Plasma Hydrogenation of Carbon Nanotubes

PTOLEMY collaboration meeting Nov 21st 2024

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ANDROMeDA
Aligned Nanotube Detector for Research On MeV Darkmatter

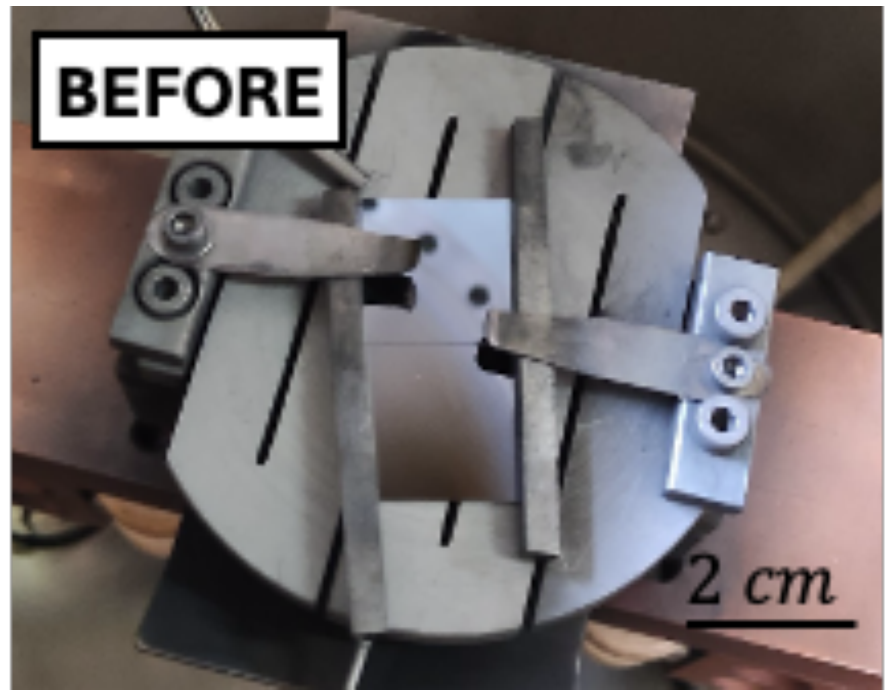
INFN
Istituto Nazionale di Fisica Nucleare

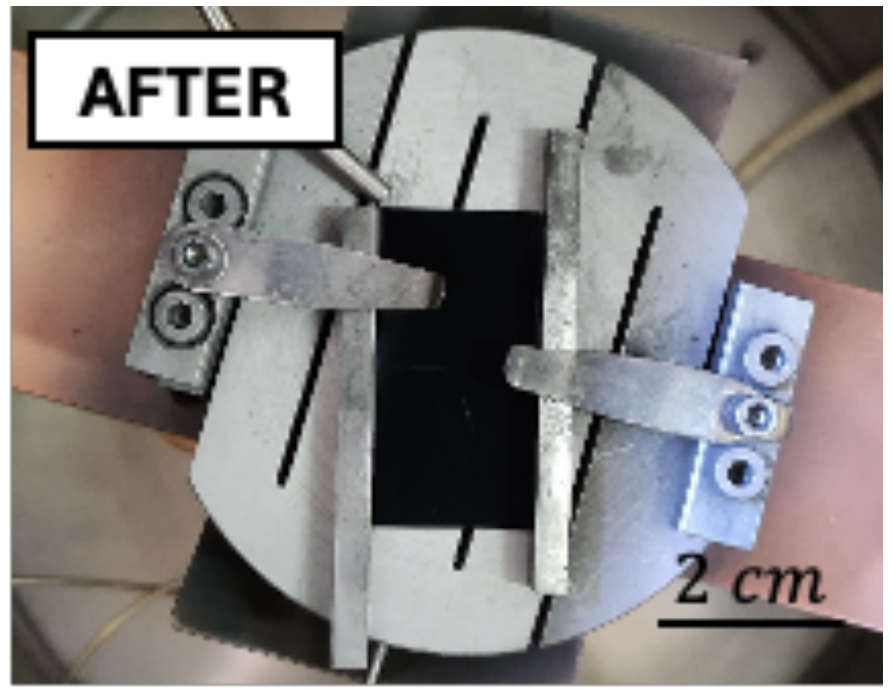
LAboratorio di Spettroscopie Elettroniche e di Correlazione
LASEC

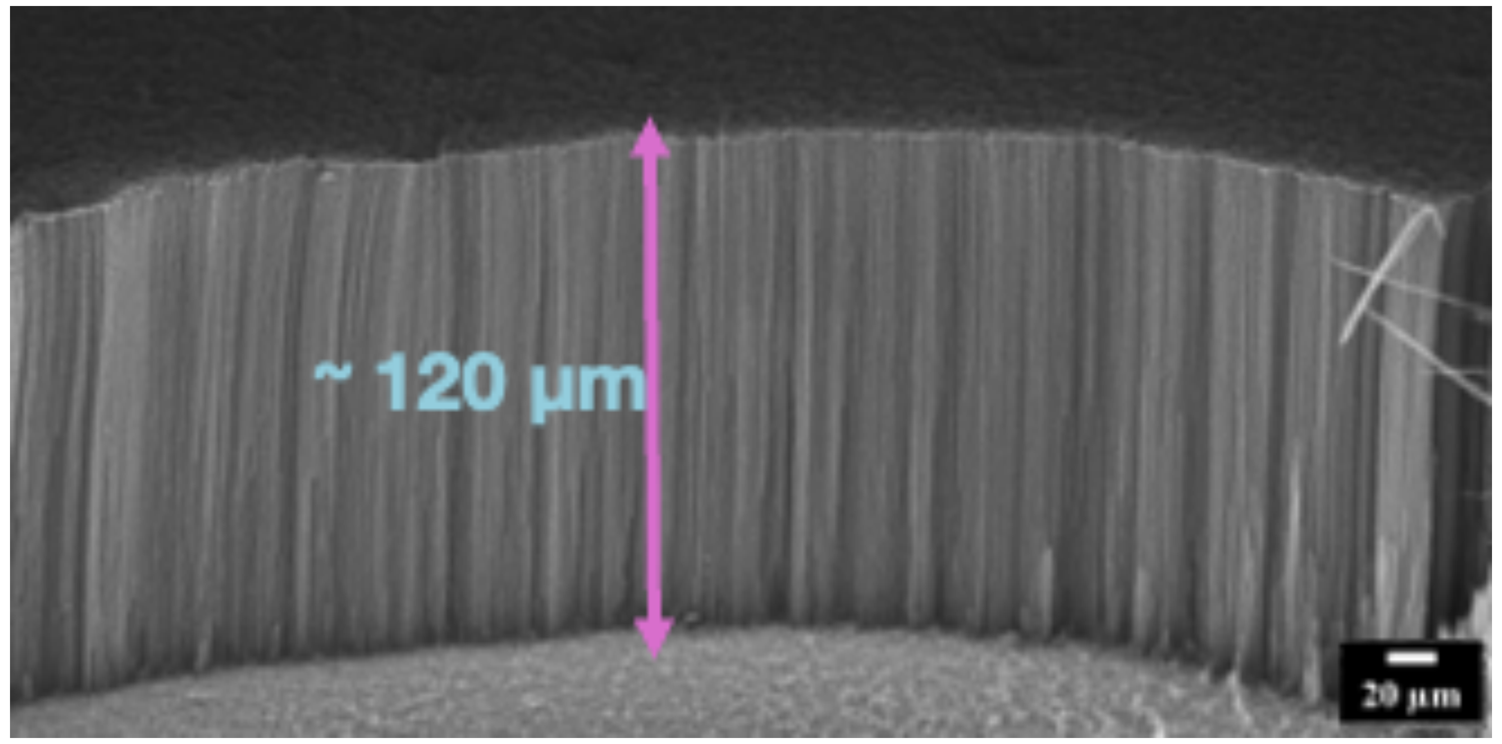
ROMA TRE
UNIVERSITÀ DEGLI STUDI

CVD chamber @ La Sapienza

VACNT growth







Plasma Hydrogenation Recipe

Two samples from the same batch

Annealing 650 °C in CVD chamber

CNT pristine

Annealed at ~ 550 °C

Used as a reference

CNT plasma H

Exposed to hydrogen plasma:

