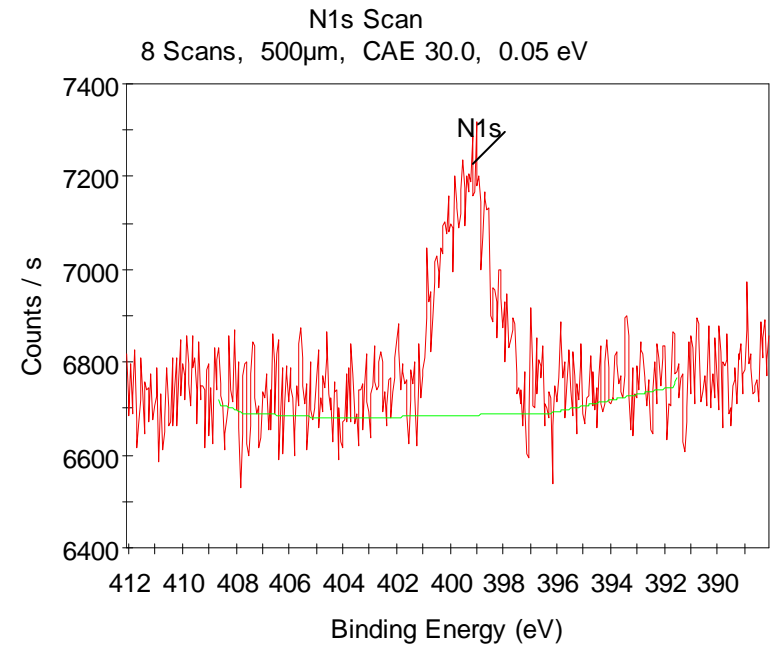
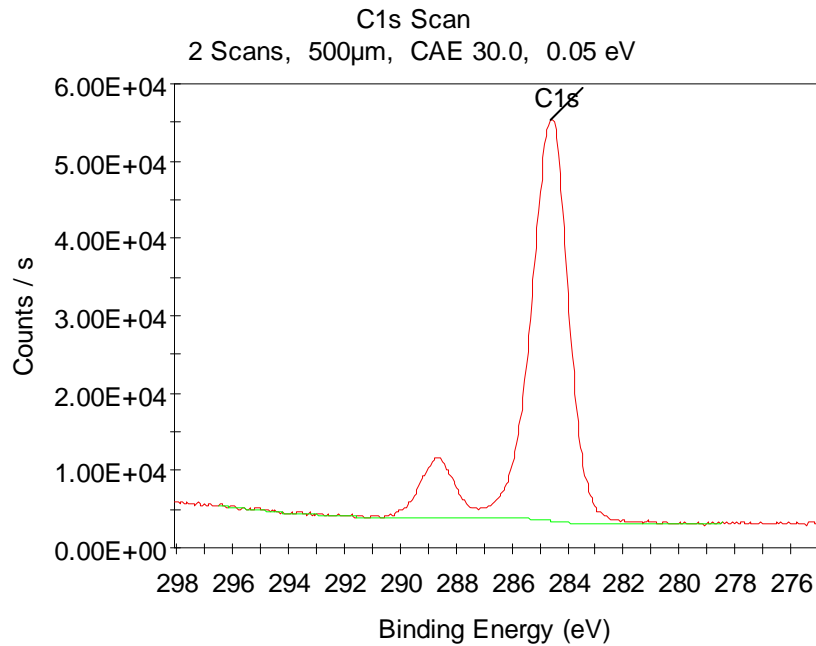


T3
0eV

样品颗粒细，压片均匀、厚度合适，谱峰窄且计数率高

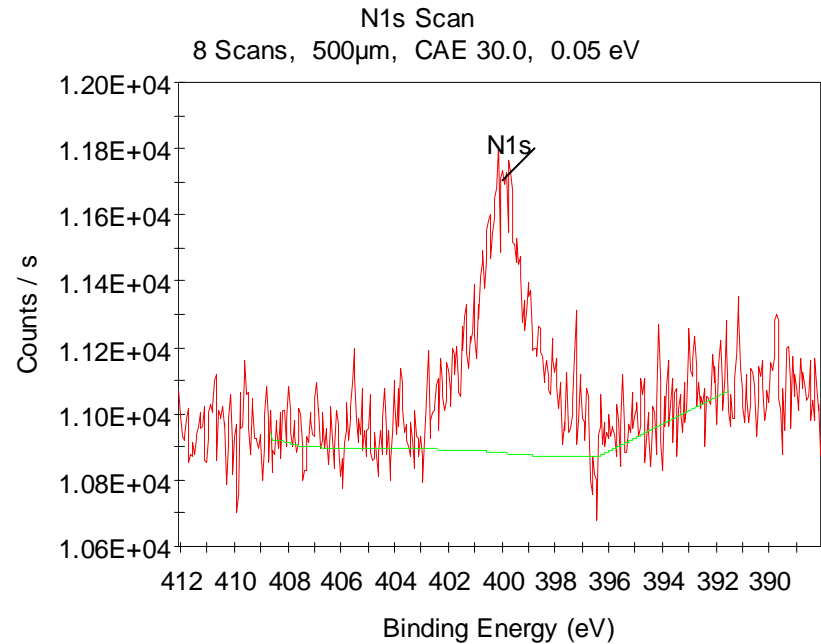
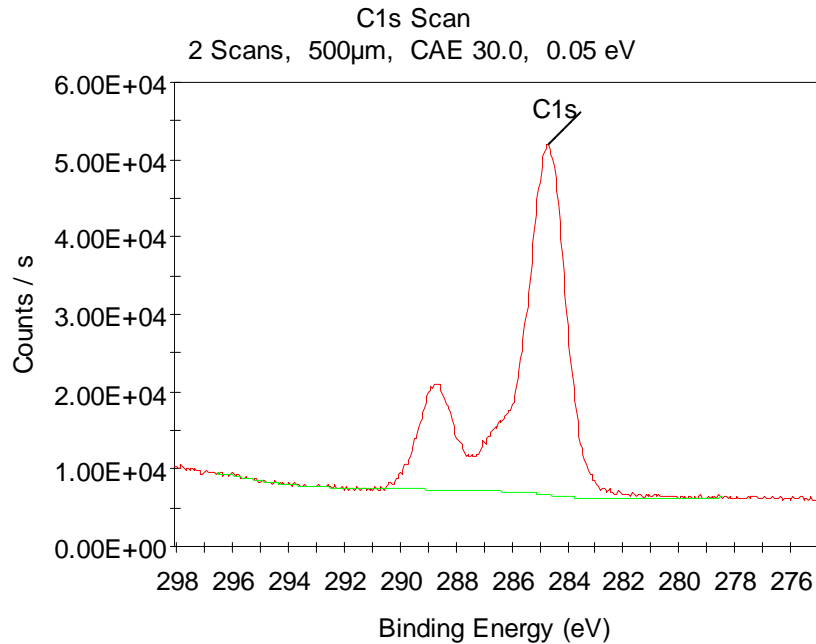


T4
0.05eV



T1
0.2eV

样品颗粒细，压片均匀、厚度合适，谱峰窄且计数率高



T2
0.1eV

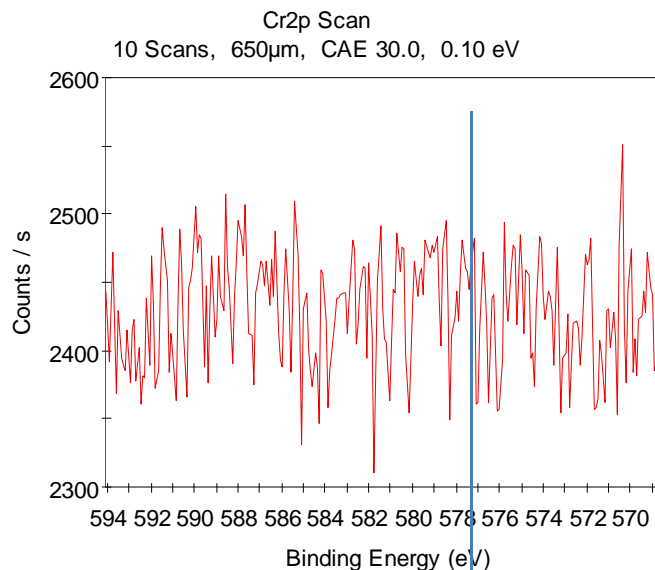
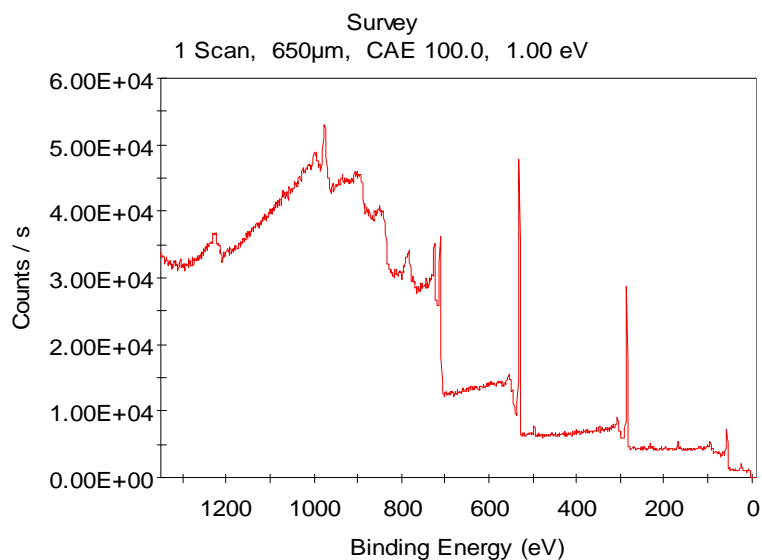
样品准备

- 小束斑双阳极（非单色化）XPS（常规分析）的样品
 - 双阳极易荷电中和，表面粗糙度要求低于Mono XPS；
 - 安装样品时，注意增大样品间的间隔，实际X射线照射面积较大，以防X射线损伤周围的样品
 - 根据分析区域大小，选择合适的电子光学透镜参数，而小束斑单色化XPS分析区域大小取决于X射线束斑（微聚焦X-ray）；

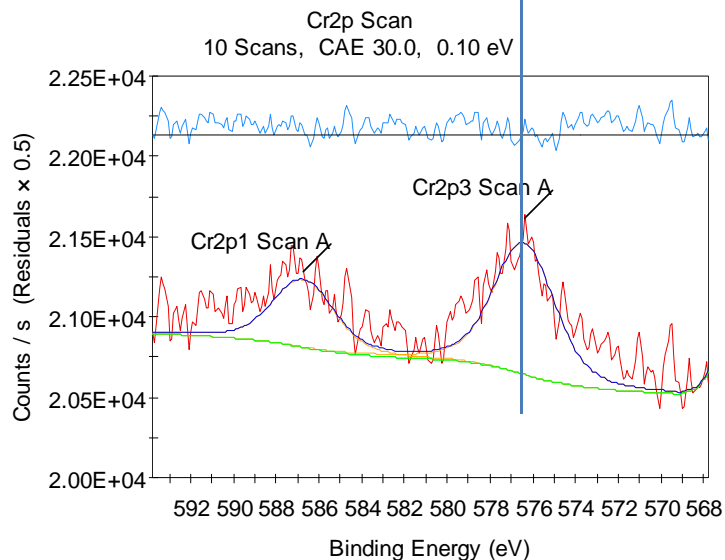
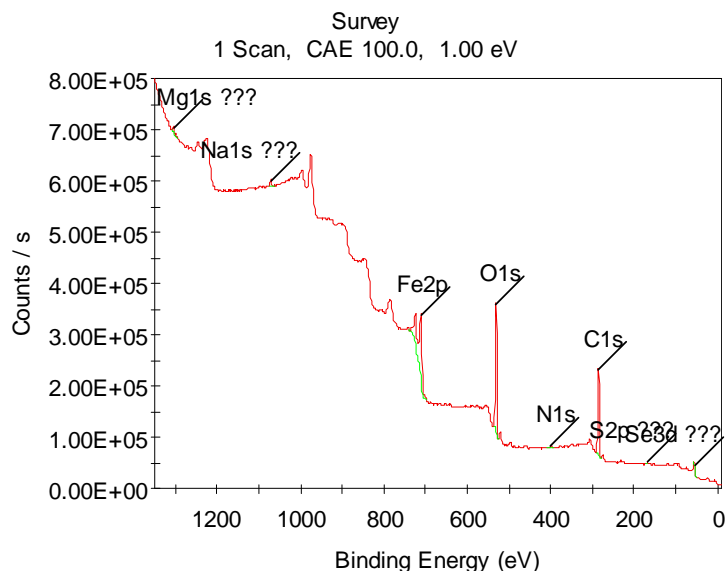
样品准备

- 大束斑双阳极（非单色化）XPS（常规分析）的样品
 - 双阳极易荷电中和，表面粗糙度要求低于Mono XPS;
 - 安装样品时，注意增大样品间的间隔，实际X射线照射面积较大，以防X射线损伤周围的样品
 - 要求样品耐X射线辐照，尺寸~10mm，应该选用合适的电子光学透镜参数，得到最佳高灵敏信号，一般高于Mono XPS;

案例：双阳极XPS可增加灵敏度。测量铁基材料中测量低含量Cr等元素



单色XPS,
分析面积0.65mm
标准静电模式



双阳极 AlKa XPS
静电模式
标准静电 约1mm
提高计数率10倍
如采用Large area
模式可得更高强度

样品准备

- XPS测量价态谱样品
 - 样品表面没有荷电积累
 - 样品一般需加负偏压，增加电子发射、防止样品费米边价带谱失真
 - 说明：
 - 样品表面无荷电积累并不意味着样品材料一定为非绝缘材料：1) 小体积、薄样品；2) 入射电子数等于发射电子数

样品准备

- 溅射样品（深度剖析）
 - 样品均匀、表面平整
 - 要求样品尺寸较大，一般大于 Ar^+ 溅射面积2倍以上，如5mm。为了XPS分析中心位于 Ar^+ 有效溅射区域内，一般刻蚀面积3~5倍于分析面积
 - 控制样品荷电，因为荷电也会影响刻蚀位置和速率

样品准备

- 磁性（含软磁）材料样品
 - 退磁/消磁；
 - 采用磁透镜模式测量：应该尽量减少样品尺寸，以降低磁场对发射电子的干扰，这也表现了小束斑XPS的优越性；
 - 采用静电透镜模式（不使用电磁透镜）：当磁性较强，无法减小样品尺寸，使用标准模式透镜无法获得正确谱时，采用静电透镜模式，装样时远离其它样品，最好单独安装在样品台上；
 - 注意：一般在静电模式下，信号强度、分辨率、荷电中和效果均不及标准模式

样品准备

- 绝缘基底上导电薄膜样品或厚样品
 - 用导电胶带或导电细丝缠绕表面，或者用铜网、带孔的铝箔包裹样品，尽量减少或消除测试表面荷电。

样品准备

- 角分辨XPS（ARXPS）样品
 - 适用于形状规整的片状或块状大样品（一般 >5mm）；
 - 成分均匀、表面平整；
 - 安装样品尽量安装在样品台中心（转抽）附近，保证在转角整个过程中，XYZ等在允许的范围內；
 - 说明：
 - 如果样品表面粗糙，出现阴影、角度不准、荷电不均等现象，影响 $I(\theta, E_b)$ 谱；
 - 不采用磁透镜；
 - 实验中当 θ 渐渐增大时，实际涉及样品探测面积增大 $1/\cos(\theta)$ 倍。（ θ 为光电子在样品上的出射角）

样品准备

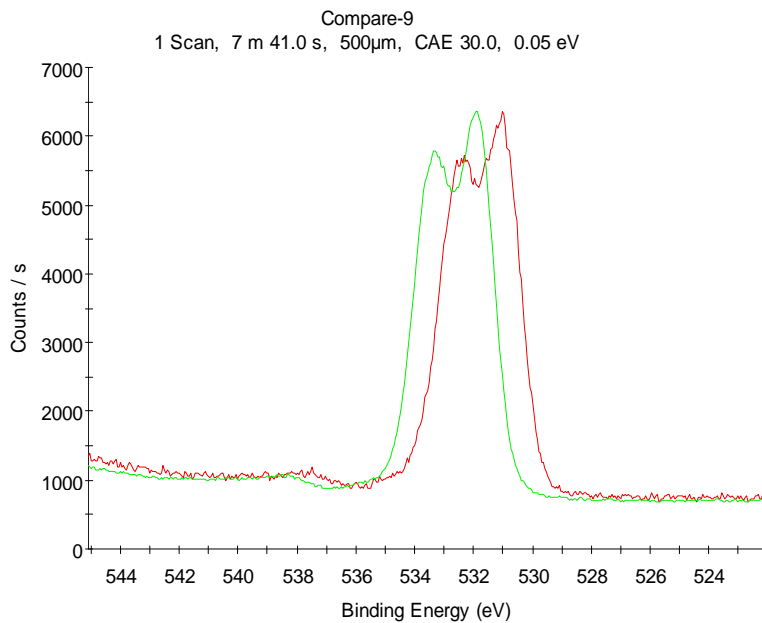
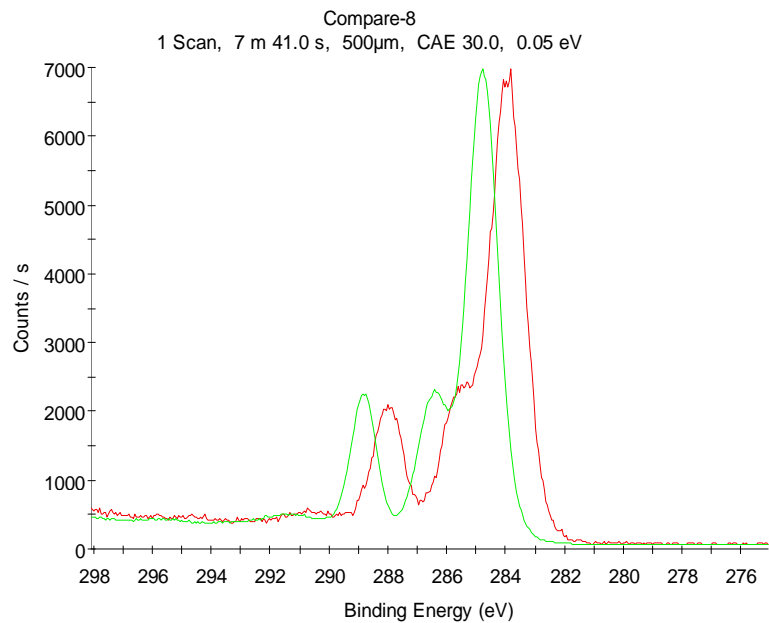
- 实验结束后，应退出样品，长时间存放在仪器真空室内，可能污染真空。

谱图处理

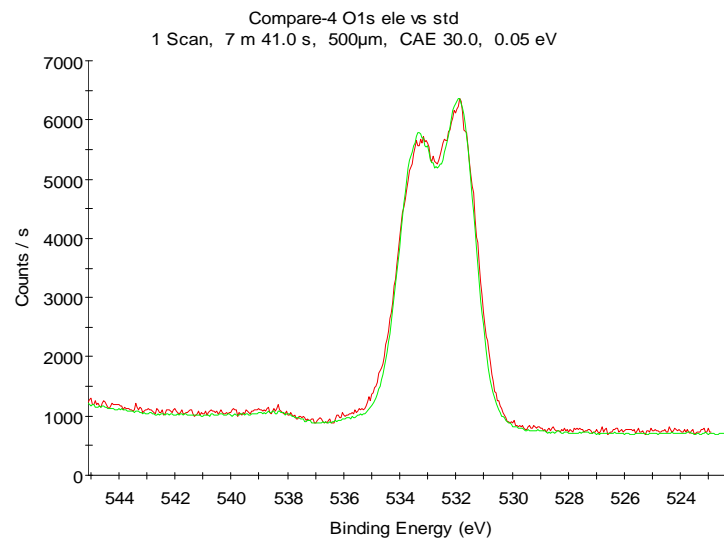
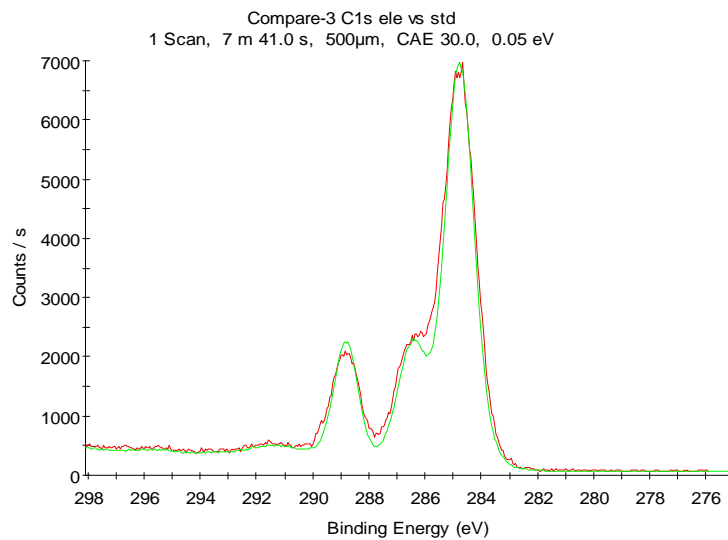
- 荷电校准
- 谱峰识别（指认）
- 分峰/价态分析
- 能量去卷积
- 平滑/去噪声
- 定量分析
- 深度剖析结果处理
- 角分辨结果处理
- 价带谱结果处理
- 结果报告
-

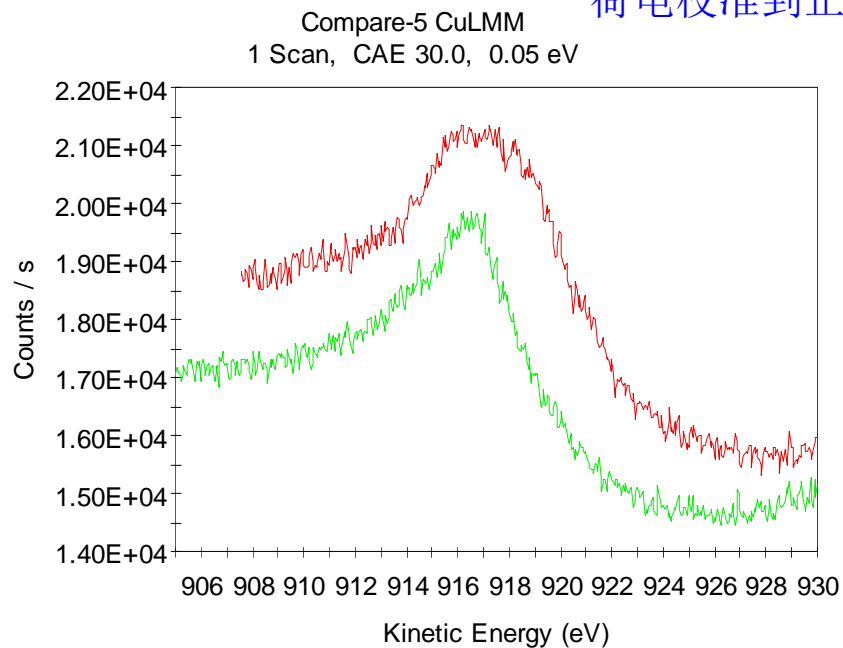
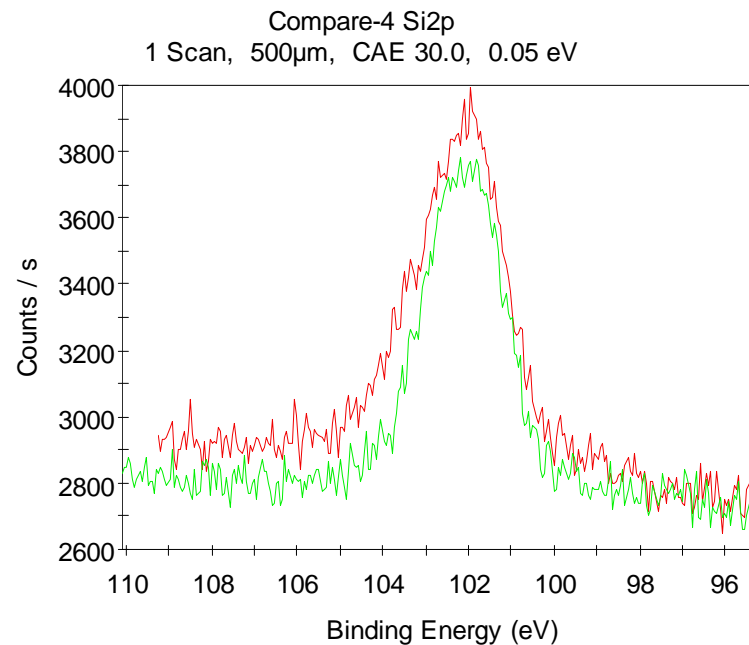
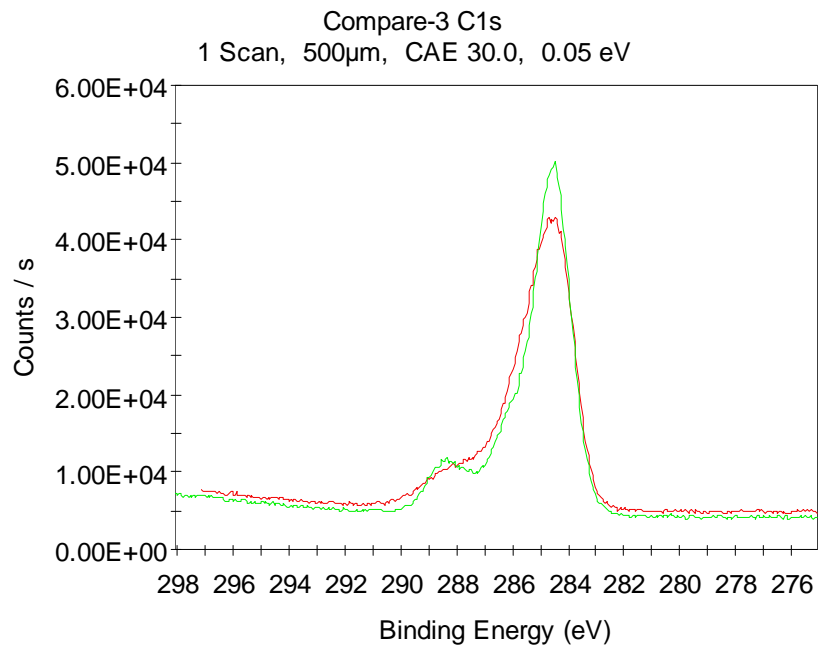
荷电校准

- XPS分析中，样品表面导电差，或虽导电但未有效接地。此时，当X射线不断照射样品时，样品表面发射光电子，表面亏电子，出现正电荷积累（XPS中荷正电），从而影响XPS谱峰，影响XPS分析；
- 样品荷电控制方法
 - 测试前：导电处理、接地；清洁样品；减薄（小）样品等；样品平整均匀以保证荷电均匀，
 - 测试中：荷电中和

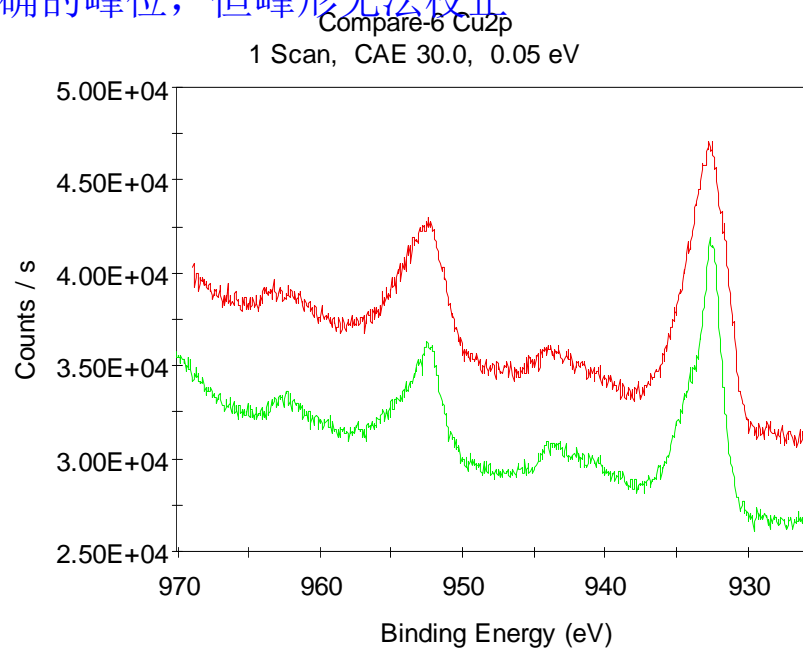


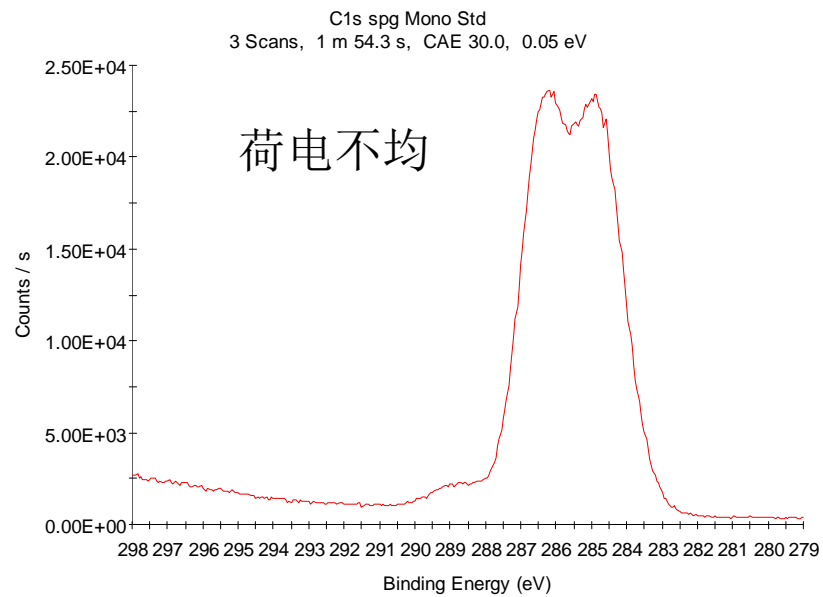
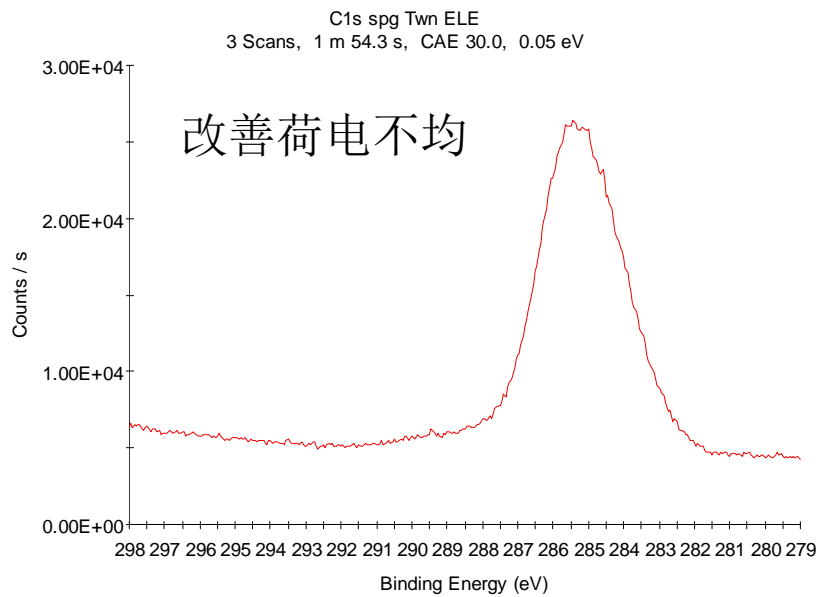
表面存在较均匀荷电，导致谱峰整体刚性移动。可以校正到正确的位置。



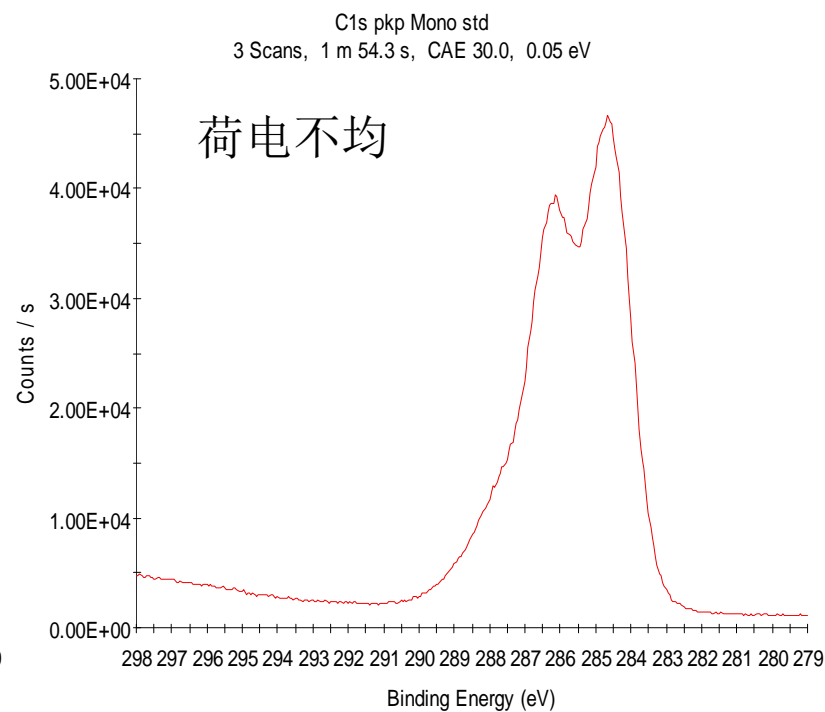
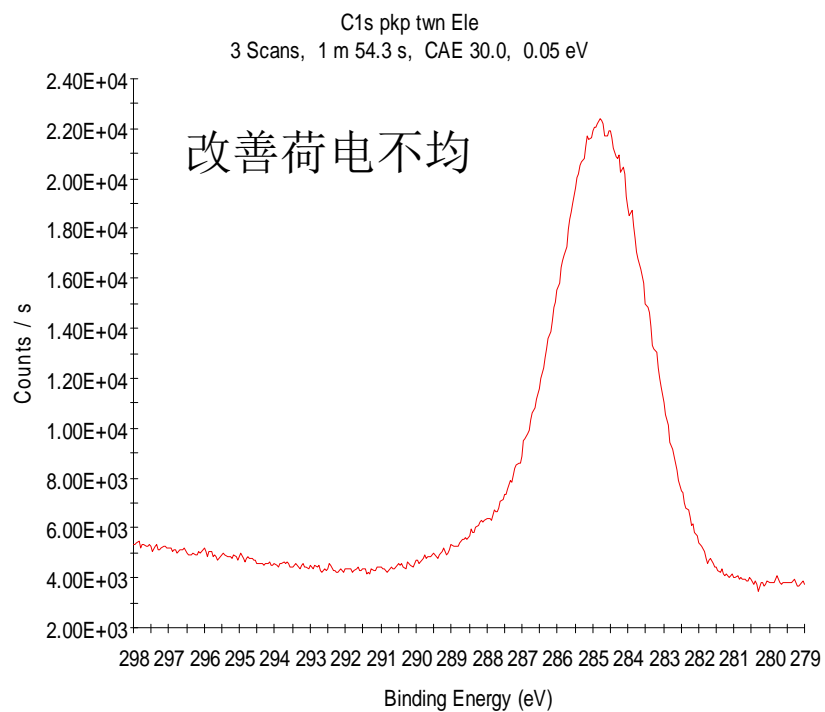


荷电校准到正确的峰位，但峰形无法校正





(a)



(b)