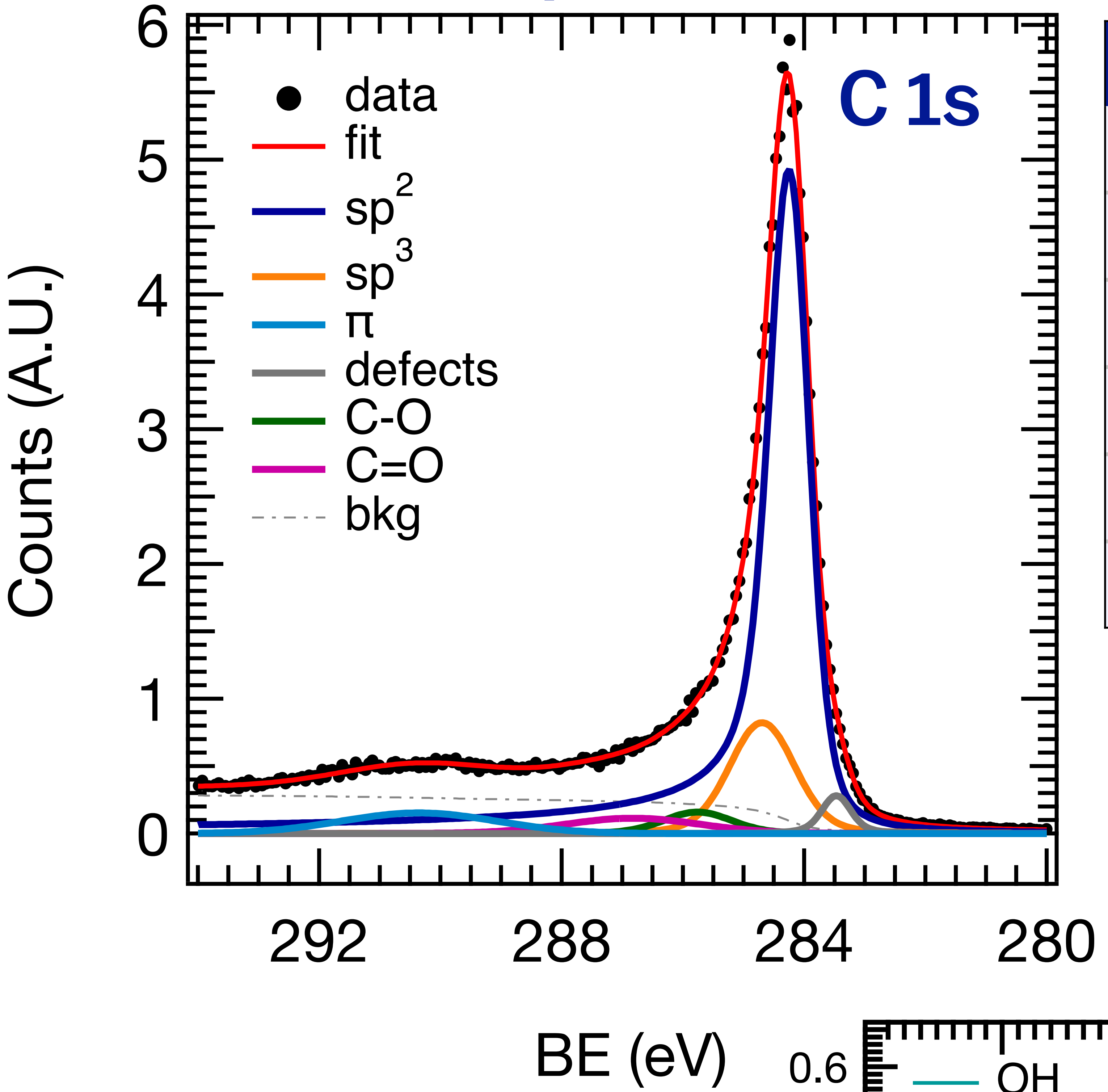
- 100 W
- 0.7 mbar H_2, 300 sccm
- 1 h

Kept in low vacuum during transfer

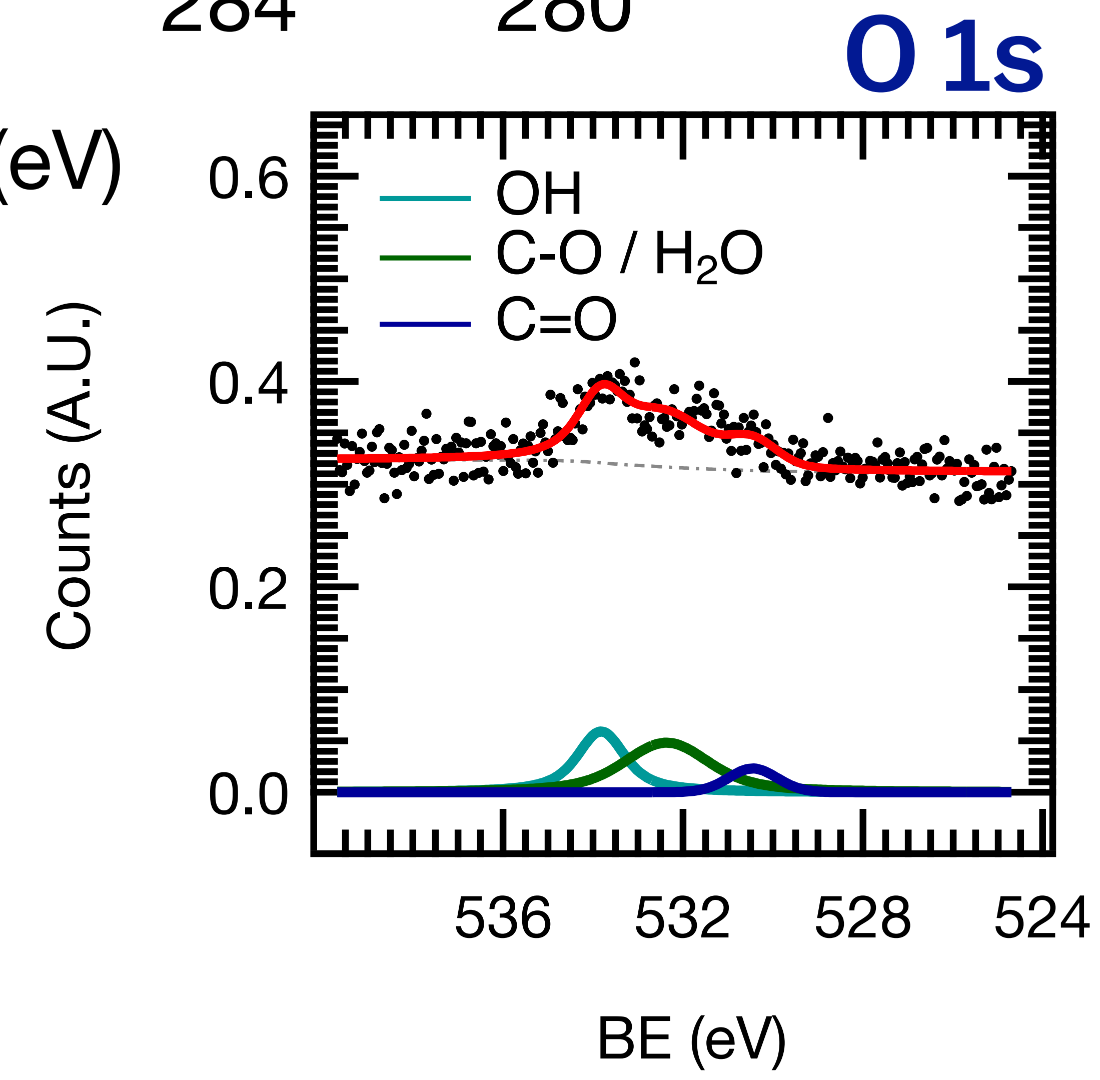
Annealed at ~ 230 °C

XPS analysis: from sp² towards sp³

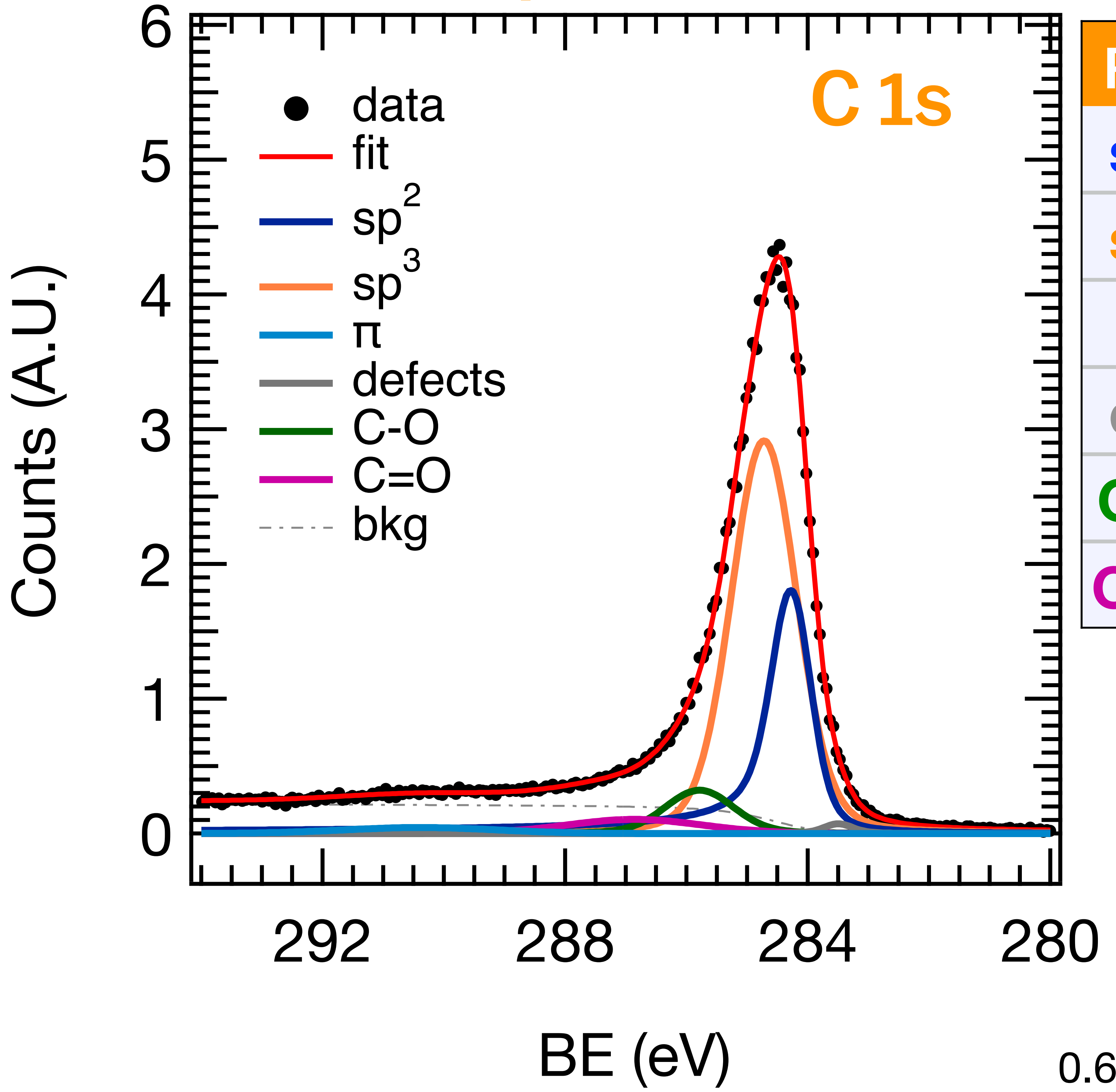
CNT pristine



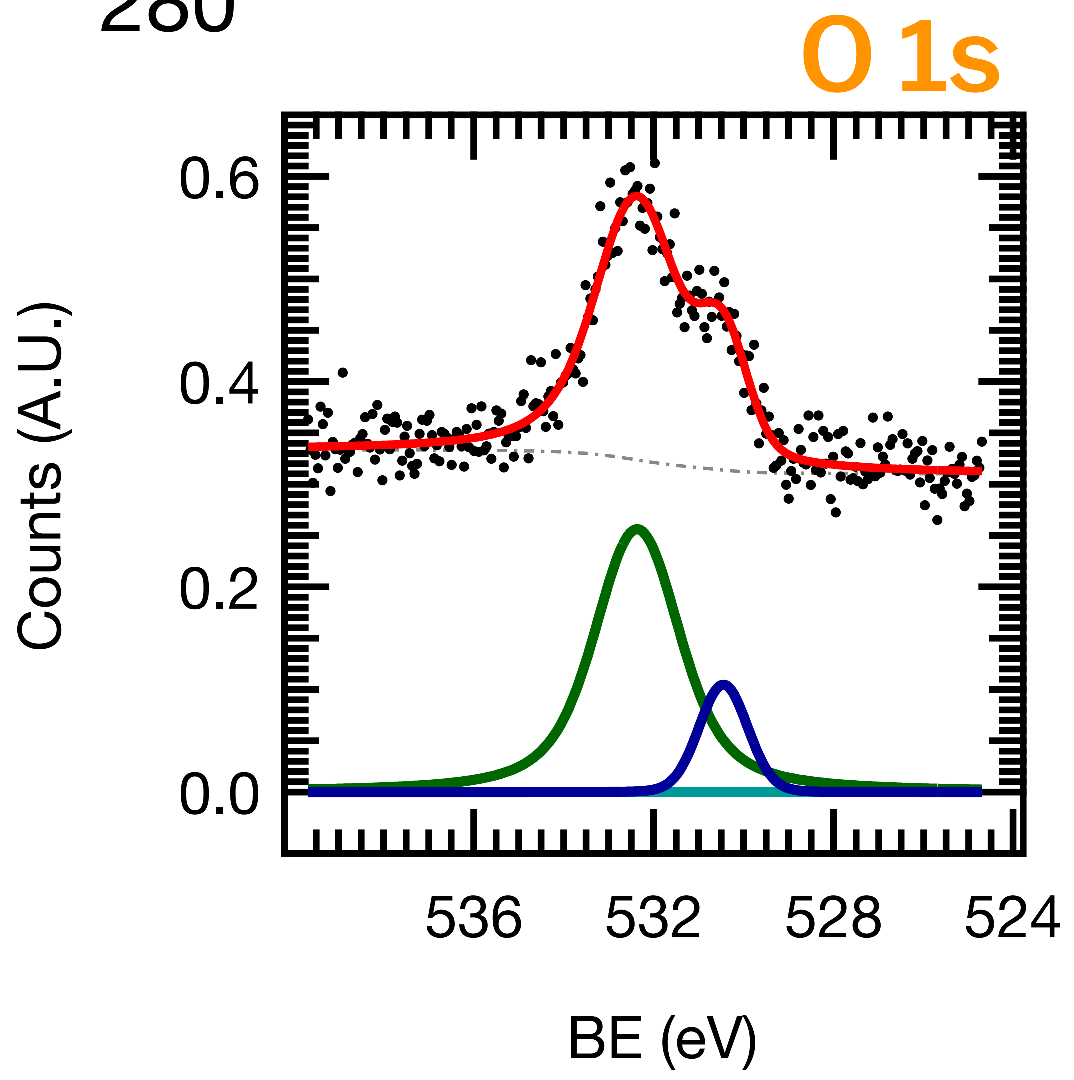
Rel intensity (I_x / I_{tot})	
sp²	0.66 ± 0.02
sp³	0.14 ± 0.02
π	0.06 ± 0.03
def	0.02 ± 0.004
C-O	0.03 ± 0.02
C=O	0.04 ± 0.02



CNT plasma H

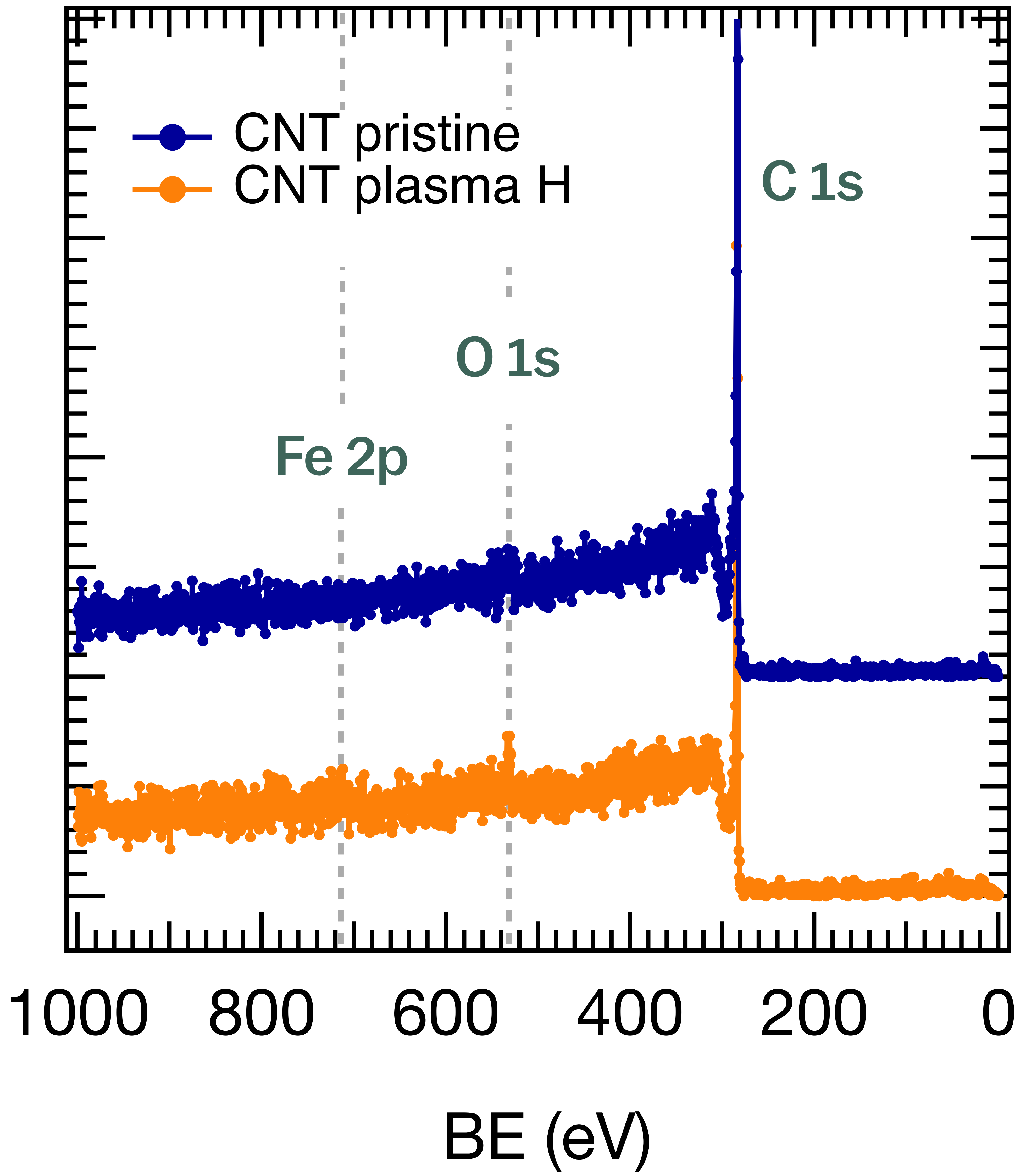


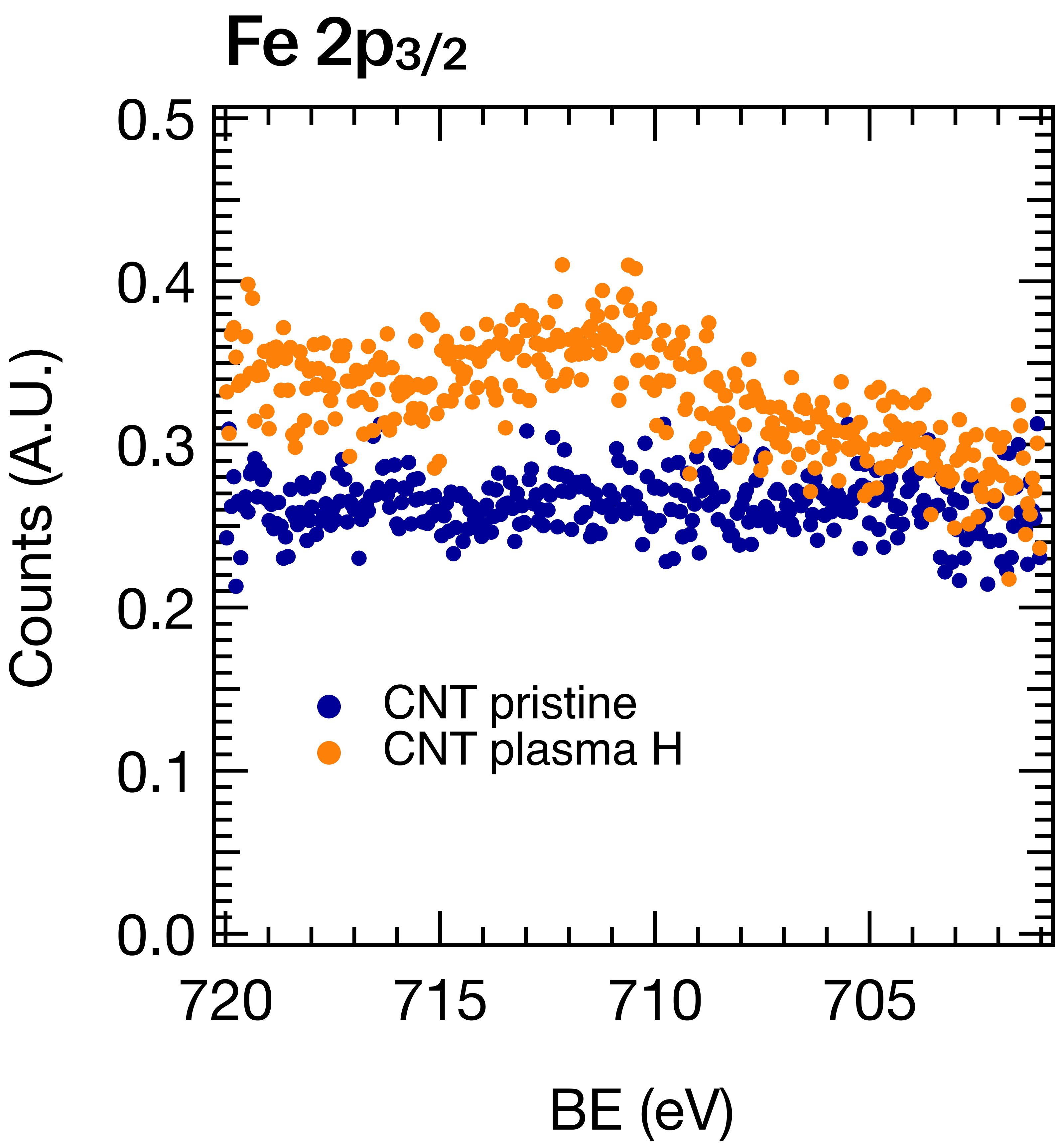
Rel intensity (I_x / I_{tot})	
sp²	0.28 ± 0.03
sp³	0.56 ± 0.04
π	0.02 ± 0.01
def	0.01 ± 0.003
C-O	0.06 ± 0.03
C=O	0.04 ± 0.02