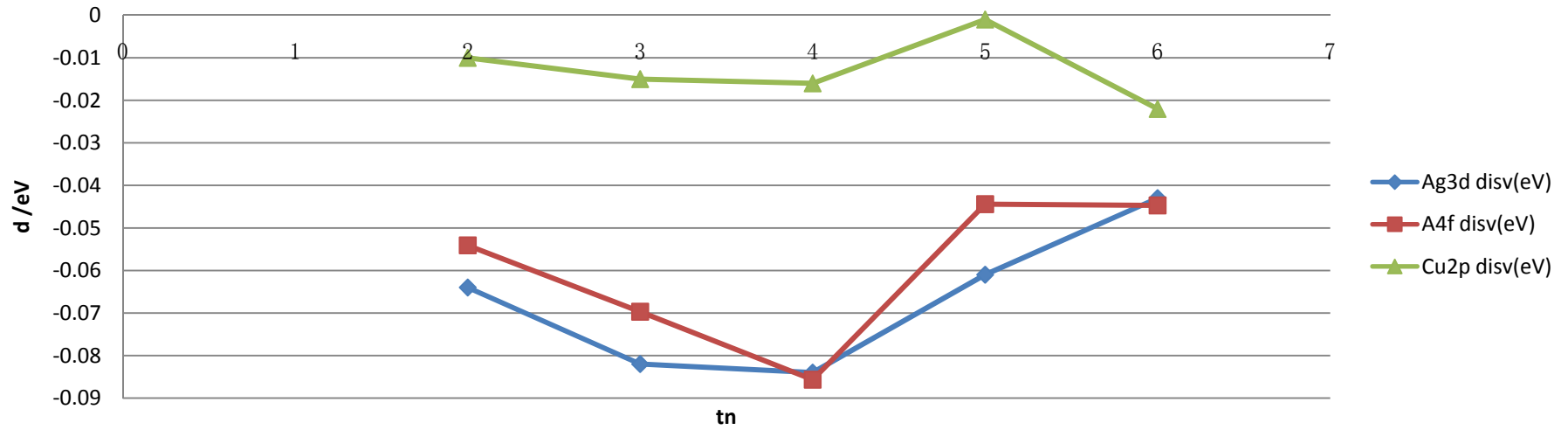
荷电校准方法

- 对于XPS测试后，已经出现的荷电，应该采用合适的方法校准：
 - 内标方法
 - 外标方法

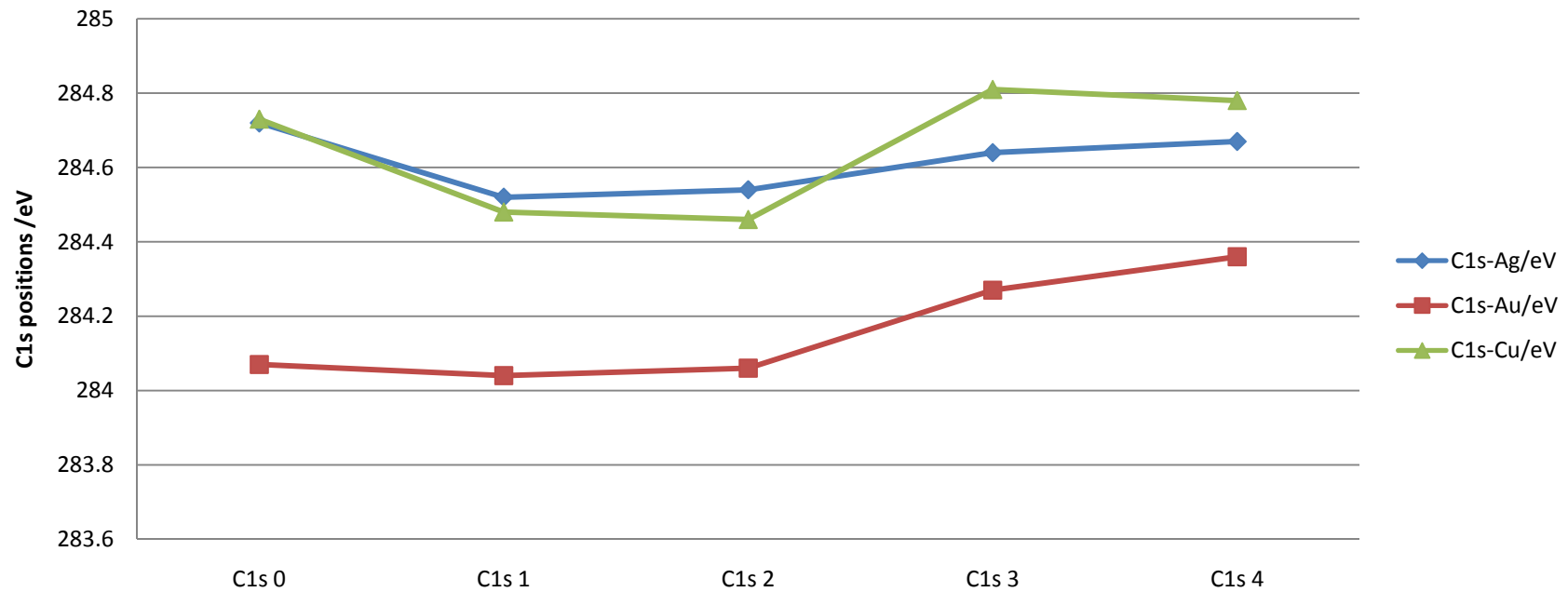
荷电控制与校准

- 污染C1s校准，最方便，被广为采用，但是污染C来源复杂未知，一般认为284.8eV，也有284.6eV, 285eV。
- 准确性？
- 标准样品台上Ag、Au、Cu经过Ar⁺刻蚀后，污染C小于Ag/Au/Cu主峰的2%。随着时间的推移，这些金属表面在真空中又逐渐沉积污染C，测量污染C1s峰，研究它们峰位变化。

Ag-368.27, Au-84.00, Cu-932.66



在Ag, Au 和Cu上, C1s峰位随沉积时间变化, 间隔~4h



荷电控制与校准

- 不同材料上污染C，差异 $\sim 0.5\text{eV}$;
- 同一材料上不同厚度污染C，差异 $\sim 0.4\text{eV}$;
- 不同来源的污染C也可能存在差异，? eV

其它元素峰的校准

- Ar2p (242.1eV in C)
- Au4f、Pt4f、.....
- 以样品上已知元素的校准
- 在Avantage中污染C1s 取284.8eV，可以直接对同一样品中的所有谱峰校准。

谱峰指认与谱峰重叠

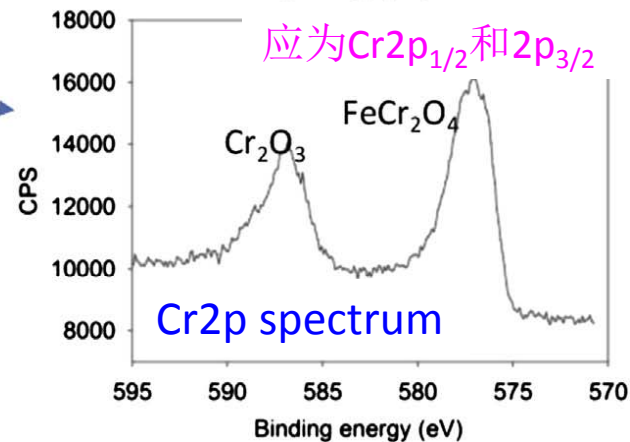
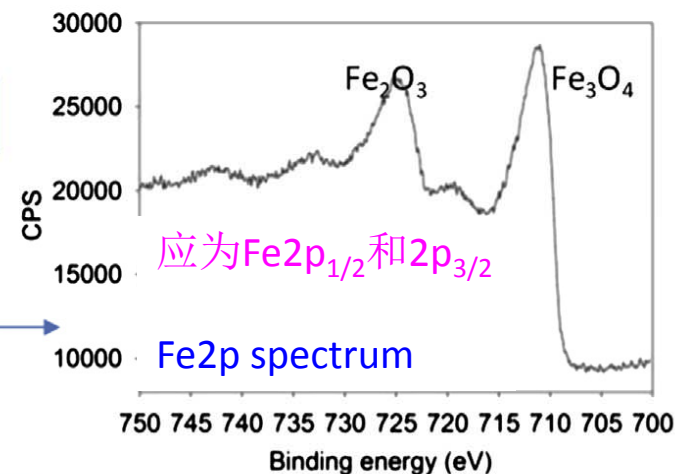
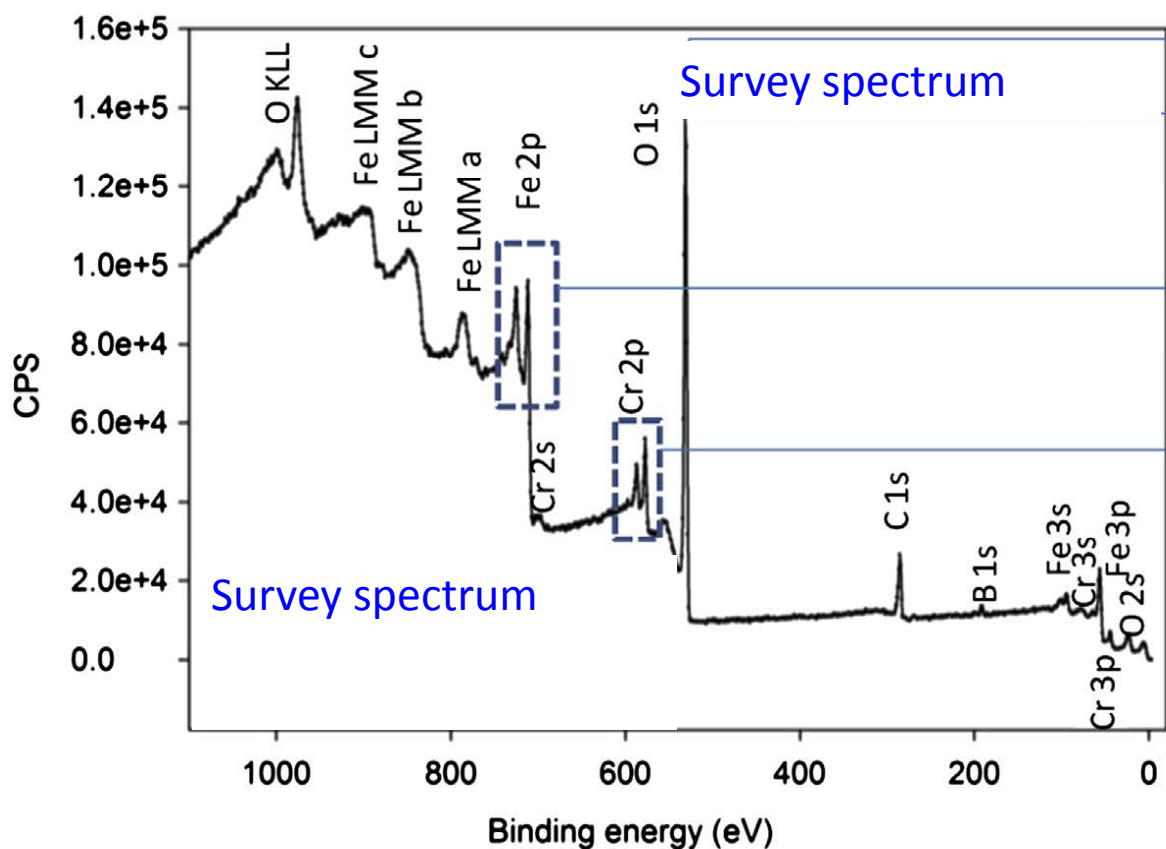
- 对照能级识别，在Avantage中智能识别；
- Knowledge Base 帮助在峰位和峰形上举行分析、识别
- 常出现谱峰重叠，影响元素和化学态指认
- 通过案例说明，

理论基础：需要掌握的要点

- 光电发射过程；
- 俄歇过程；
- 固体材料中的元激发；
- 电子弹性散射和非弹性散射；
- 三阶段理论：激发、电子输运、表面跃迁空态；
- 电子能级和能带；
- 化学（物理）位移、自旋轨道分裂、终态效应；
- 峰强、峰位、峰宽所表示的信息；
- 定性和定量分析基础；
-

XPS分析中 自旋轨道劈裂峰误认为元素不同化学态峰

样品中含Fe Cr O C等元素



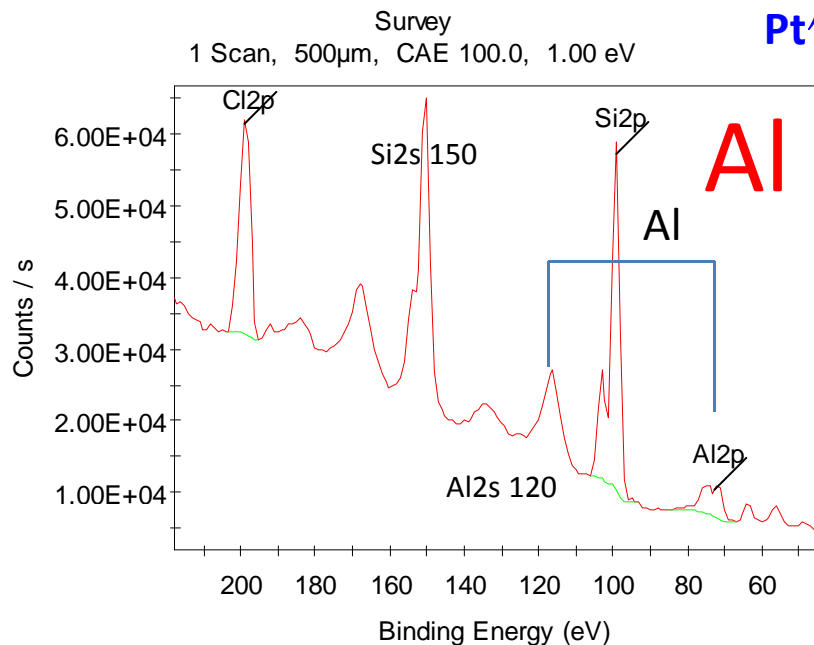
XPS谱峰重叠和干扰

- 等离激元特征损失峰
 - 为光电子主峰的伴峰，具有特征性，等能量间距多级峰
- 俄歇谱峰
 - 复杂、多峰，俄歇峰群
 - 特征性，与光电子峰能量间距与光子能量有关

等离子激元干扰XPS谱峰

- 单质Si、Al等及其氧化物出现等离子激元峰，分布范围（BE）较宽；
- 案例：Si和Al的等离子激元对关注谱峰的影响

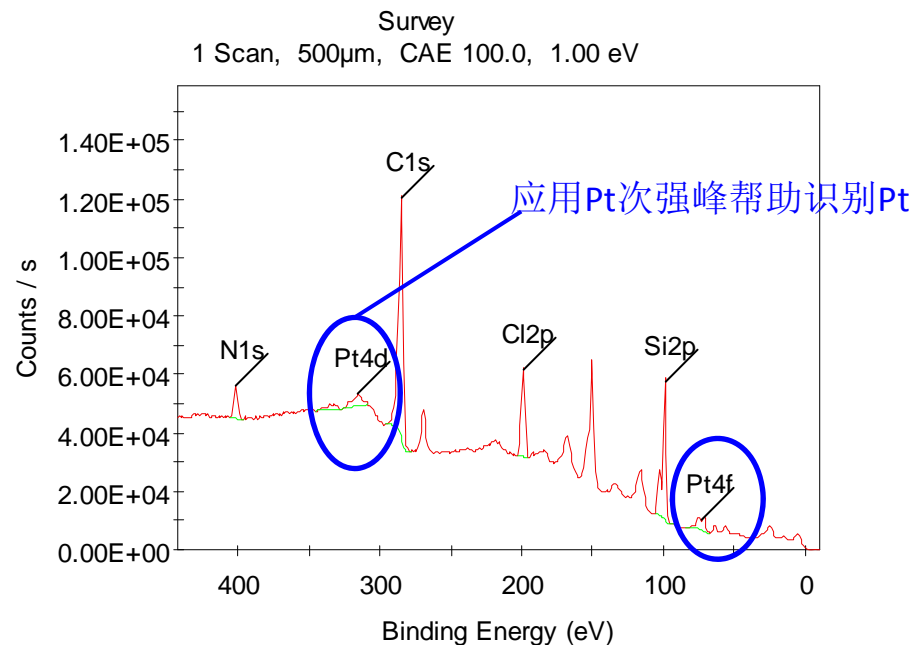
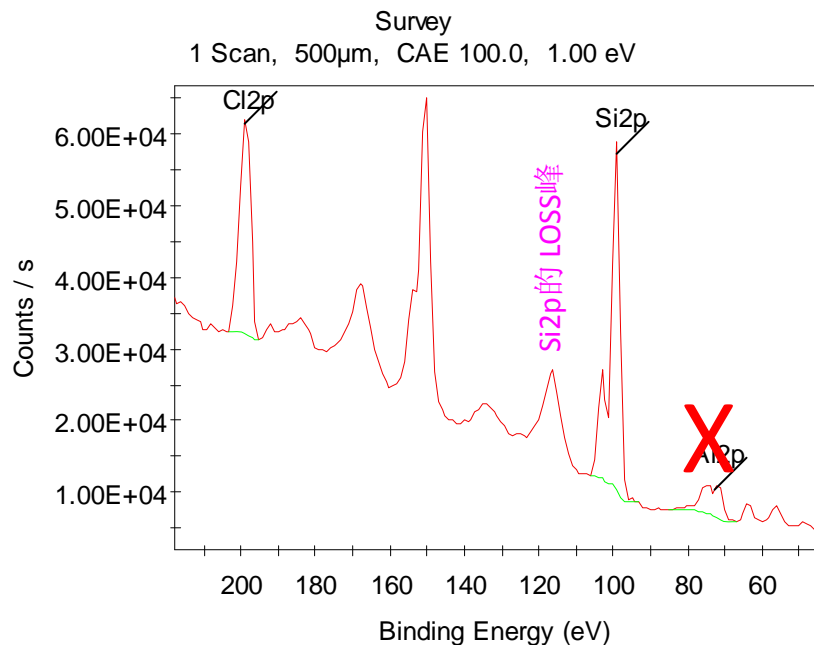
Pt催化剂样品(Pt+SiO₂), X-ray:mono AlKa

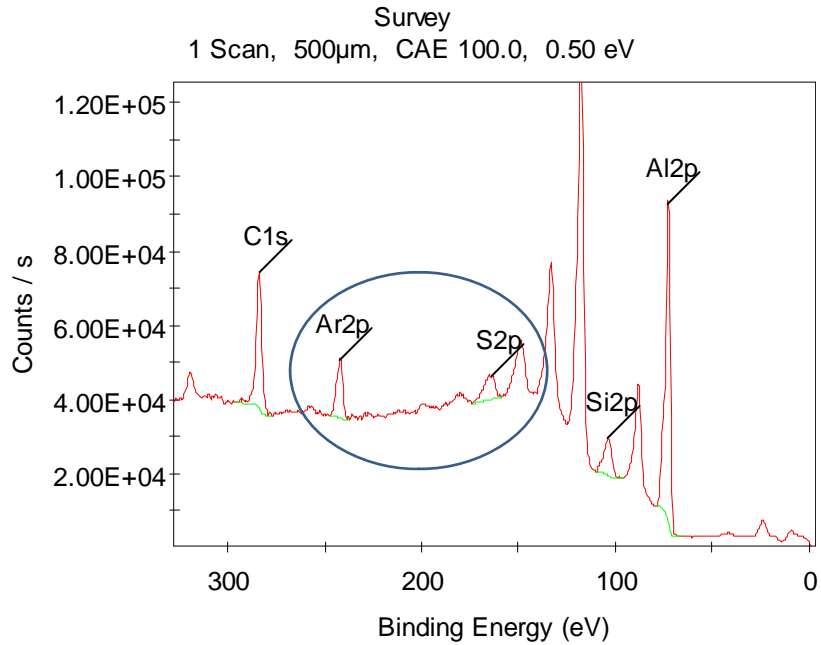


软件识别出Al, 归属于Al?
答: 不能全指认Al, 因为: 1) Al2p峰强不应小于Al2s峰; 2) 峰形, 峰宽; 3)

将Pt4f峰和Si2p等离激元损失峰分别误认为Al2p和Al2s。两个峰的高度比偏离正常的Al2p和Al2s

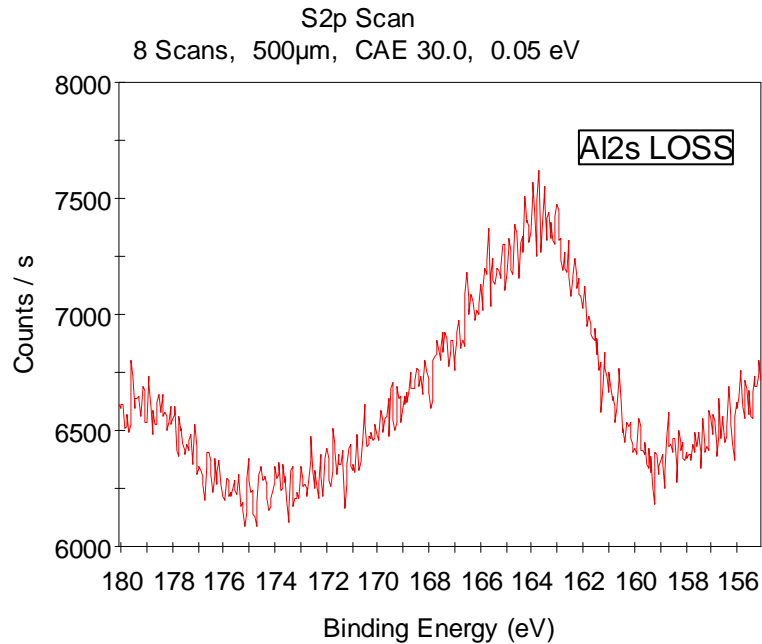
样品中应该含Pt



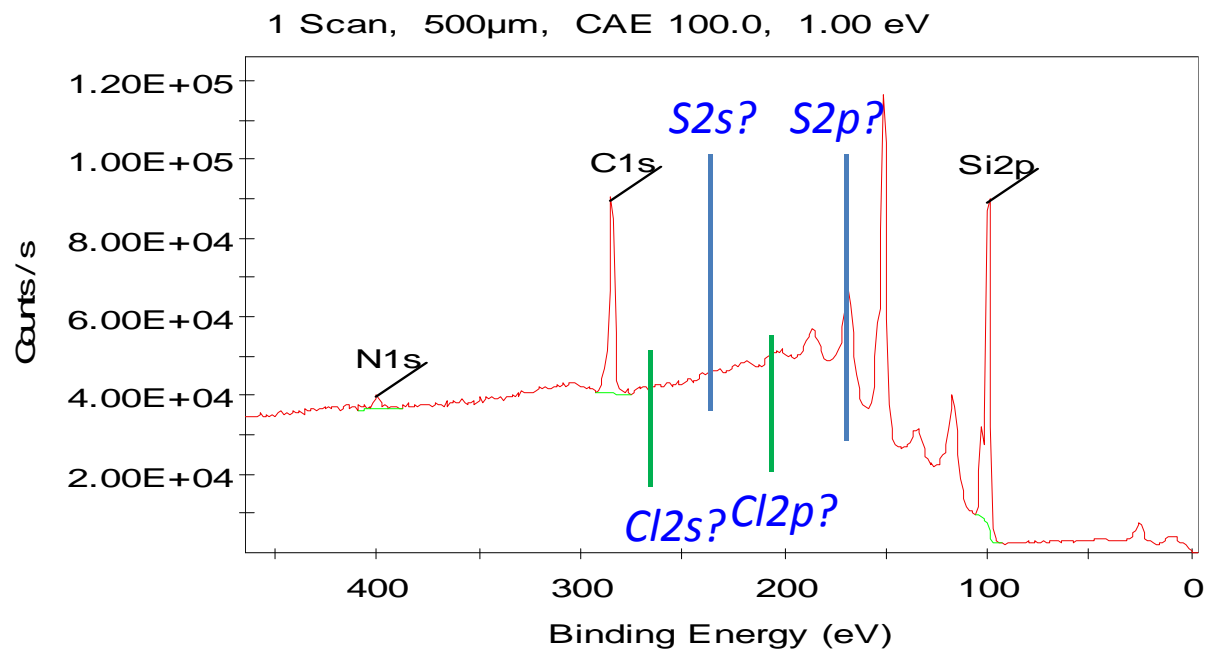
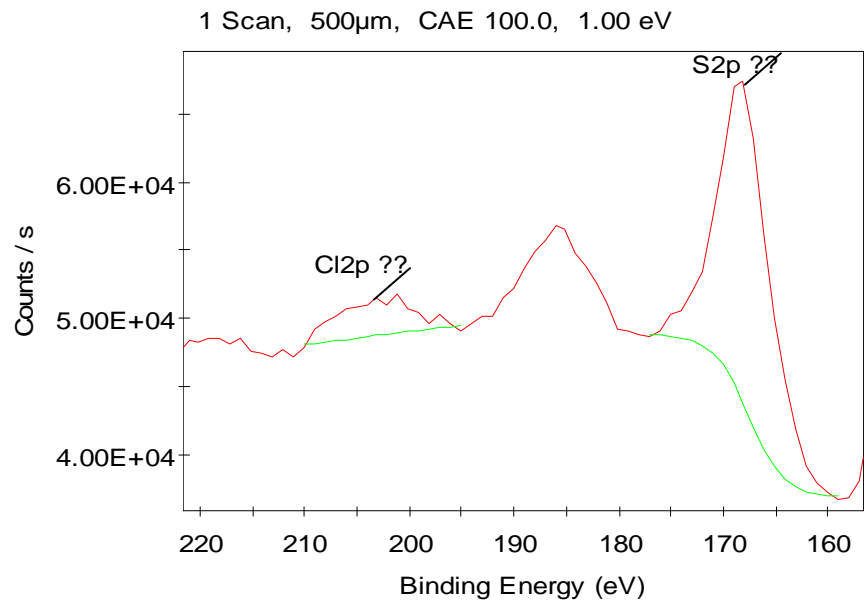


氧化铝基样品中含S?

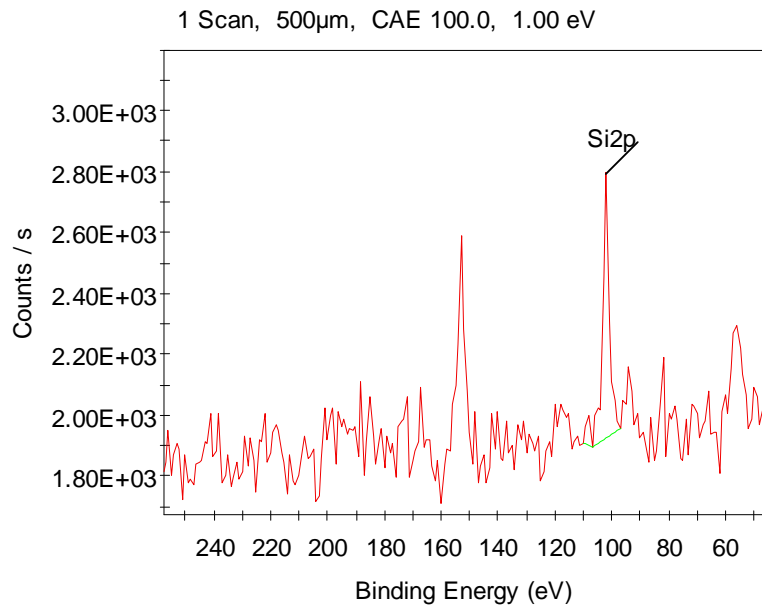
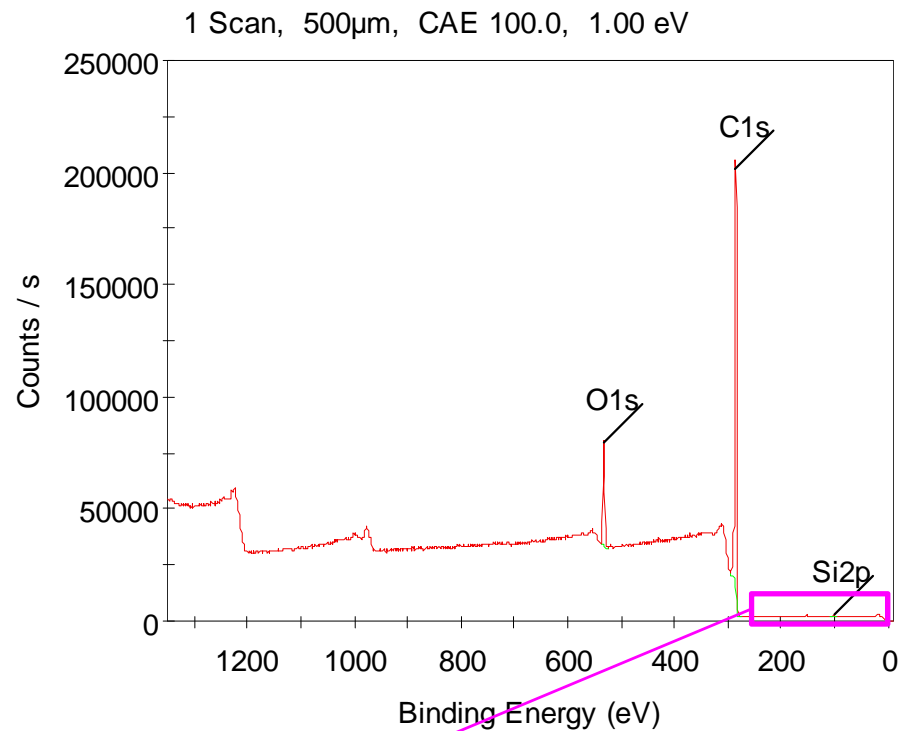
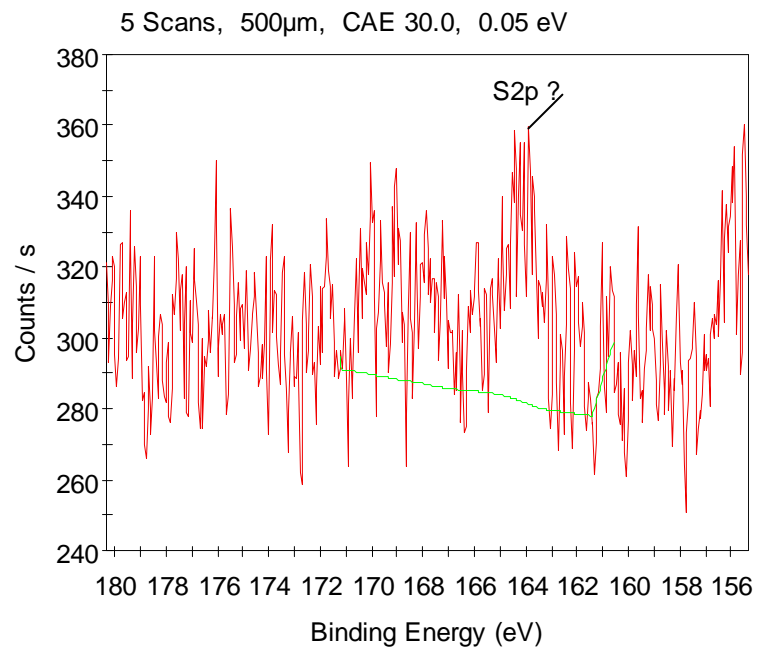
答: 虽然S2p (164eV) 与Al 2s 等离子激元峰重叠。但S2s (229eV, S2p强度0.5倍) 不明显, 因此, 样品中不含S元素。



样品中含元素s和Cl?



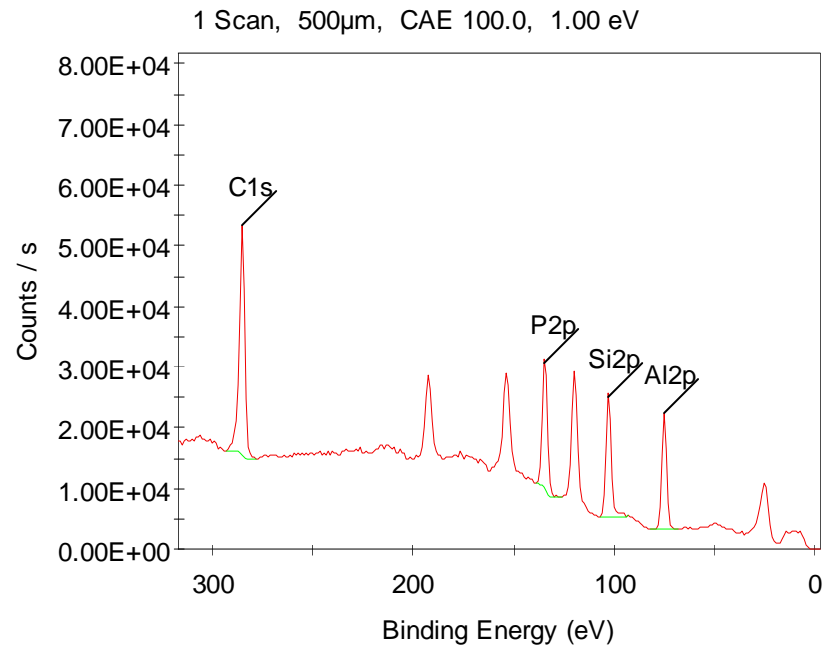
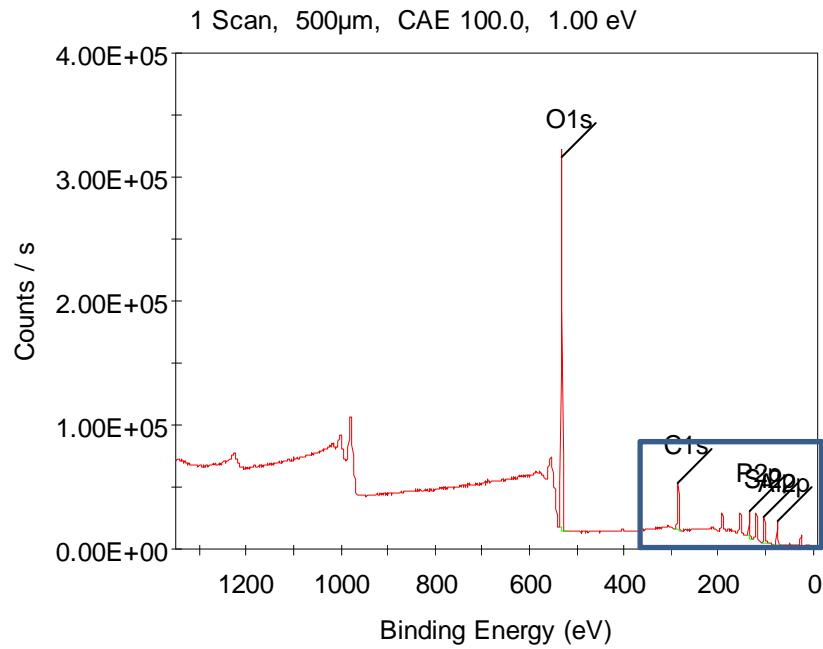
XPS确定某个样品中是否含有关键元素S



等离子激元

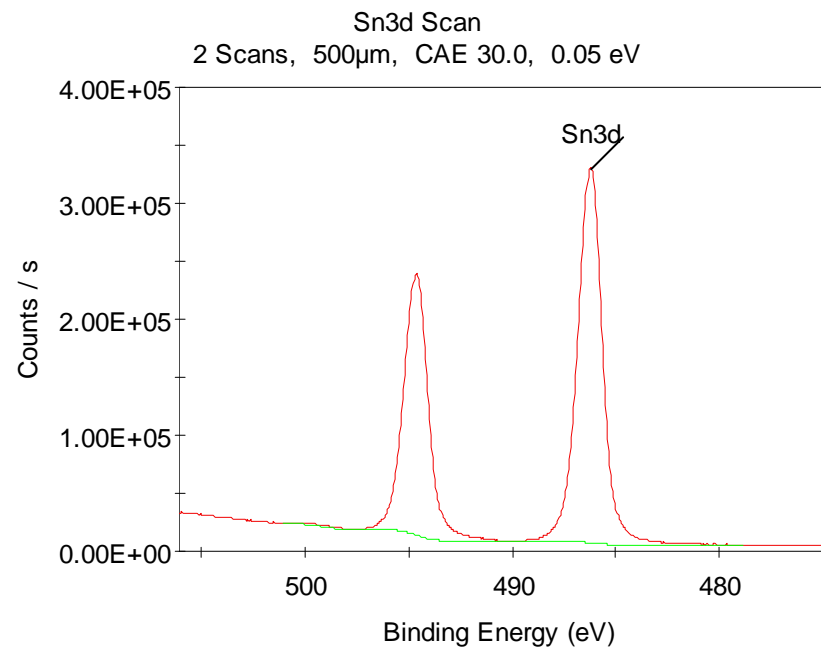
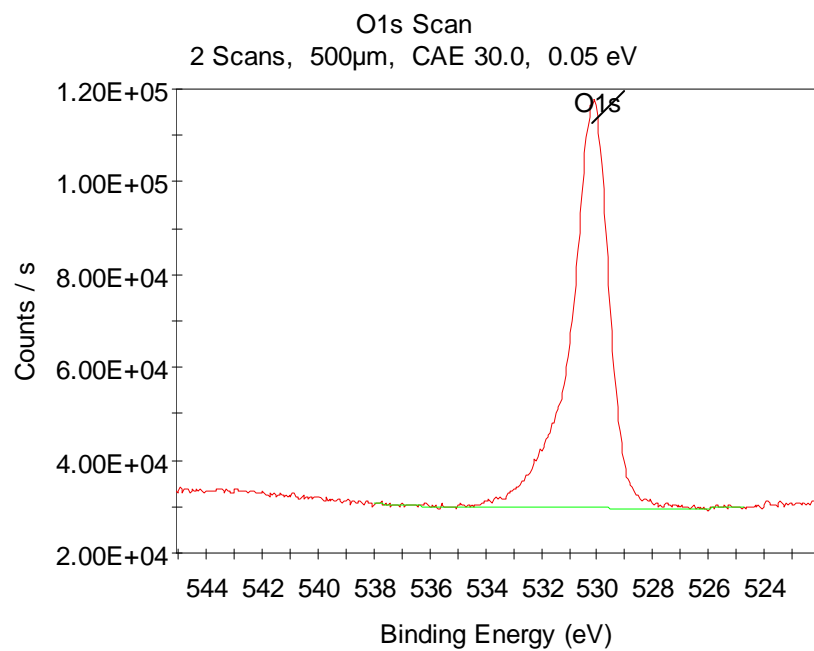
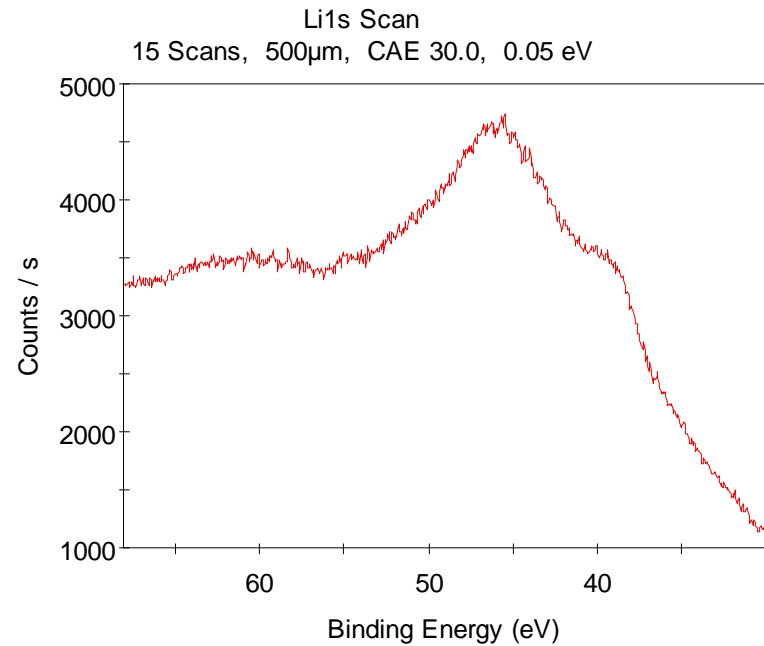
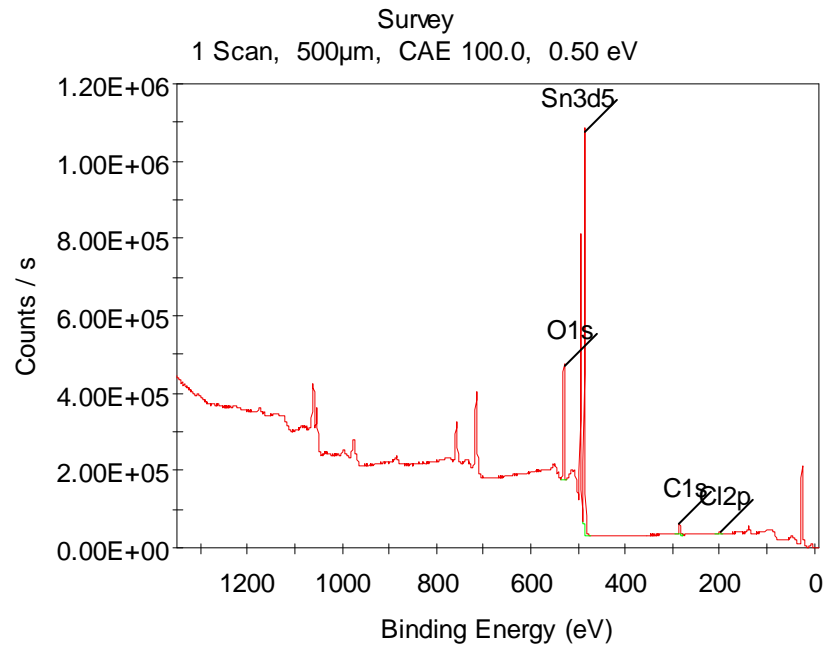
- 等离子激元？
 - 等离子体--固体中自由电子气的集体振荡，被认为是物质的第四态
 - 具有固有频率 ω_p , ω_s
 - 在激发的固体中很常见，
- 电子能谱与等离子激元
- 多峰，与光电子峰重叠，在低BE段影响谱峰的定性和定量分析

样品: SiO₂+Al₂O₃



在0~200eV范围内集中了多个峰，使得谱图复杂，谱峰难以指认

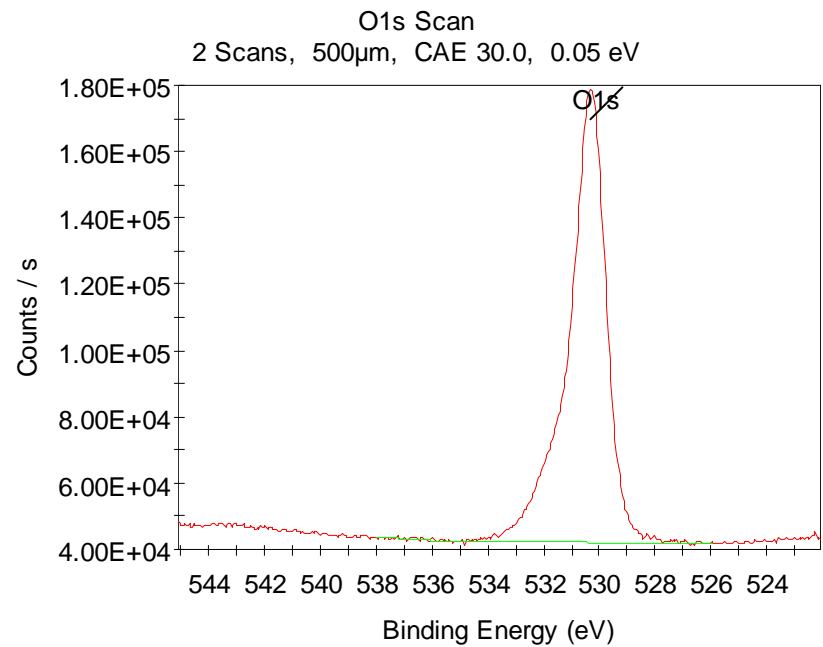
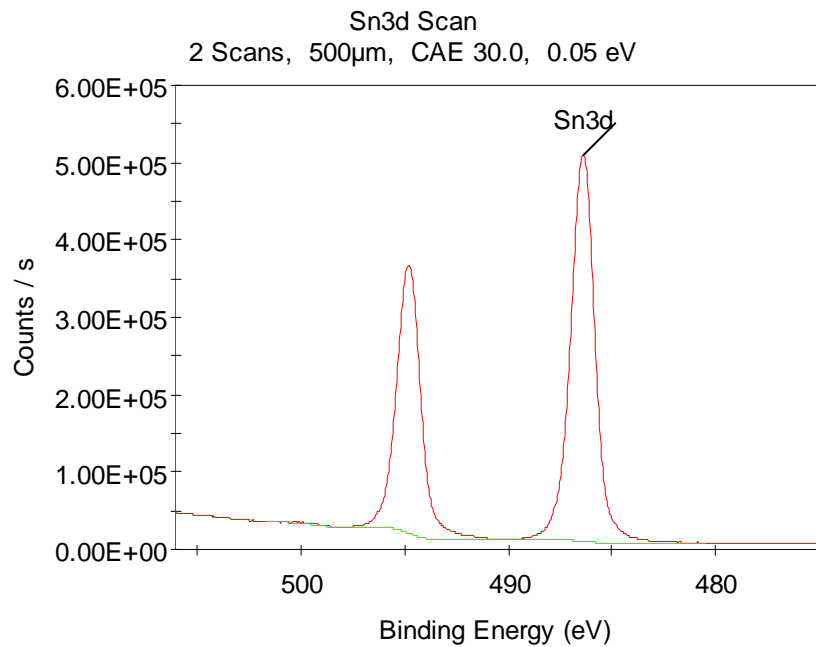
案例：SnO₂掺入关键元素Li（低含量）



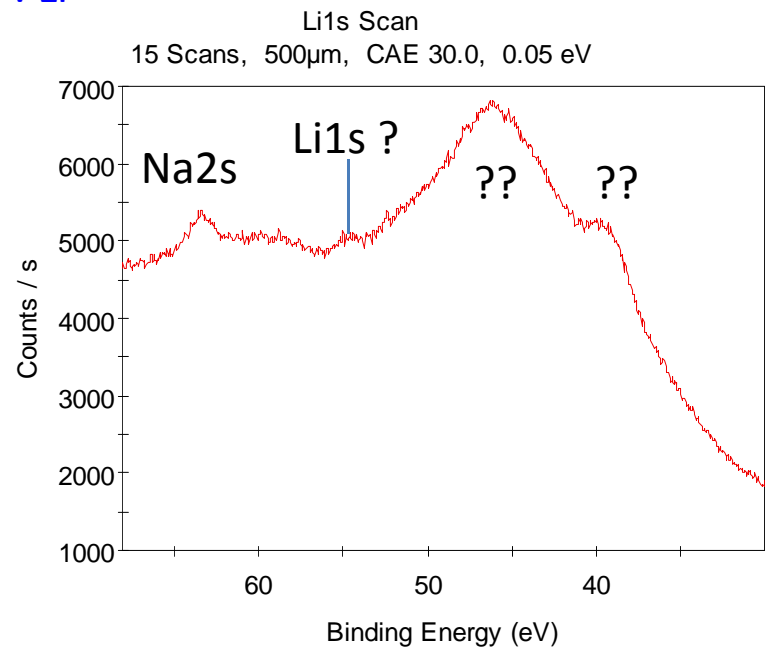
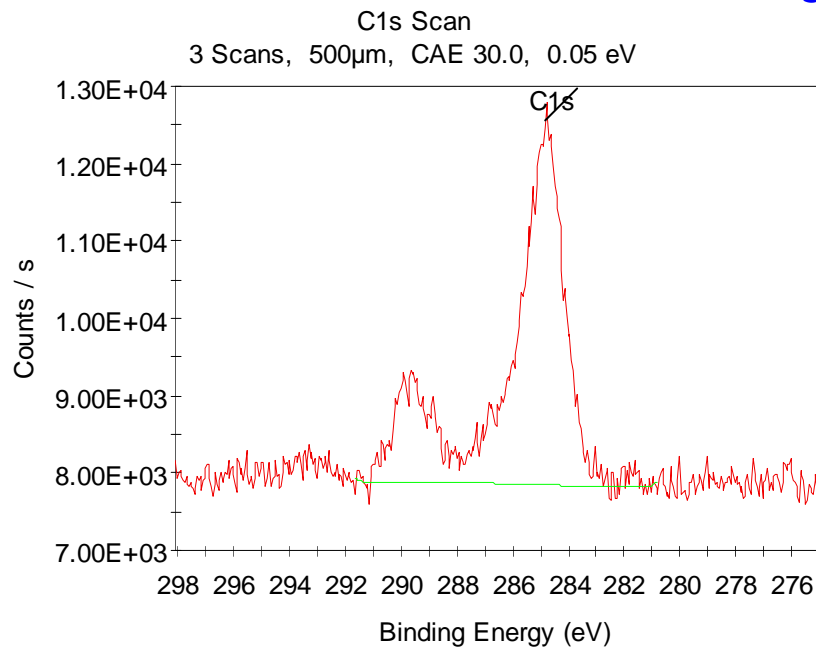
Experiment Descriptions

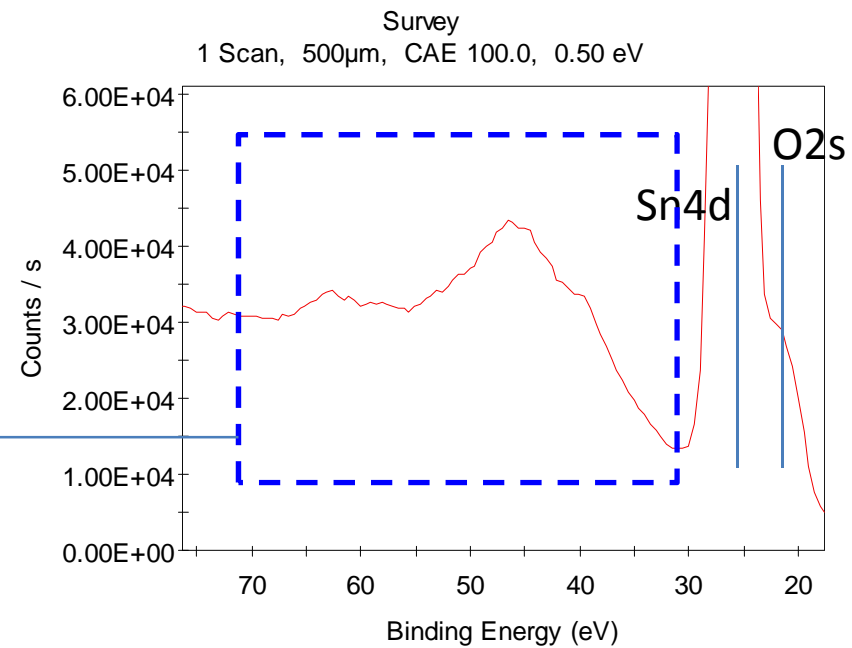
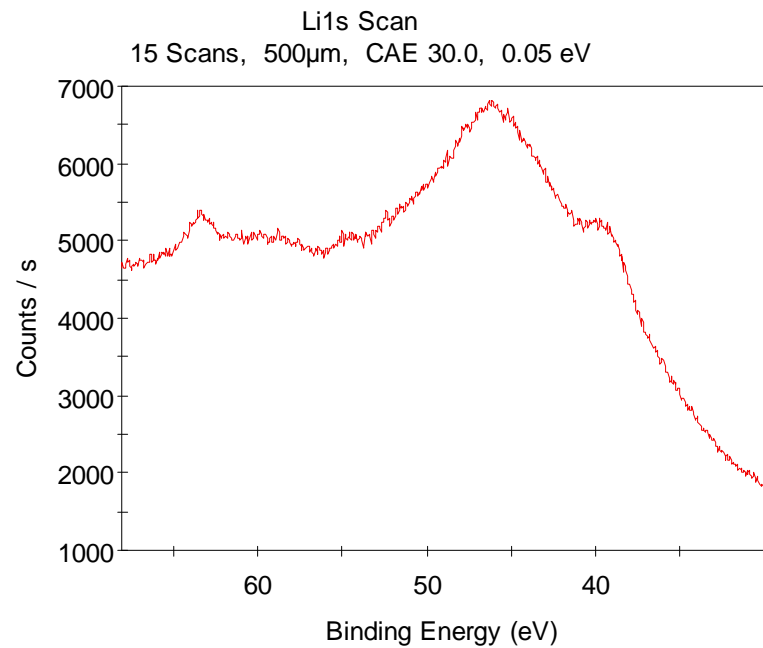
140729-Wangy-Lidy-z\Mono 500µm\Sn1

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHERMO1	TXFN	Backgn	Title
Sn3d5	490.080	486.204	474.480	1030475.923	2.318	2631499.3457	0.0000	0.000	Standard		22.000	5630.199	Smart	Survey
O1s	535.880	530.191	524.680	295598.506	2.515	833616.1511	0.0000	0.000	Standard		2.881	5681.658	Smart	Survey
C1s	297.280	284.703	276.080	28227.892	2.612	96996.0016	0.0000	0.000	Standard		1.000	5411.536	Smart	Survey
Cl2p	211.280	198.604	192.880	6163.338	3.501	26002.1950	0.0000	0.000	Standard		2.741	5325.560	Smart	Survey
C1s	294.280	284.663	277.830	6413.537	1.419	13894.3291	0.1754	15.207	Standard	Y	1.000	1110.786	Smart	C1s Scan
Sn3d	501.080	486.219	478.880	322380.128	1.265	796665.6990	0.2886	25.025	Standard	Y	37.257	1195.147	Smart	Sn3d Scan
O1s	537.980	530.146	524.730	87382.474	1.299	144636.9054	0.6893	59.768	Standard	Y	2.881	1215.615	Smart	O1s Scan

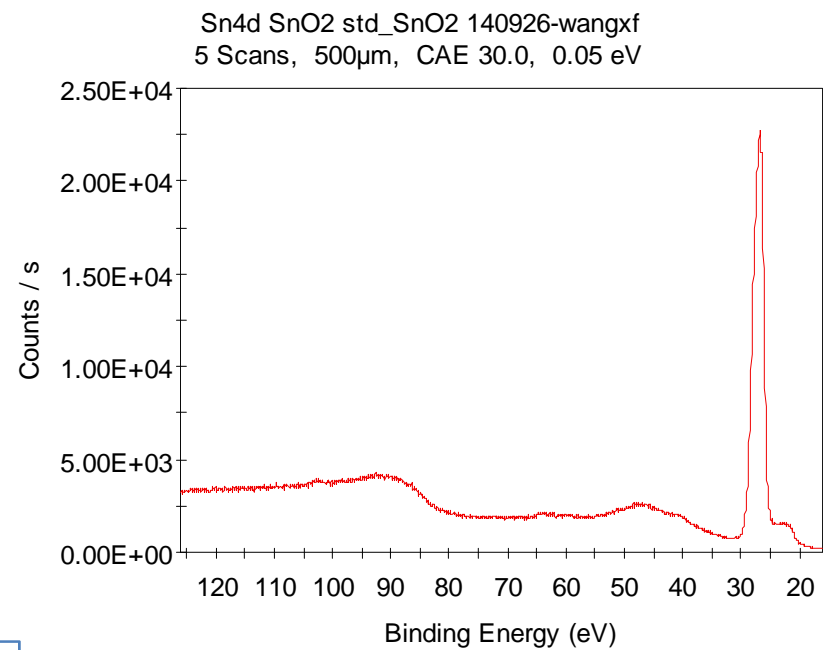
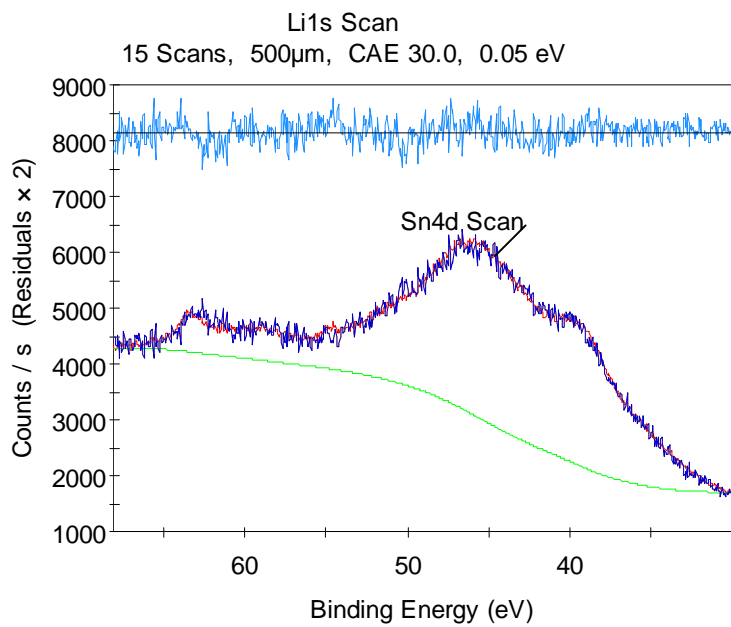
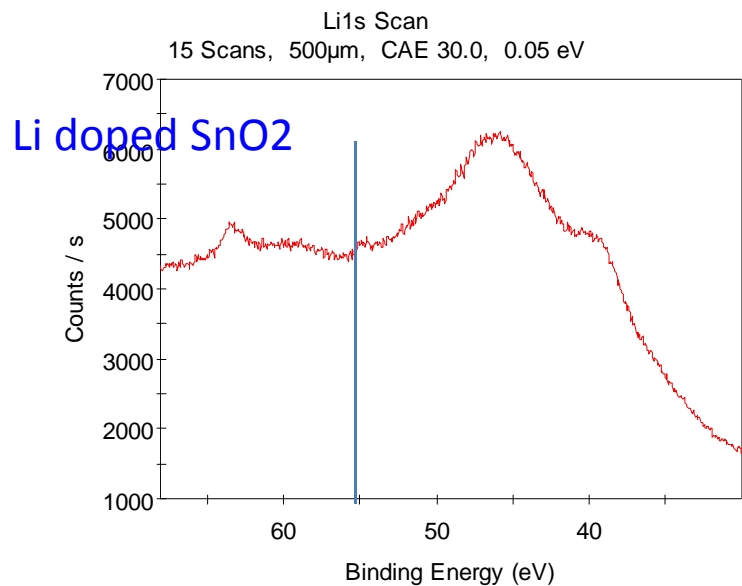


SnO₂ : Li

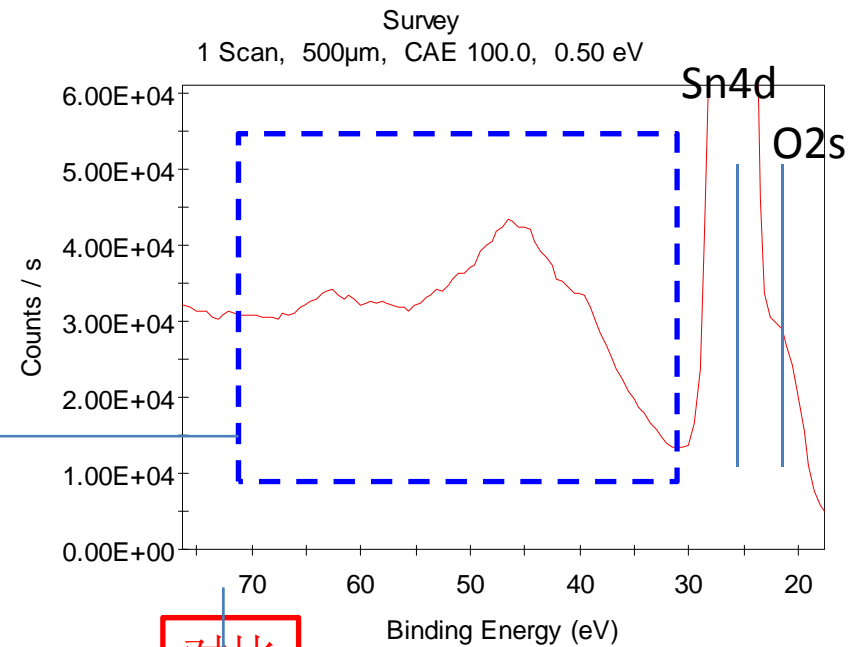
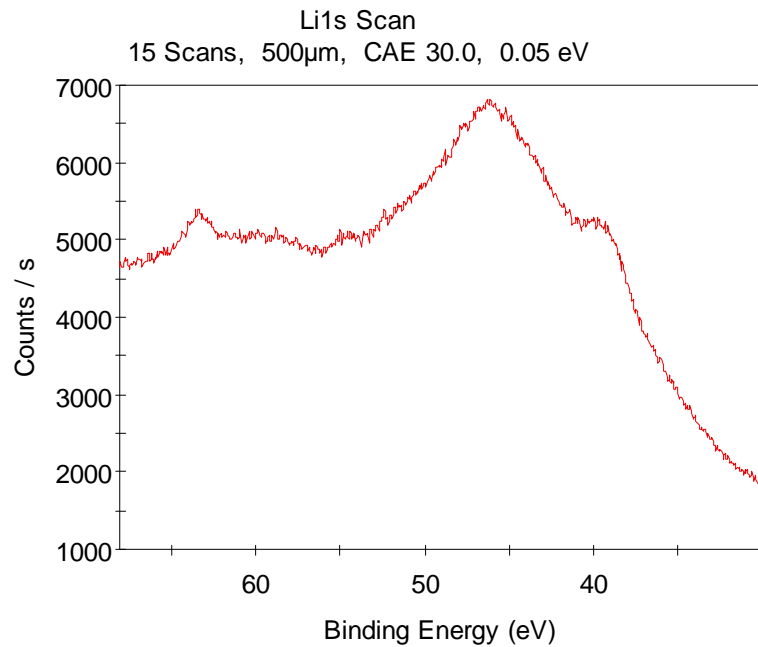




全谱范围宽，视野大。查看全谱，



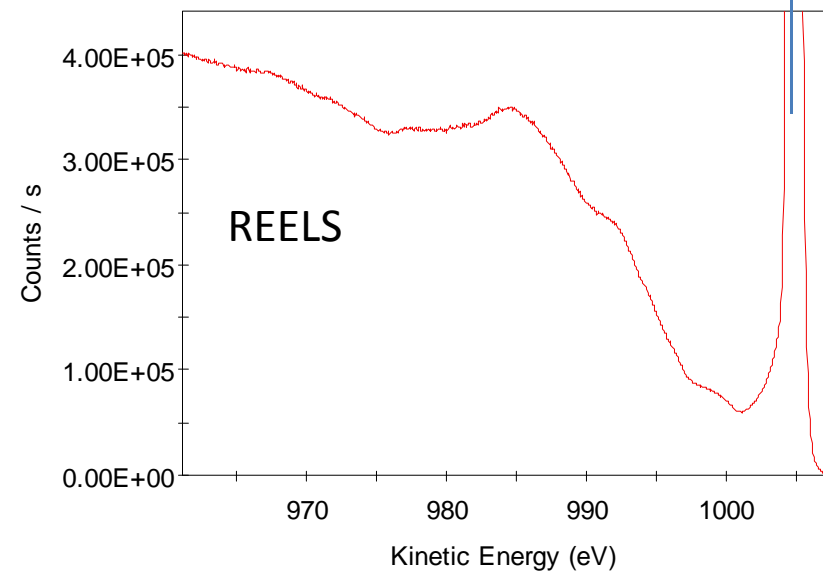
谱峰完全与标准SnO₂谱重合，故不存在Li



对比

Scan 979eV #002 Lensmode-Std
2 Scans, CAE 5.0, 0.05 eV

$E_0=1\text{keV}$



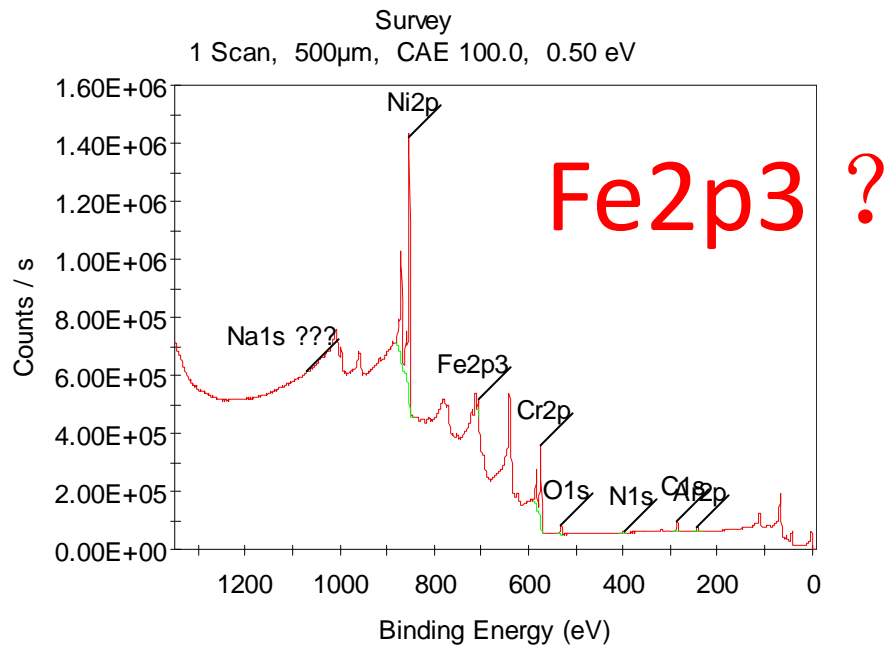
结论: **Sn4d**的能量损失谱与**Li1s**重叠,
干扰了对**Li1s**的分析。
无法分析**SnO2**中微量**Li**。
XPS不是无所不能的分析工具。

XPS谱中俄歇谱峰干扰

- 损失峰/携振峰干扰光电子峰;
- 俄歇峰 (**XAES**) 干扰光电子峰;
- 光电子峰干扰另一光电子峰, 如:
 - Cu2p/Pr3d;
 - S2p/S2s分别与Se3p/Se3s重叠干扰;
 -
- 卫星峰/鬼峰/阳极靶交叉峰干扰光电子峰;
- 双阳极XPS中, 韧致辐射X射线激发谱峰及背景的干扰;
-

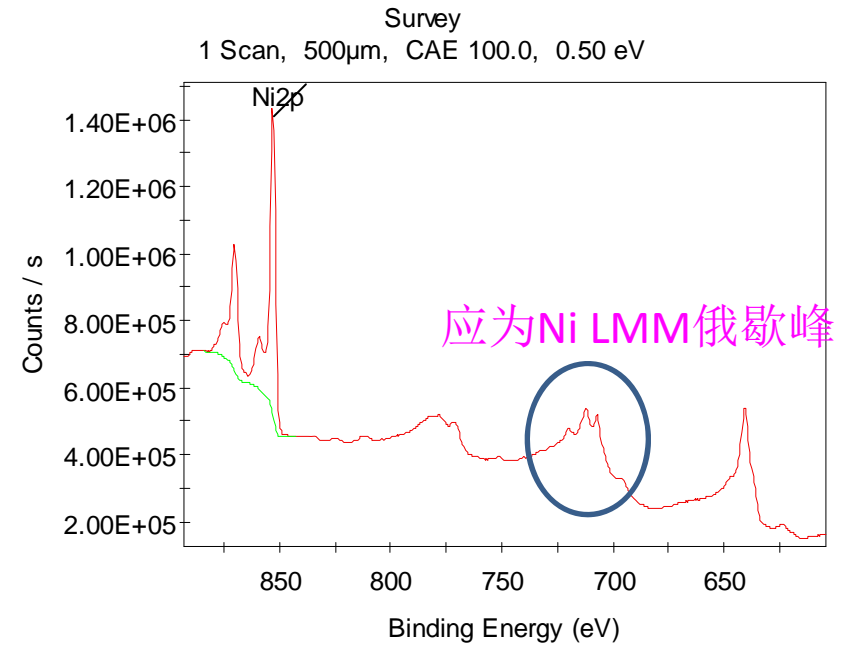
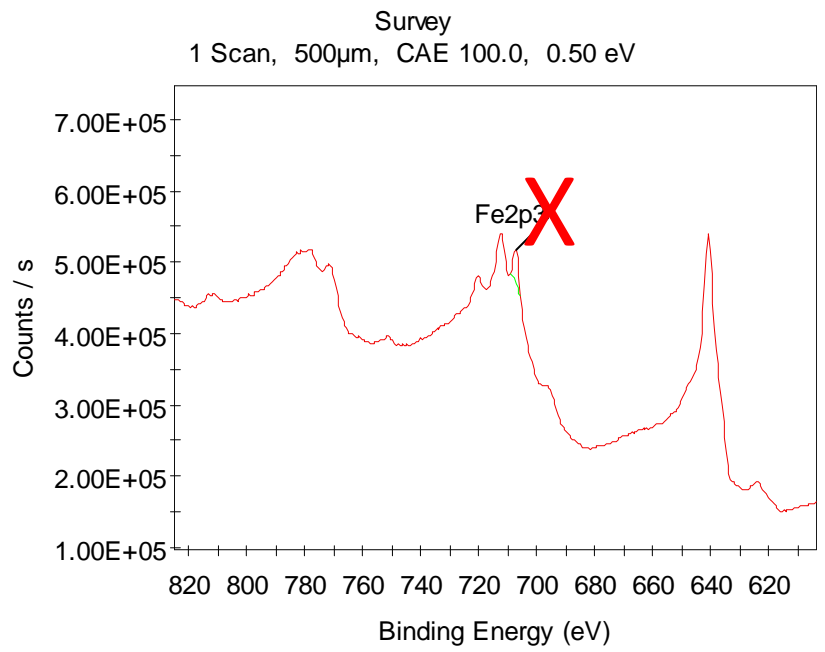
XPS谱中俄歇谱峰干扰

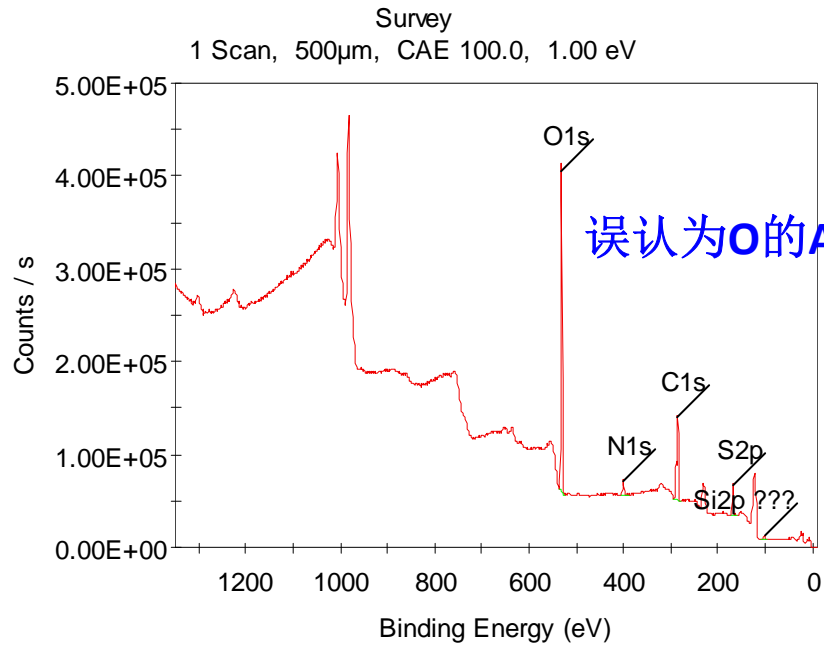
- 伴随光电发射，产生俄歇发射，XPS中伴随出现俄歇谱峰；
- 案例：Mono AlK α XPS 中 Fe2p-Ni LMM，Nd3d+OKLL



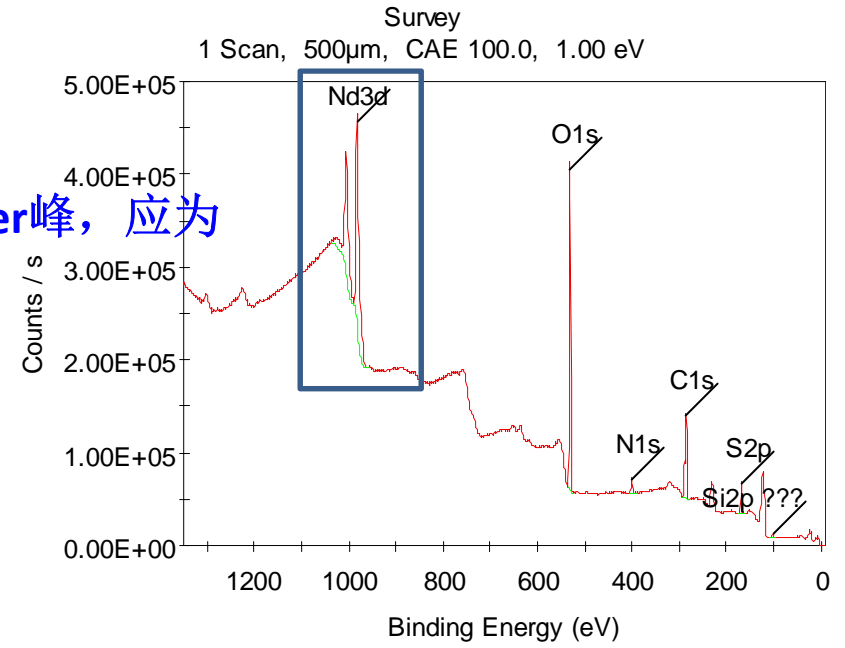
NiCr合金样品，
激发条件：Mono AlKa

将NiLMM峰，误认为Fe2p3



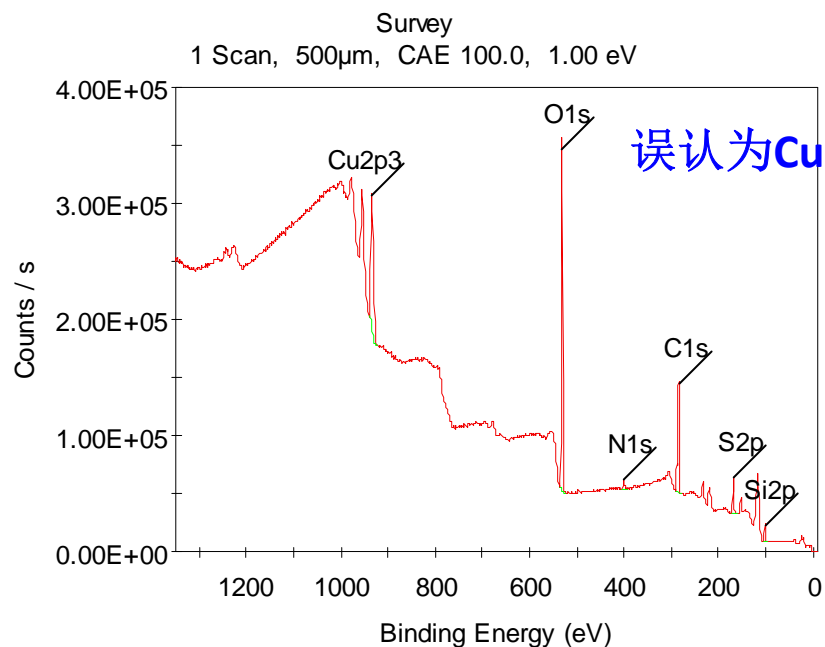


误认为O的Auger峰, 应为

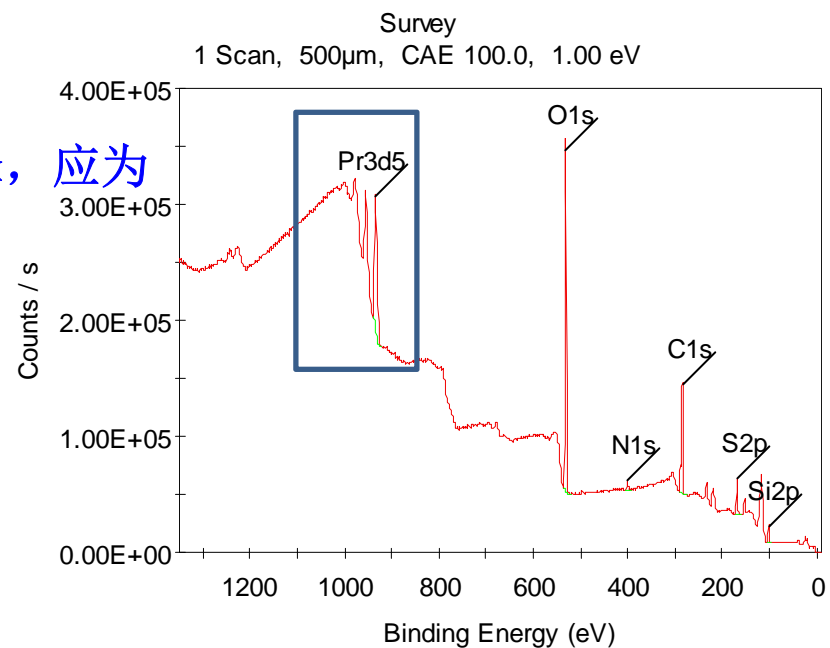


XPS谱中俄歇谱峰干扰

- 损失峰/携振峰干扰光电子峰;
- 俄歇峰 (XAES) 干扰光电子峰;
- 光电子峰干扰另一光电子峰, 如:
 - Cu2p/Pr3d;
 - S2p/S2s分别与Se3p/Se3s重叠干扰;
 -
- 卫星峰/鬼峰/阳极靶交叉峰干扰光电子峰;
- 双阳极XPS中, 韧致辐射X射线激发谱峰及背景的干扰;
-