- **sp²** decreases, **sp³** increases (x4)
- **C-O** and **C=O** increases

XPS Survey Scan Reveals Iron Traces in Hydrogenated CNTs

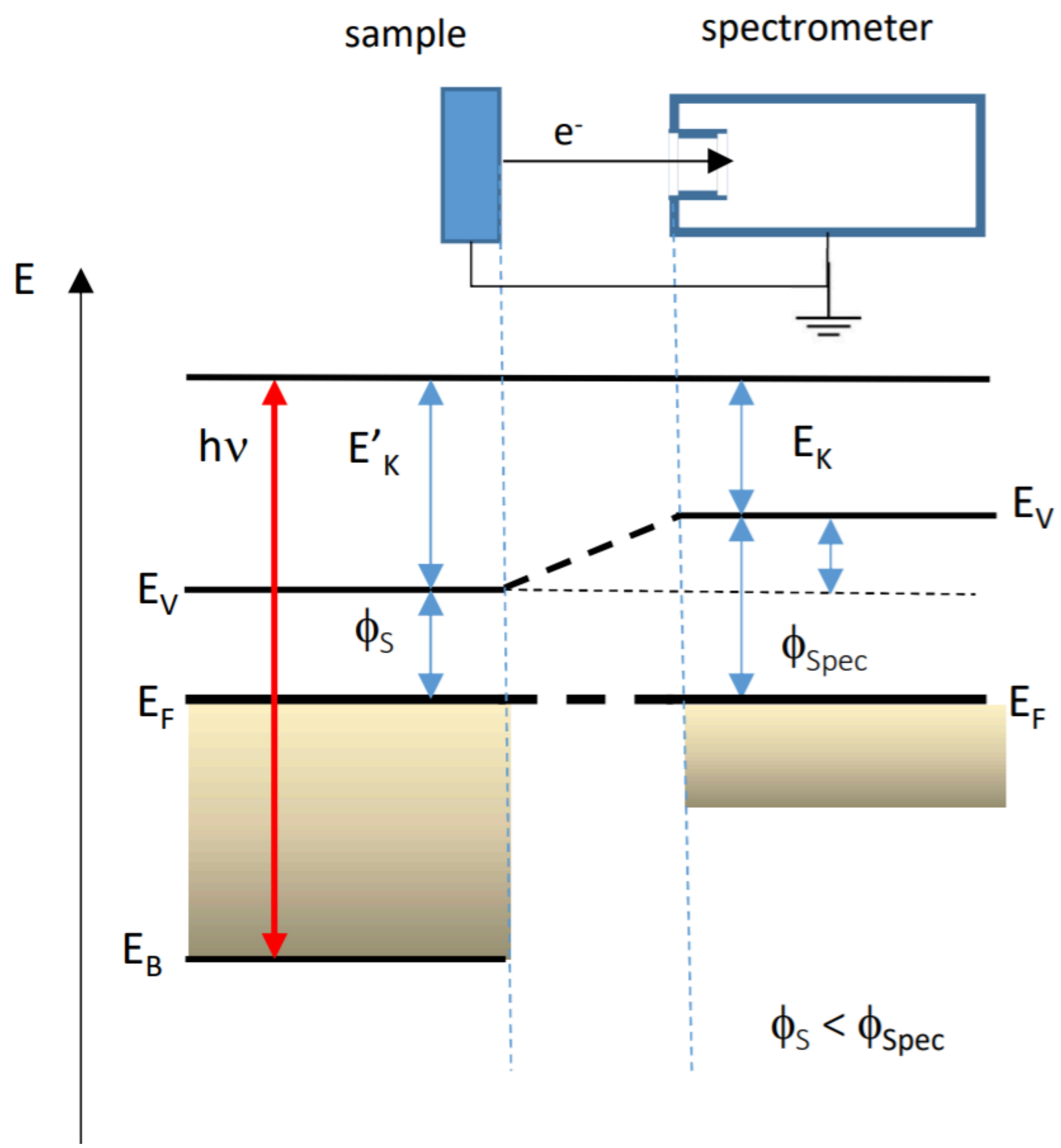




Why a higher Fe 2p intensity in hydrogenated CNT?

It may require SEM investigation

How to measure a Work Function



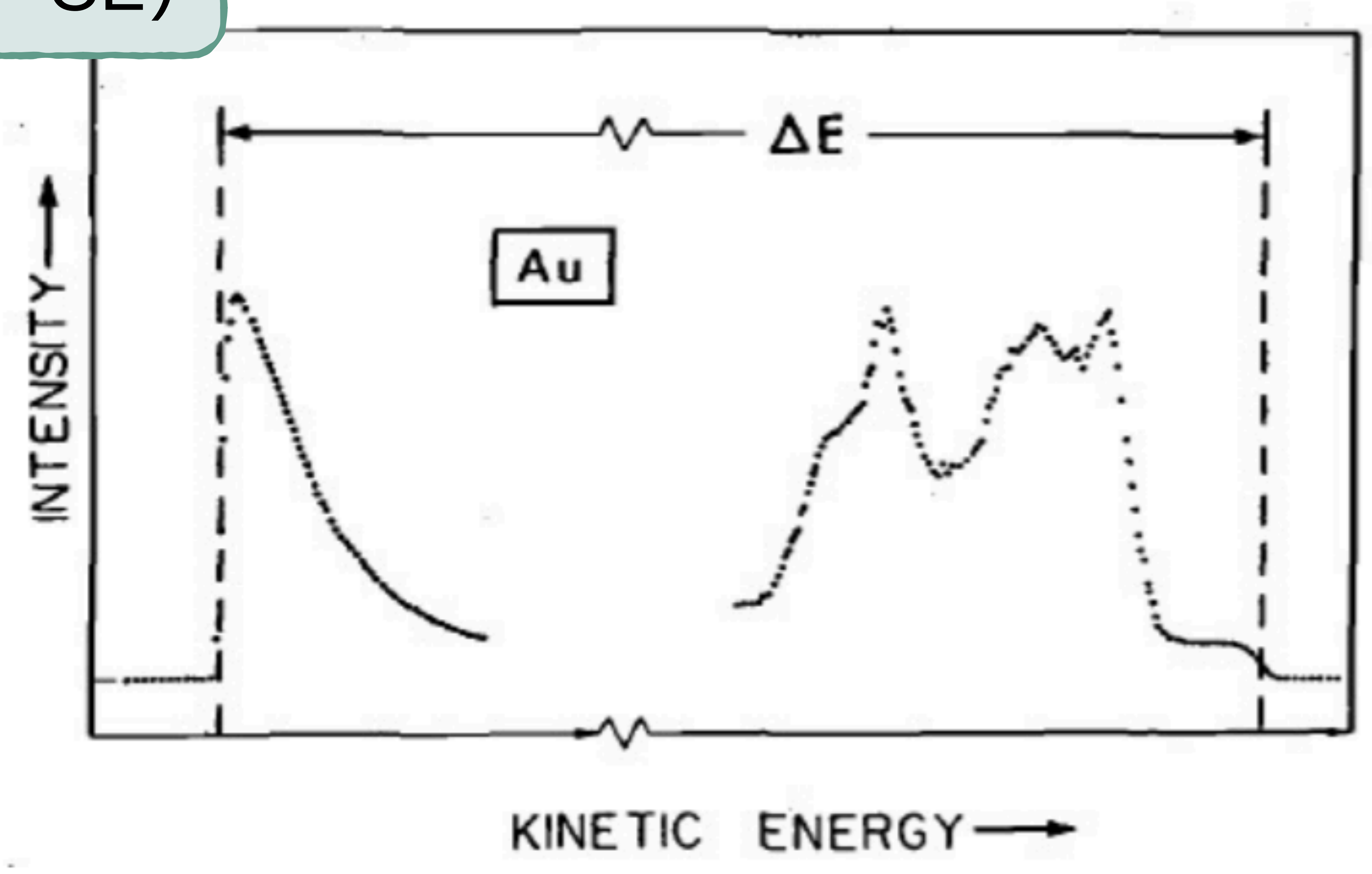
Analyzer point of view

$$E_K^{min} = \phi_S - \phi_{Spec}$$
$$E_K^{max} = h\nu - \phi_{Spec}$$

ΔE_K depends only on the sample

$$\Delta E_K = E_K^{max} - E_K^{min} = h\nu - \phi_S$$

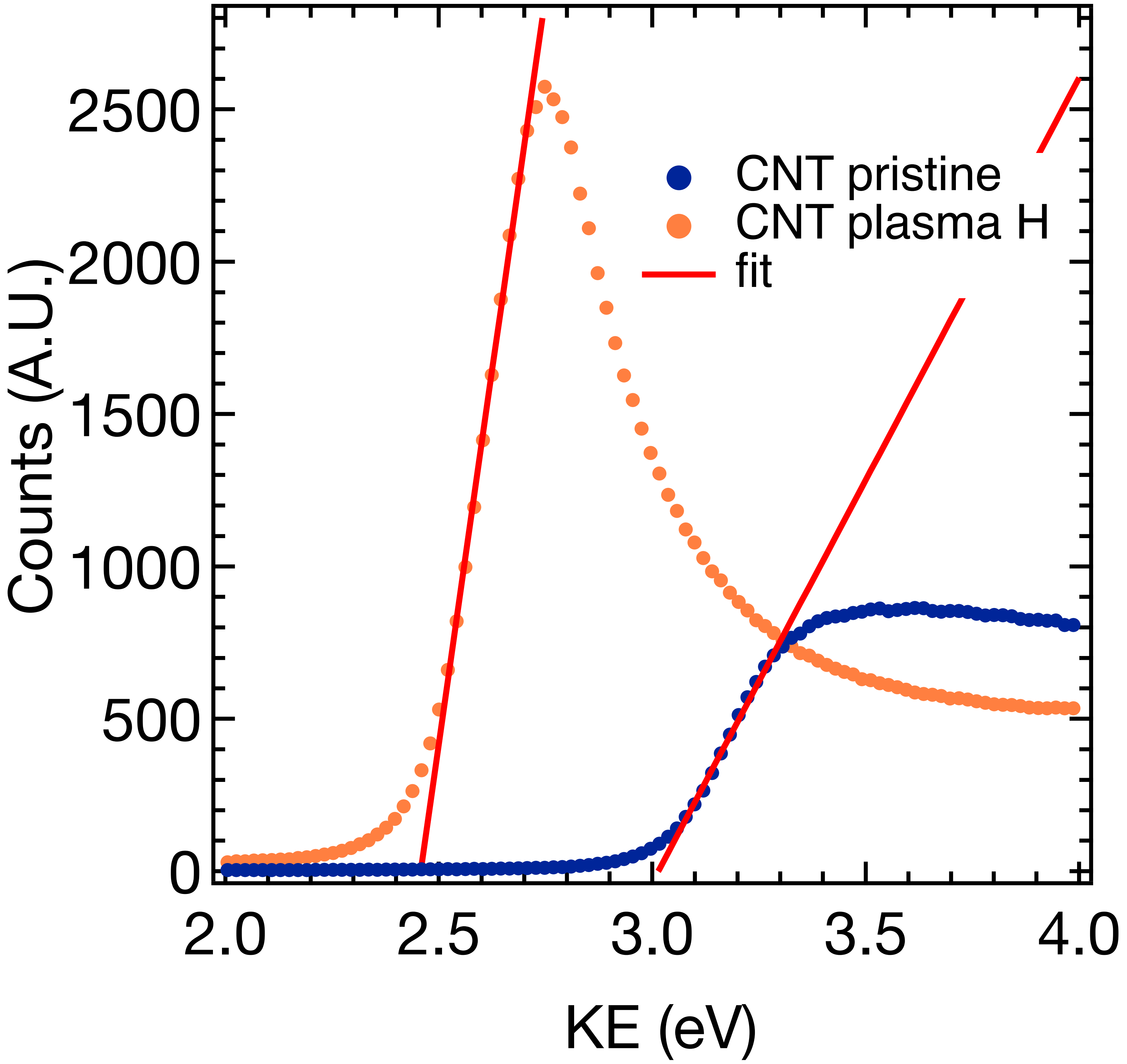
$\phi_{sample} = h\nu - \Delta E_k = h\nu - (FL - SE)$



Bias voltage applied to the sample to measure the secondary electron onset

UPS: Work Function Changes and Band Gap Opening

Secondary Electron onset (SE)



$V_{BIAS} = -3$ V

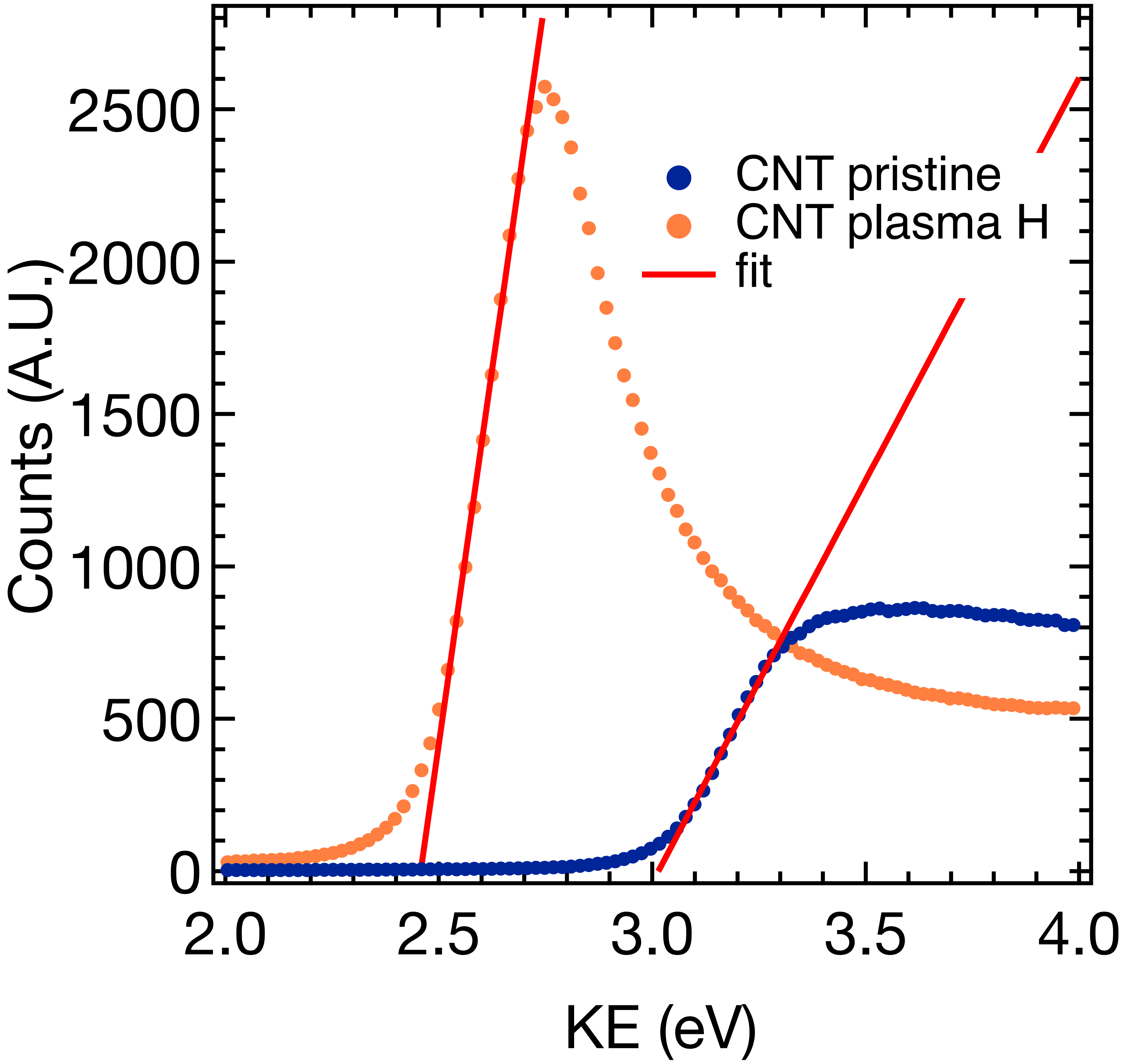
Work Function measure: $\phi_{sample} = h\nu - \Delta E_k = h\nu - (FL - SE)$

Surface dipole changes:

- **WF lowers** from 4.33 ± 0.05 eV to 3.81 ± 0.05 eV

UPS: Work Function Changes and Band Gap Opening

Secondary Electron onset (SE)