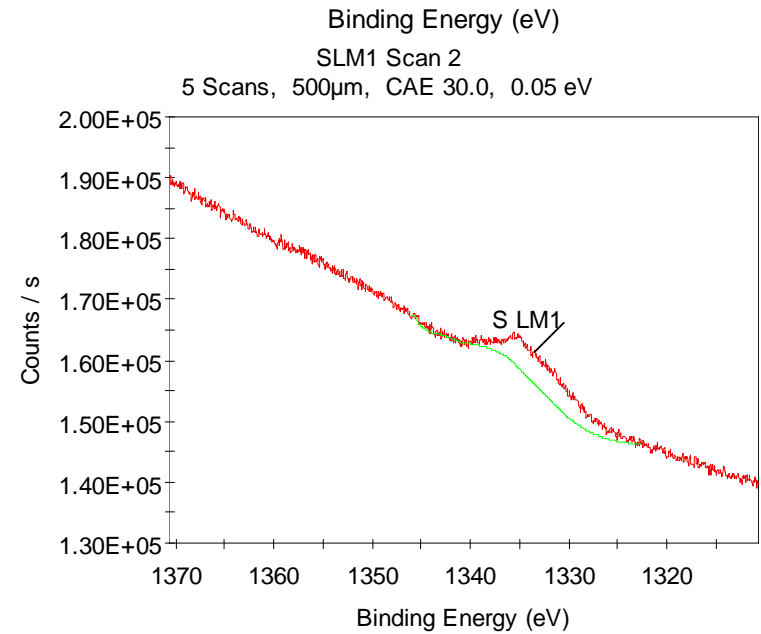
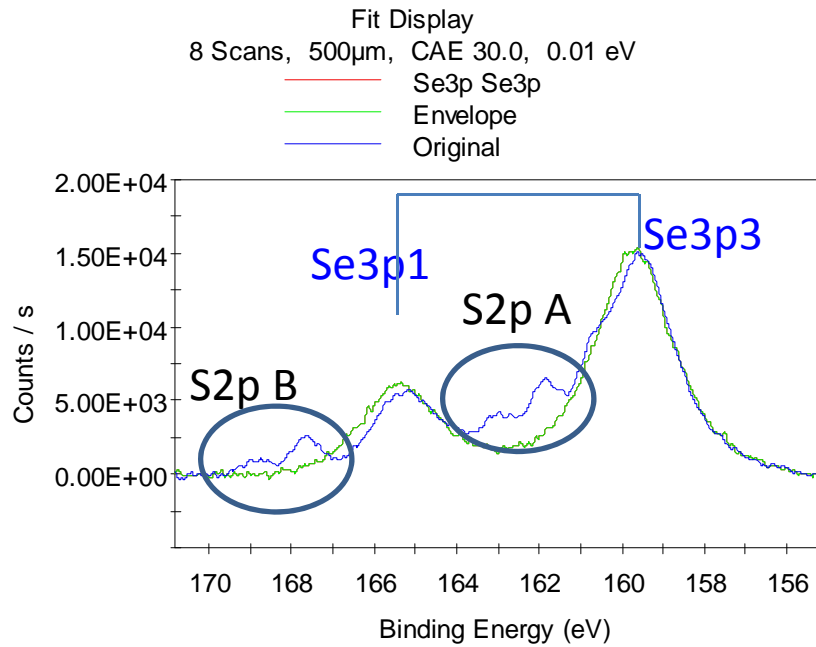
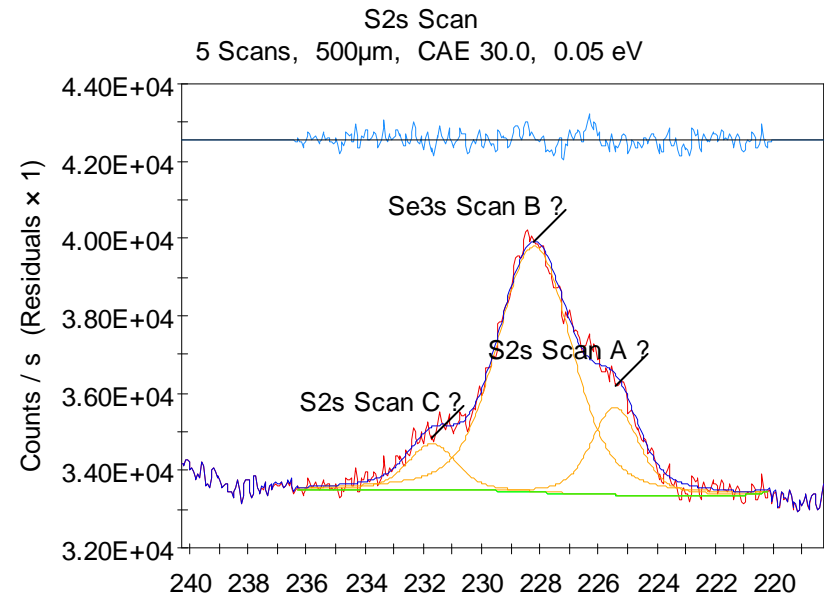
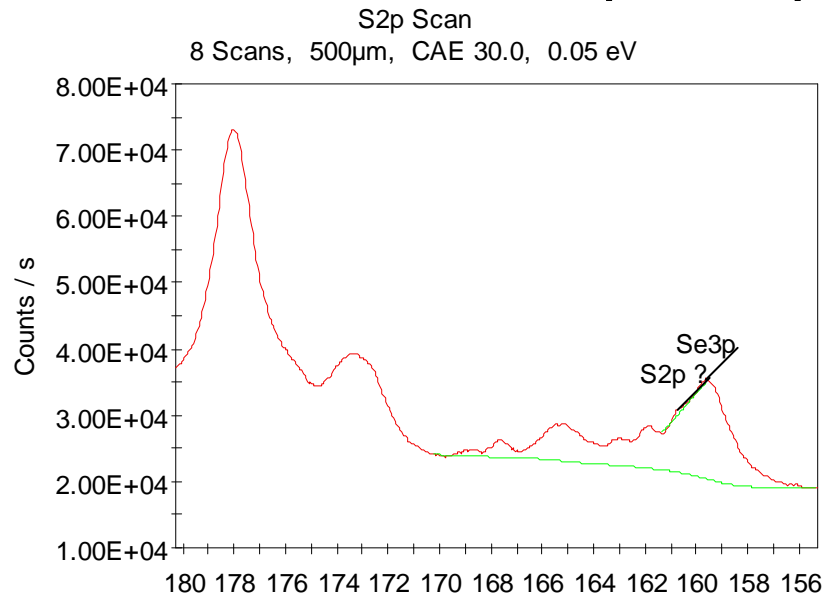


误认为Cu2p峰, 应为



可采用其它能级峰判别指认, 例如: 采用Pr4d, 而Cu不存在4d峰。
如果两种元素Cu/Pr同时存在, 谱峰重叠。则3d峰无法直接使用, 需要分峰;
或者采用其它谱峰Cu (3p) /Pr (4d) 的进行分析。

S2p -Se3p and S2s-Se3s



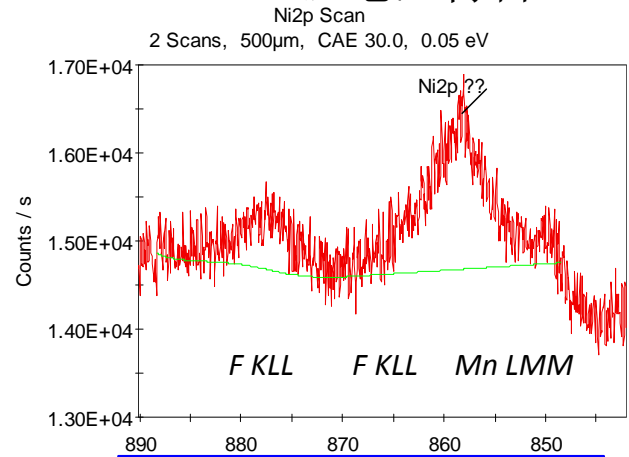
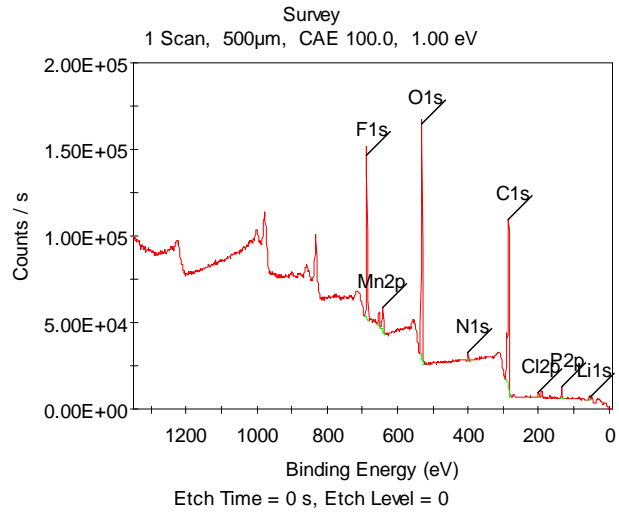
解决重叠峰干扰的方法

- 对于俄歇干扰光电子峰，更换X射线光子能量（激发源，AlKa更换为MgKa）可以改变重叠干扰，得到正确的实验结果；
- 在结合能BE坐标中，某光电子特征峰EP与某俄歇特征峰EA之间的差值 δ 与激发X射线的光子能量 $h\nu$ 有关，表示为：

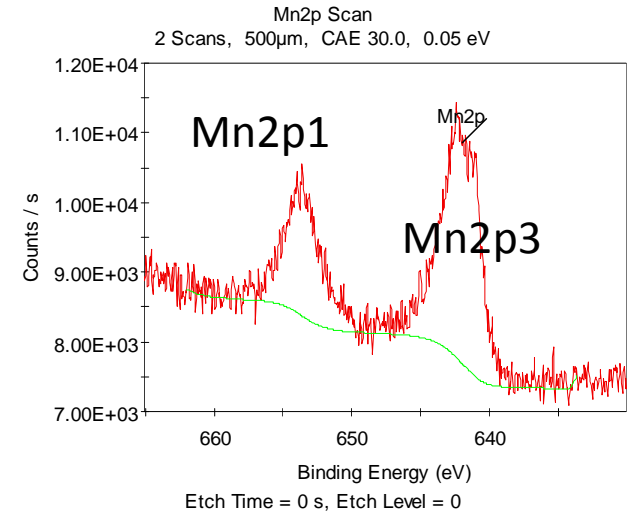
$$\delta(h\nu) = EP(BE) - EA(BE)$$
$$\delta(h\nu) = EP(BE) - [h\nu - EA(KE)]$$

如AlKa切换为MgKa， δ 变化 -233eV，即俄歇峰向低BE方向移动233eV (=1486.6eV-1253.6eV)

X-ray: Mono AlKa。样品含F O Mn N Cl P Li (锂电池材料)



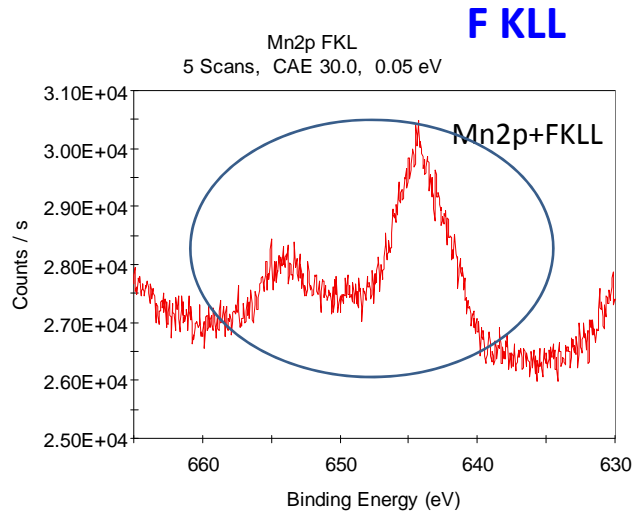
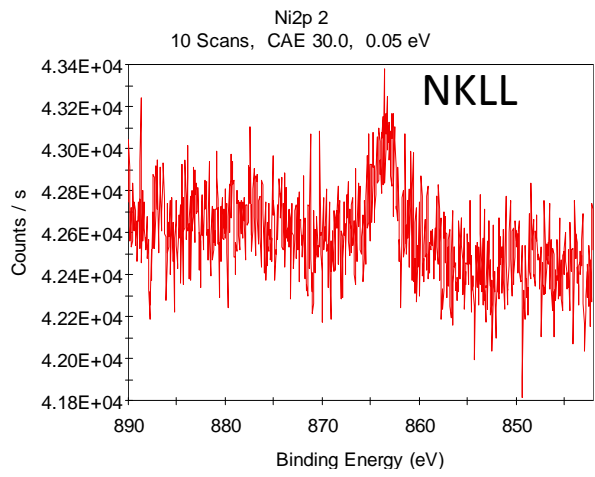
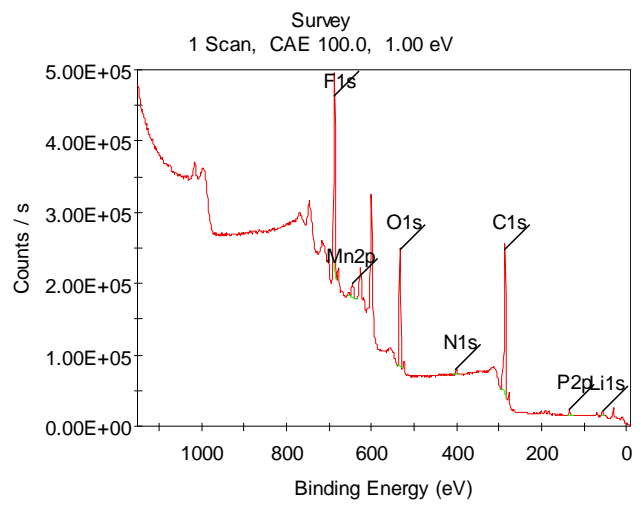
出现Ni2p信号?



Mn2p3与2p1强度比应为2:1

X-ray: MgKa。样品含F O Mn N Cl P

Ni2p为双峰结构

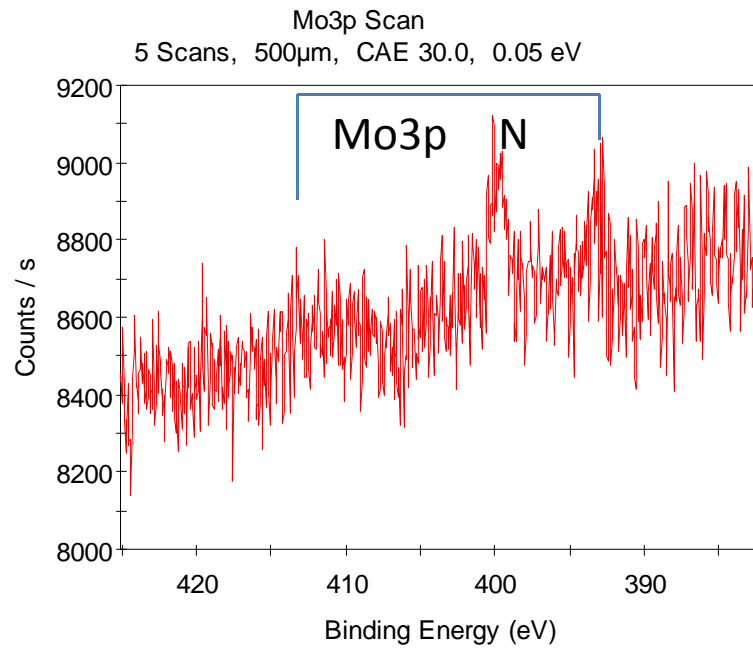
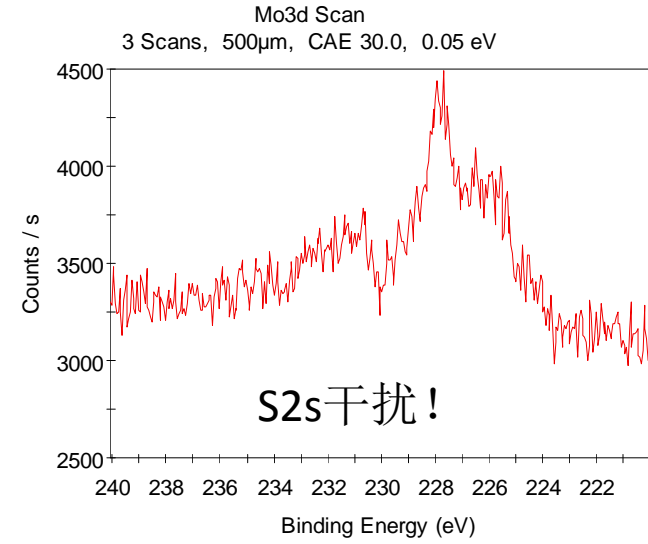
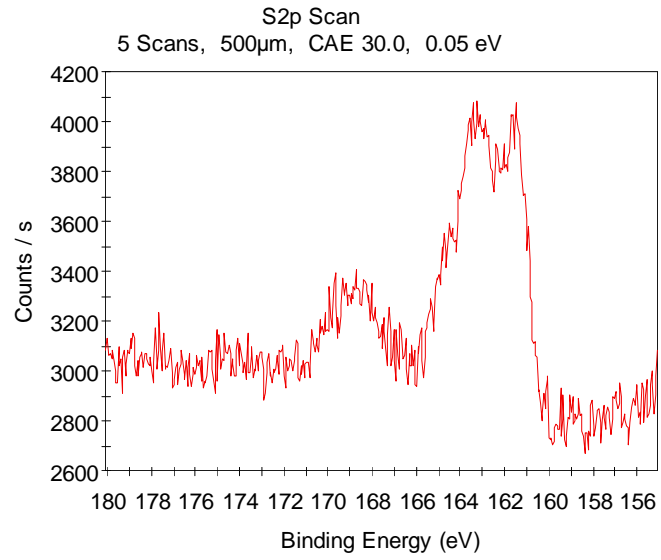


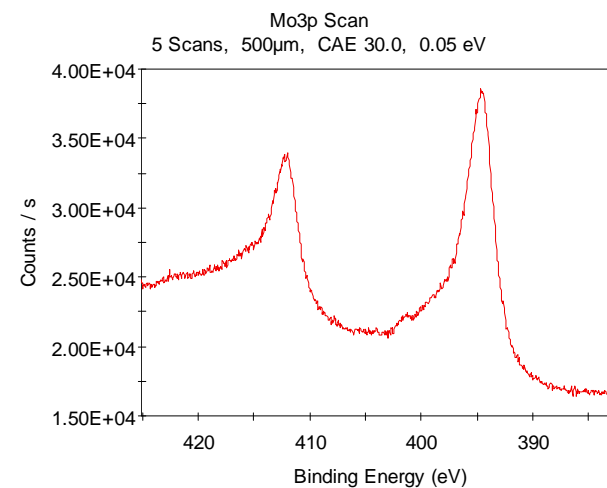
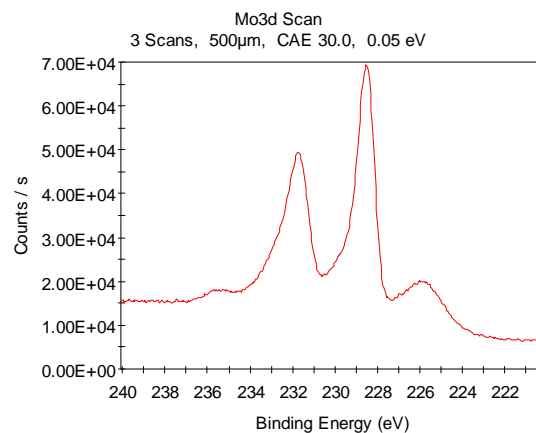
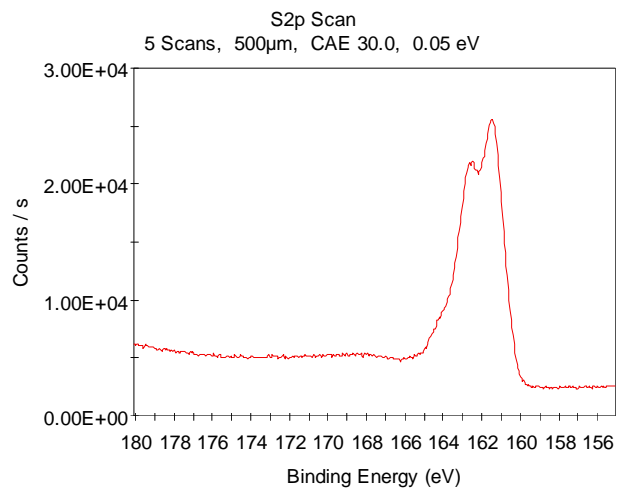
光电子峰 (XPS) 出现的同时, 伴随俄歇峰 (XAES) 出现

解决重叠峰干扰的方法

- 对于光电子峰、等离激元峰的干扰可采用
 - 选用次强峰或俄歇峰
 - Pt+Al₂O₃中 Pt4f(Al2p)→Pt4d;
 - MoS₂中Mo3d(S2s)→Mo3p;
 - 分峰处理，包括非线性拟合 (NNLSF)
 - MoS₂ (Mo3p) +N: 将N1s峰从Mo3p的包络中剥离;
 - Sb3d+O1s: 将Sb3d双峰从O1s中剥离;
 - Ru3d+C1s: 将Ru3d双峰从C1s中剥离;
 - Nd3d+OKLL: 采用非线性拟合剥离;

样品: S+Mo ?

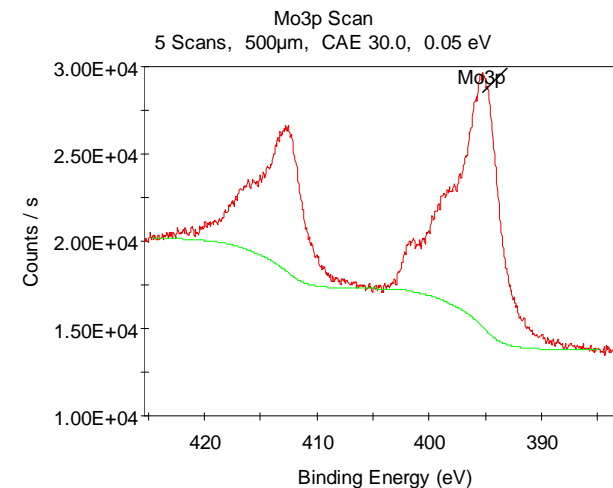
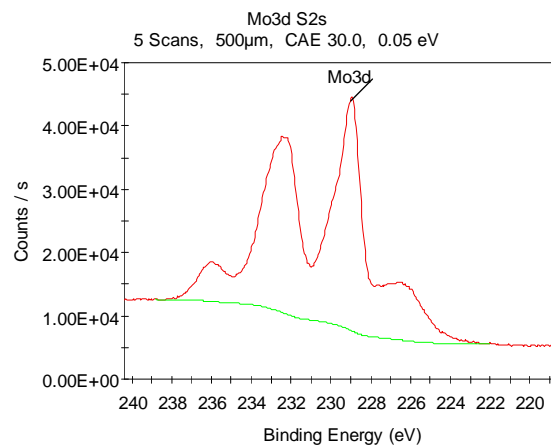
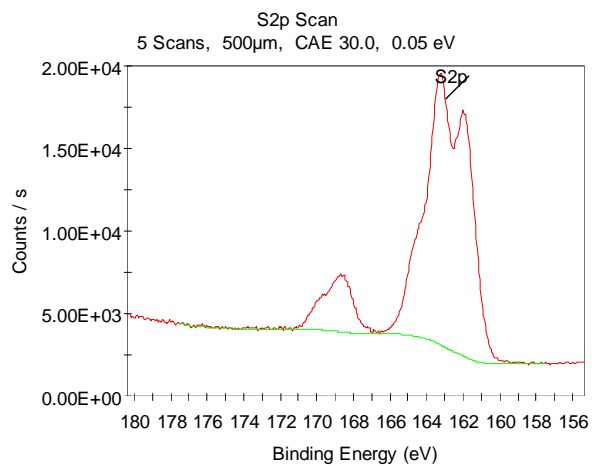




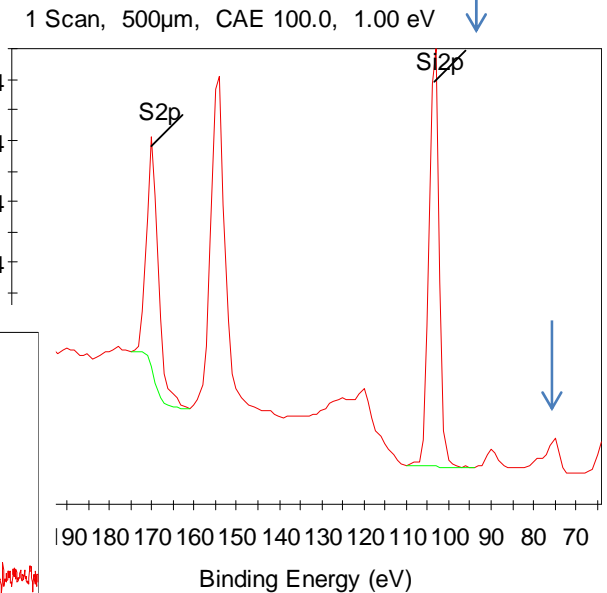
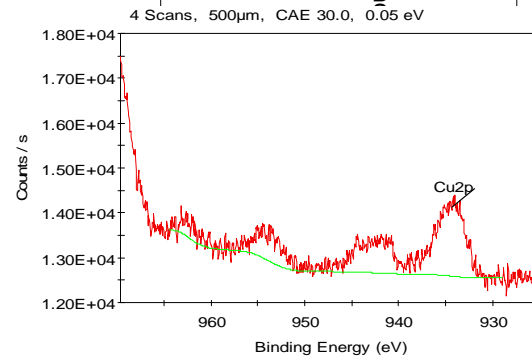
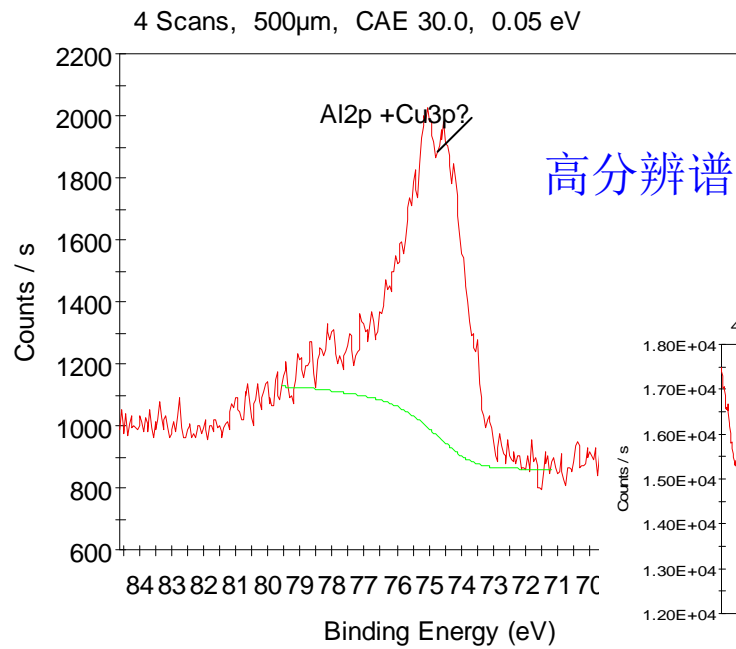
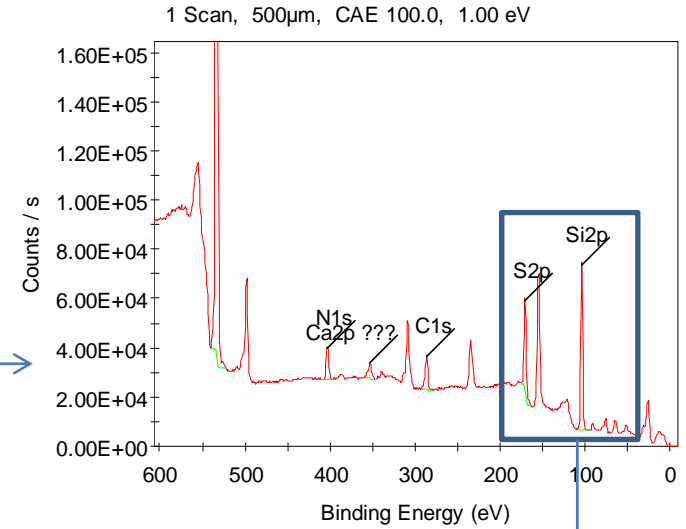
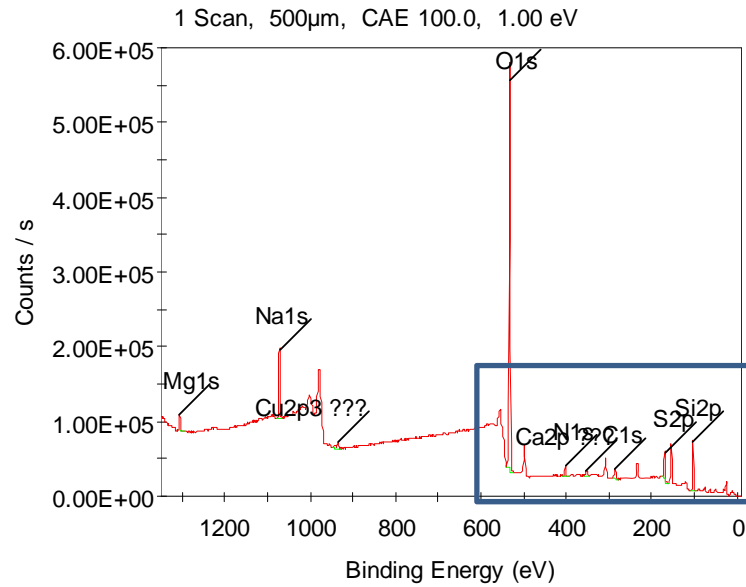
XPS分析两种MoS₂样品

最强峰Mo3d受S2s干扰

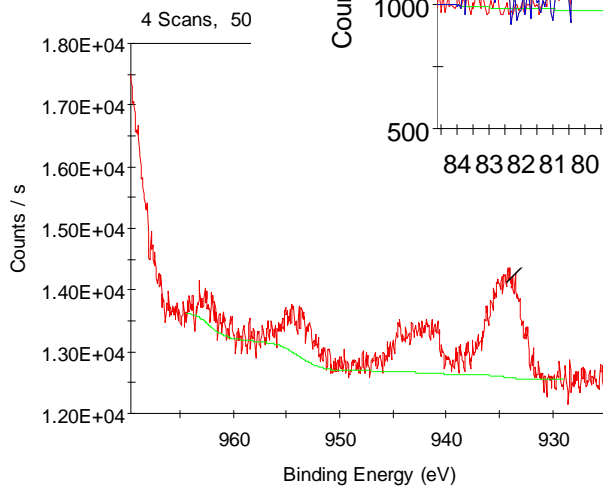
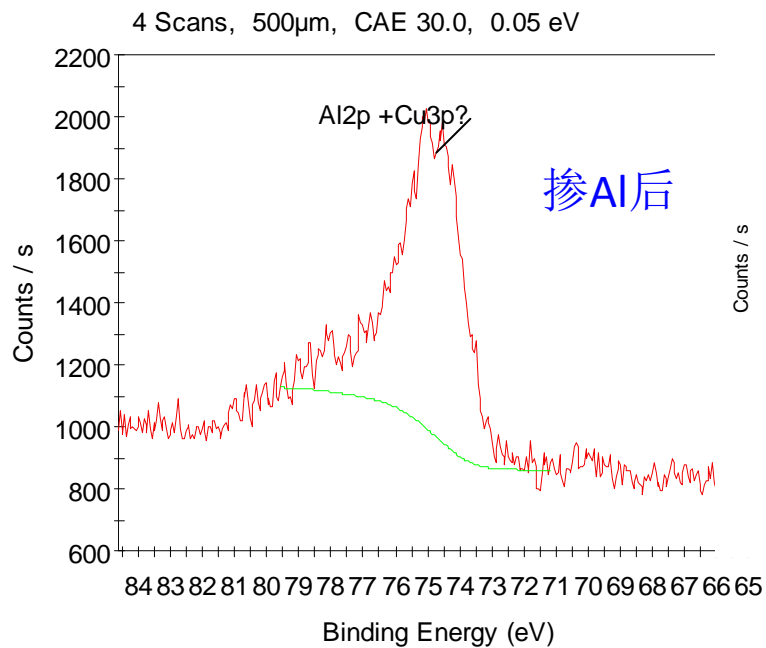
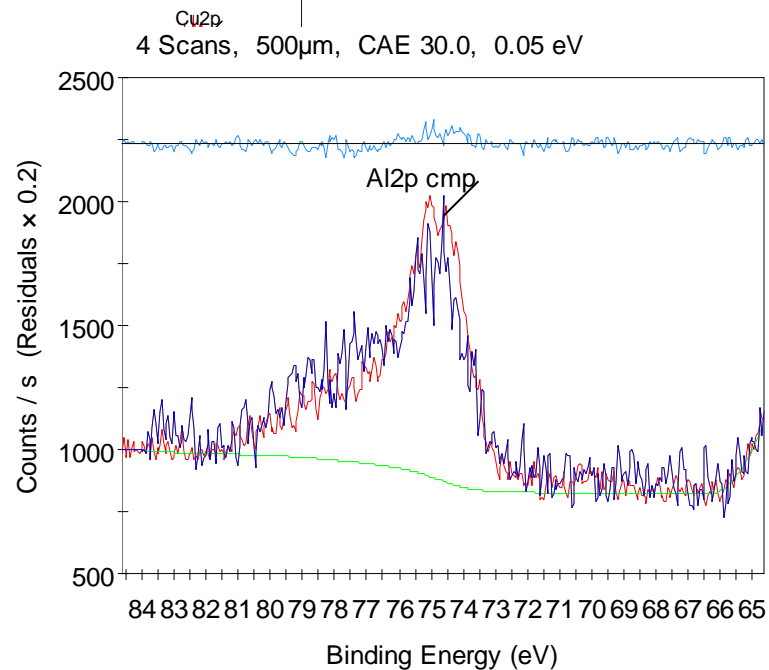
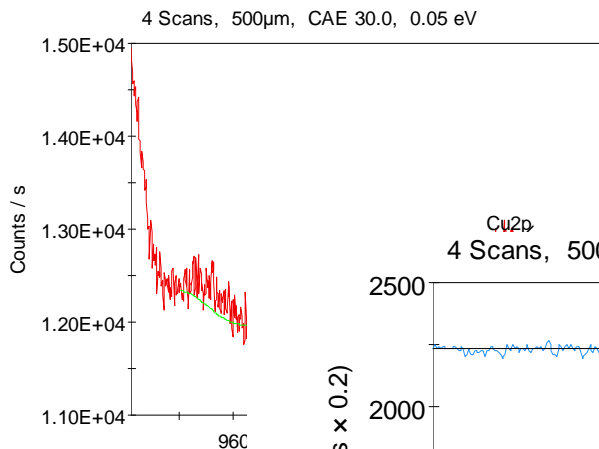
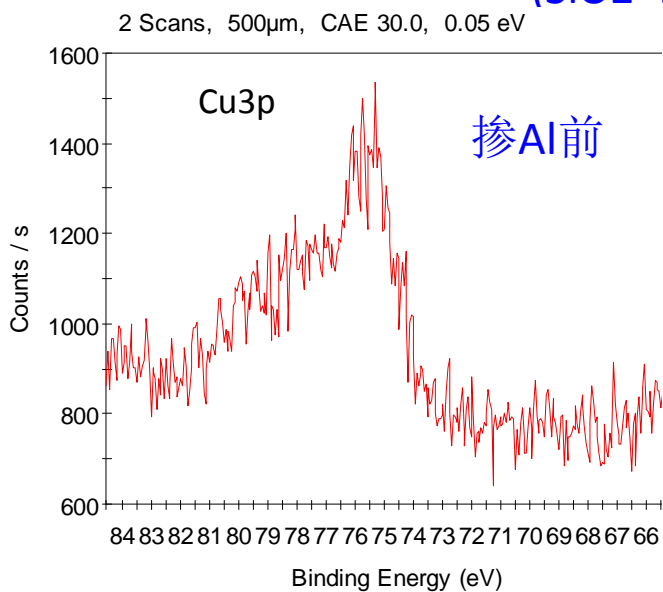
选用Mo3p表征Mo的价态



(SiO₂+MgO :Cu)样品中掺有Al ?