V_{BIAS} = - 3 V

Work Function measure: $\phi_{sample} = h\nu - \Delta E_k = h\nu - (FL - SE)$

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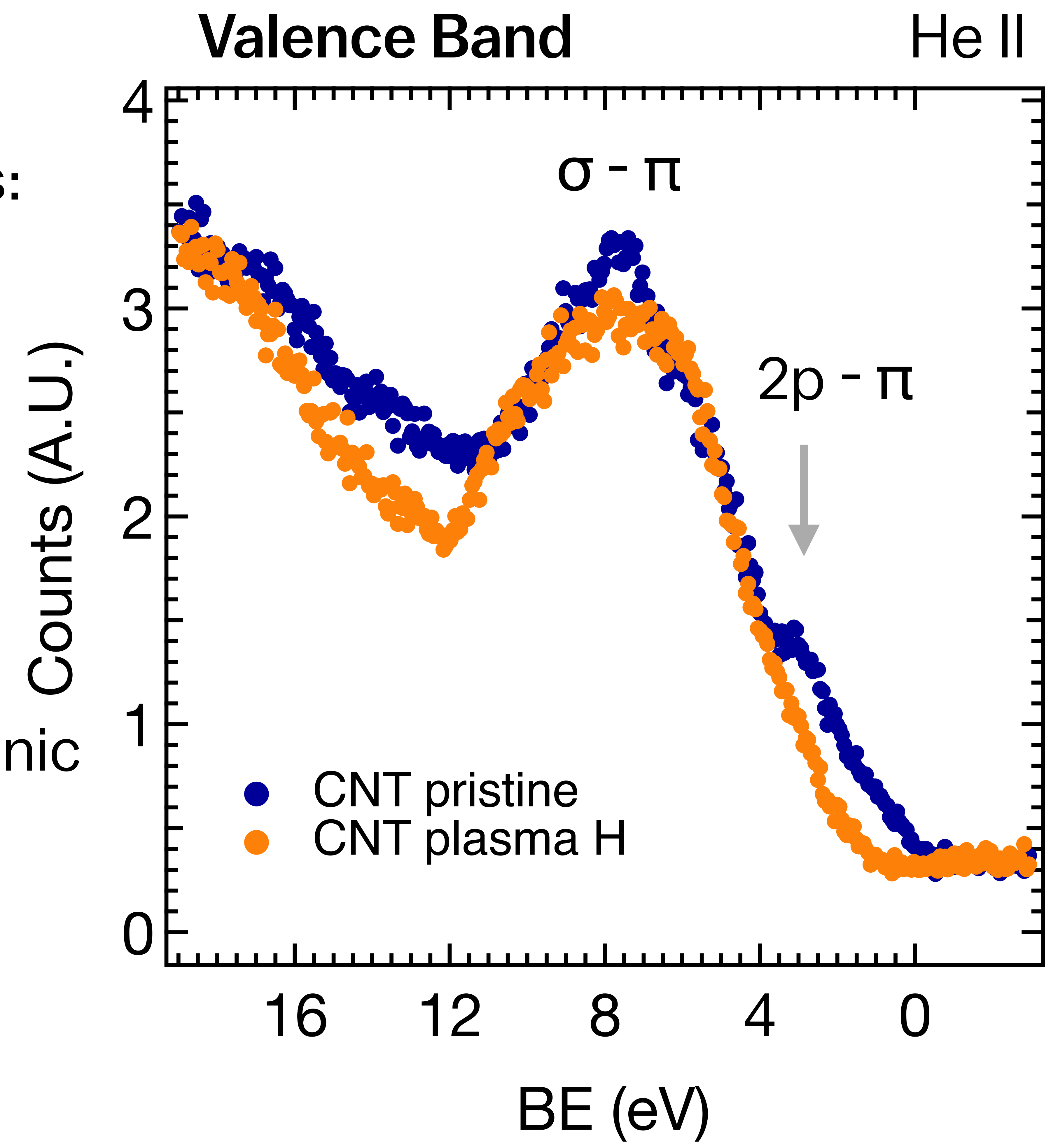
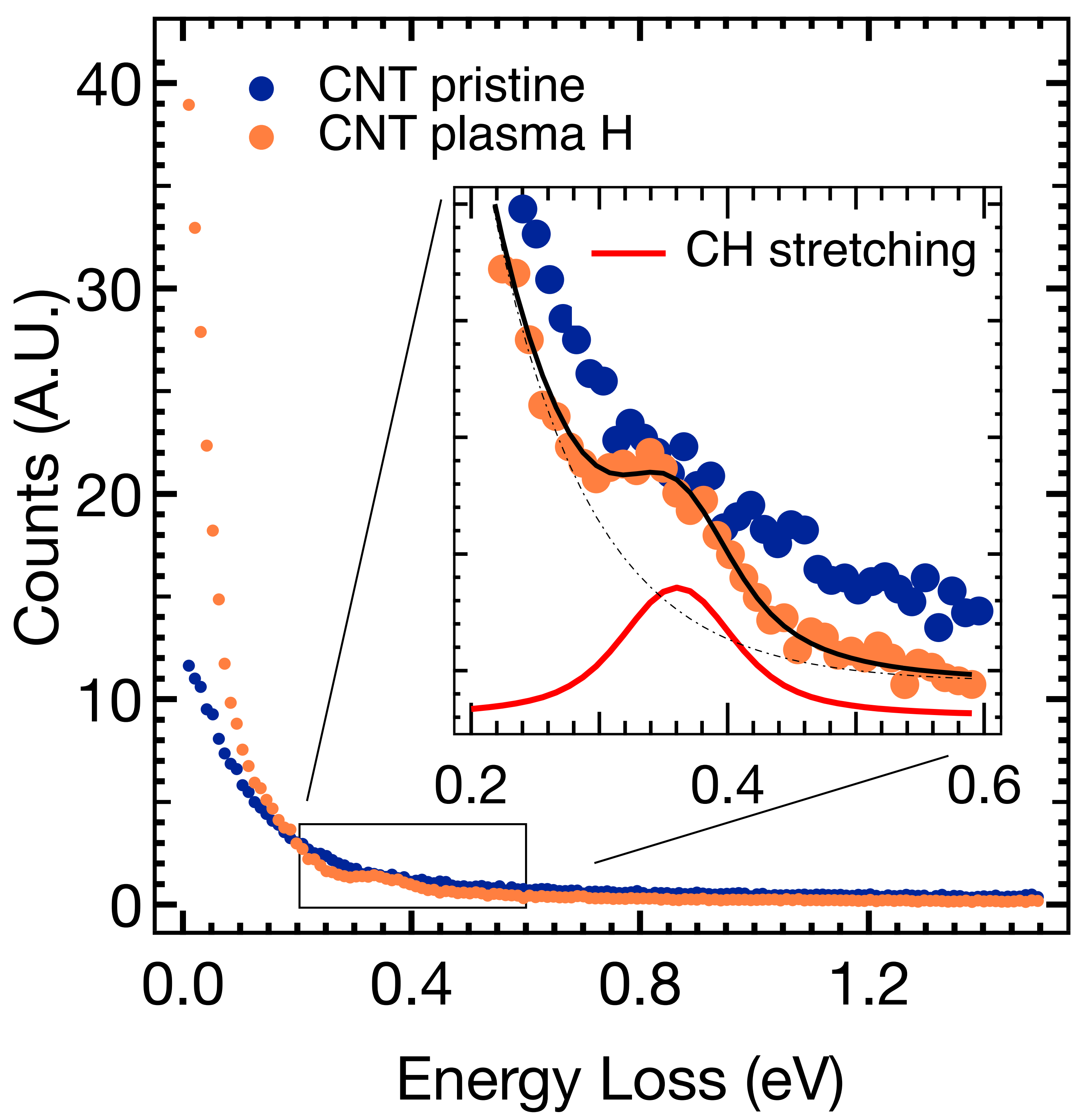
Depletion of the electronic levels near Fermi level

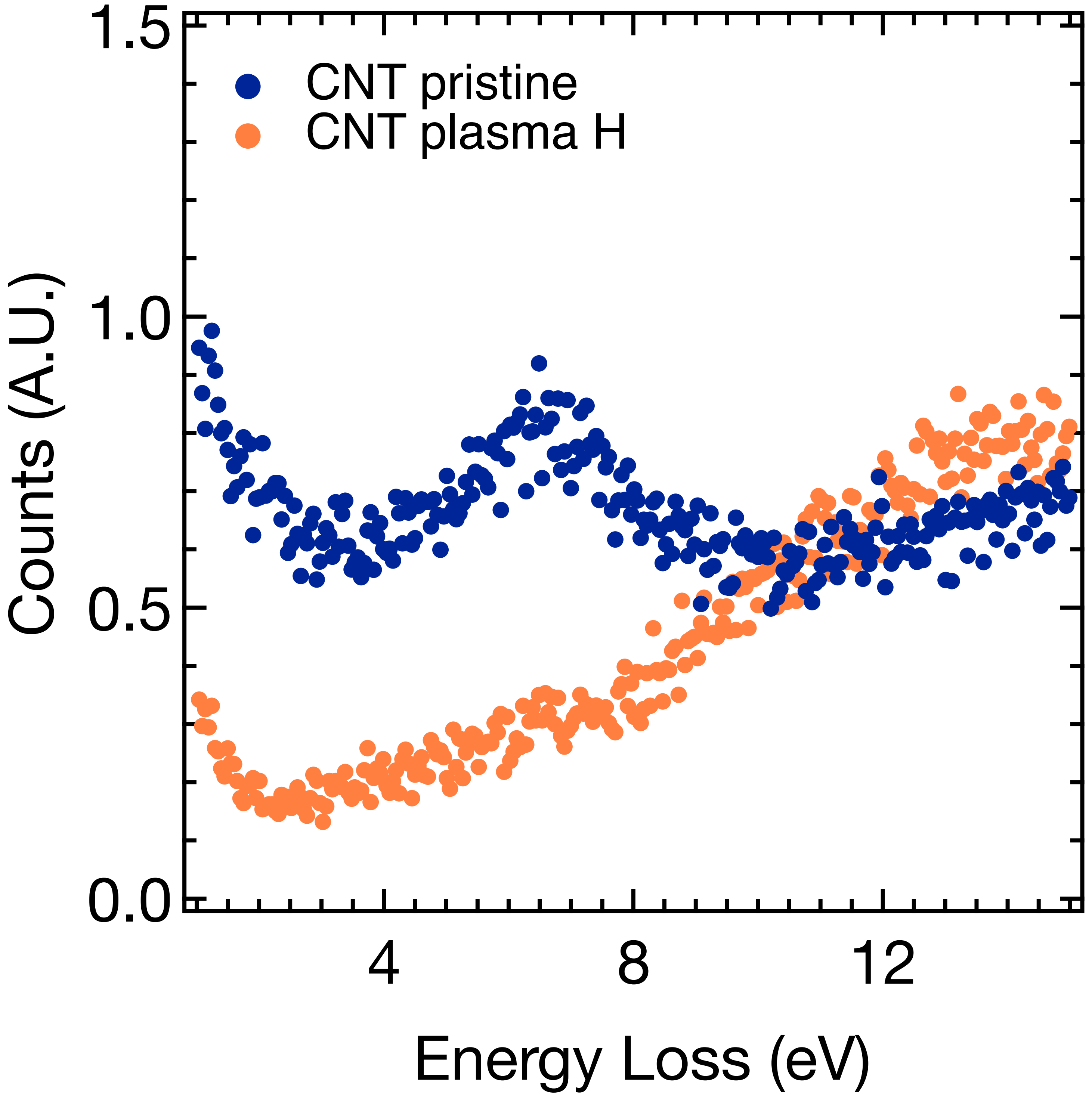
- **Gap opening**

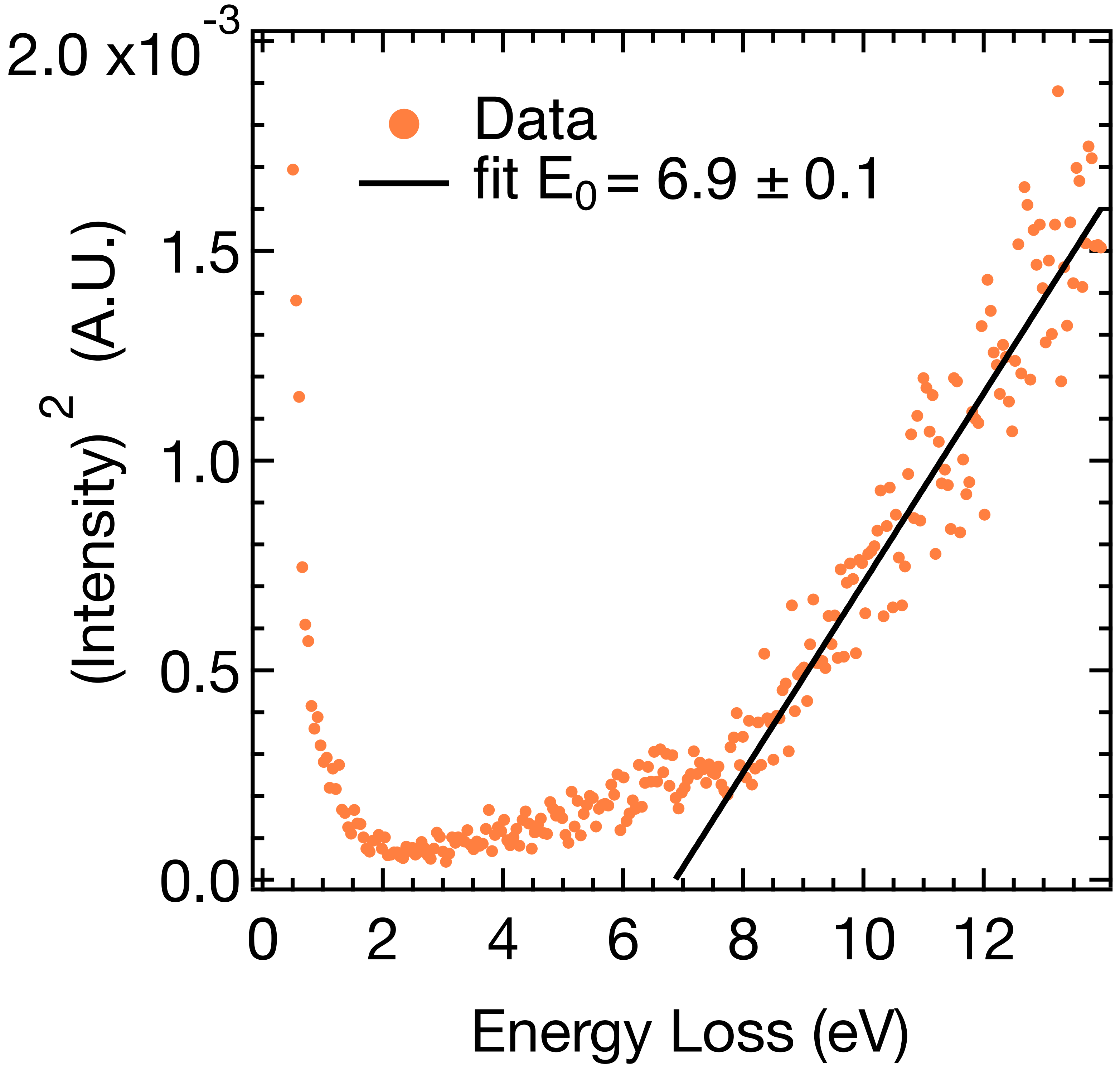


Hydrogenation Signatures in Energy Loss Spectroscopy

Electron Energy Loss Spectroscopy

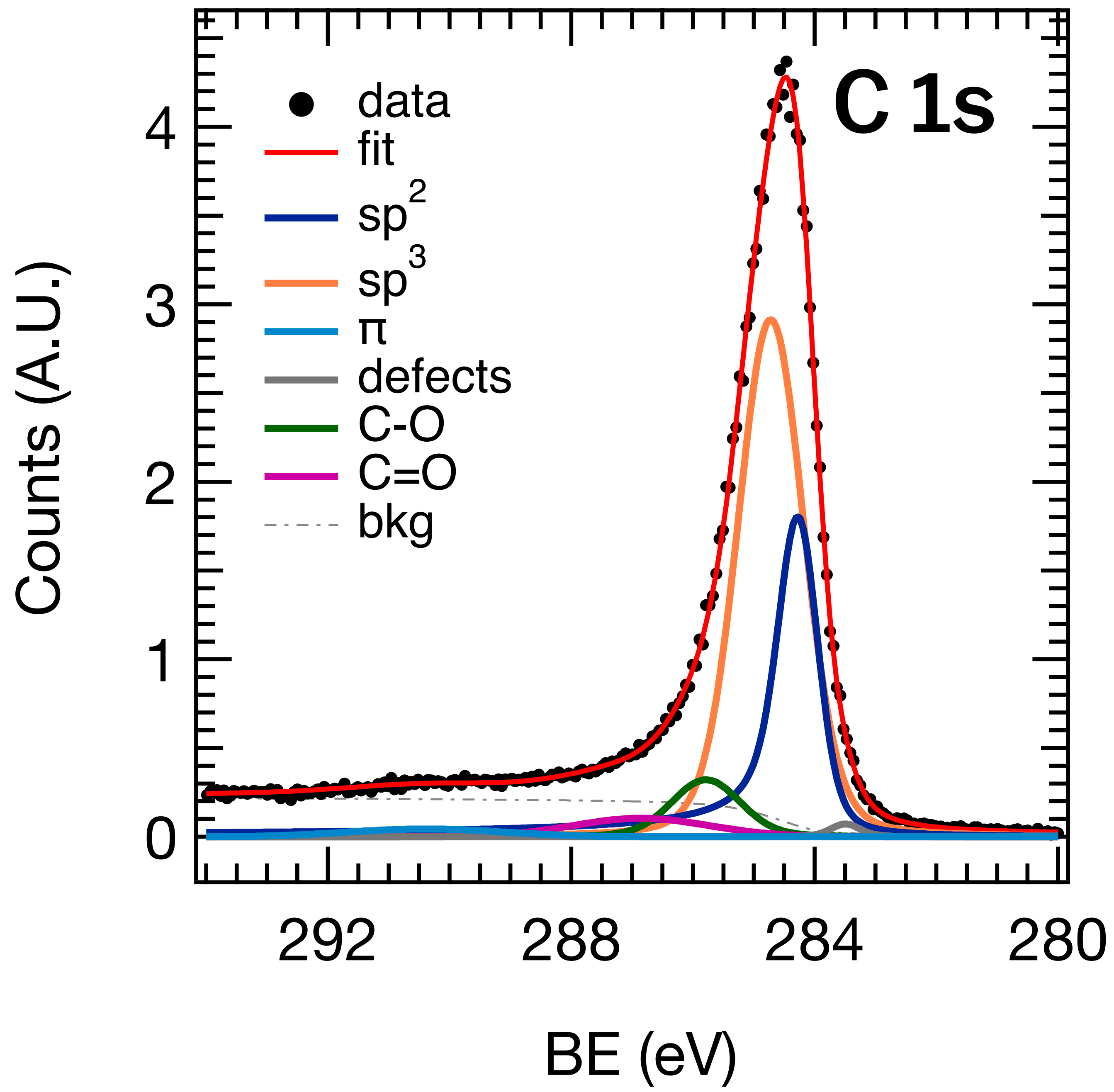






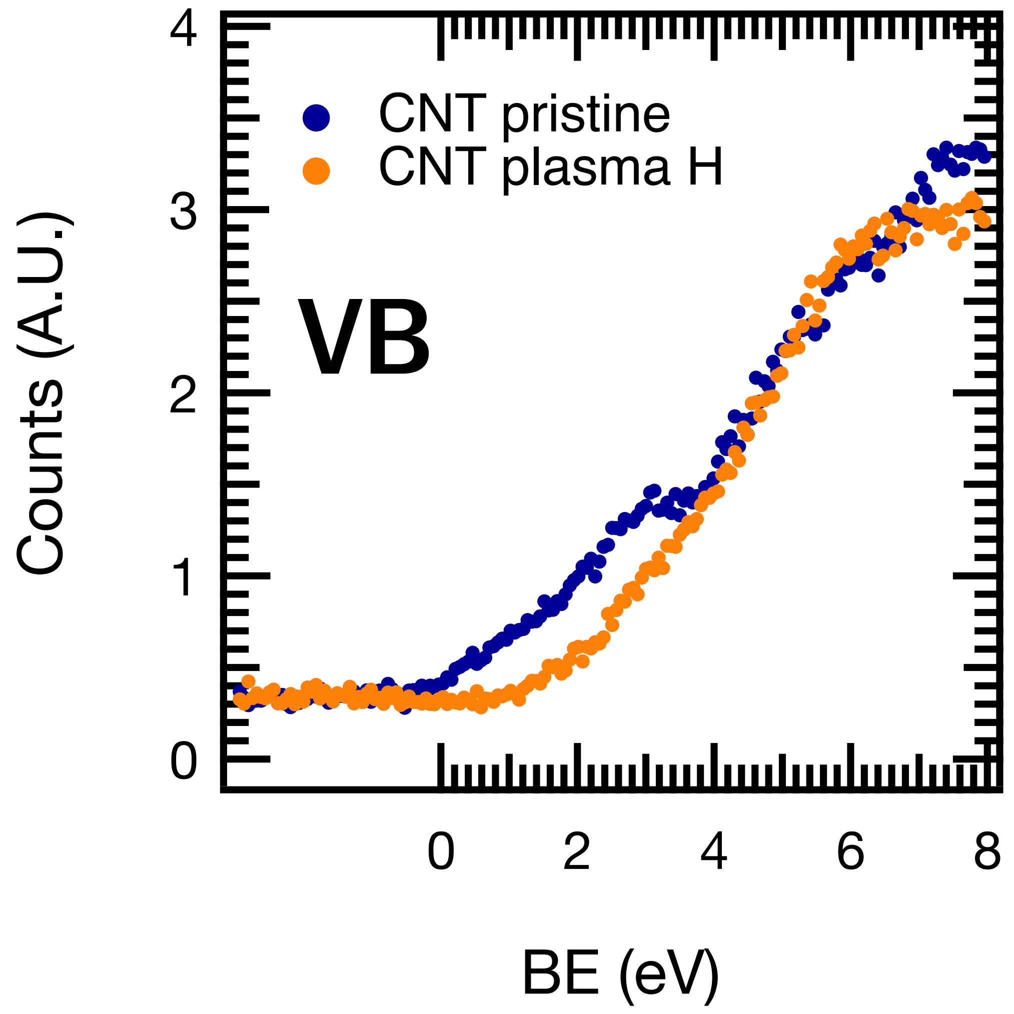
- **CH stretching** appears at ~ 0.36 eV
- Quenching of the **π plasmon** and low energy losses
- Wide **band gap** opening ~ 6.9 eV

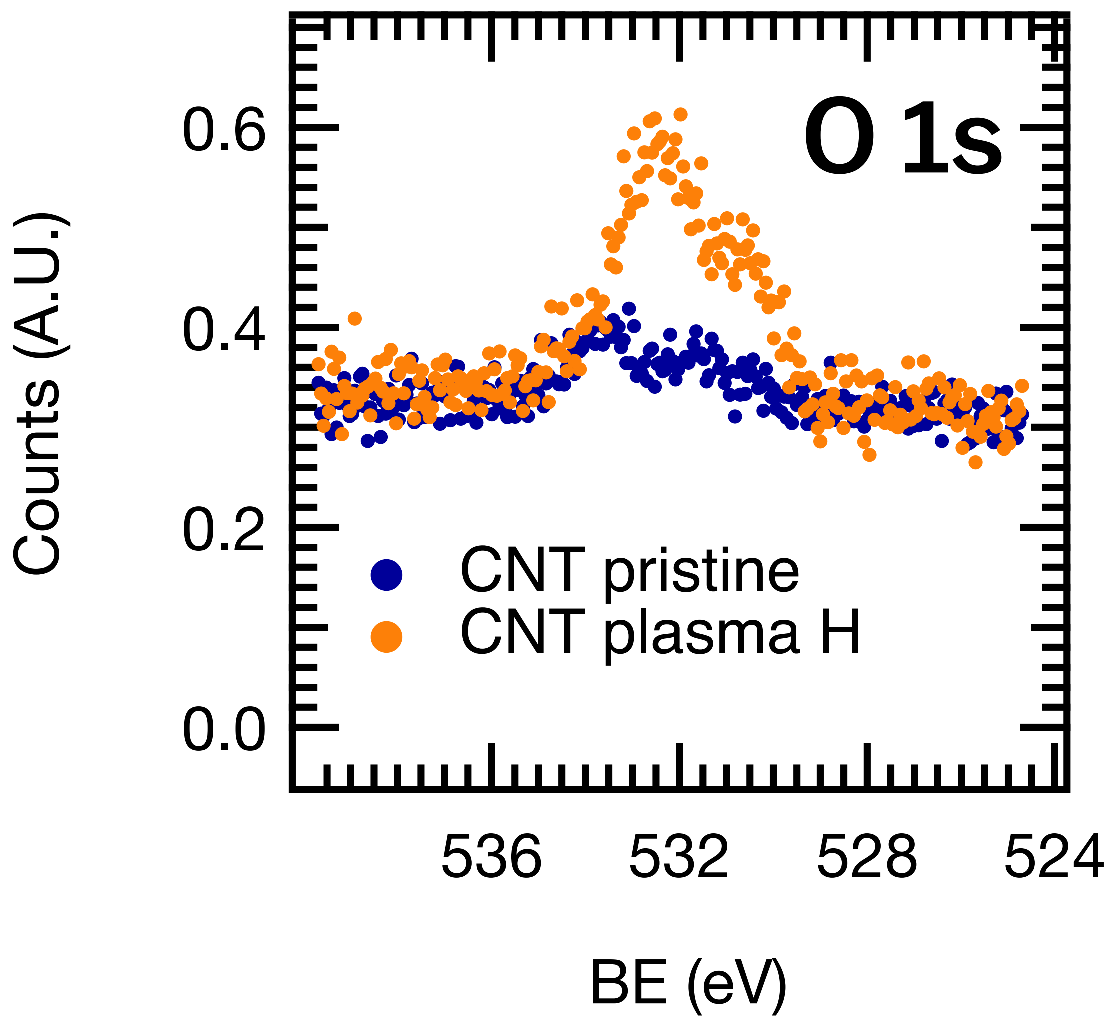
Hydrogen Plasma *vs* Thermal Cracking Hydrogenation



$I_{sp3} / (I_{sp2} + I_{sp3}) \simeq 67\%$

WF = 3.81 ± 0.05 eV



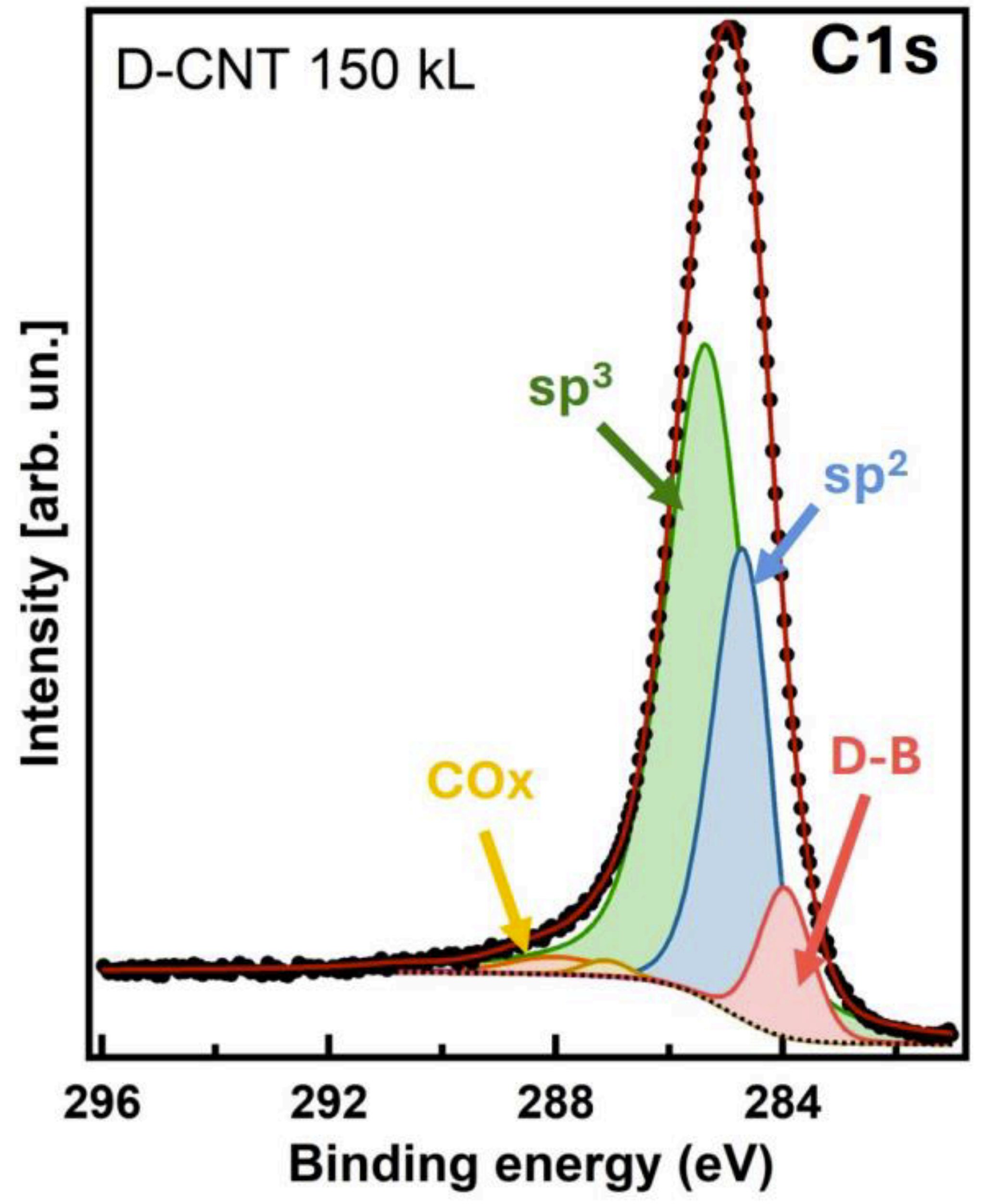


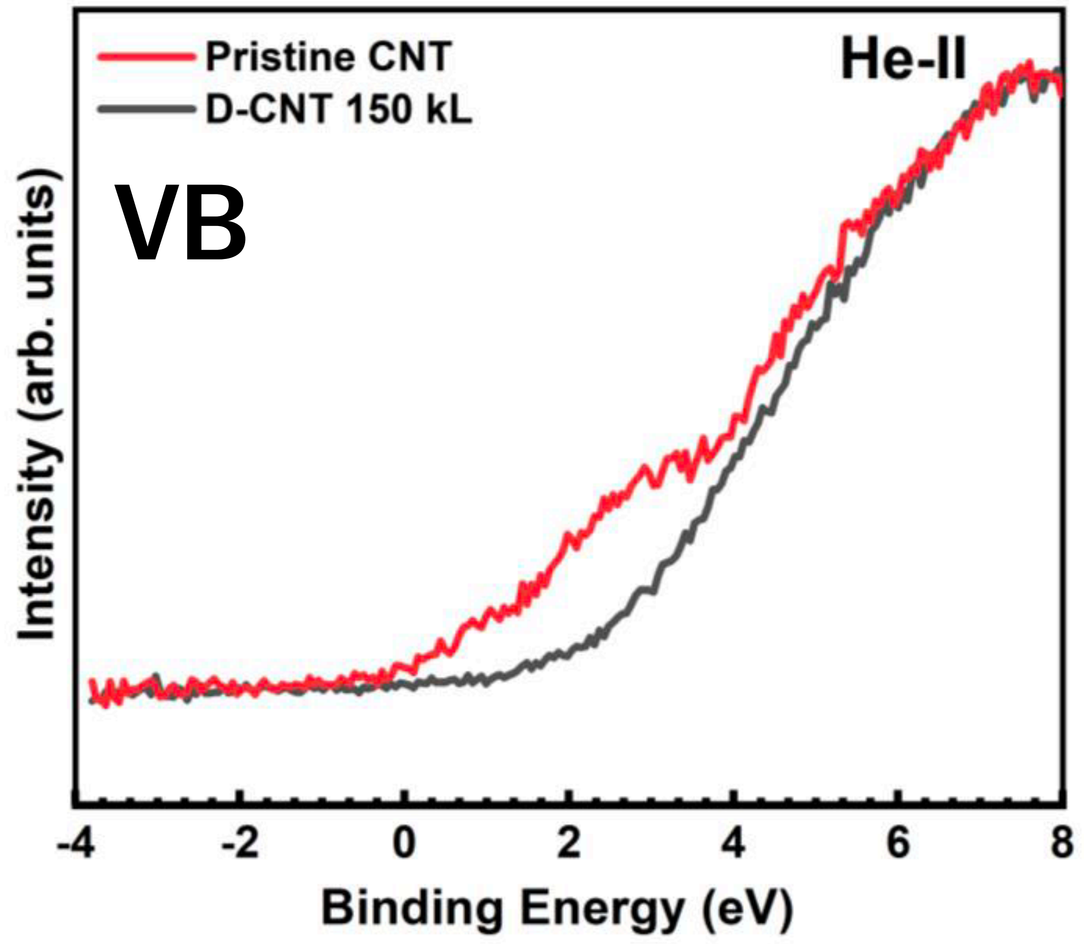
Atomic Deuterium bonding to Multi-Walled Carbon Nano Tubes