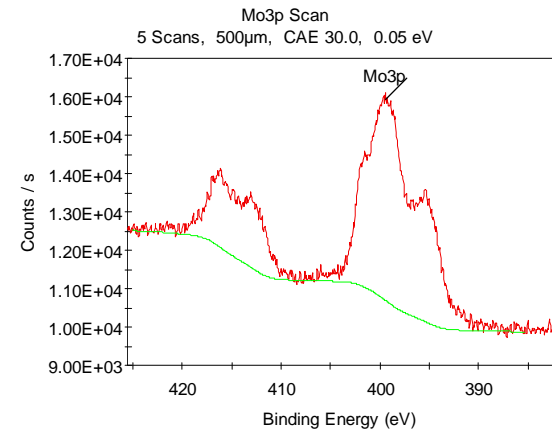
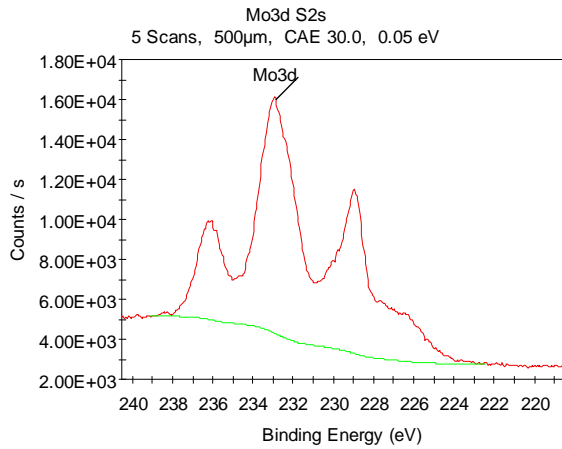
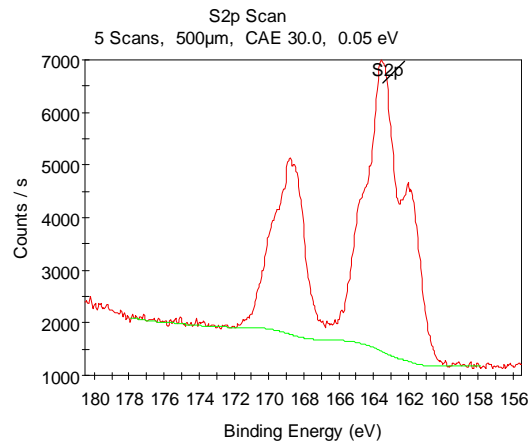


(SiO₂+MgO :Cu)样品 掺Al前后对比



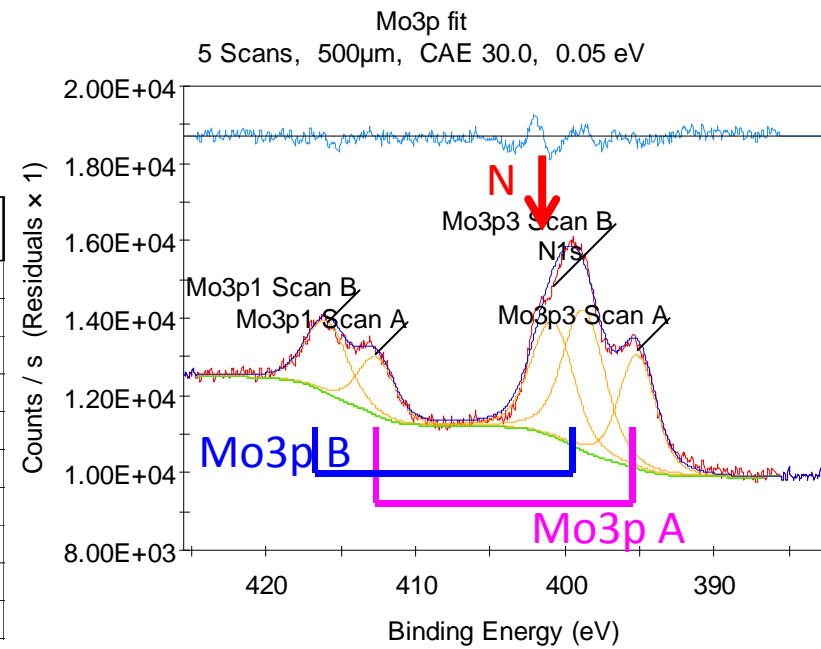
解决重叠峰干扰的方法

- 对于光电子峰、等离激元峰的干扰可采用
 - 选用次强峰或俄歇峰
 - Pt+Al₂O₃中 Pt4f(Al2p)→Pt4d;
 - MoS₂中Mo3d(S2s)→Mo3p;
 - 分峰处理，包括非线性拟合 (**NNLSF**)
 - MoS₂ (Mo3p) +N: 将N1s峰从Mo3p的包络中剥离;
 - Sb3d+O1s: 将Sb3d双峰从O1s中剥离;
 - Ru3d+C1s: 将Ru3d双峰从C1s中剥离;
 - Nd3d+OKLL: 采用非线性拟合剥离;



线性拟合

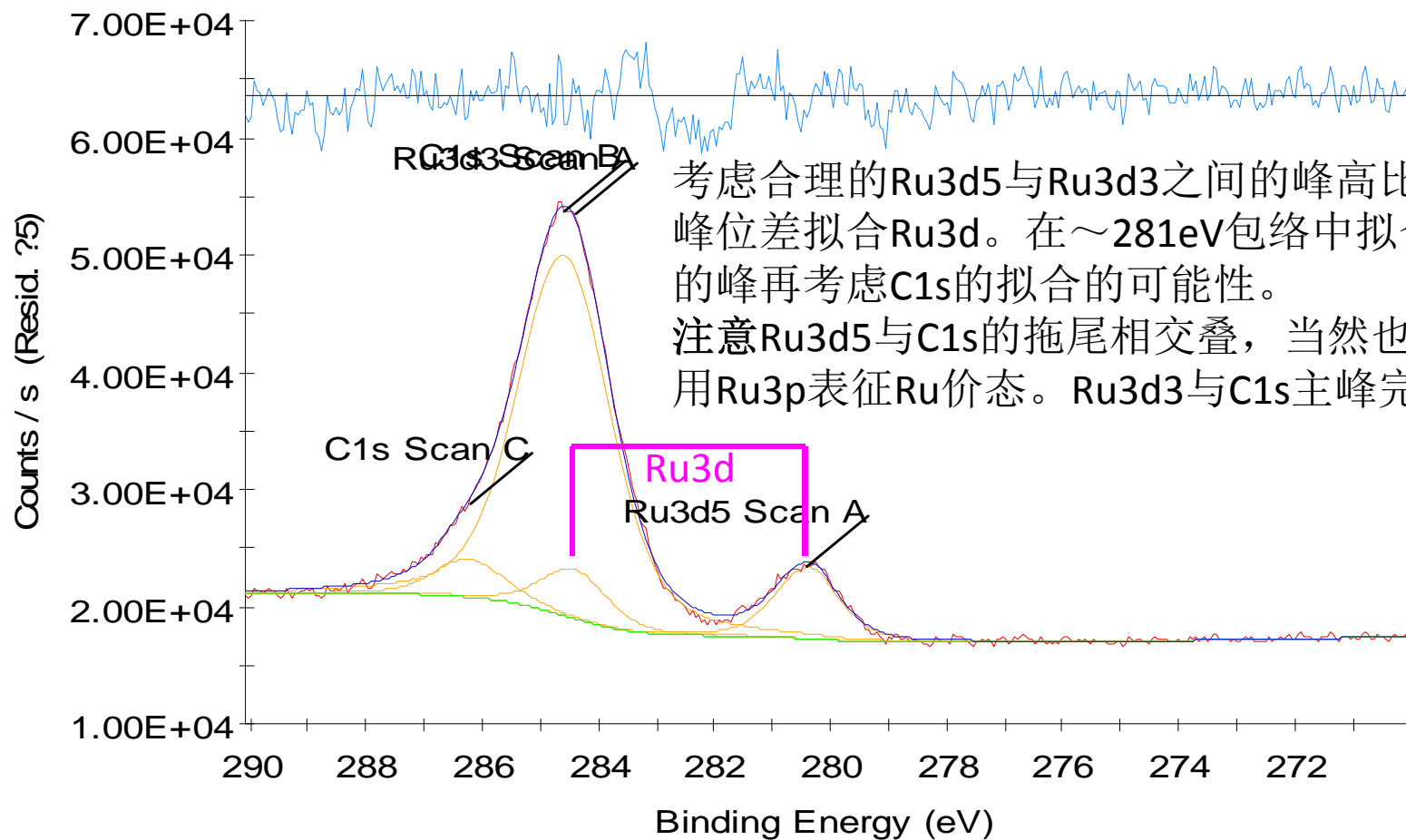
Ref.	Name	Peak BE	Height CPS	Height Ratio	Area CPS.eV	Area Ratio	FWHM fit param (eV)
A	Mo3p3 Scan A	395.13	2945.82	0.81	10023.47	0.70	2.90
							0.5 : 3.5
B	Mo3p1 Scan A	412.61	1507.62	0.41	5129.86	0.36	2.90
		A+17.20 (+0.9 -0.35)	A*0.512				A*1
C	Mo3p3 Scan B	398.71	3652.32	1.00	14325.56	1.00	3.34
							0.5 : 3.5
D	Mo3p1 Scan B	415.95	1869.20	0.51	7327.34	0.51	3.34
		C+17.20 (+0.9 -0.35)	C*0.512				C*1
E	N1s	400.81	2976.30	0.81	11827.56	0.83	3.39
							0.5 : 3.5



Ru3d与C1s峰

ESCALAB 250Xi in ATC BNU

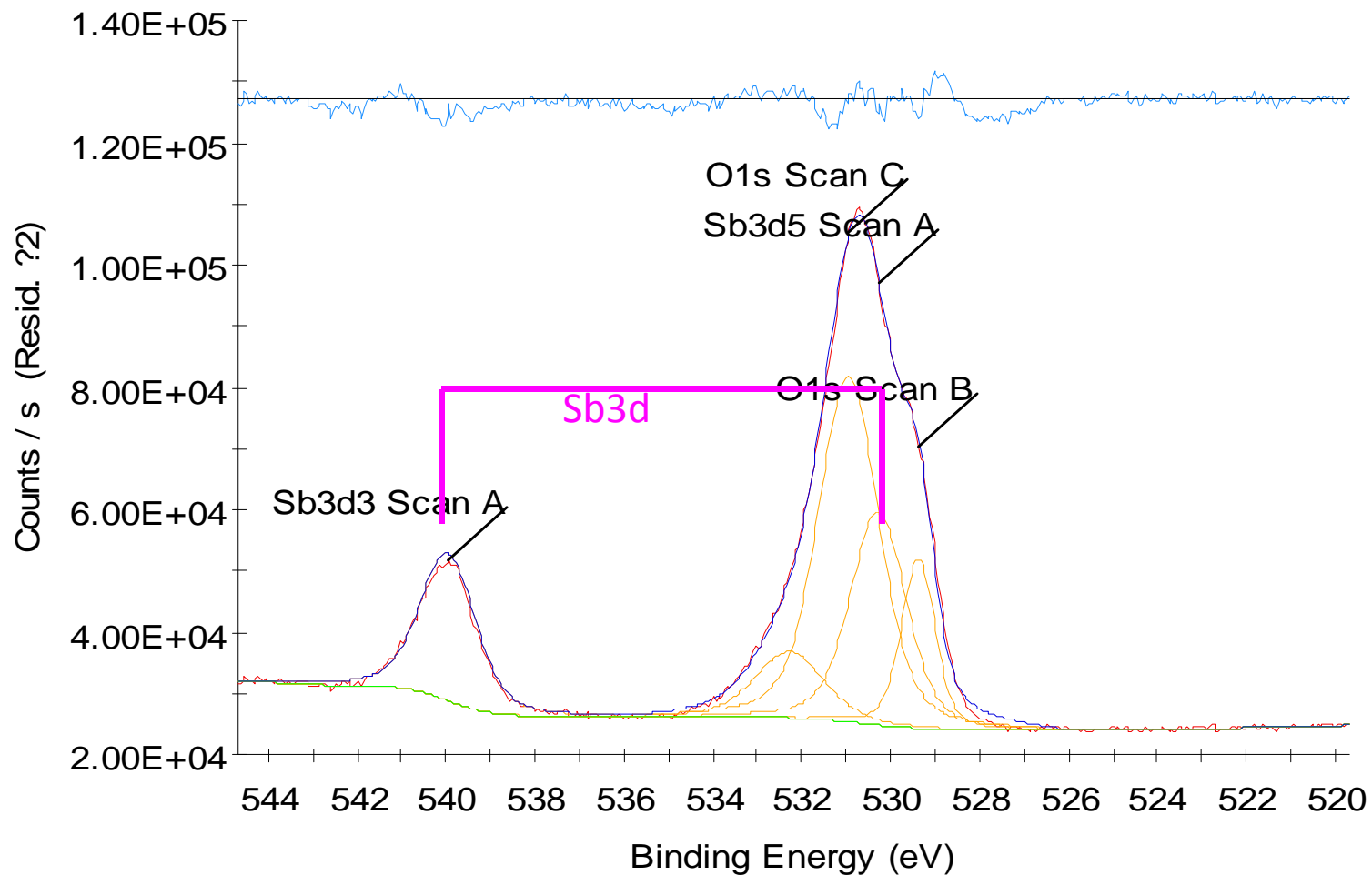
2 Scans, 1 m 20.2 s, 500衞, CAE 30.0, 0.05 eV

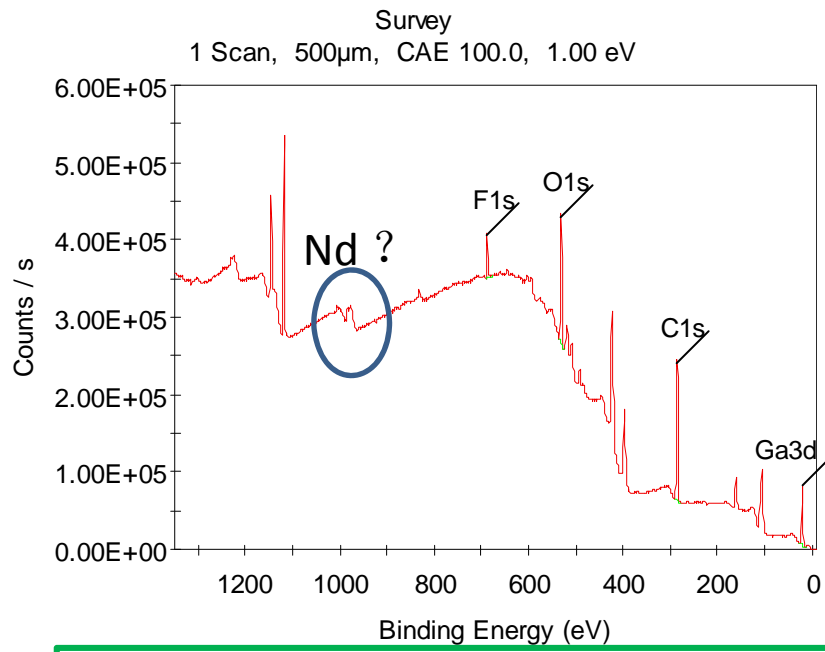


Sb3d与O1s峰

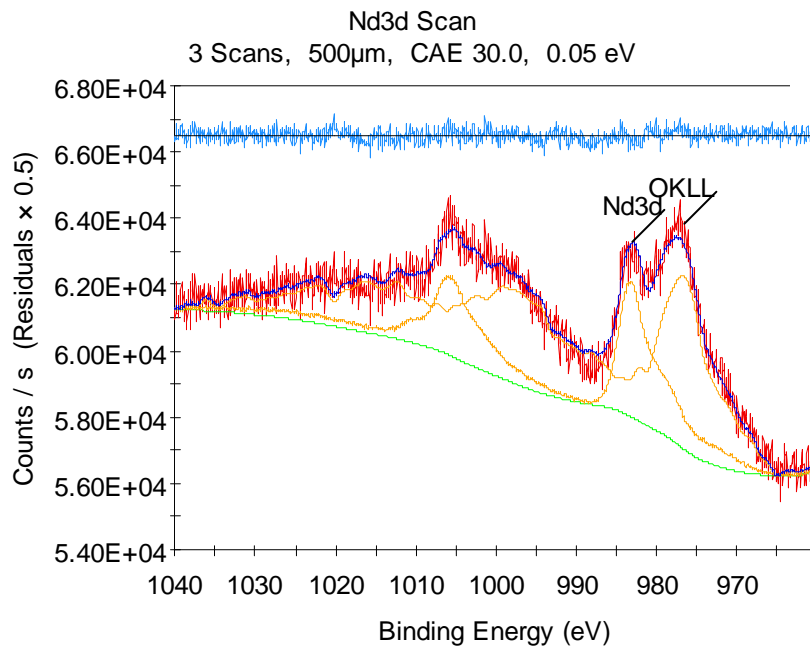
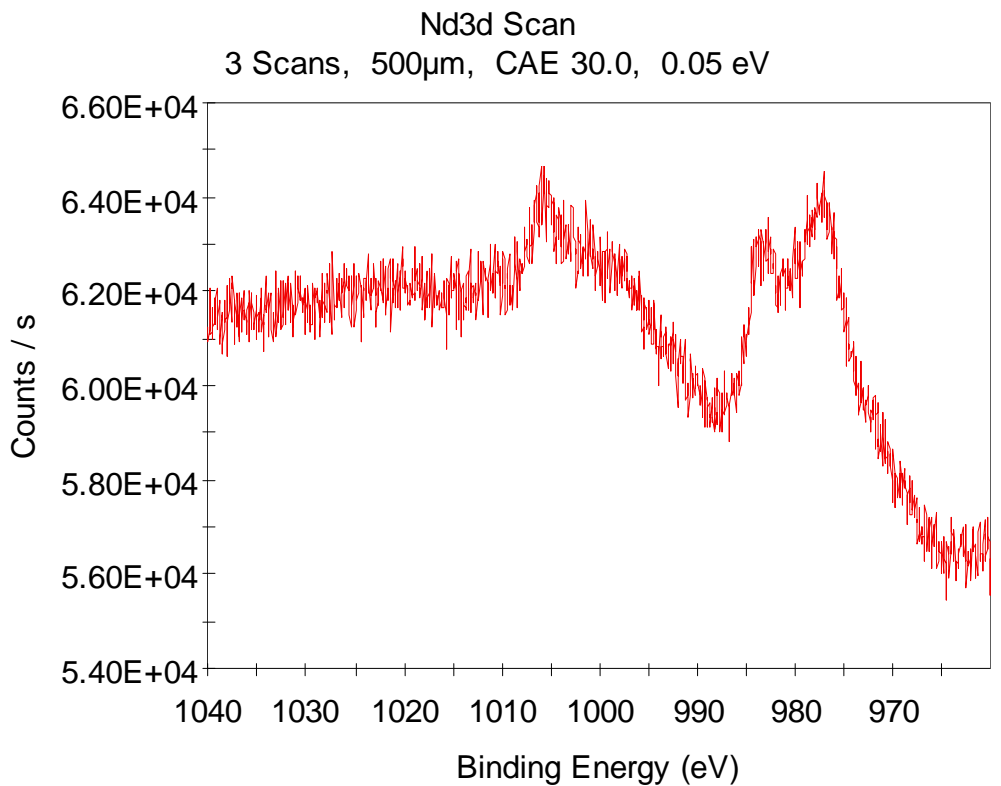
ESCALAB 250Xi in ATC BNU

2 Scans, 1 m 40.2 s, 500衞, CAE 30.0, 0.05 eV





OKLL与Nd3d重叠，有Nd3d信号出现



Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
Ga3d	26.980	20.250	14.980	20264.415	1.494	37970.7426	0.3173	7.866
C1s	292.930	284.674	278.880	57293.610	1.210	88560.3095	1.1179	27.711
O1s	541.880	531.071	525.880	39579.822	2.438	103147.5280	0.4917	12.190
Ga2p	1151.930	1118.540	1112.180	93115.243	1.761	423841.7510	0.0000	0.000
OKLL	1040.080	976.530	960.080	5218.891	6.895	117990.3594	2.0937	51.902
Nd3d	1040.080	983.080	960.080	4092.605	4.699	51498.1527	0.0134	0.331

灵敏度因子有误！

射线束辐照诱导变化产生的假峰

- XPS-X射线
- AES/SAM-电子束
- REELS-电子束
- 样品清洁/深度剖析-离子束（如Ar⁺）
- ISS /SIMS—离子束 Ar⁺, He⁺
- UPS-UV射线
- *应该注意：射线辐照对样品有损伤，可能会产生假峰！*

射线对结果的影响

- 化学态变化
 - 氧化态的还原(如:TiO₂)
 - 化学键断裂(如:有机高分子)
 - 电子损伤(REELS 测量宽禁带,有机高分子)
- 组分变化
 - 吸附
 - 脱附
 - 分凝

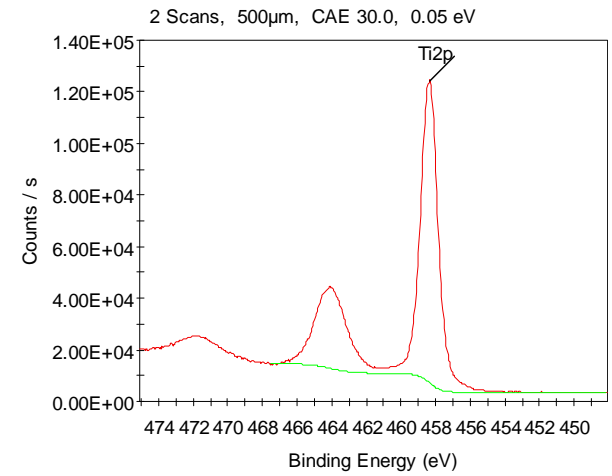
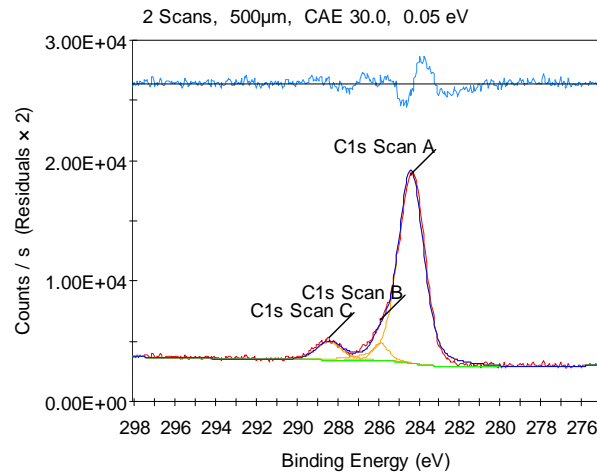
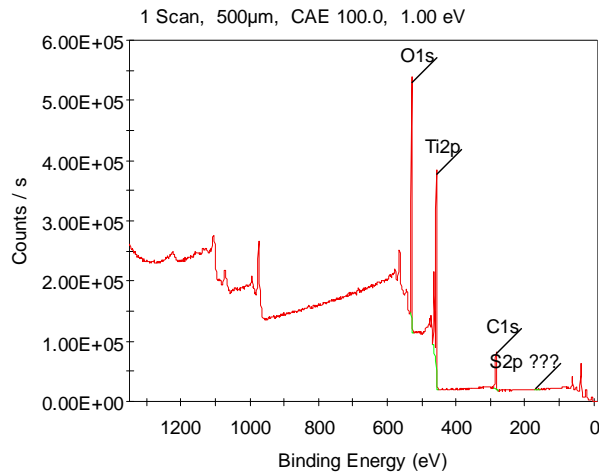
氩离子 (Ar^+) 刻蚀

- 电子能谱仪器中常配有 Ar^+ 源，用于：
 - 清洁样品
 - 深度剖析
 - 中和负电
 - 离子谱
 -
- 参数（例如Thermo EX06）：
 - 能量（200eV—3000eV）
 - 束流（~10 μA -2 μA ）
 - 扫描区间（~10² μm ~4mm）
 - 时间（根据需求设定）

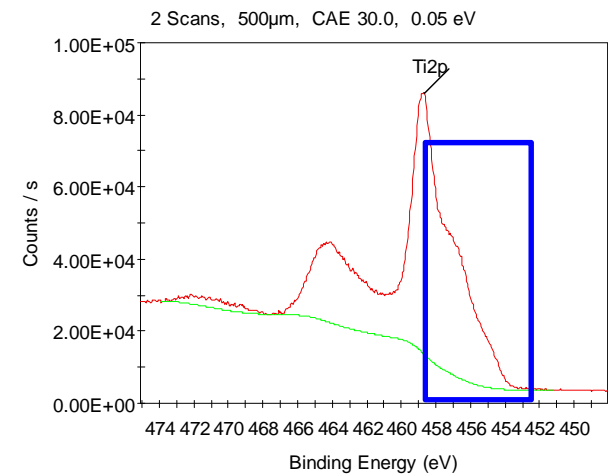
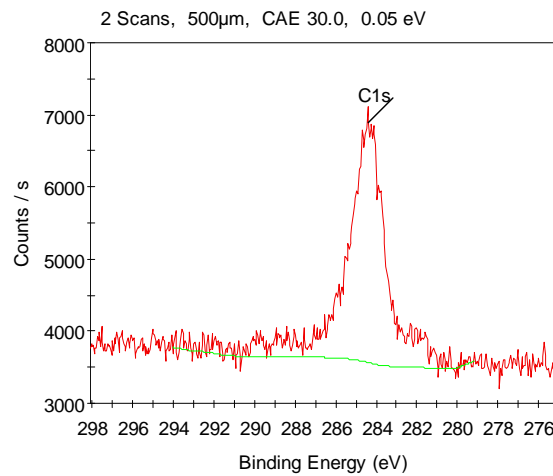
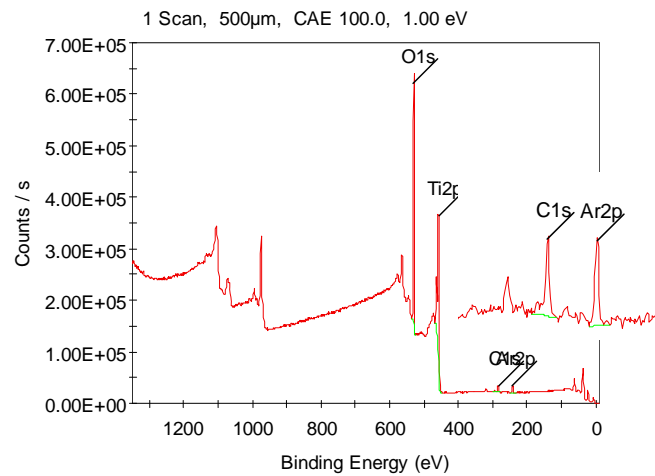
Ar⁺刻蚀nano-TiO₂

- Nano-TiO₂表面出现了污染，出现较强C峰
- Ar⁺ 清洁？

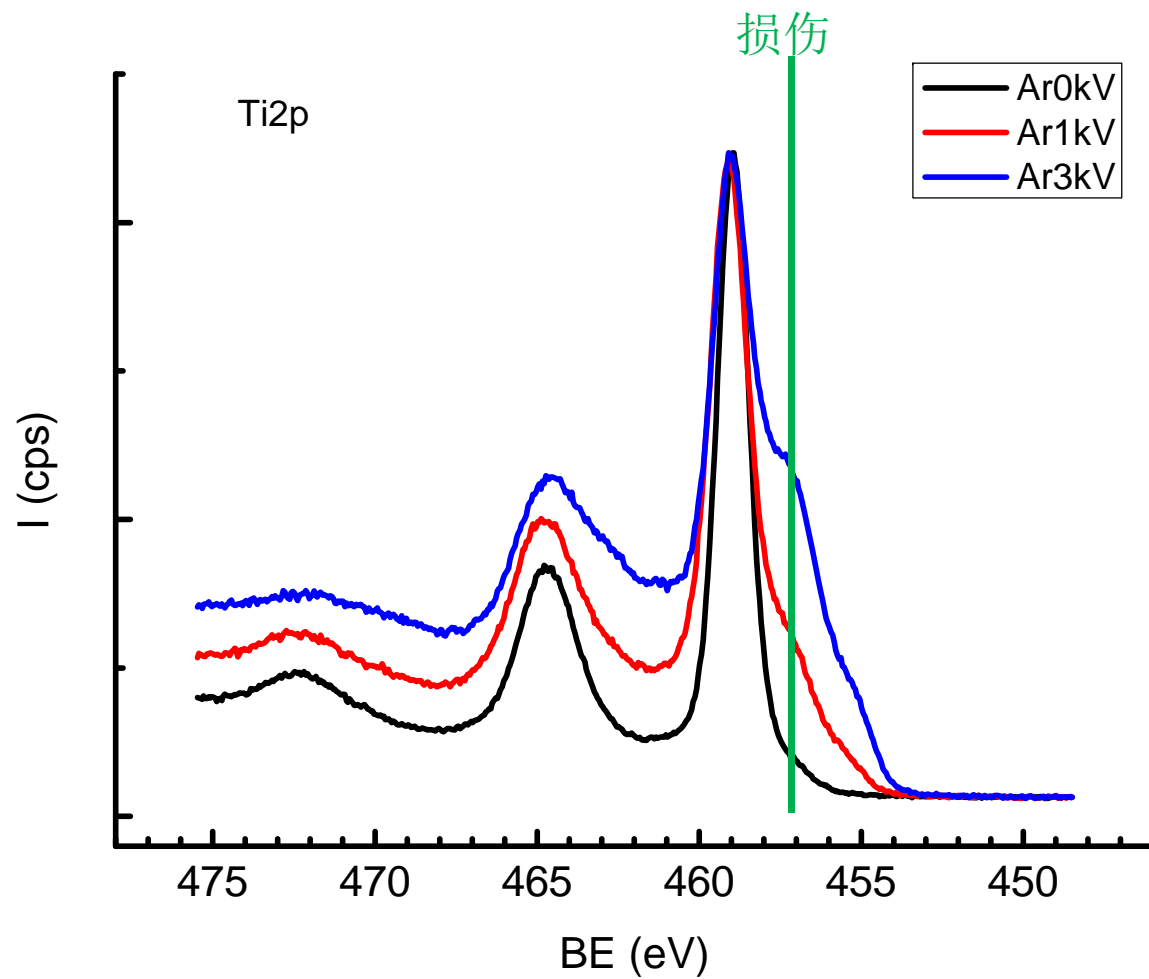
未经Ar+刻蚀 原始样品上出现较强的C1s峰 ~20 kcps



Ar+ 刻蚀 3keV 60s 后, C峰虽然大大降低 ~7kcps, Ti2p 还原, 结果失真!



Ar⁺刻蚀nano-TiO₂



其它条件相同：
Ar⁺刻蚀60s；
~50uA/cm²

Ar⁺刻蚀损伤

- 离子注入
- 择优溅射
- 离子混合效应
- 溅射污染、诱导吸附环境物质、离子钉入
- 破坏样品表面结构、组分
- 长时间溅射表面粗糙，弧坑效应，
-

Ar⁺刻蚀损伤：减小损伤

- 减少Ar⁺刻蚀引起的损伤：
 - 尽量不使用Ar⁺刻蚀，采用其它物理和化学方法处理样品；
 - 尽量低通量Ar⁺，适当时间；
 - 尽量低能量E₀，（ESCALAB 250Xi 可至200eV）；
 - 尽量减少Ar⁺辐照时间，保持原始样品特征；
 - 其它技术：原子团簇枪；
- 综合优化Ar⁺溅射条件：能量、束流密度、时间、离子束斑、角度、旋转样品台参数；

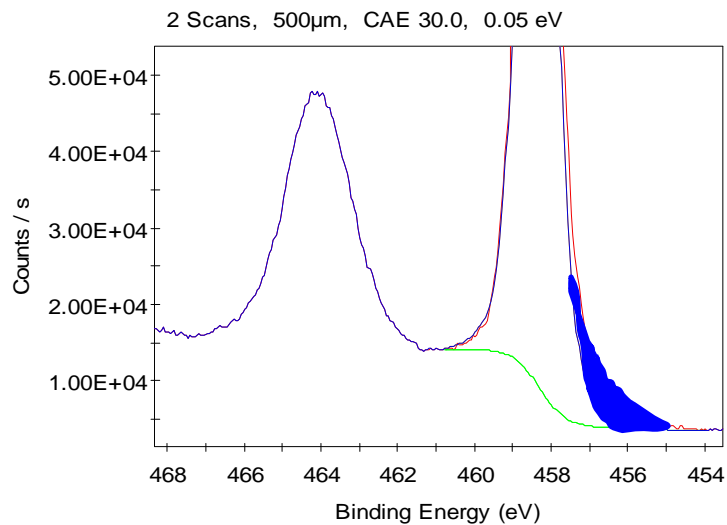
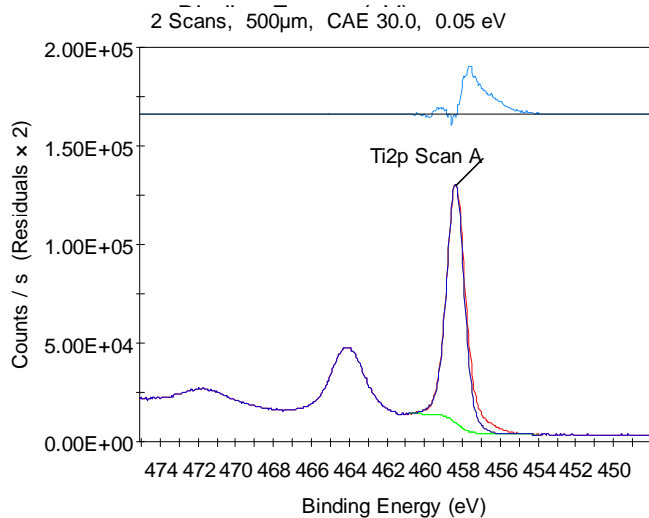
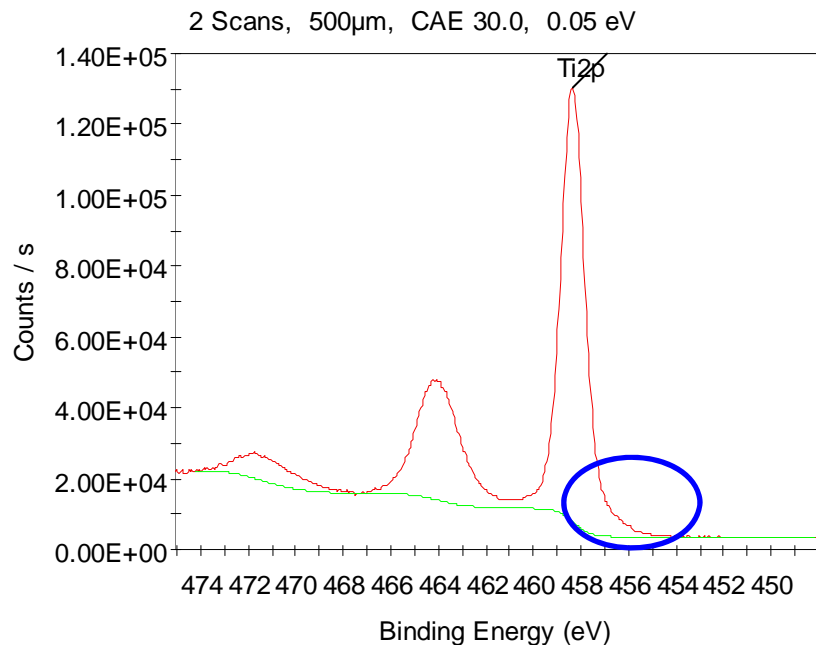
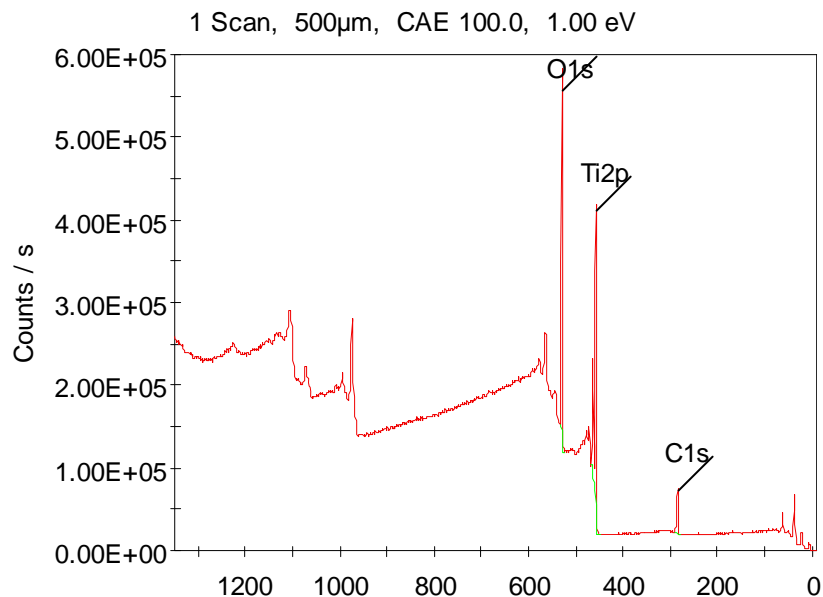
氩离子（ Ar^+ ）刻蚀样品诱导变化

- Ar^+ 离子荷电并具有质量、能量，刻蚀清洁样品表面时，可能诱导表面不同程度的损伤；
- 损伤现象常见，分析时应引起足够的注意；
- 正确评估结果；

X射线辐照样品诱导变化（损伤）

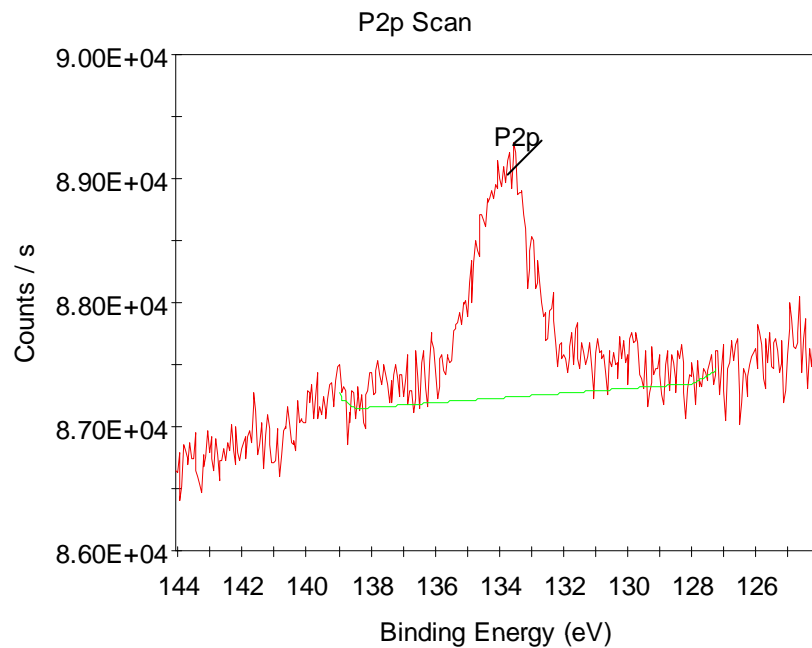
- 一般X射线辐照损伤比Ar⁺小，但也普遍存在于XPS分析中；

X射线辐照TiO2诱导变化

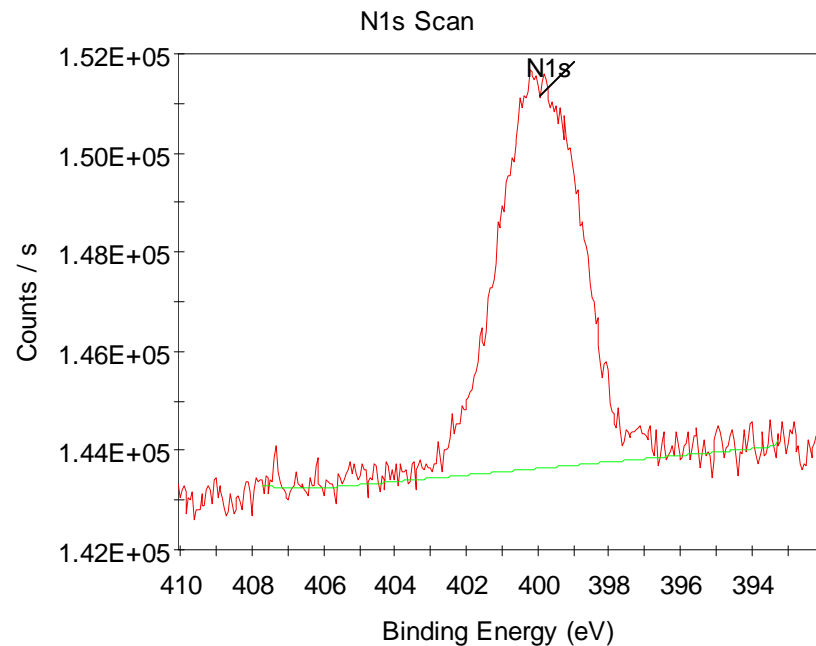


金表面修饰DNA分子：XPS测量 低含量元素P、N

- 为了得到弱信号P2p、N1s采用长时间反复扫描，但需要检查样品是否损伤。

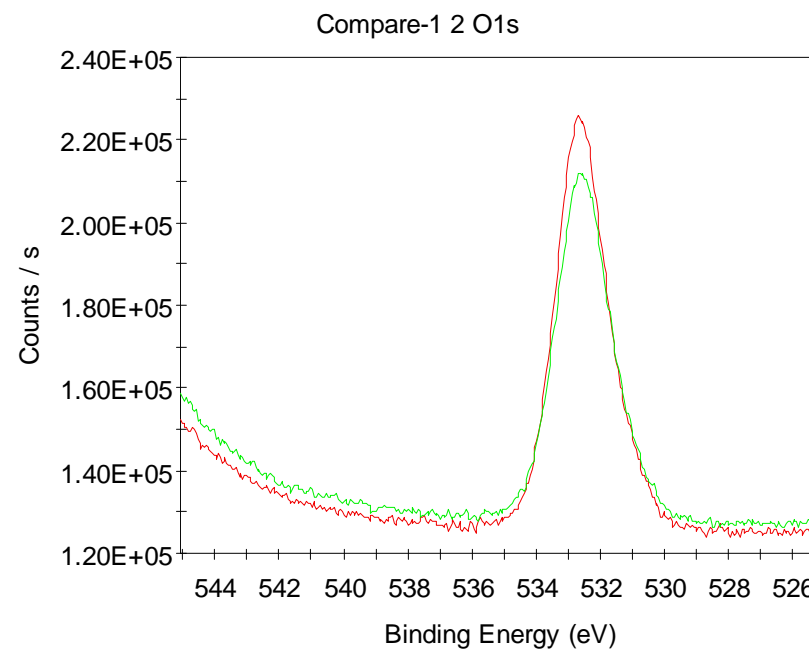
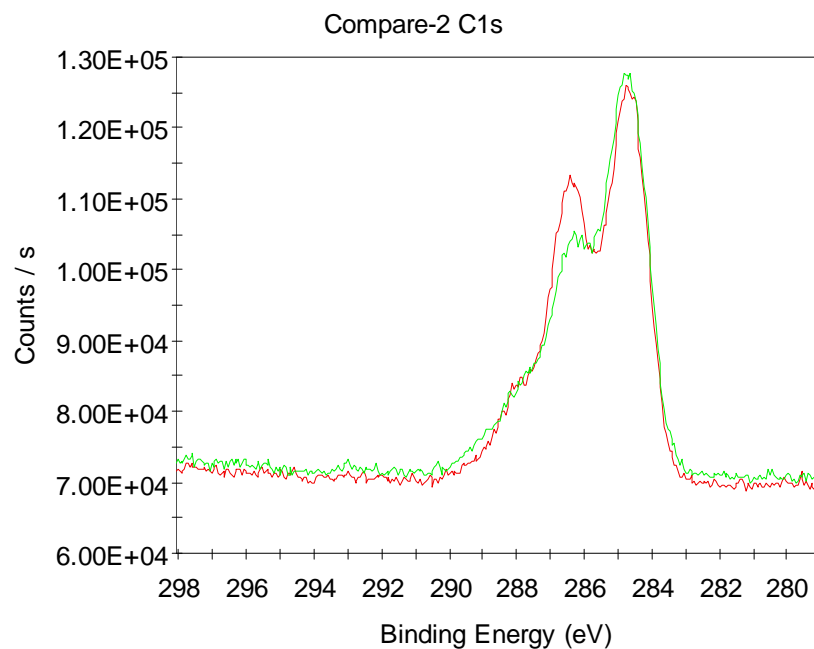


扫描20次，约15mins



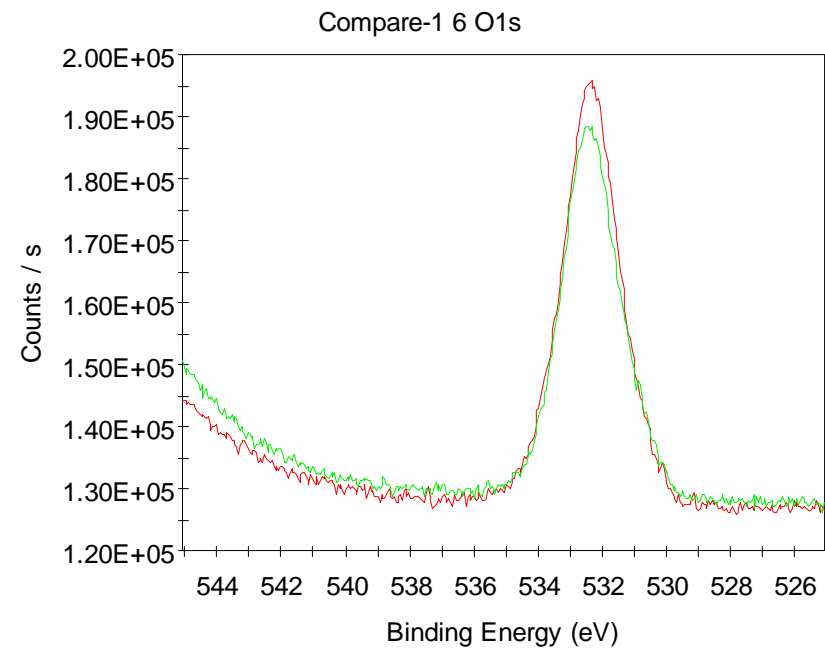
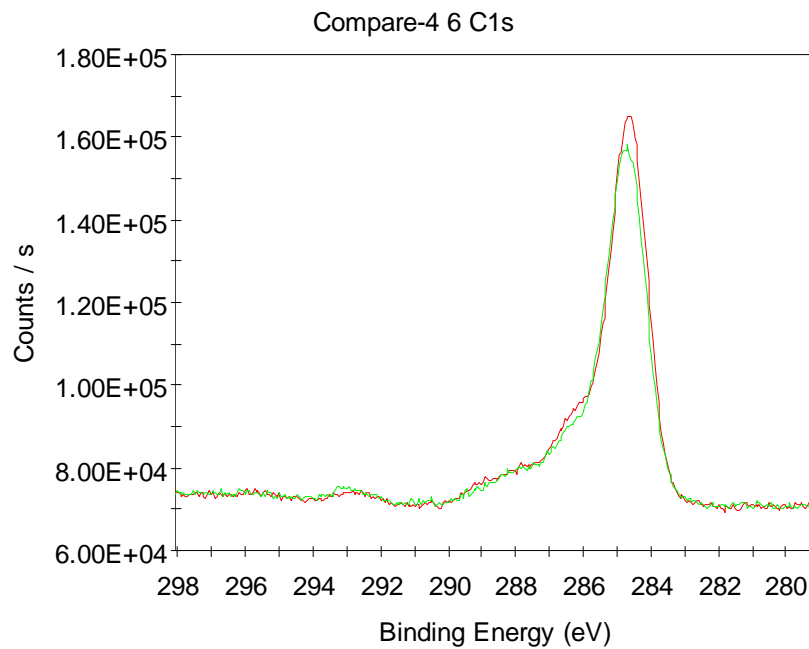
扫描20次，约15mins

XPS测量过程中，经过X辐照主元素能谱变化



2 # 样品经X射线45mins辐照前 (红色) 后 (绿色) C1s和O1s变化

XPS测量过程中，经过X辐照主元素能谱变化



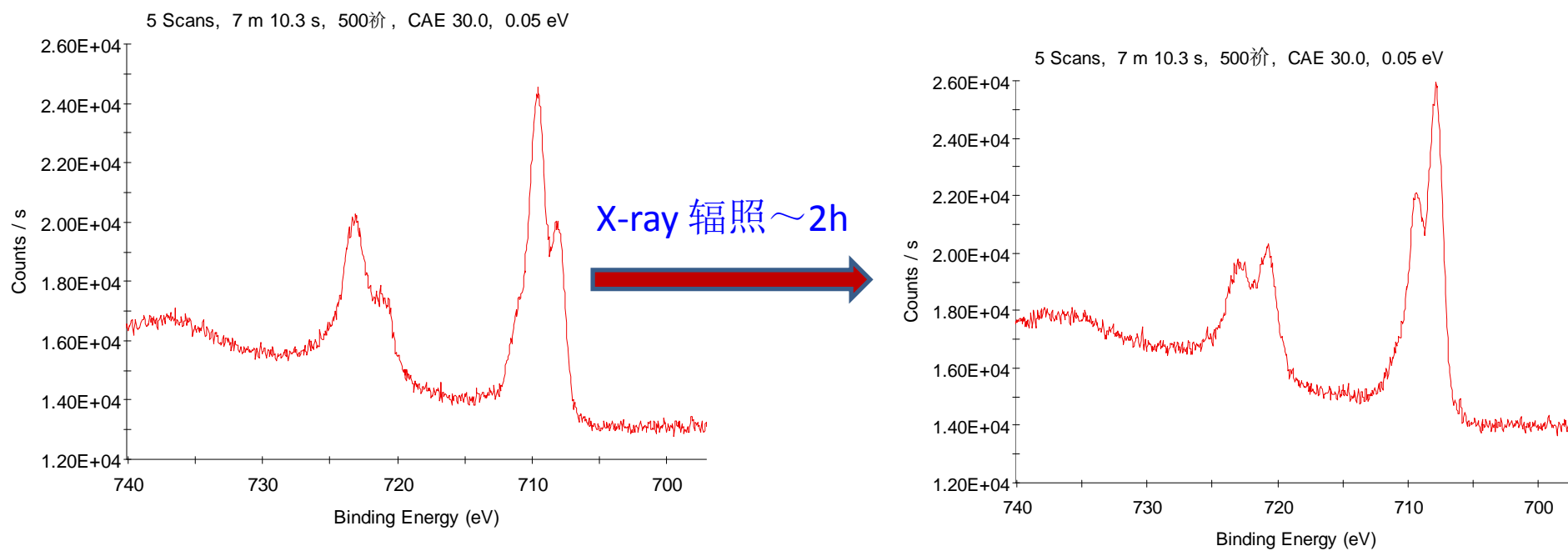
不同样品损伤程度不同。

6# 样品经X射线45mins辐照前（红色）后（绿色）C1s和O1s变化，此样品在X-ray照射45min后损伤程度小。

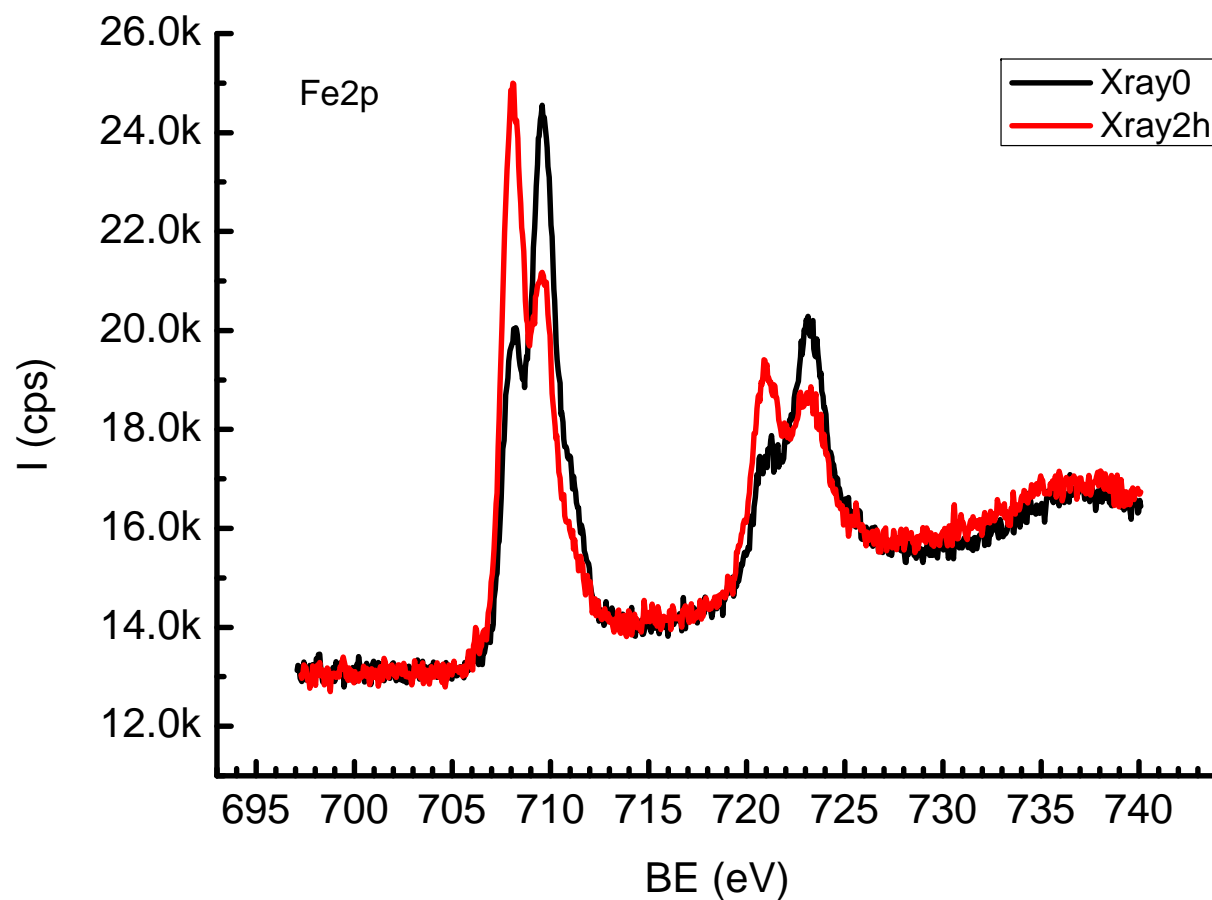
X射线辐照损伤

- 电子能谱测量过程中样品被辐照损伤是普遍现象（可参考电子能谱有关资料书籍）；
- 稀土氧化物和过渡金属氧化物受X射线辐照被还原；
- 损伤程度与X射线强度，辐照剂量等有关；
- 损伤机理：
 - 光化学反应、电子激发；
 - 辐照产生温升；

氧化铁在X射线照射下被还原

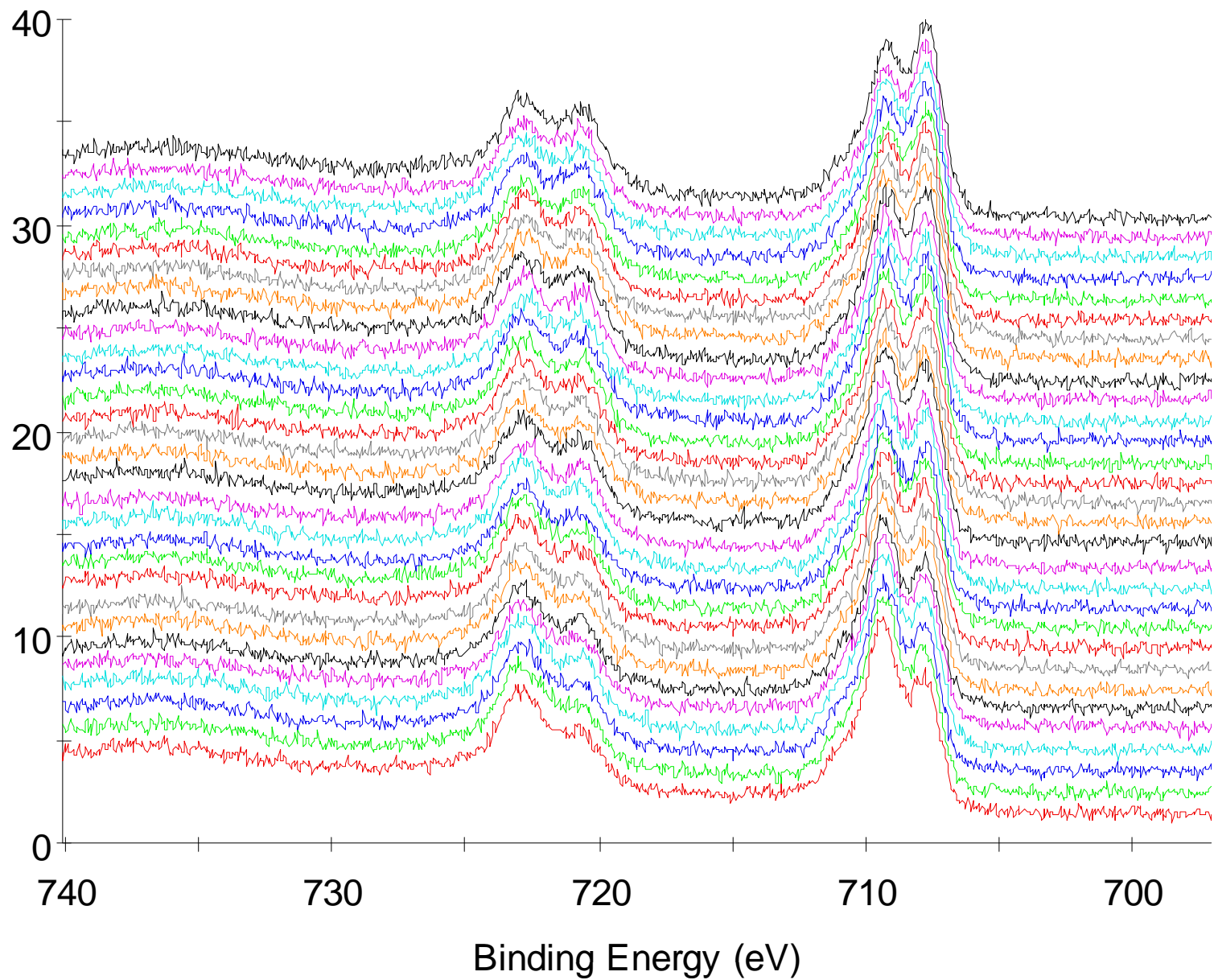


氧化铁在X射线照射下被还原



X-ray 辐照 (~2h) 氧化铁样品的前后对比

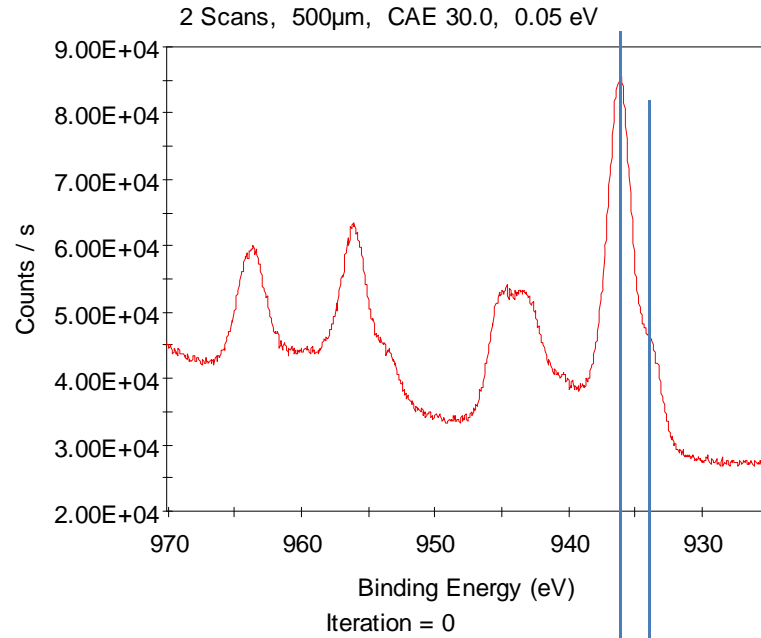
1 Scan, 1 m 26.1 s, 900衞, CAE 40.0, 0.05 eV



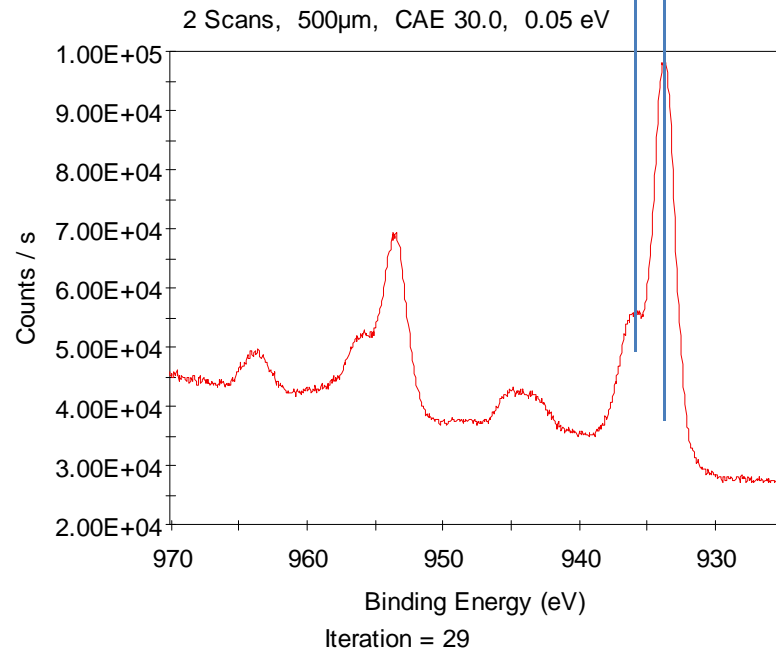
含Fe氧化物中Fe2p谱随X-ray 辐照时间变化 (~2h)

CuO在X-ray辐照下的诱导变化

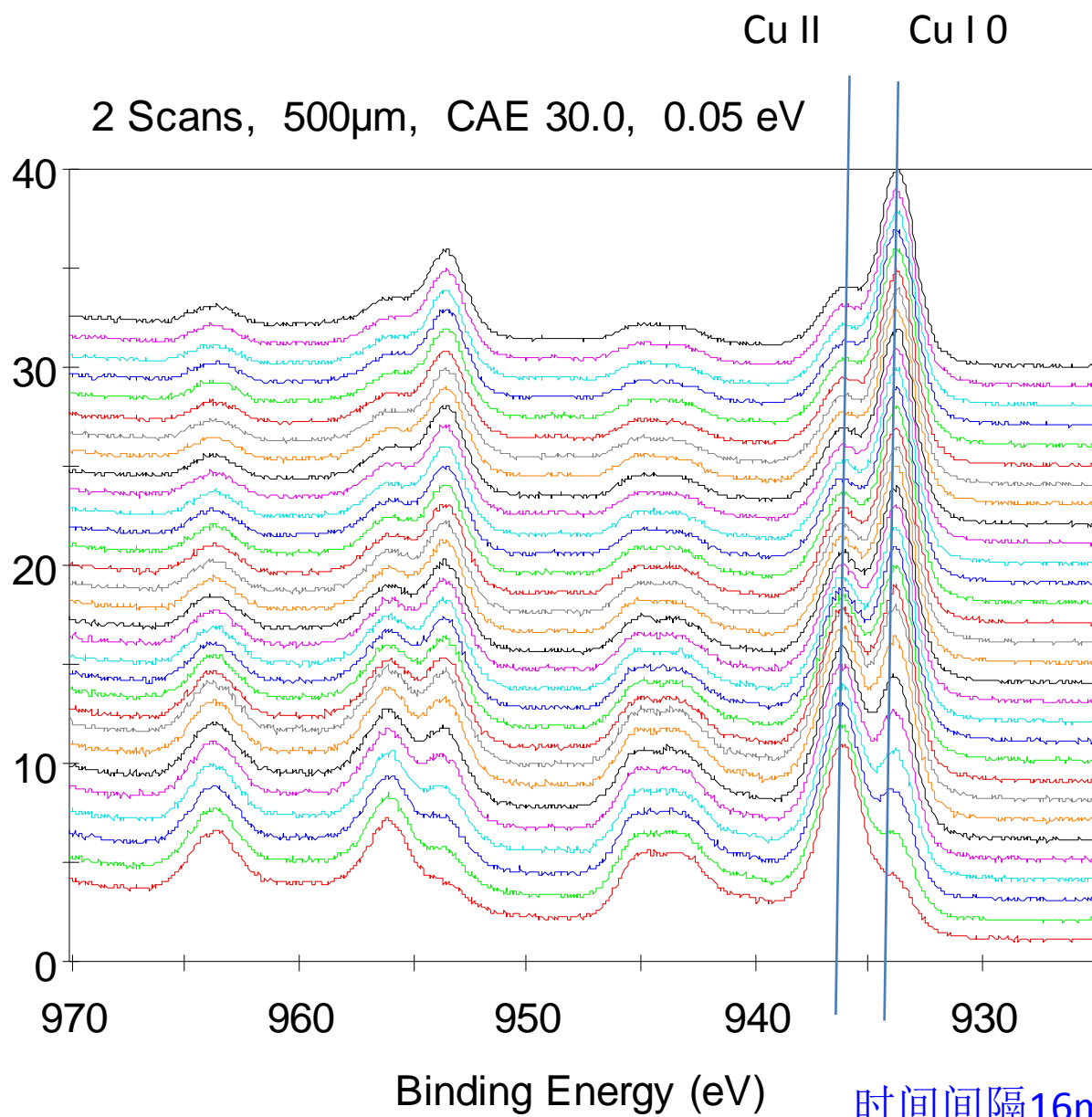
第1次 XPS



第30次 XPS

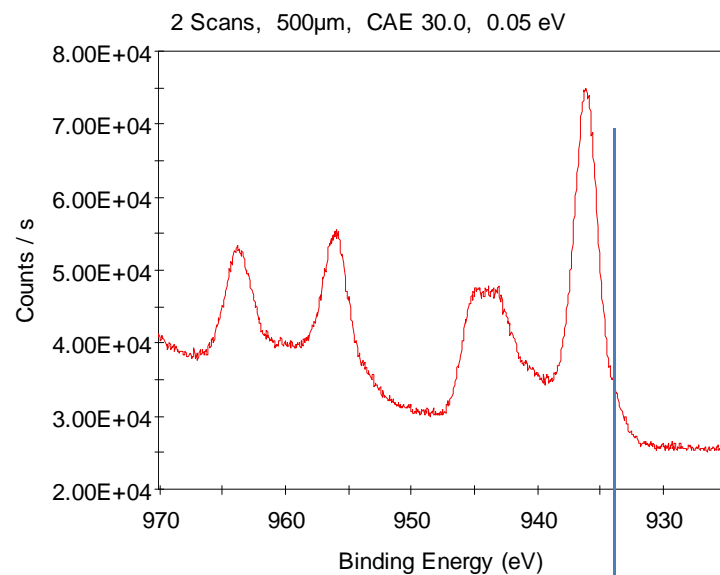


某氧化铜

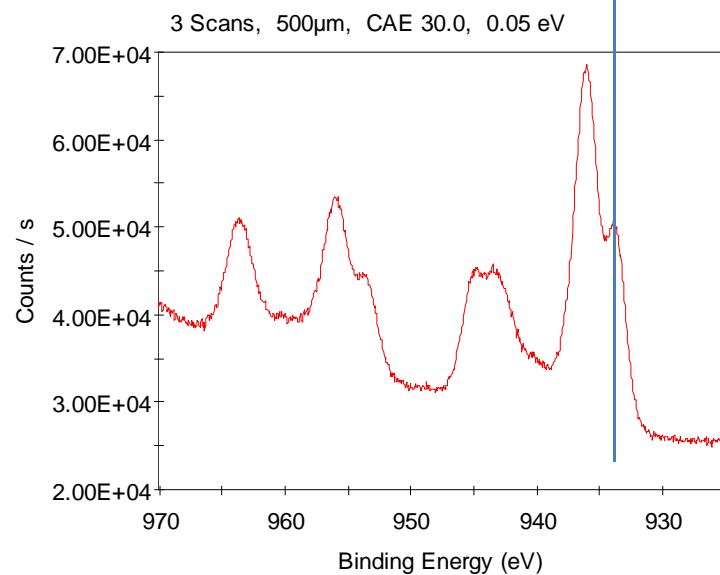


时间间隔16min
X射线功率150W/500 μ m

从真空中取出，在自然环境空气中放置数天后，重新测试发现恢复CuO态



经过8h X-ray辐照的铜
氧化物样品，放置空气中
数天后，重新测试结果

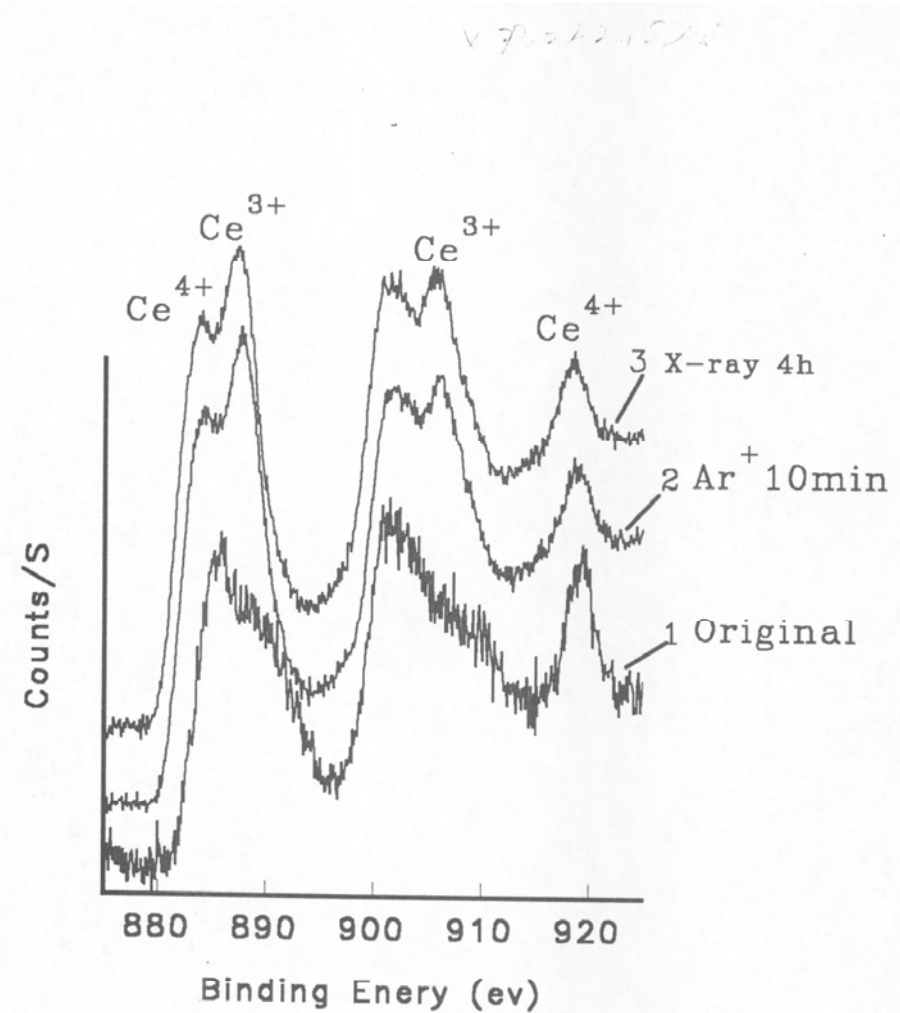
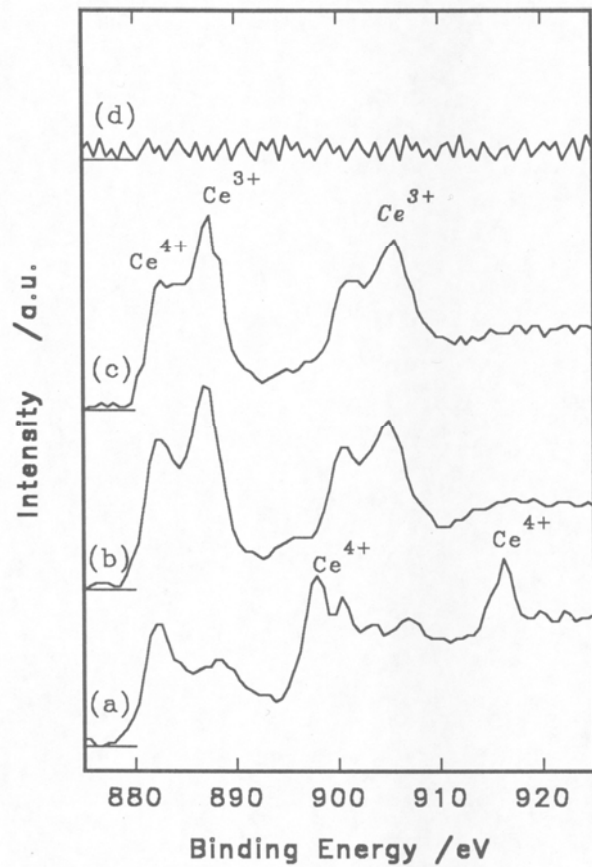


X-ray辐照约20min

XPS分析稀土CeO₂样品

- 稀土RE氧化物不仅受离子辐照会诱导还原，且受X射线辐照也同样会诱导还原反应

XPS分析稀土CeO₂样品



Ce3d XPS's after Ar⁺ etching CeO₂, a:2min b:33min c:
d:81min

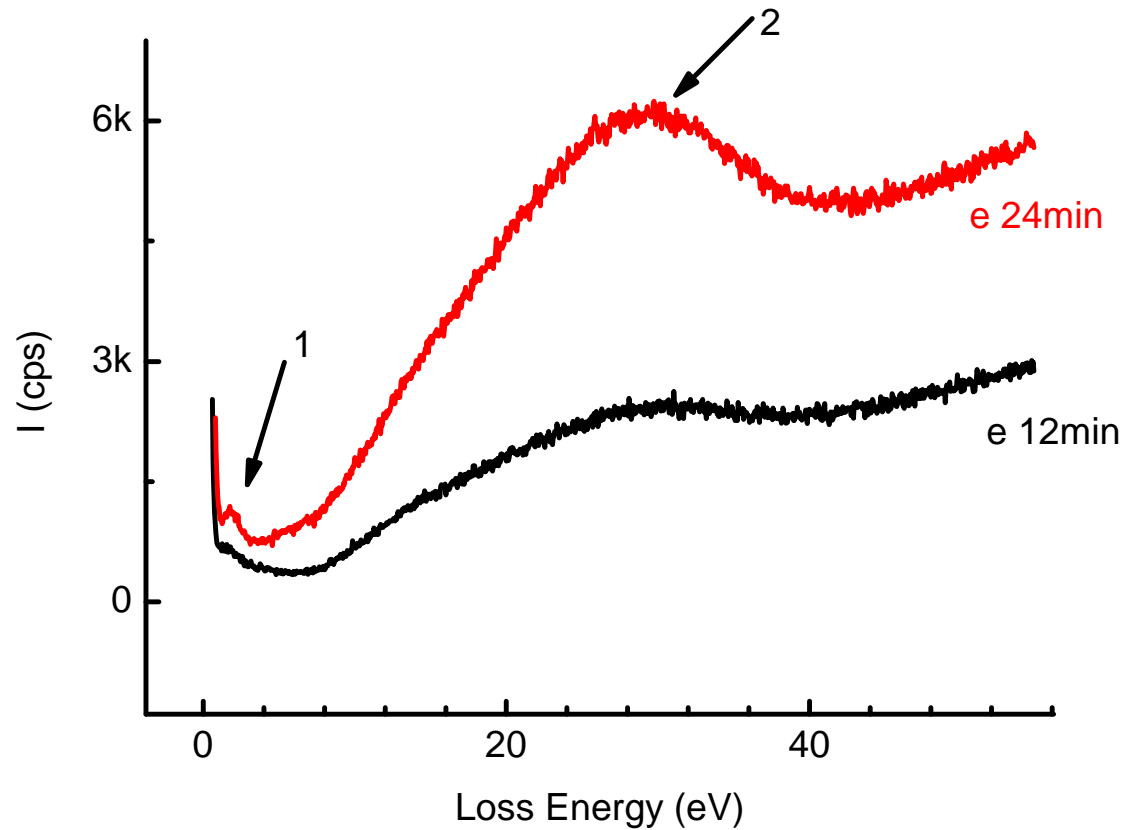
如何减少X射线引起的损伤

- 尽量减小X光枪功率、照射样品面积、照射时间等；
- 为保证测量信噪比可以采用低功率，适当增加通能、延长时间。
- 对于易受X射线损伤的样品或区域，在优化参数调试好参数后，应考虑换位置采谱；
- 优化实验参数：对于热效应引起的损伤，采用低照射功率（激发功率），延长采谱时间，以保证信噪比；
- 优化实验参数：对于辐照易损伤样品需牺牲信噪比；

电子辐照损伤

- 采用电子源激发能谱：
 - 俄歇电子能谱
 - 反射式电子能量损失谱（REELS）

电子辐照损伤：DLC的REELS谱



REELS测量条件：电子能量1keV，束流~200uA

AES分析中电子辐照

- 在AES中电子能量一般大于或等于3keV，可能诱导样品的变化

UPS分析中UV辐照

- UV辐照会诱导样品变化？
- UPS分析高分子聚合物

能量去卷积 (Deconvolution, PSF)

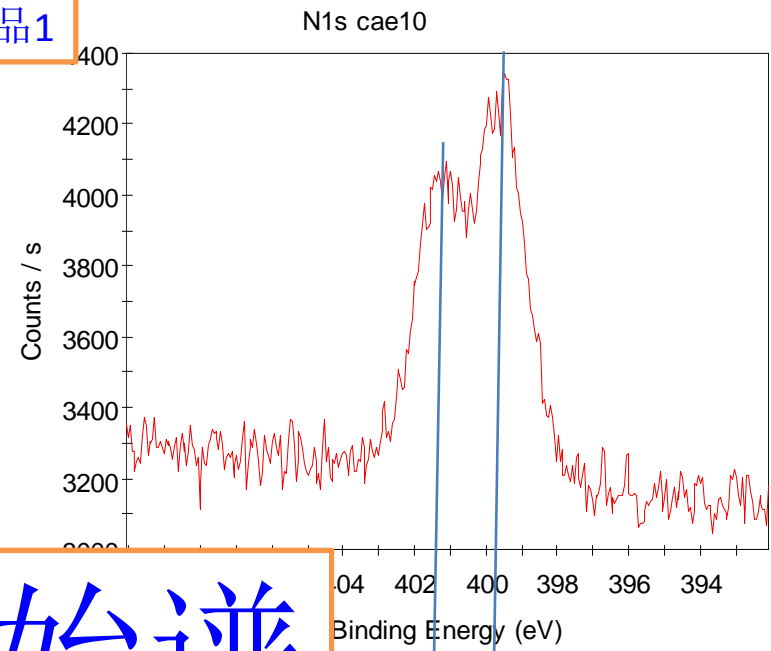
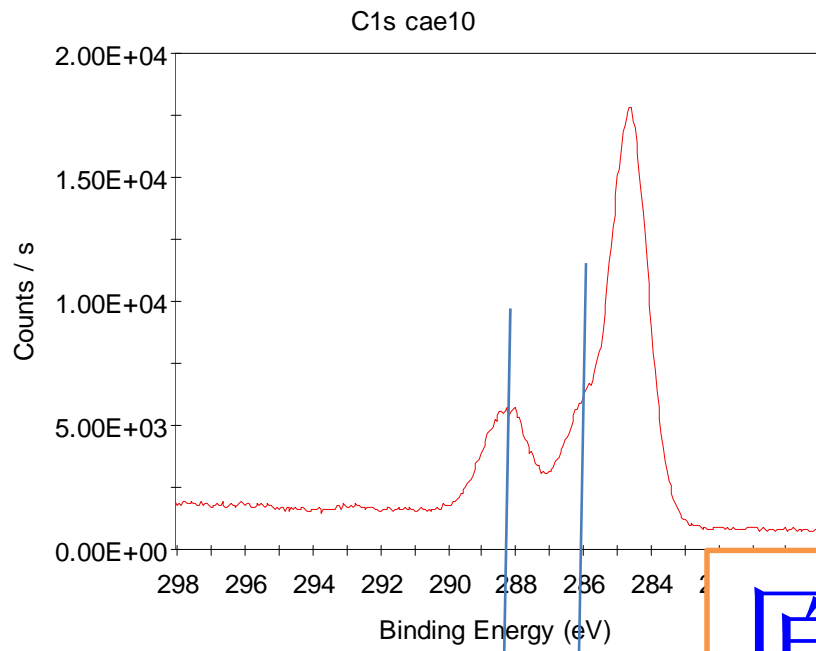
PSF基础