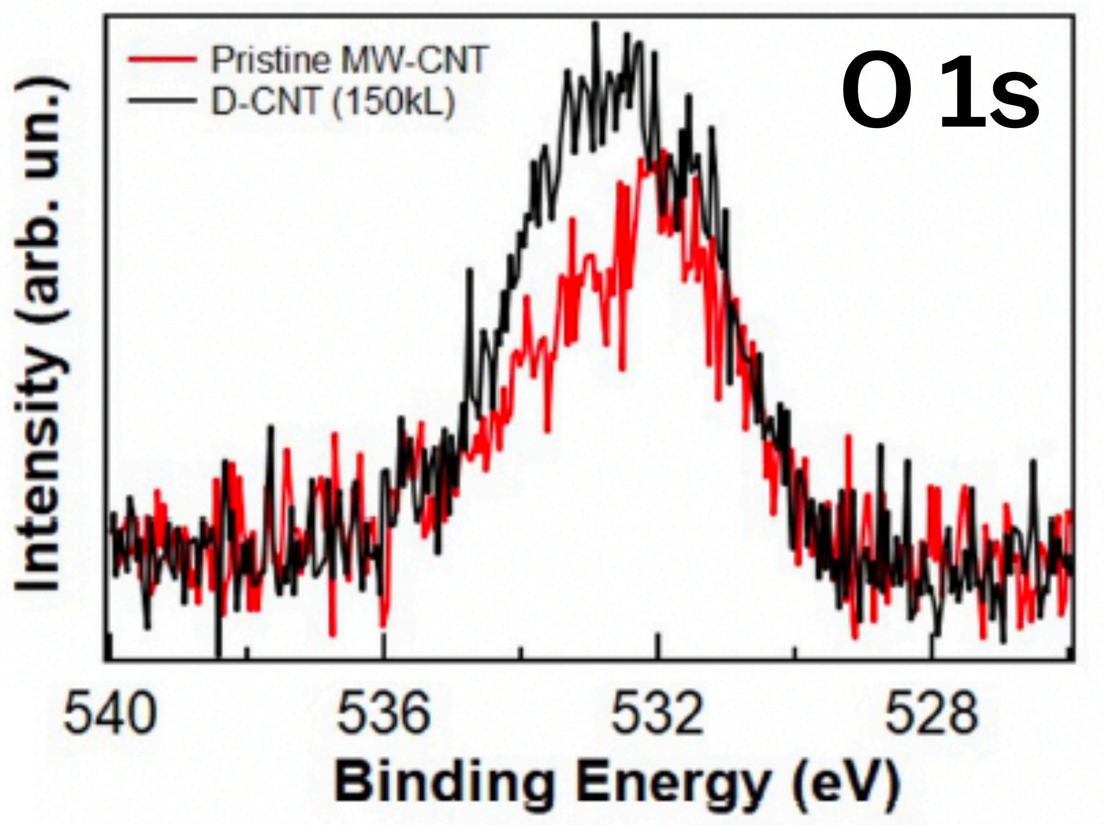
Sammar Tayyab et al., to be published

$I_{sp3} / (I_{sp2} + I_{sp3}) \simeq 70\%$

WF = 3.84 ± 0.05 eV







Key Insights and Future Steps

A successful plasma hydrogenation of CNT

- **sp^2** and **π plasmon** lowering, **sp^3** increasing
- **Work function** decreases
- **C-H** vibration appears
- **Gap** opening

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Large amount of hydrogen!

Is it hydrogenated also in depth?

...but it is not perfectly clean

Also **C-O** and **C=O** increase

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Present/Future steps:

1. **Compare thermal cracking and plasma hydrogenation in depth**

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Present/Future steps:

1. **Compare thermal cracking and plasma hydrogenation in depth**
2. Make plasma hydrogenation **during CNT growth**

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A successful plasma hydrogenation of CNT

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Large amount of hydrogen!

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...but it is not perfectly clean

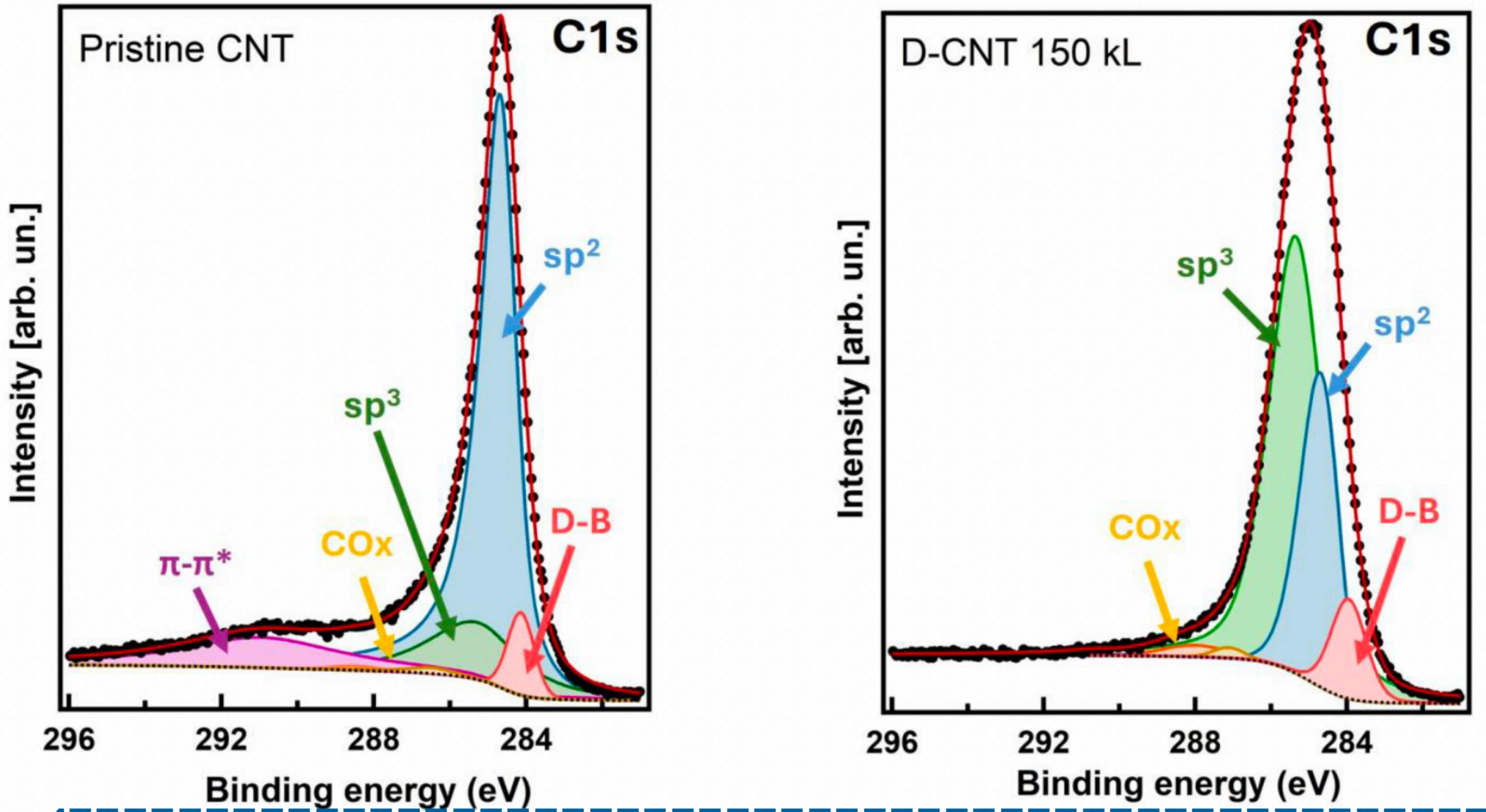
Also **C-O** and **C=O** increase

Present/Future steps:

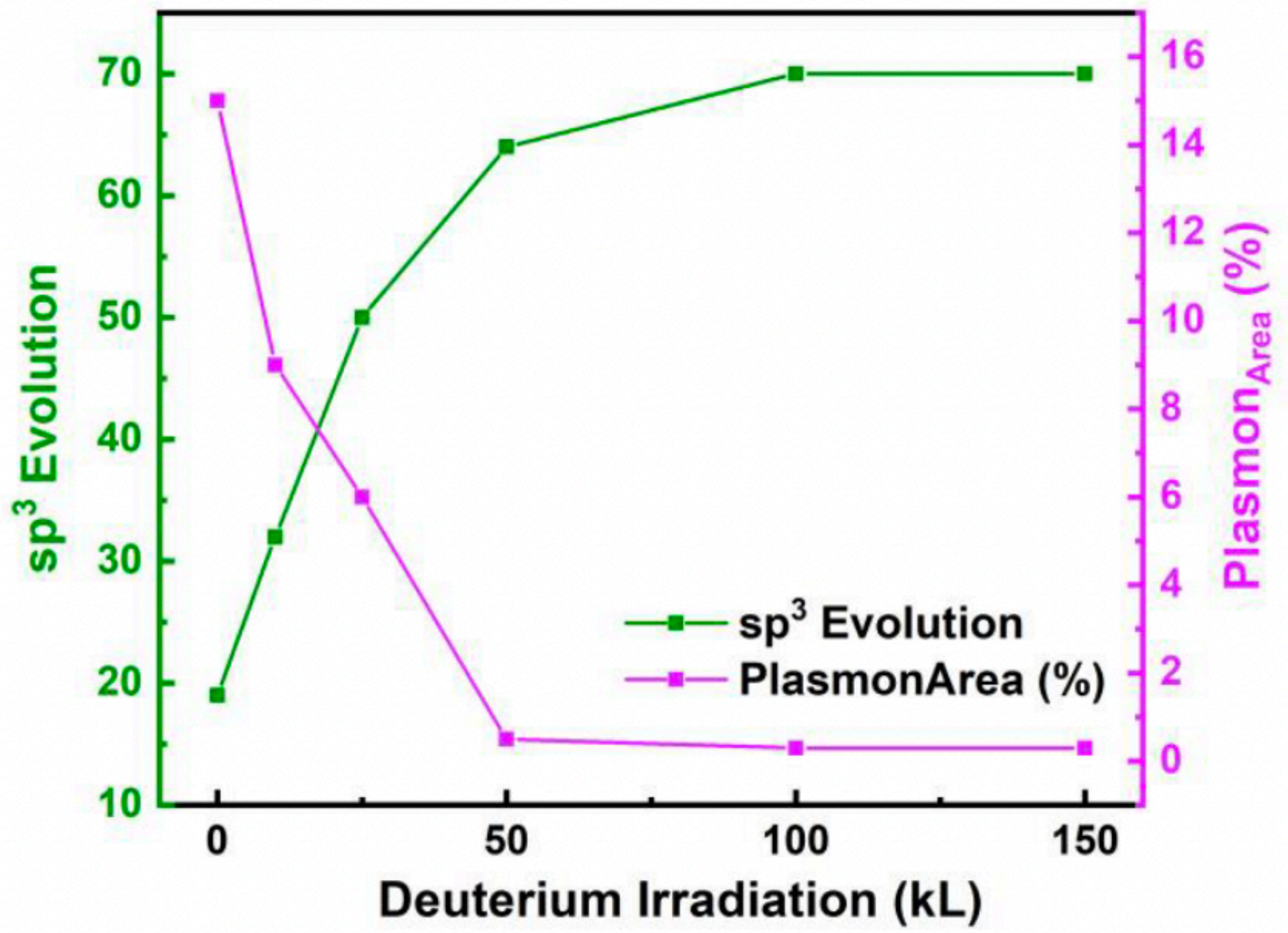
1. **Compare thermal cracking and plasma hydrogenation in depth**
2. Make plasma hydrogenation **during CNT growth**
3. Fine tuning of the parameters to **limit oxygen contaminations**

Back-up

C1s core level lineshape of Pristine and Highly Deuterated CNT sample. A Quantitative Analysis:



	Pristine MWCNTs	D-CNT (150 kL)
Atomic D upload [sp3/(sp3+sp2)]	19%	70%



sp^2 component representative of perfect planar C bonding.

sp^3 component is a sign of bond deformation and D C bonds.

plasmon associated to the π collective excitations.

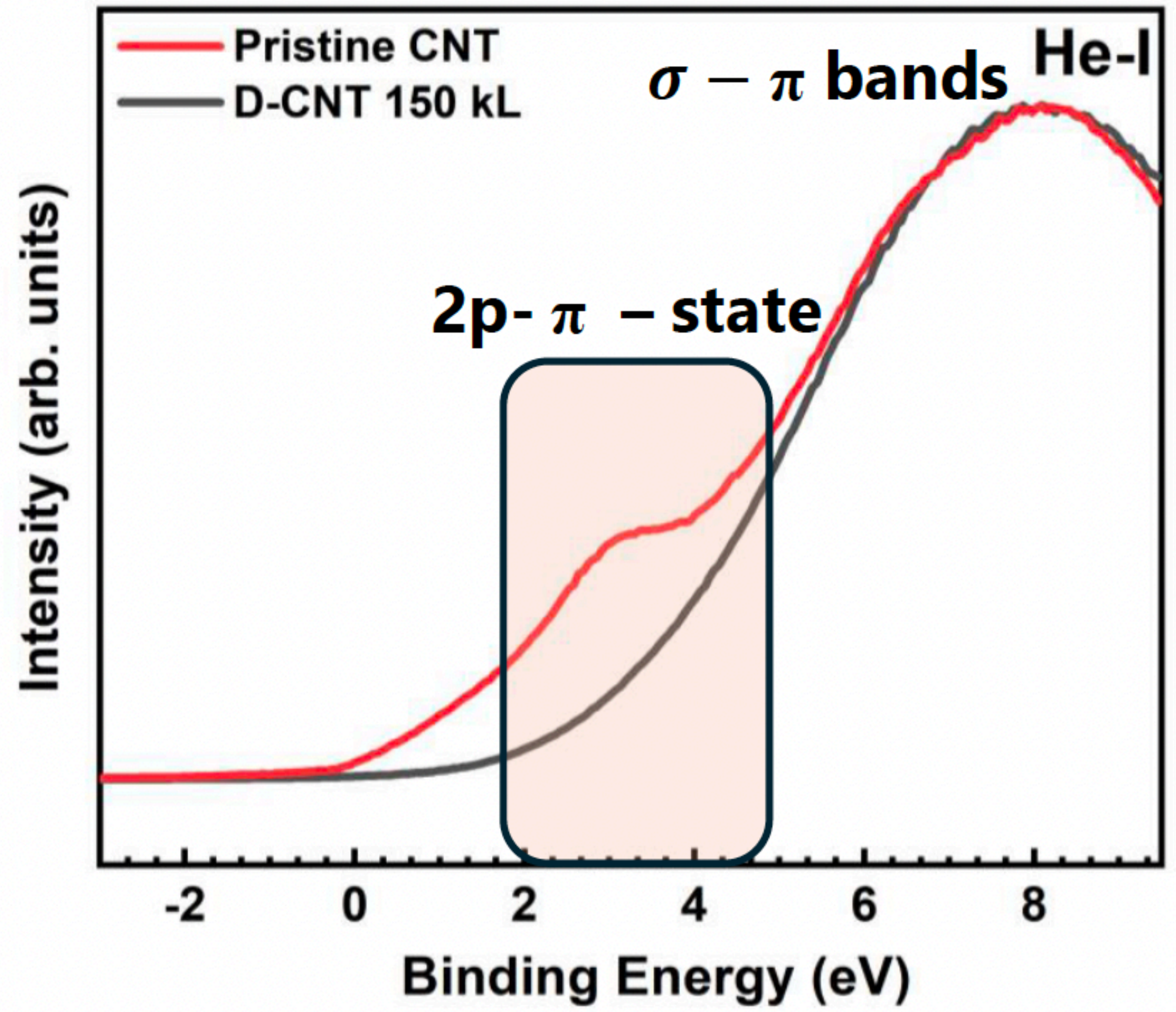
*** ~ 50% D-nanoporous graphene**

* Mahmoud Mohamed Saad Abdelnabi et al, Nanomaterials (2021), 11, 130.