- 定义：
与样品相关的谱函数 F_0 ；
与仪器相关的谱函数 R_t ；
- 测量谱 $I(E)=F_0 \odot R_t$ (1)
 $I(E)$ 为仪器测量出的谱，称为**表观谱**；
 R_t 为**仪器响应函数**，与仪器构造、设置参数有关，对于固定的仪器和设置参数，可以用已知样（如Ag）测出，预存在计算机中
以备调用。

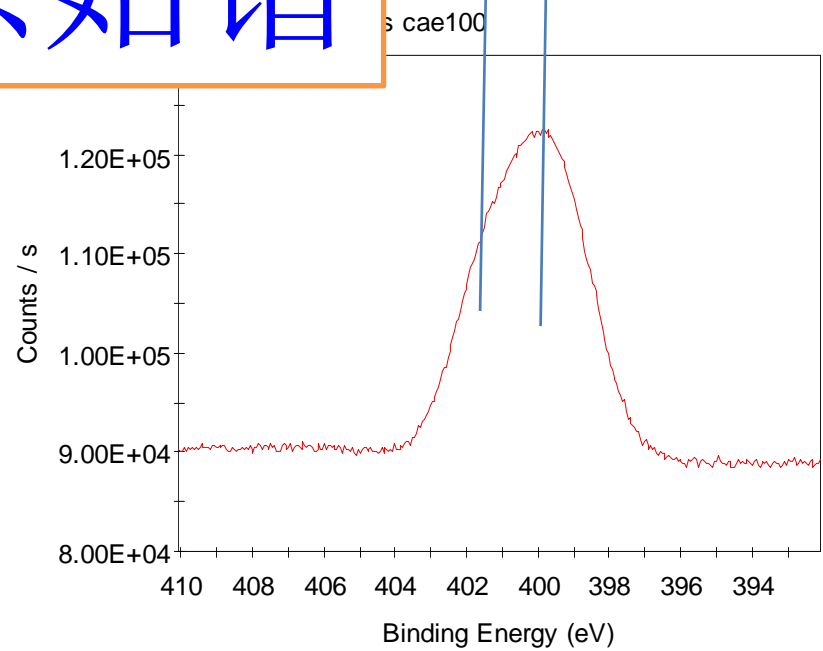
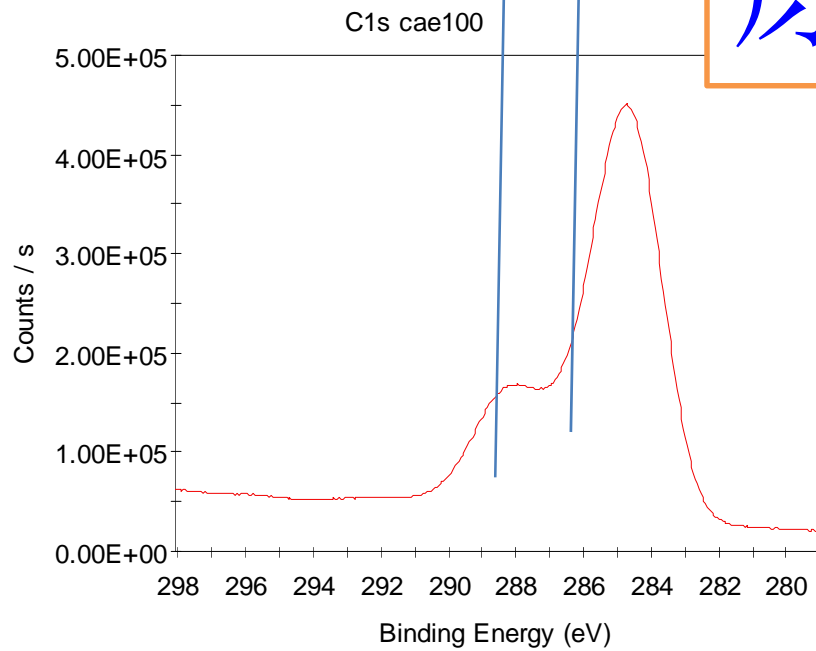
PSF基础

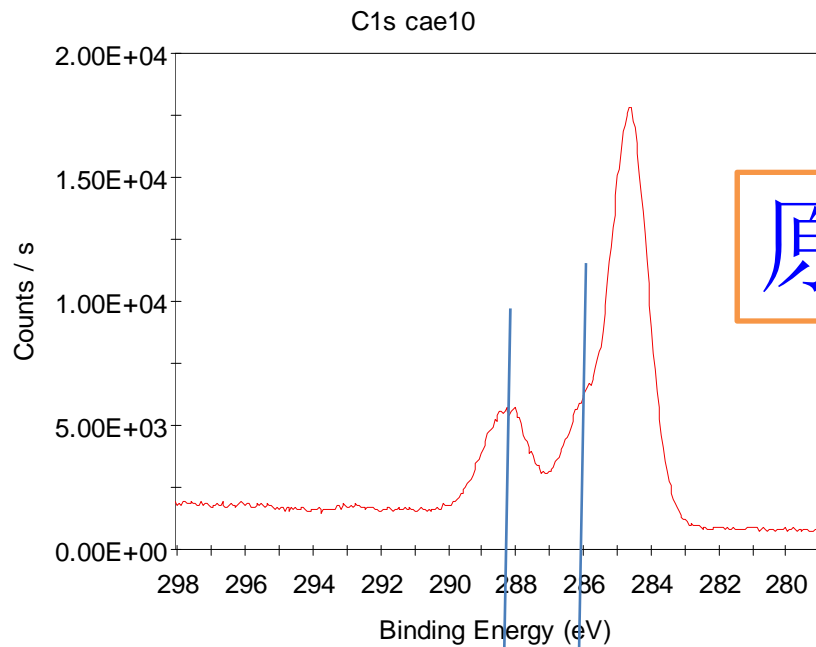
- $I(E) = F_0 \odot R_t$ (1)
.....
- 从公式 (1) 中解出 $F_0(E)$ 的过程称为 **去卷积** 或 **退卷积 (deconvolution)**，表示为：
 $F_0(E) = I \odot^{-1} R_t$ (2)
与表观谱 $I(E)$ 相比， $F_0(E)$ 剔除了 $I(E)$ 中仪器 R_t 展宽贡献，所以提高了分辨率。
- 在Avantage中有此计算功能，操作简单，选择功能执行（**Processing ... Modify Spectra ... Energy Deconvolution**）。

样品1

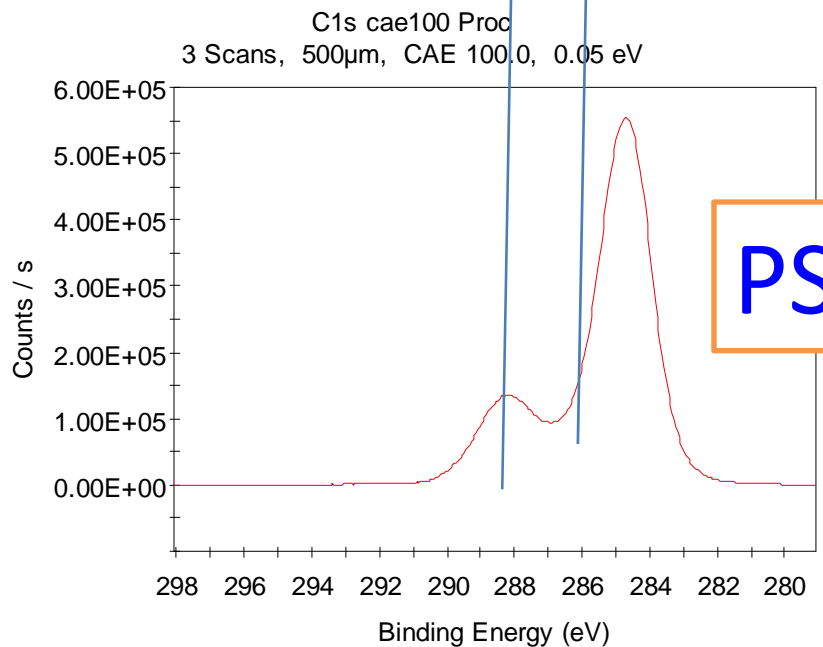
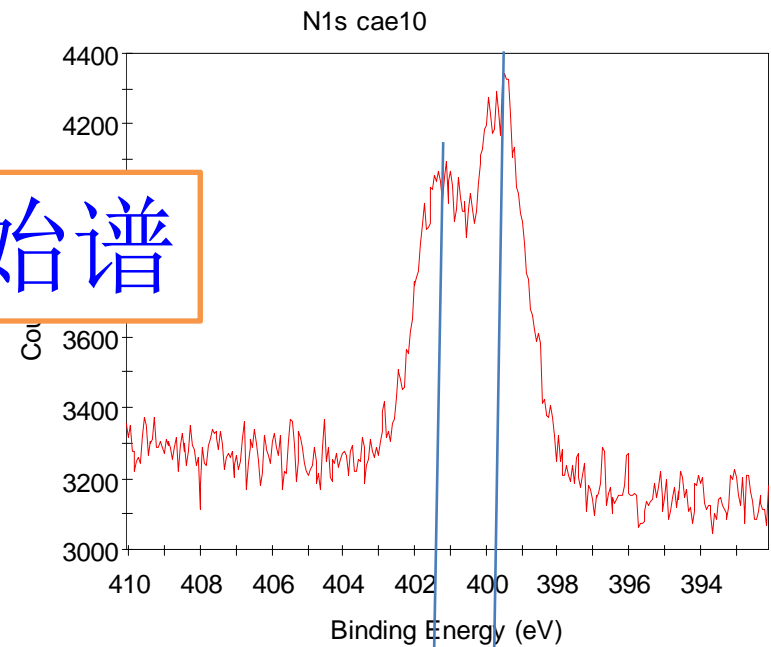


原始谱

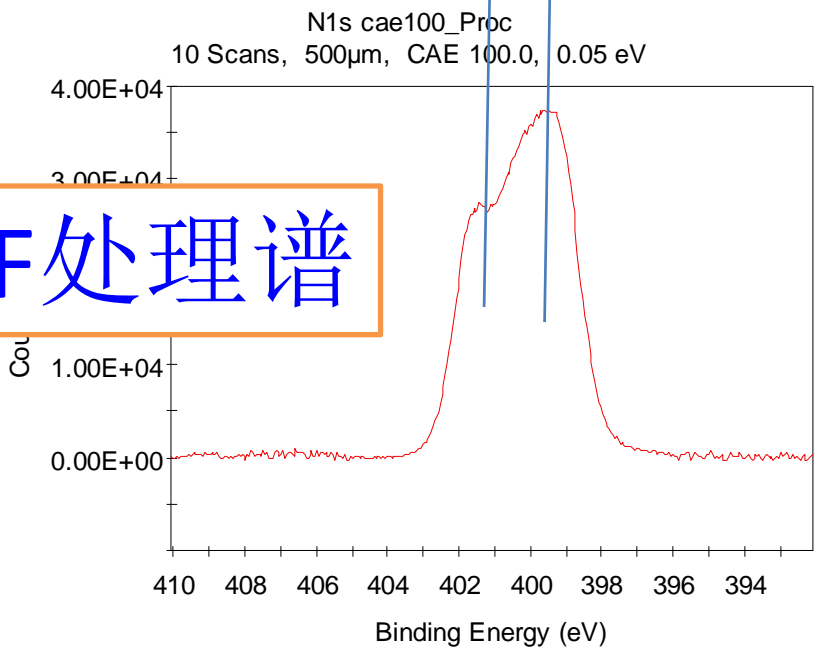




原始谱

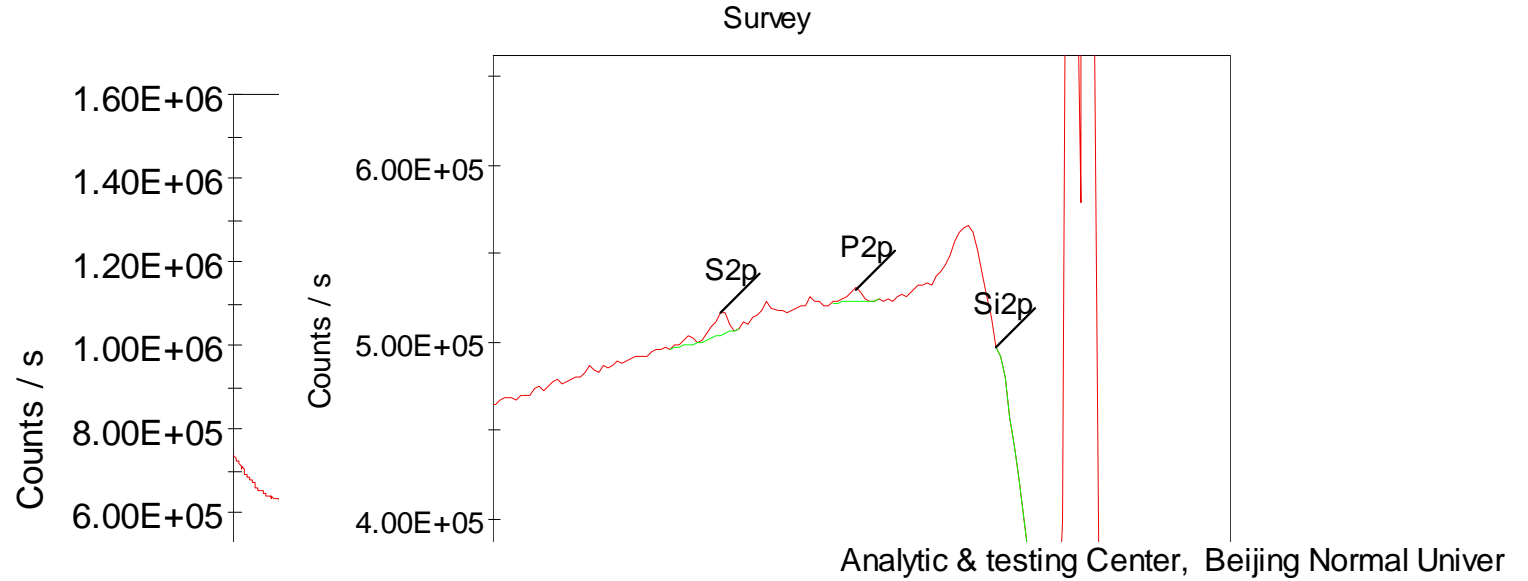


PSF处理谱



PSF应用：低含量元素的测量分析

- Au表面修饰DNA分子及其它有机分子；
- 测量分子单层中的N、P等元素；
- P含量很低，粗测Survey谱没有发现；

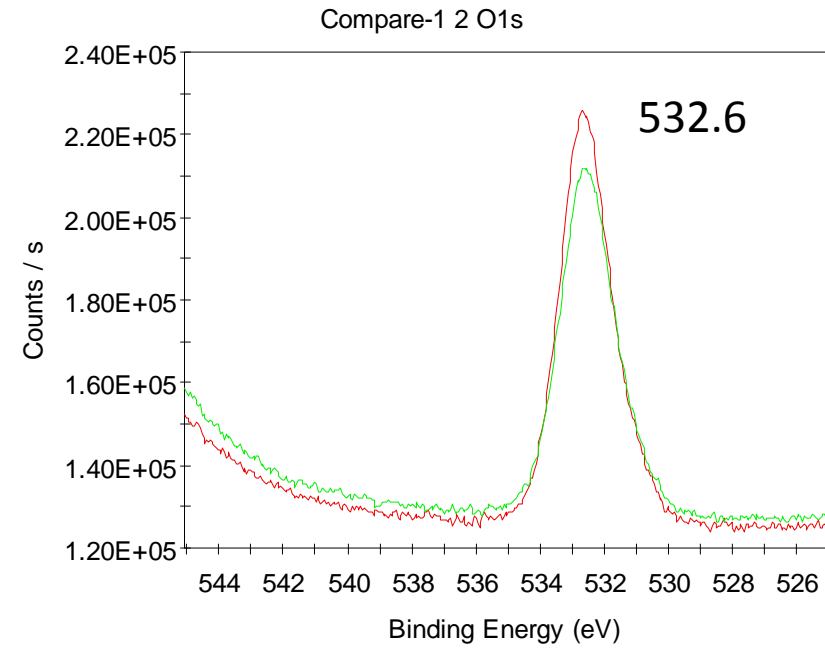
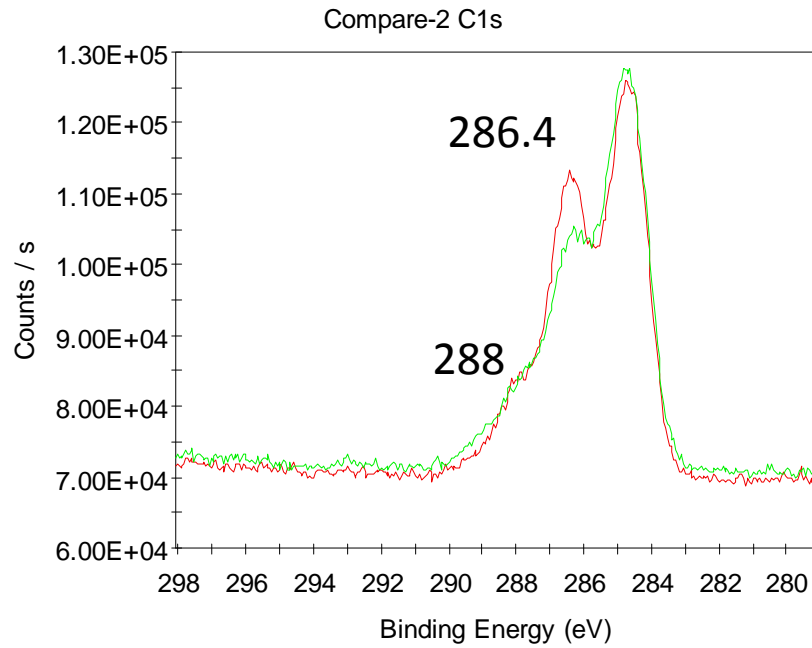


Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHERMO1	TXFN	Backgn	Title
Au4f	92.580	84.258	78.580	1085058.675	2.701	5412966.9915	0.6227	13.298	Standard	Y	20.735	5217.303	Smart	Survey
O1s	537.080	532.735	527.080	367667.616	2.933	1210066.5328	1.2357	26.390	Standard	Y	2.881	5684.679	Smart	Survey
C1s	291.580	285.828	278.080	225197.351	3.994	947255.9956	2.4556	52.444	Standard	Y	1.000	5412.686	Smart	Survey
N1s	407.580	400.168	394.580	35946.071	3.431	147604.2230	0.2411	5.149	Standard	Y	1.676	5533.597	Smart	Survey
S2p	174.080	163.127	159.580	12387.344	4.044	64076.3316	0.0838	1.790	Standard	Y	1.881	5291.279	Smart	Survey
P2p	139.000	134.244	129.449	7068.817	2.983	24212.7944	0.0435	0.929	Standard	Y	1.353	5263.839	Smart	Survey

全谱中低含量元素峰

测量含量更低的P元素

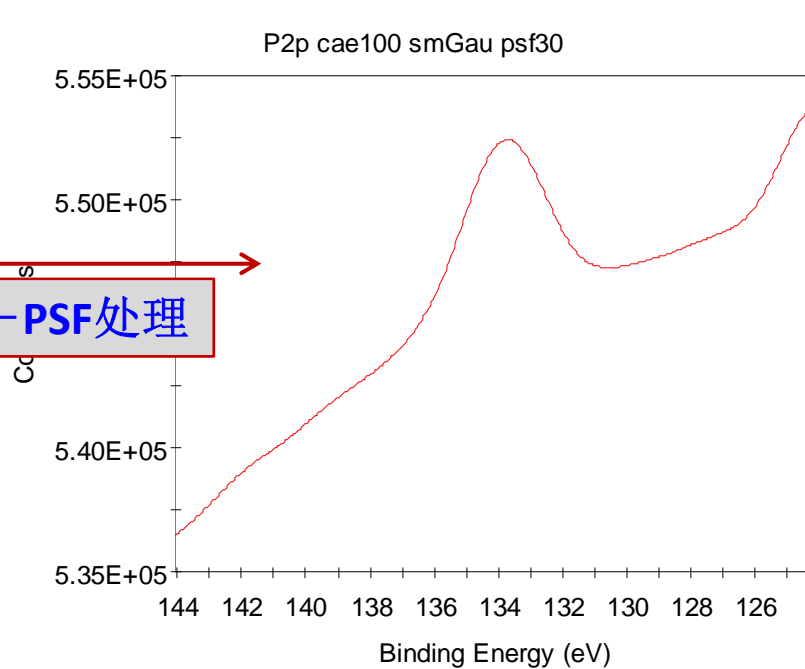
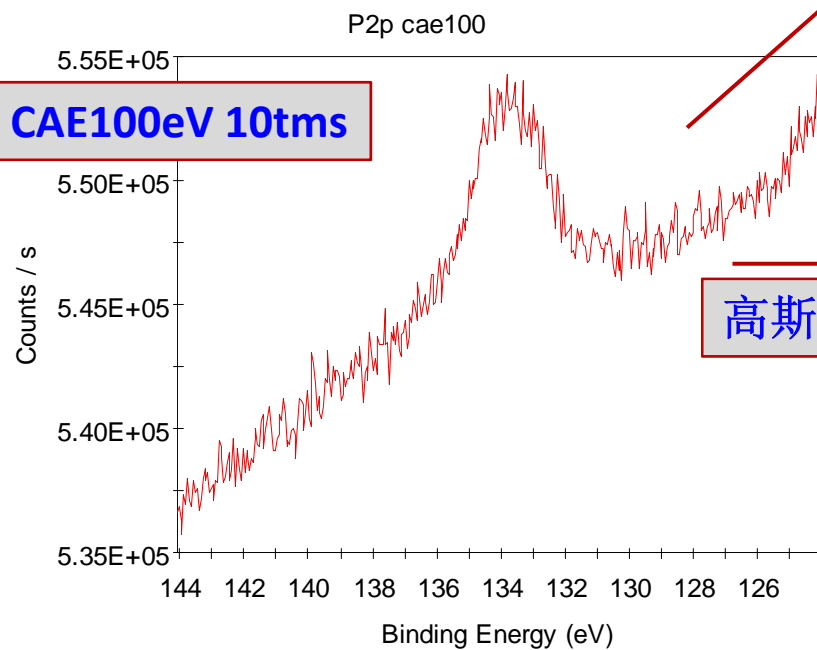
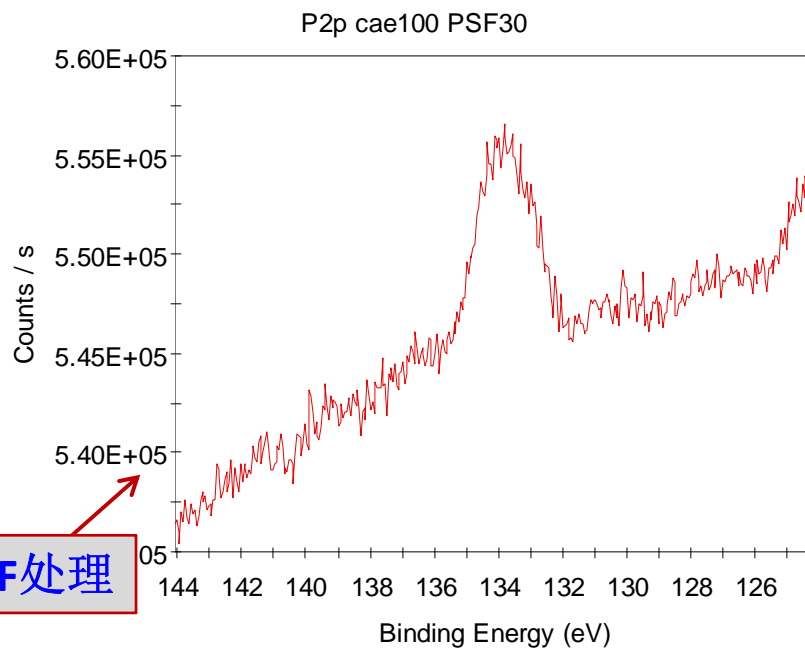
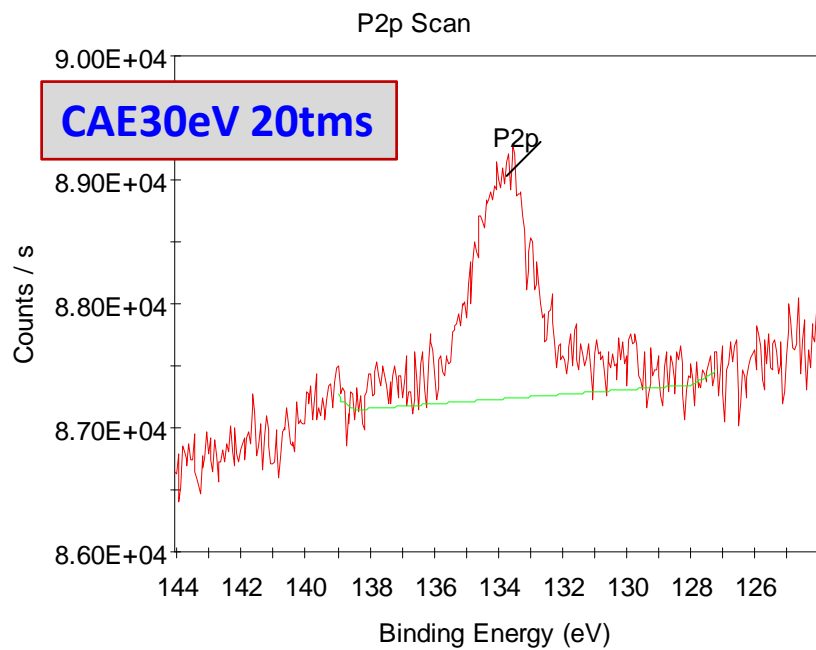
X射线辐照40mins后，表面明显损伤



Red--before X-ray irradiation,
Green-- after X-ray irradiation

降低XPS分析中辐照损伤效应

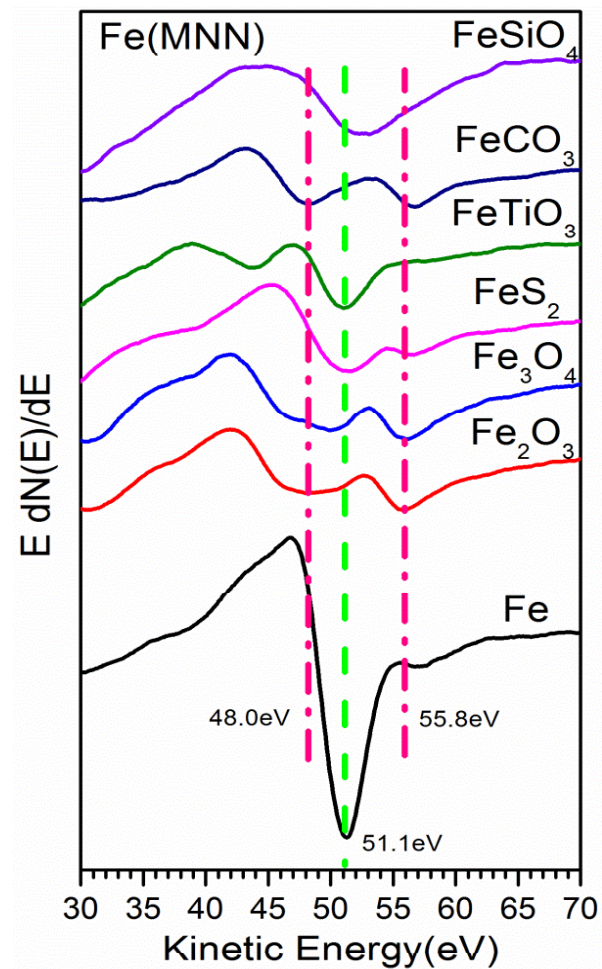
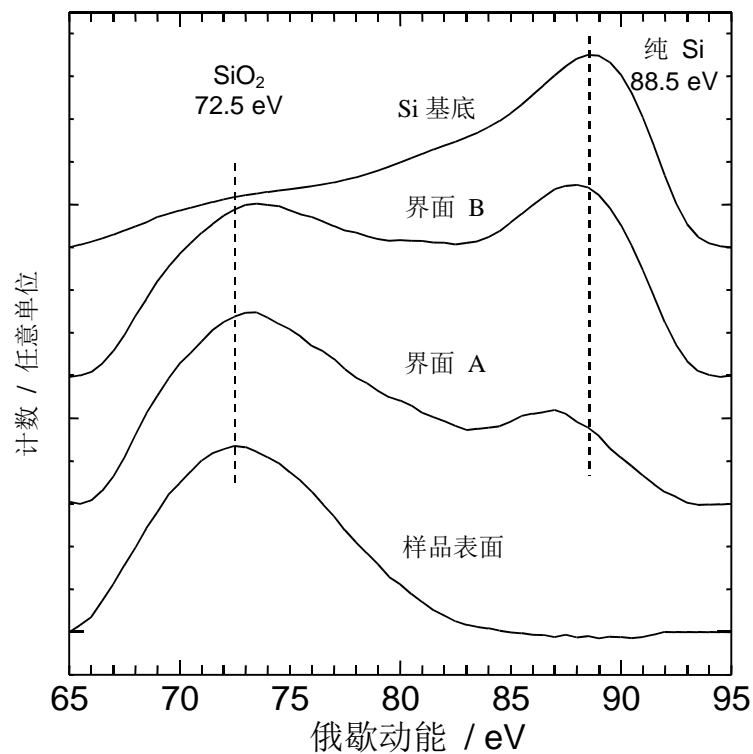
- 为了减少损伤，应降低X光功率、减小收集谱时间，但此时低含量P等元素谱峰的信噪比水平降低。如何解决此矛盾？
- 解决办法：低分辨率+高灵敏度模式（即最大通能如100eV），对采集谱PSF处理得到高分辨谱。



Knowledge功能

- 集结了各元素的谱（光电子谱及其伴峰，俄歇谱及其伴峰）详细信息，化学态信息，测量参数，实验技术，等等信息。
- 例如：在分析分析化学态时，与以往简单地对照谱峰位置信息相比，利用Knowledge对照分析谱图，可以很方便得到更丰富的信息。

峰形分析--化学态分析



不只是使用峰位比对进行化学态分析，利用参考谱峰进行峰形比对指认化学态

Thermo Advantage

File Edit View Window Help

Experiment

Analysis Compare and Overlay Modify Profile Arithmetic Image Utilities Angle Resolved XPS

Display Modes Display Options Reporting

Image Large 2

ZnO-Spercent ZnO-Cl-prtag_ZnLMM-NLS 2-ZnO-Cl-Op2prtag 1-ZnO-Cl-5prtag 3-ZnO-Cl-Op05prtag 4-ZnO-Cl-0prtag XPS Knowledge View

Zn

Primary XPS region Zn2p Overlapping regions O KLL, V LMM

Binding energies of common chemical states

Chemical state	Binding energy Zn2p _{3/2} / eV
Zn metal	1021.7
ZnO	1021.3

Oxide charge referenced to adventitious C1s peak at 284.8eV

Experimental information

- Small binding energy shifts of some compounds compared to zinc metal.
 - Chemical state differentiation with can be difficult with XPS only.
 - Collect principal Zn LMM peak as well as Zn2p.
 - Bigger chemical shifts observed for Zn LMM compared to Zn2p.

Interpretation of XPS spectra

- Zn2p peak has significantly split spin-orbit components ($\Delta_{\text{metal}}=23\text{eV}$).
- ZnO has an unusual O1s spectrum with two peaks possibly indicating either Zn (OH)₂, ZnCO₃ or oxygen vacancies.
- Zinc shows only a small binding energy shift in the Zn2p_{3/2} region (1021eV-1023e, modal value).
 - Peak width may broaden in the presence of more than one Zn species.
- Zn2p peaks often accompanied by Auger peak at Kinetic Energy=990eV.
 - If zinc is buried (under carbon, for example), Zn Auger peak may be observed even if Zn2p is not (due to difference in electron kinetic energy).
 - Similarly, Zn3p (very high kinetic energy) may be observed even if Zn2p is not.
- Use X-ray induced Zn LMM Auger peaks, which have a larger shift with chemical state.
 - Use Wagner plot to help assign chemistry.

X-ray induced Zn LMM Auger spectra

Zn2p spectra of ZnO and Zn metal

Experiment Root Object

Data Folders Settings General

Main Folder C:\Avantage\Projects Browse

Project Misc

Project Description Miscellaneous project

Apply Reset Close

Zoom 100

X-Ray Ion Flood

22:01 2013/12/9

Thermo Advantage

File Edit View Window Help

Experiment

Analysis Compare and Overlay Modify Profile Arithmetic Image Utilities Angle Resolved XPS Display Modes Display Options Reporting

ZnO-5percentCl ZnO-Cl-prtag_ZnLMM-NLS 2-ZnO-Cl-0p2prttag 1-ZnO-Cl-5prttag 3-ZnO-Cl-0p05prttag 4-ZnO-Cl-0prttag XPS Knowledge View

Zn

D KLL, V LMM

$3/2$ / eV

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X-ray induced Zn LMM Auger spectra

Zn2p spectra of ZnO and Zn metal

Zoom 100

X-Ray Ion Flood

22:03 2013/12/9

Zn

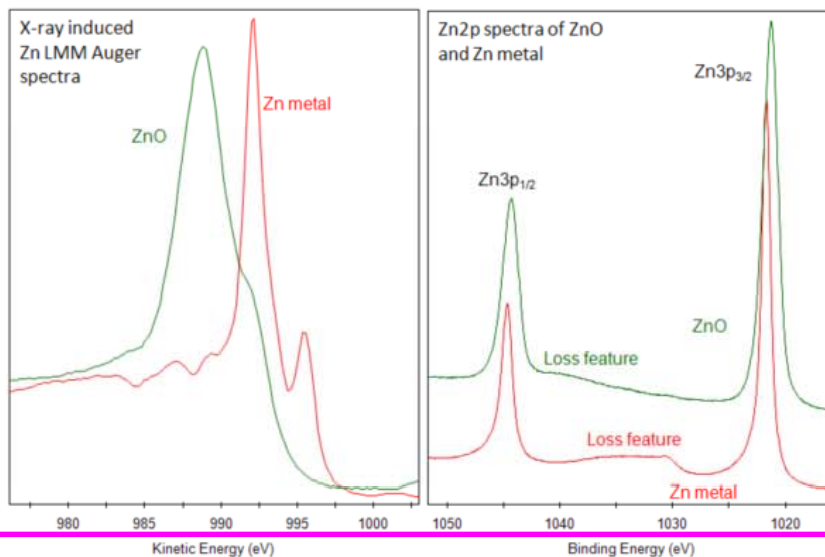
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 - o Peak width may broaden in the presence of more than one Zn species.
- Zn2p peaks often accompanied by Auger peak at Kinetic Energy \approx 990eV.
 - o If zinc is buried (under carbon, for example), Zn Auger peak may be observed even if Zn2p is not (due to difference in electron kinetic energy).
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 - o Use Wagner plot to help assign chemistry.

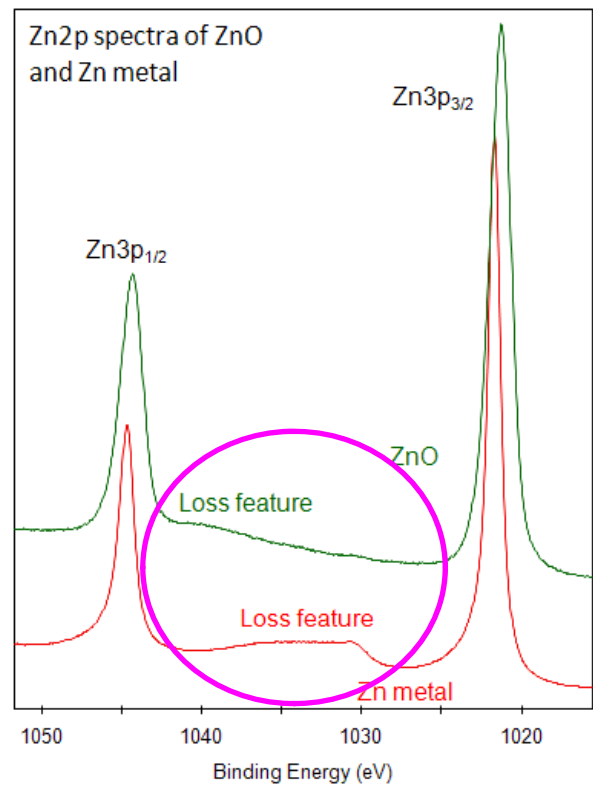
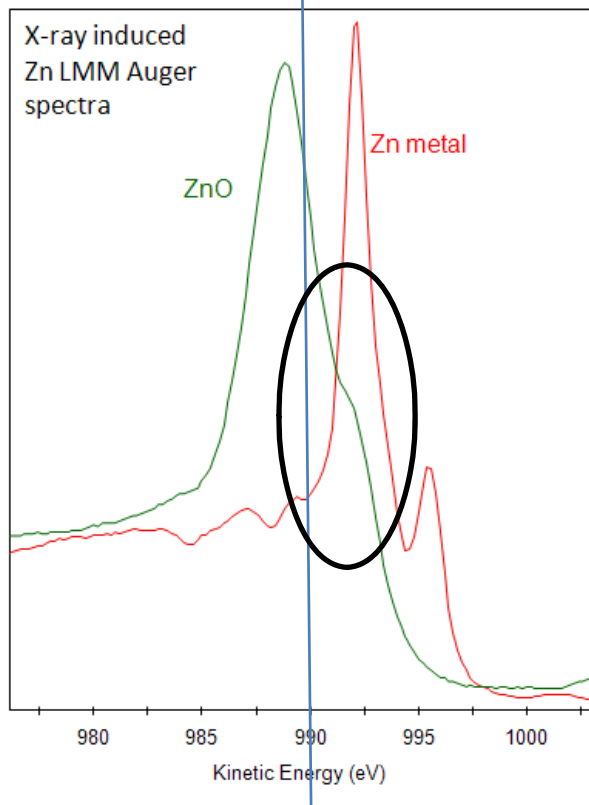
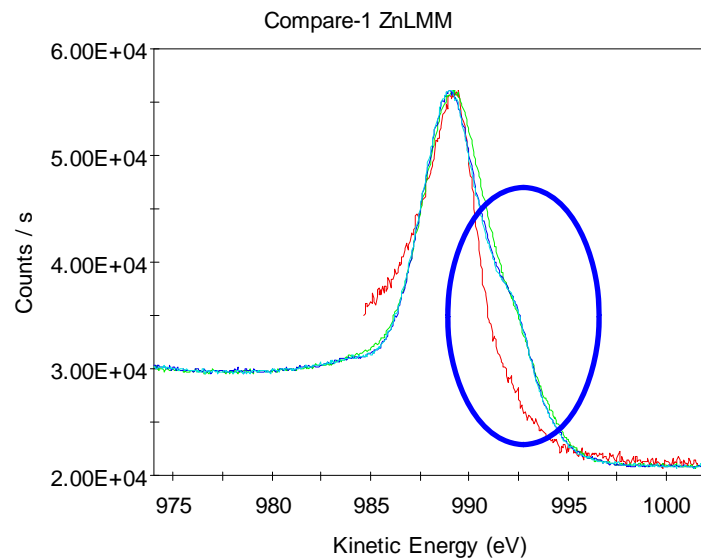
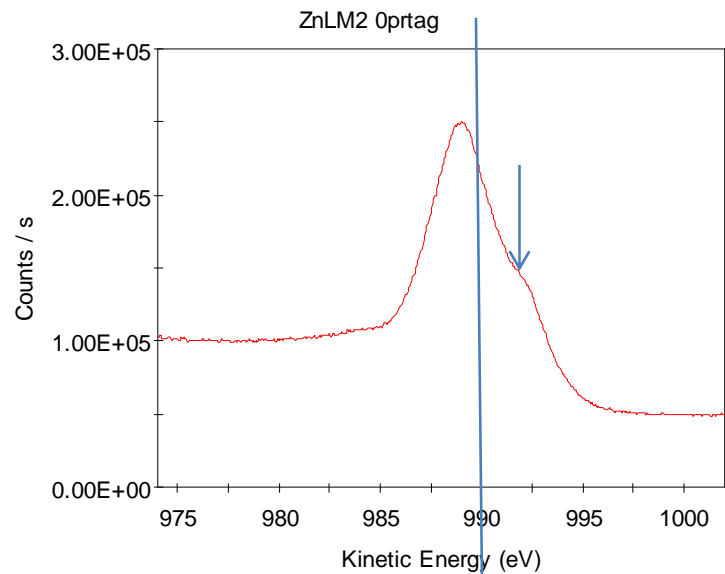
Chemical state	Binding energy Zn2p _{3/2} / eV
Zn metal	1021.7
ZnO	1021.3

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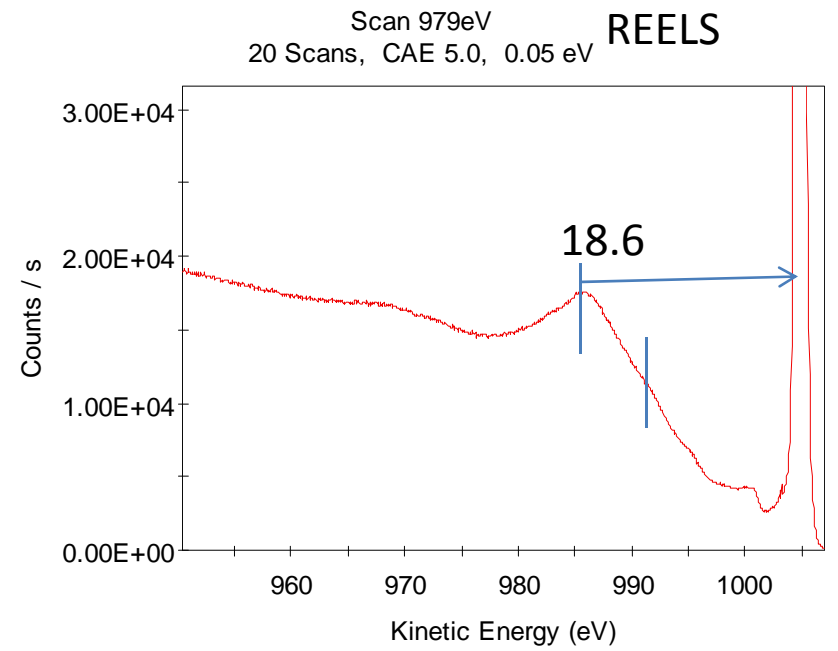
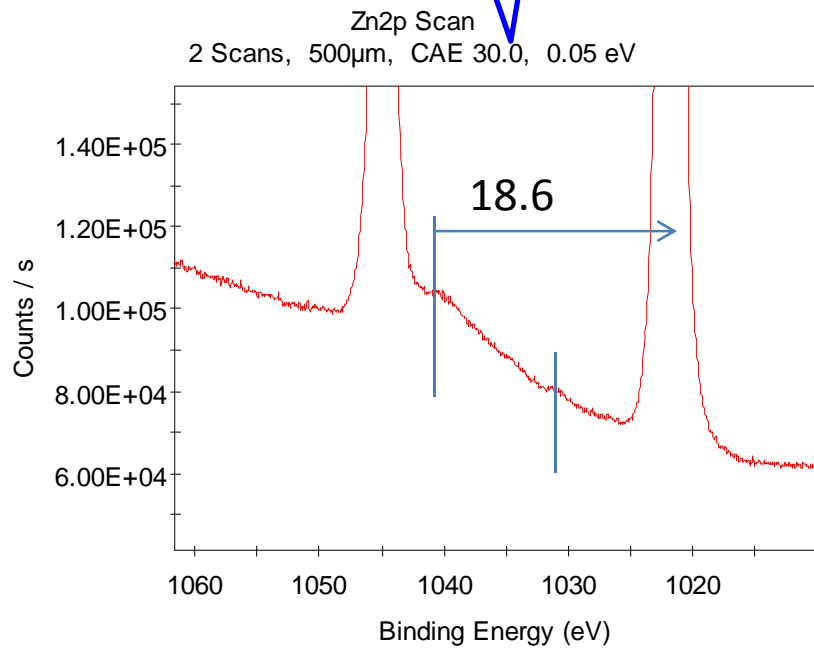
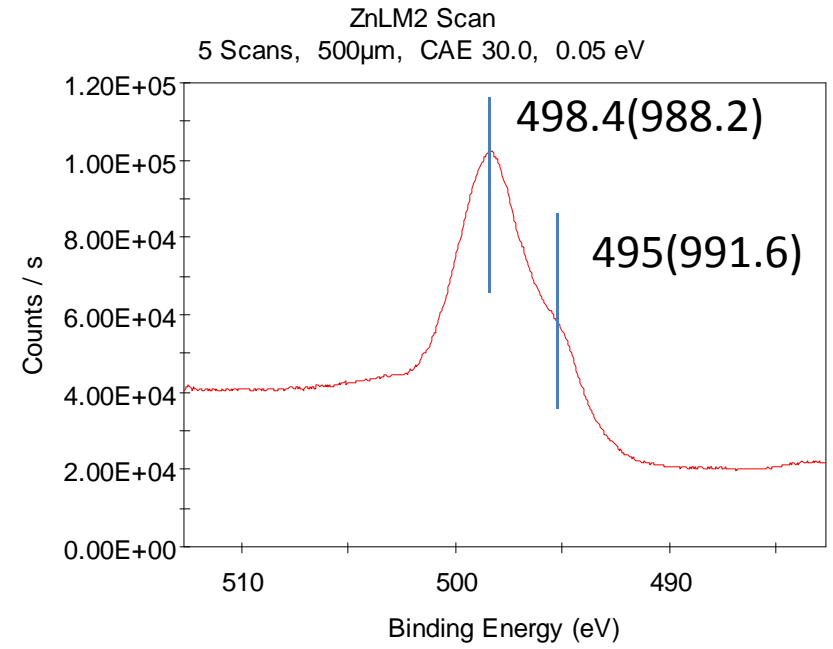
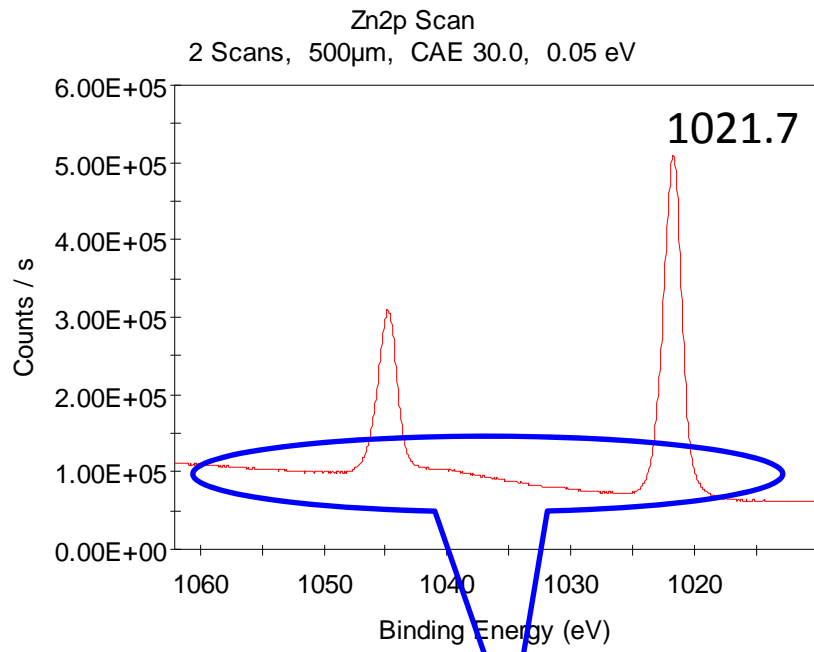


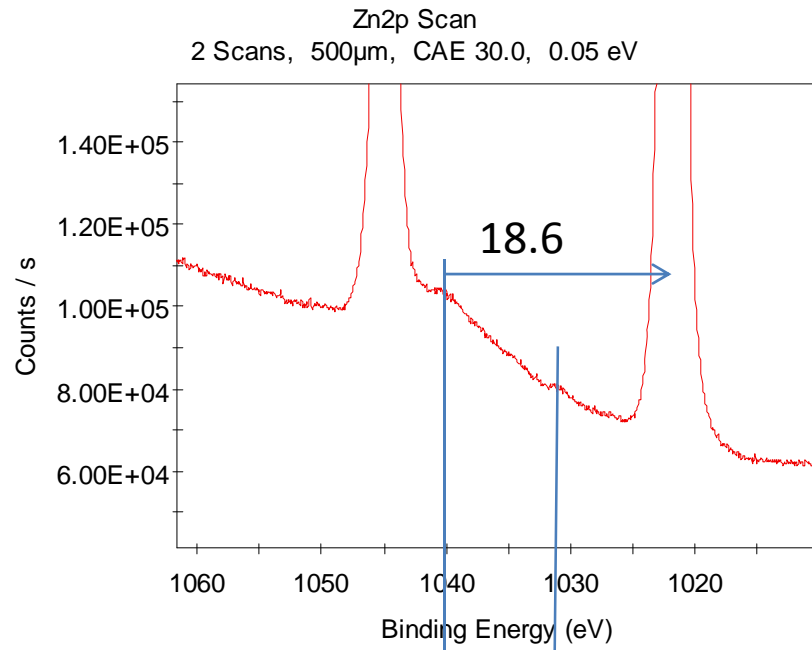
General comments

- There have been concerns about mobility of zinc in alloys and vapour pressure with concern about introducing zinc into a high vacuum environment.
 - o In practice this is not a major concern, if the sample is not heated in vacuum.

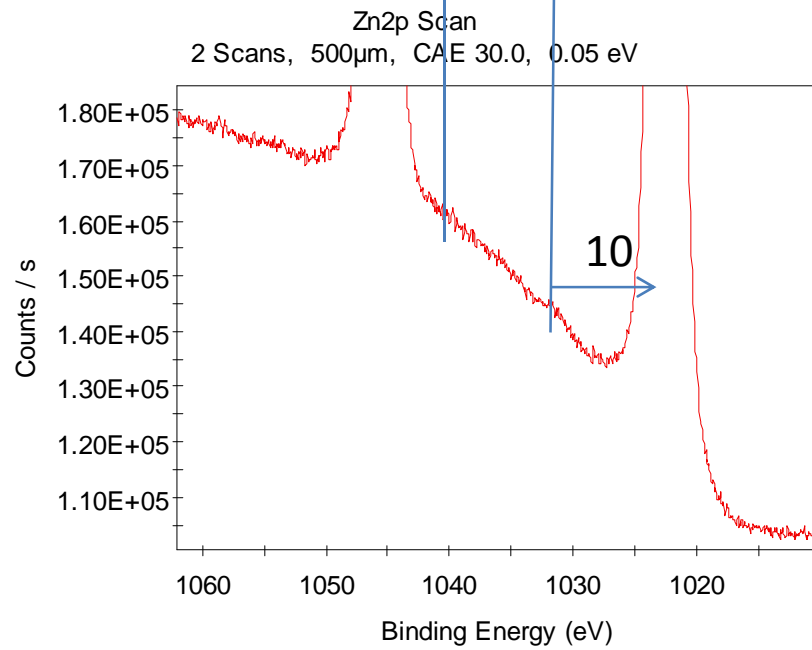


损失峰特征





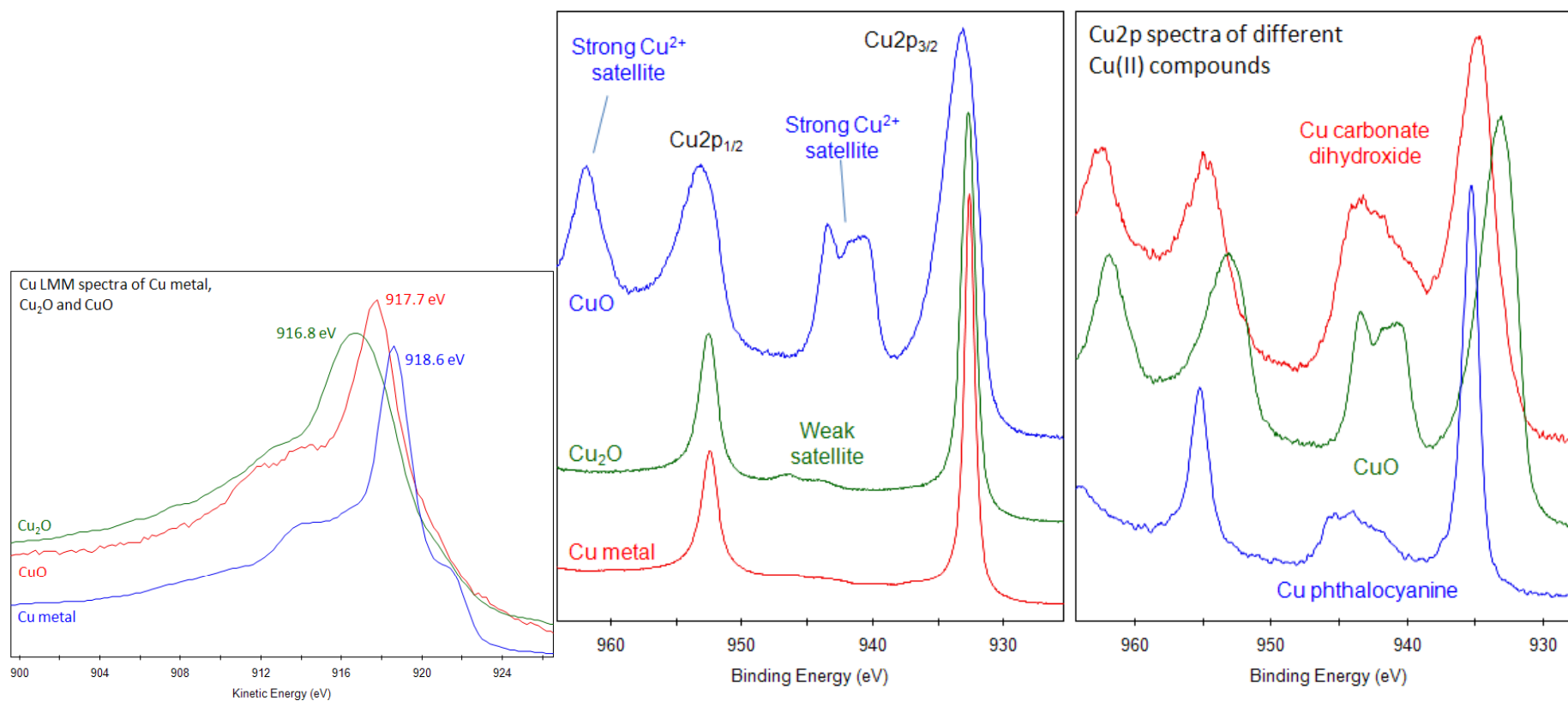
ZnO粉体



表面经Ar离子溅射后的Zn片

这些图谱可以直接调入与采集的谱对比分析，用作模板进行NLS（NLLSF）等分析。

Chemical state	Binding energy Cu2p _{3/2} / eV
Cu metal	932.6
Cu (I) oxide	932.7
Cu (II) oxide	933.1
Cu (II) carbonate dihydroxide	934.8
Cu (II) phthalocyanine	935.2

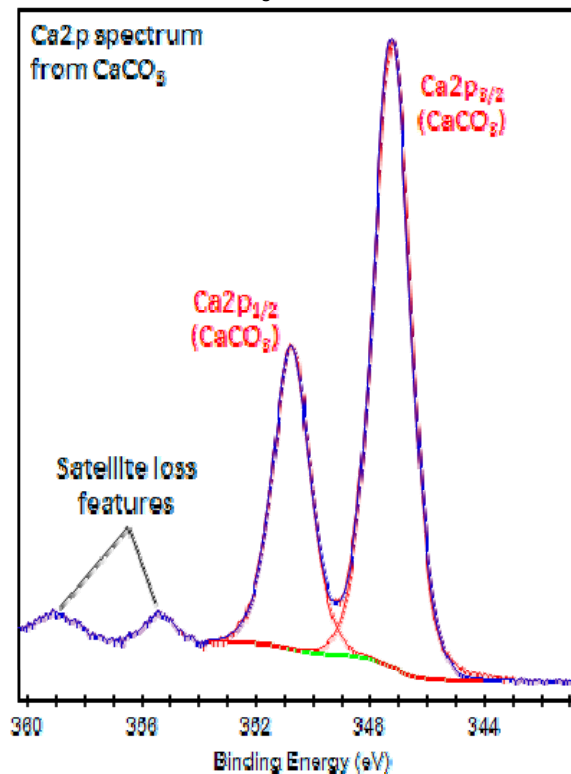


Experimental information

- In presence of a significant magnesium concentration, collect Ca2s as well as Ca2p region.

Interpretation of XPS spectra

- In presence of magnesium, check for Ca2s to prevent misinterpreting Mg KLL as Ca2p.
- There is only a small range of Ca 2p chemical shifts (<1eV) for typical compounds.
 - Limited use in determining chemistry.
- Ca2p peak has clearly spaced spin-orbit components ($\Delta_{\text{carbonate}}=3.5\text{eV}$).
- Satellite loss features are sometimes observed in the Ca2p region.
 - Reasonably strong satellites are observed for CaCO_3 , for example, but only weak satellites for tribasic calcium phosphate.



General comments

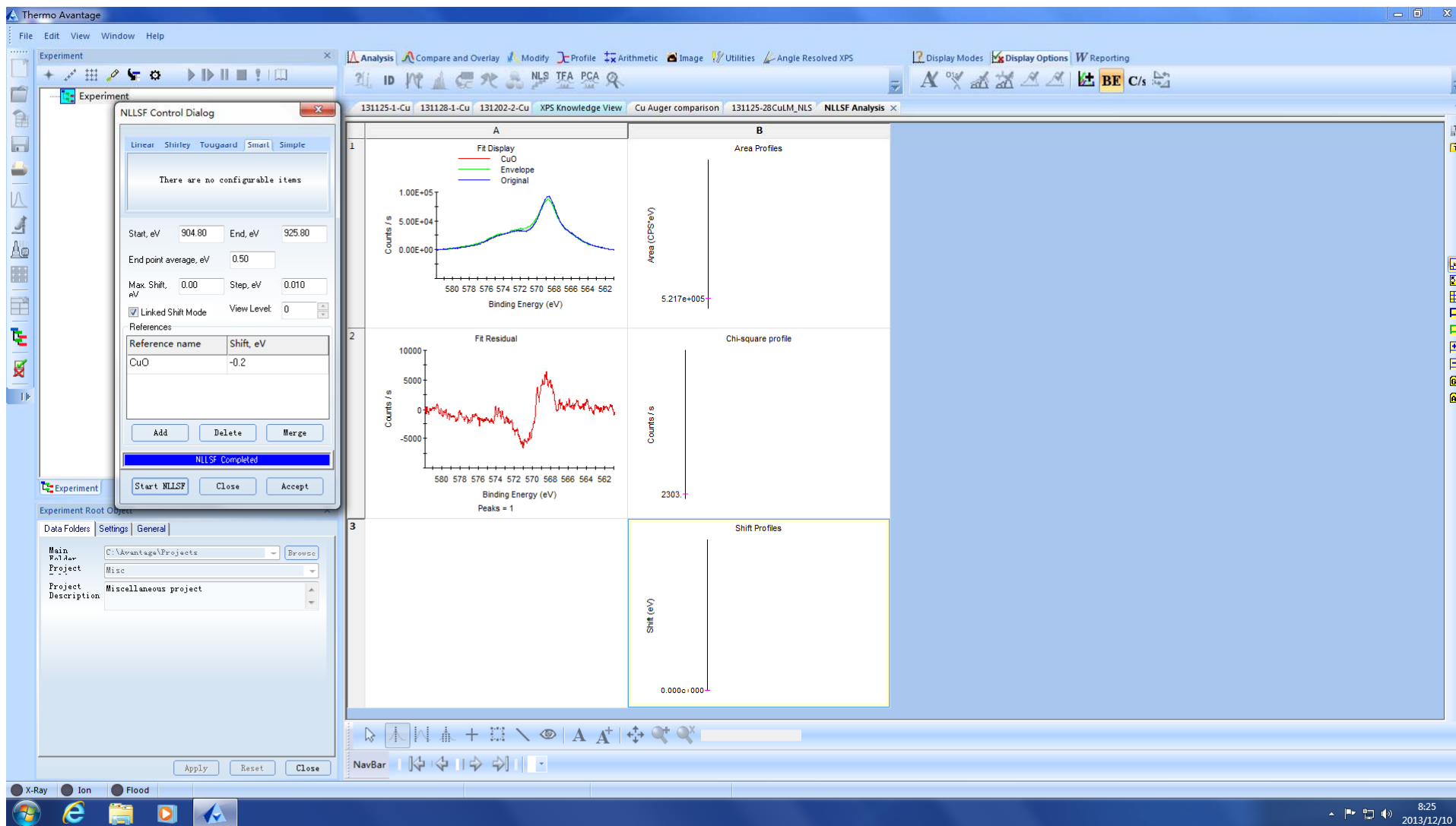
- Since calcium is a highly reactive metal, it is always present as a compound.
- CaCO_3 may degrade under prolonged X-ray exposure, giving $\text{CaO} + \text{CO}_2$.
- Calcium compounds such as calcium oxide or hydroxide may have reacted with atmospheric CO_2 , forming carbonates.

非线性拟合NLS

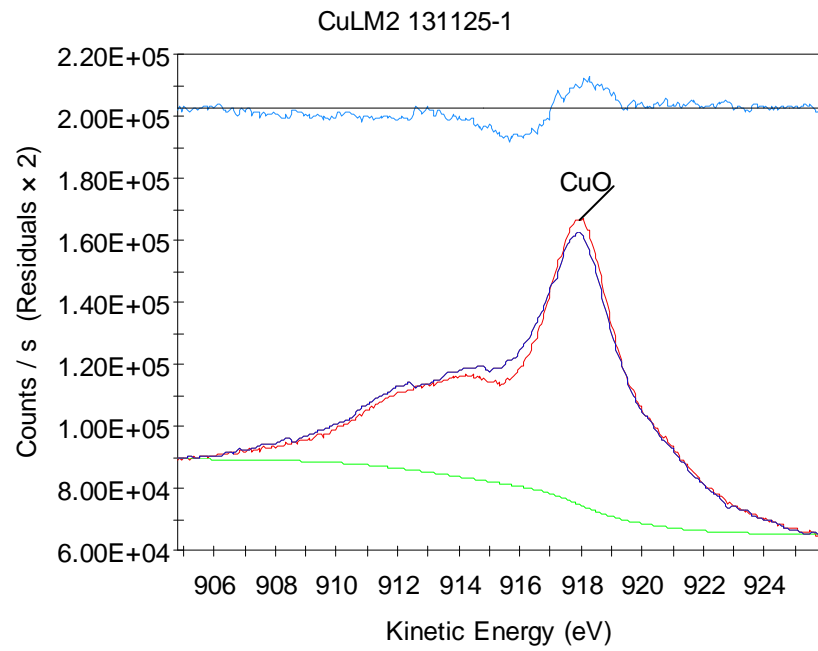
- 非线性最小二乘法谱峰拟合（Non-Linear Least Squares Fitting，NLLSF或NLS），与线性最小二乘法拟合不同，NLS是调节参考谱（数目为所含组分个数）的峰位置和强度，而不改变其形状（模板拟合），使得参考谱包络线与实际测量谱的方差最小。
- NLS能很好地应用于拟合俄歇谱、伴随有Shake-up峰的XPS谱（如一些过渡元素、稀土元素）、伴随有CK跃迁的谱，等等。
- NLS集成在Avantage中，对谱图分析很有益处。省去了用户使用第三方软件(如：CASA XPS)分析数据的麻烦。

俄歇谱峰拟合

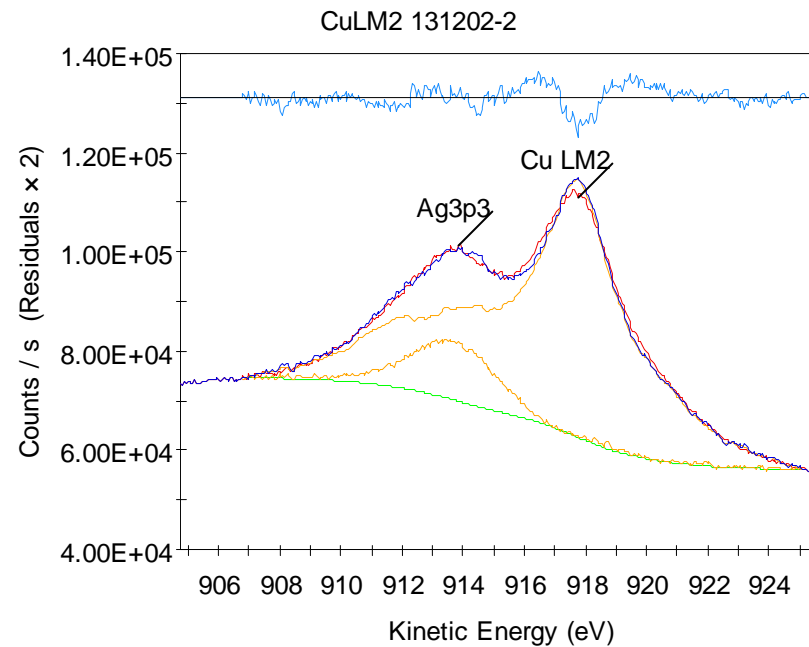
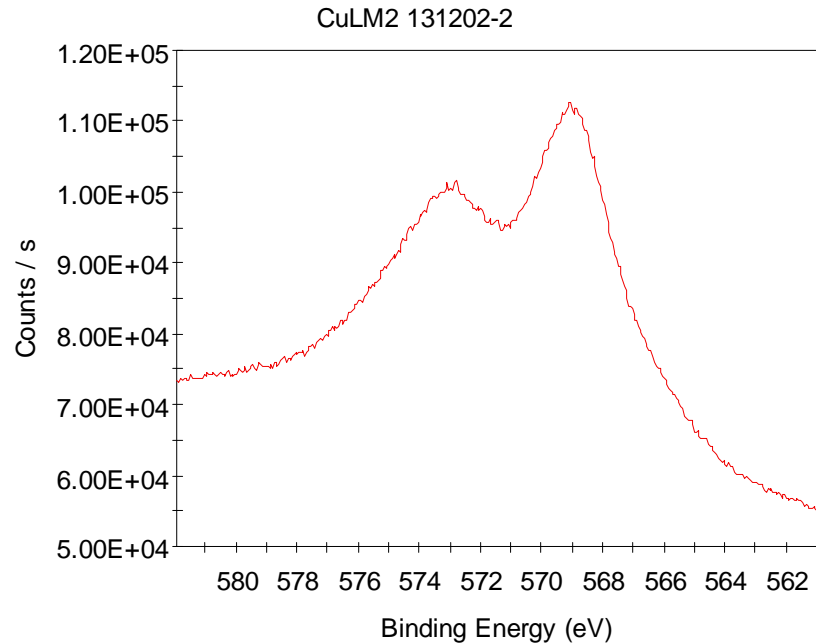
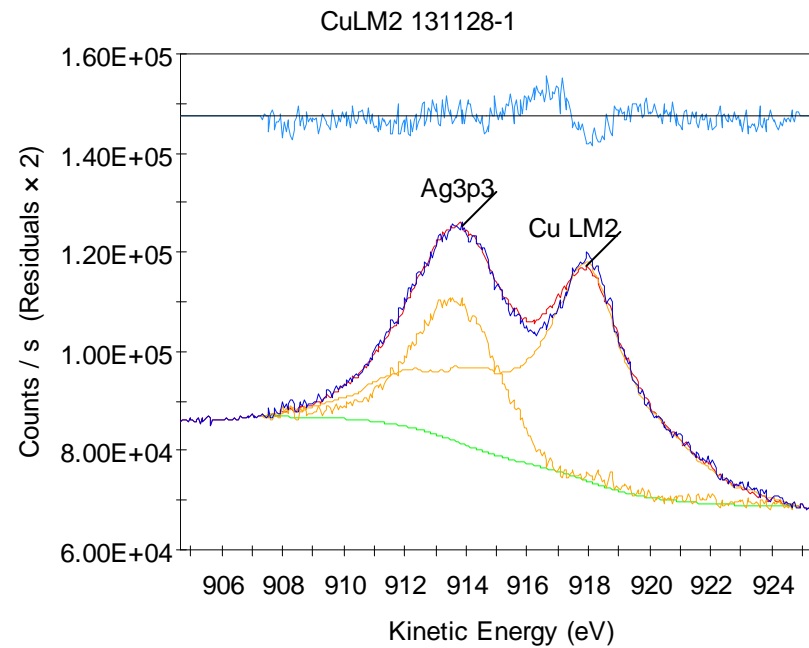
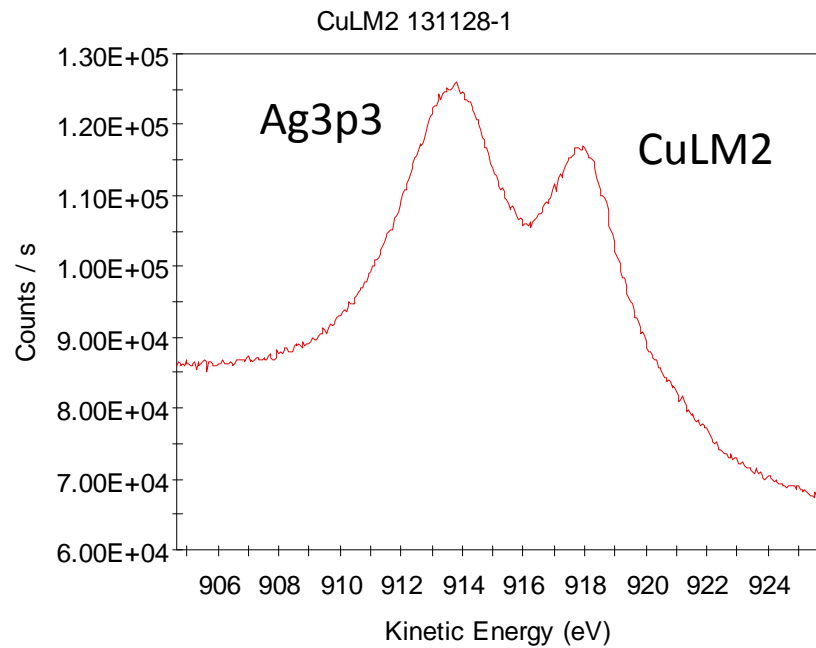
- NLS应用举例：样品Cu-Ag的CuLMM拟合；
- 分析Cu价态时常使用CuLMM。Cu-Ag样品中CuLMM峰受到Ag3p3干扰（Mono AlKa），采用NLS同时拟合CuLMM和光电子谱Ag3p。



NLS:CuLMM俄歇谱峰拟合界面

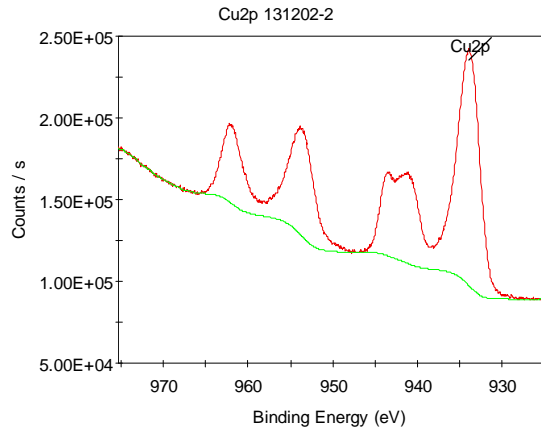
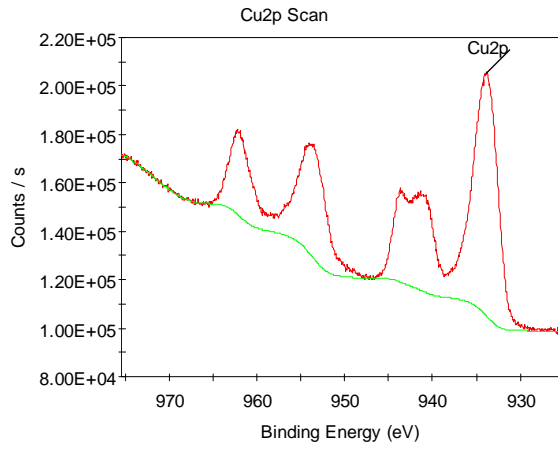
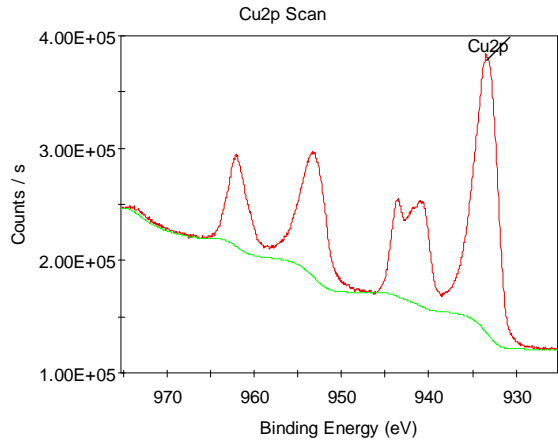


NLS:CuLMM俄歇谱峰拟合结果

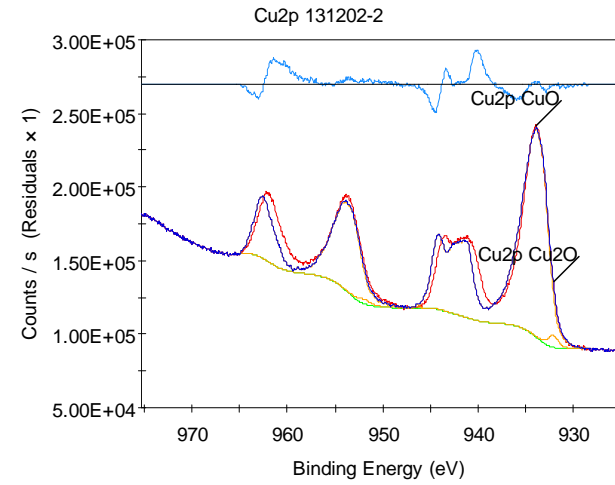
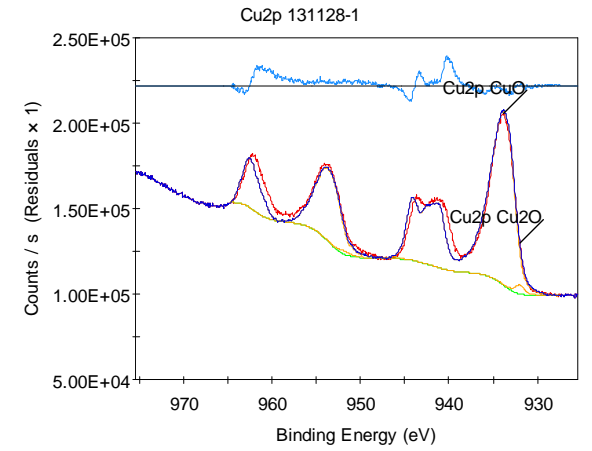
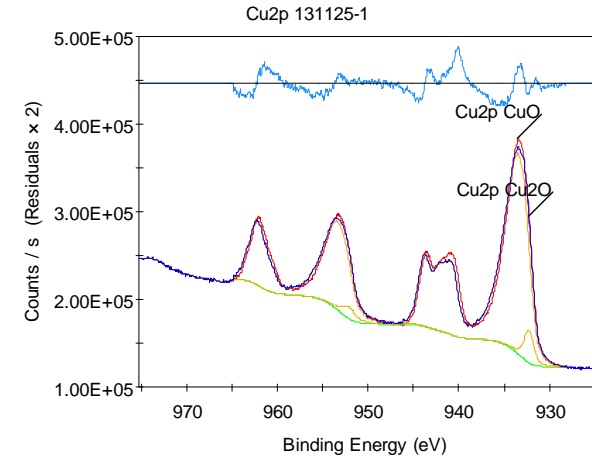
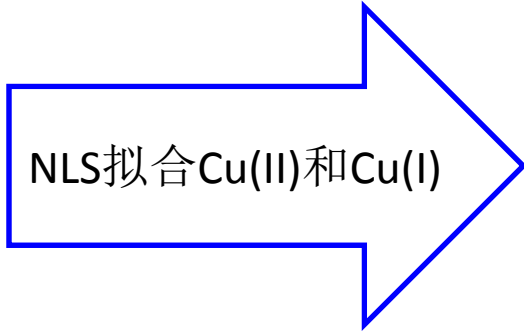


非线性拟合Cu2p谱峰

- Cu(II)有复杂的Shake-up峰（损失峰），通常的线性拟合程序难以拟合。可采用非线性拟合（NLS）程序拟合。在peaktable中报告定量结果，即NLS像LS一样可以对谱图进行定量分析
- NLS拟合所需标准或参考图谱可以调用用户自己的图谱（例如：Ag3p, Cu2p, CuLMM, ZnLMM,），也可以调用Knowledge提供的图谱。



样品: CuO 中 Cu₂O?



结 束

细节决定成败！

感谢大家，欢迎交流