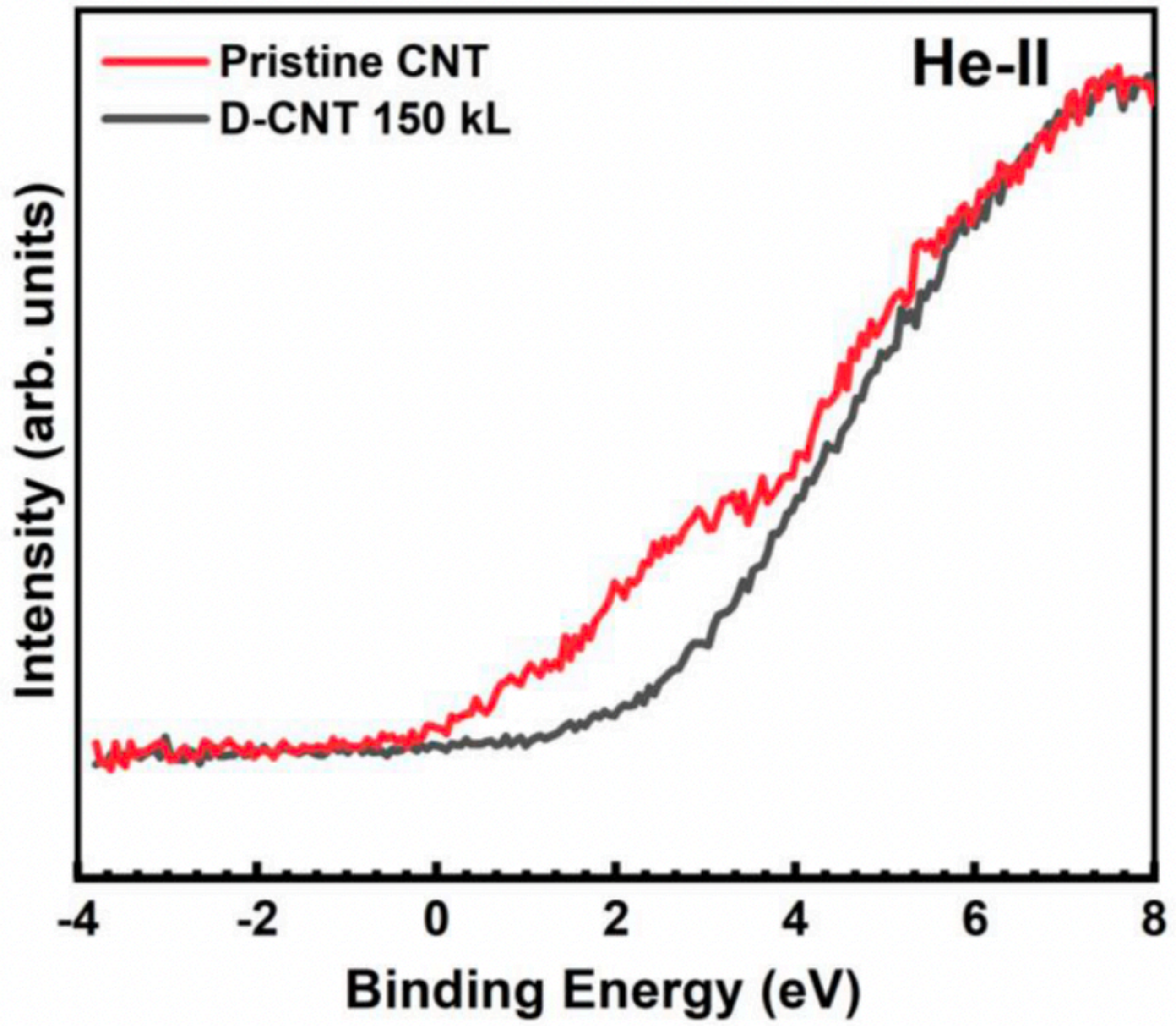
Ultraviolet Photoelectron Spectroscopy:

Valence bands Collection:

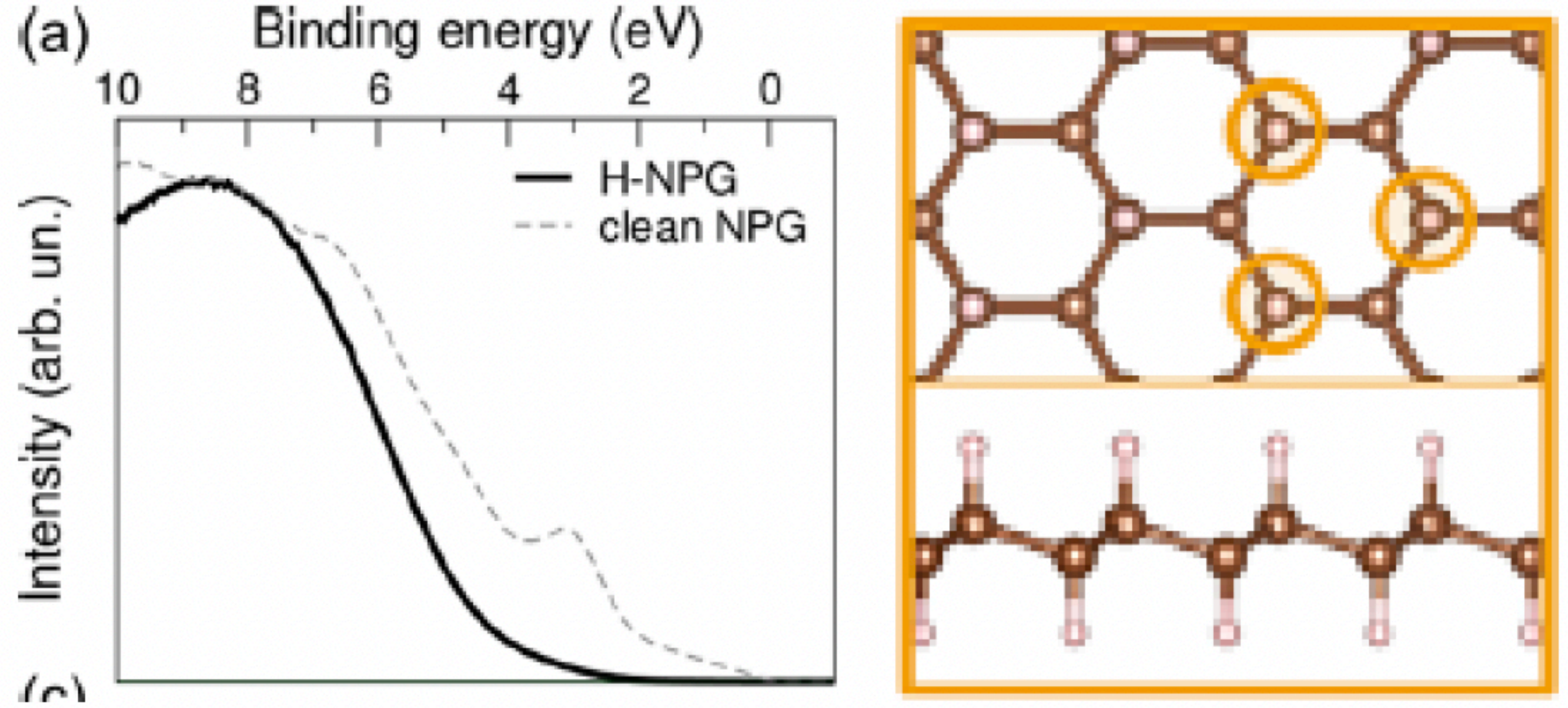
(He I photon energy 21.22 eV)



(He II photon energy 40.81 eV)



2side H-Gr



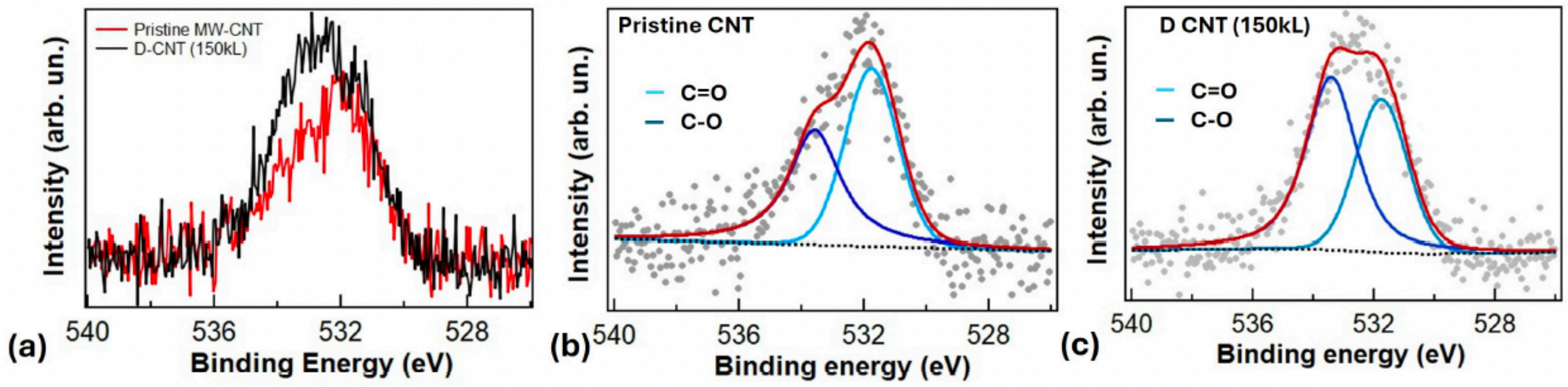
VB spectra of clean and H-Gr taken with He I.

Reduction in of 2p- π – states at 3.5 eV in D-CNT sample and

↓

Decrease in C2p- π electrons and
Reduction of graphitic carbon content

Reference: Nano Lett. 2022, 22, 2971–2977



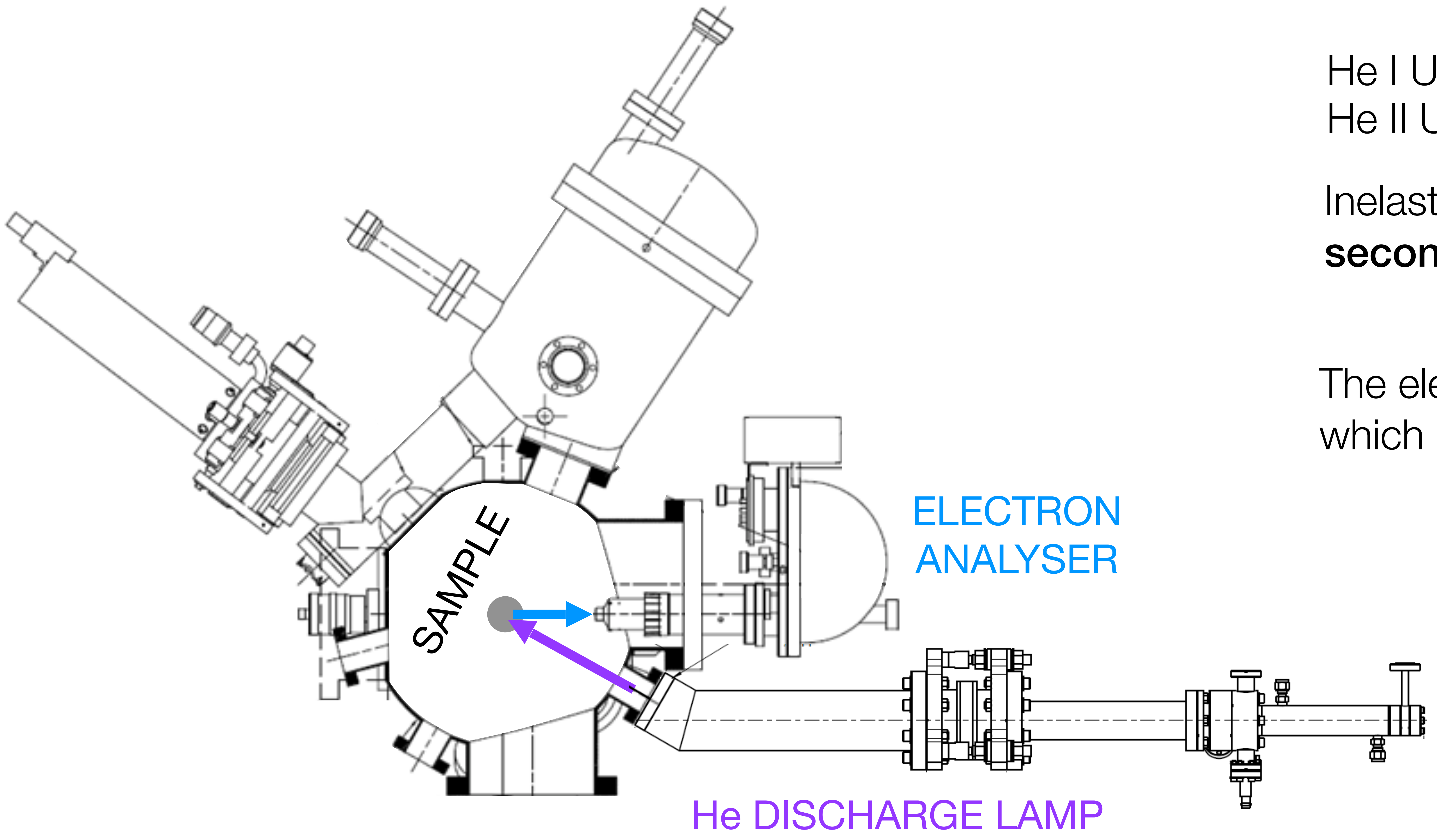
C1s component	BE (eV)	Δ BE (eV)	FWHM (eV)	Area/Area$_{total}$	Θ (%)
sp^2	284.7	0	1.1	63	19
sp^3	285.3	0.6	2.9	16	
C-O	286.5	1.8	1.5	0.8	
C=O	288.5	3.8	1.5	0.4	
π - excitation	290.9	6.2	5.0	15	
vacancy - DB	284.1	-0.6	0.8	4	

Pristine MW-CNT			
O1s component	BE (eV)	FWHM (eV)	Area/Area$_{total}$
C=O	531.8	2.1	302
C-O	533.5	1.9	276
D-CNT MW-CNT			
O1s component	BE (eV)	FWHM (eV)	Area/Area$_{total}$
C=O	531.8	1.9	335
C-O	533.4	2.1	481

C1s component	BE (eV)	Δ BE (eV)	FWHM (eV)	Area/Area$_{total}$	Θ (%)
sp^2	284.7	0	1.1	27	70
sp^3	285.3	0.6	1.8	62	
C-O	286.8	2.1	1.0	0.6	
C=O	288.0	3.3	2.1	1.6	
π - excitation	290.9	6.2	2.0	0.3	
vacancy - DB	284.0	-0.7	1.1	8	

UV **P**hotoelectron **S**pectroscopy technique and setup

The work function of a sample can be measured with **UPS**

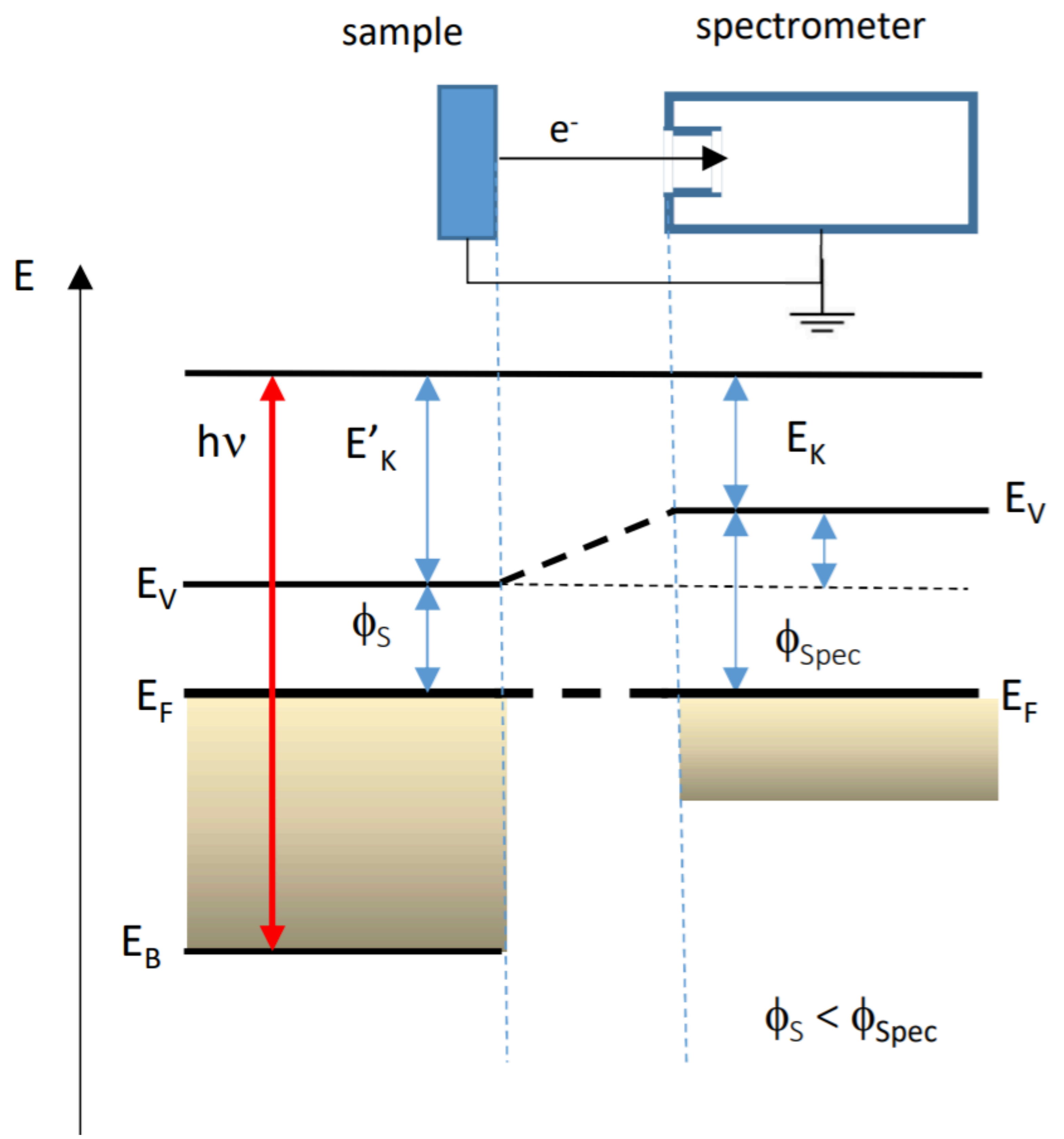


He I UV photon energy: hv = 21.22 eV
He II UV photon energy: hv = 40.8 eV

Inelastically scattered photoelectrons produce **secondary electrons**

The electrons emitted are collected by an electron analyzer which measures their **kinetic energy**

How to measure a **Work Function**

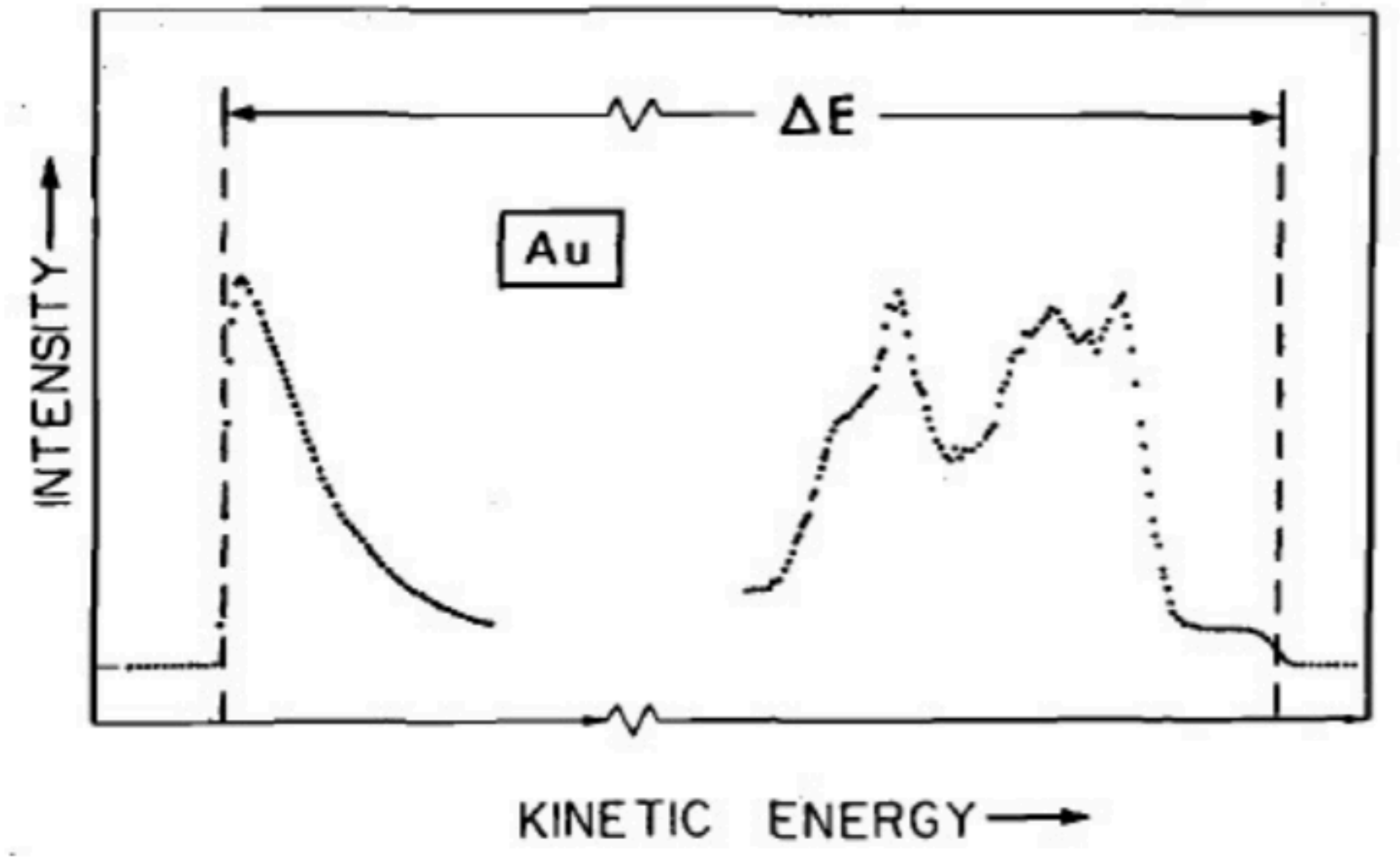


Analyzer point of view

$$E_K^{min} = \phi_S - \phi_{Spec}$$
$$E_K^{max} = h\nu - \phi_{Spec}$$

$$\Delta E_K = E_K^{max} - E_K^{min} = h\nu - \phi_S$$

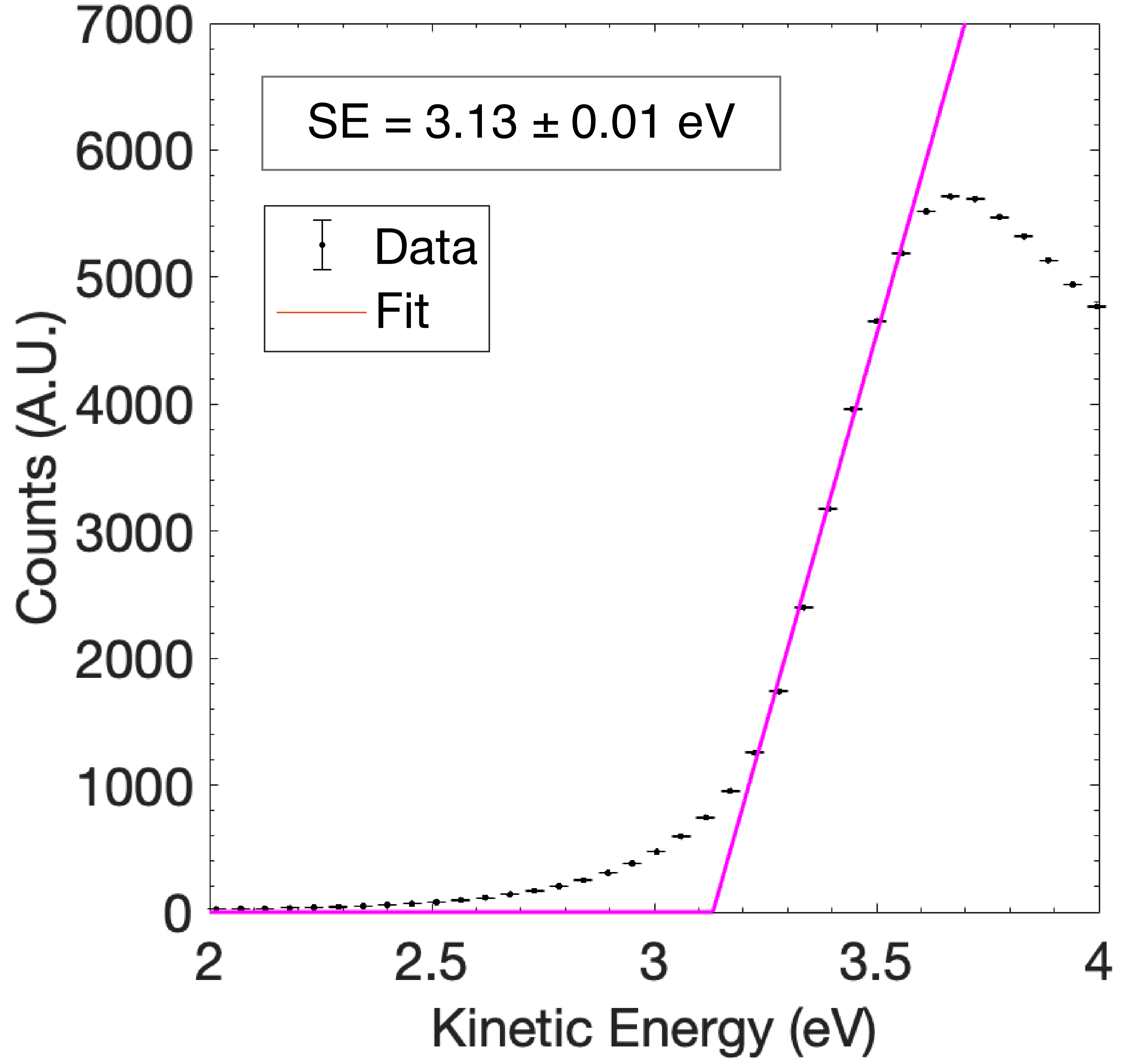
- **E_K max does not depend on the sample** but only on the analyzer's work function
- **E_K min depends on the sample and on the analyzer**
- **ΔE_K depends only on the sample**



- a **potential difference** is applied to the sample with respect to the analyzer in order to measure the secondary electron onset

Fitting procedure and calculation of ϕ_{CNT}

Secondary onset



Linear Fit

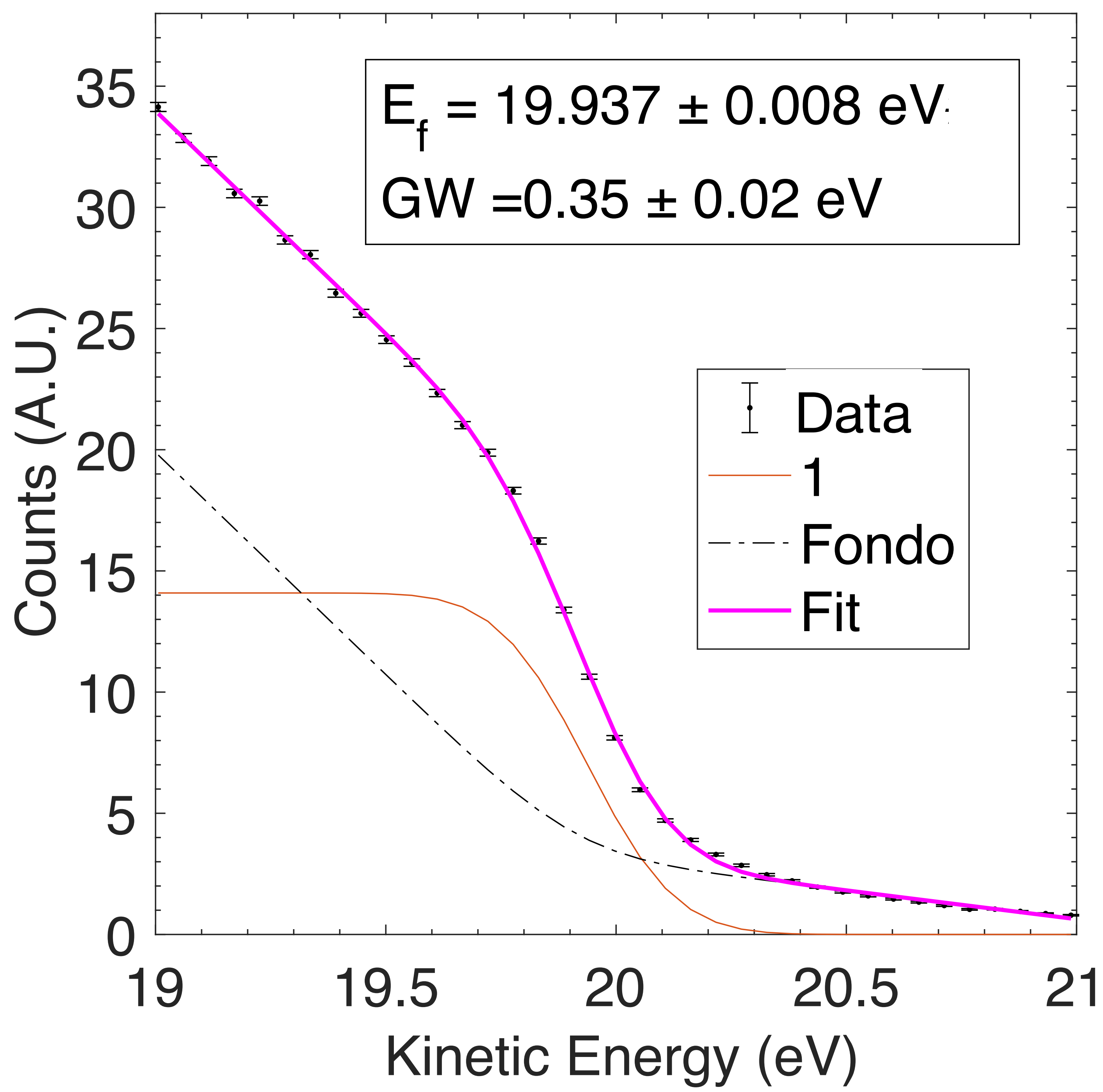
$$y = m\,x + q$$

$$SE = -\,q\,/\,m$$

Sample polarized to $V_B = -3$ V

Measured on a metal clip on the sample holder

Fermi Level



Fermi function convolution with a gaussian

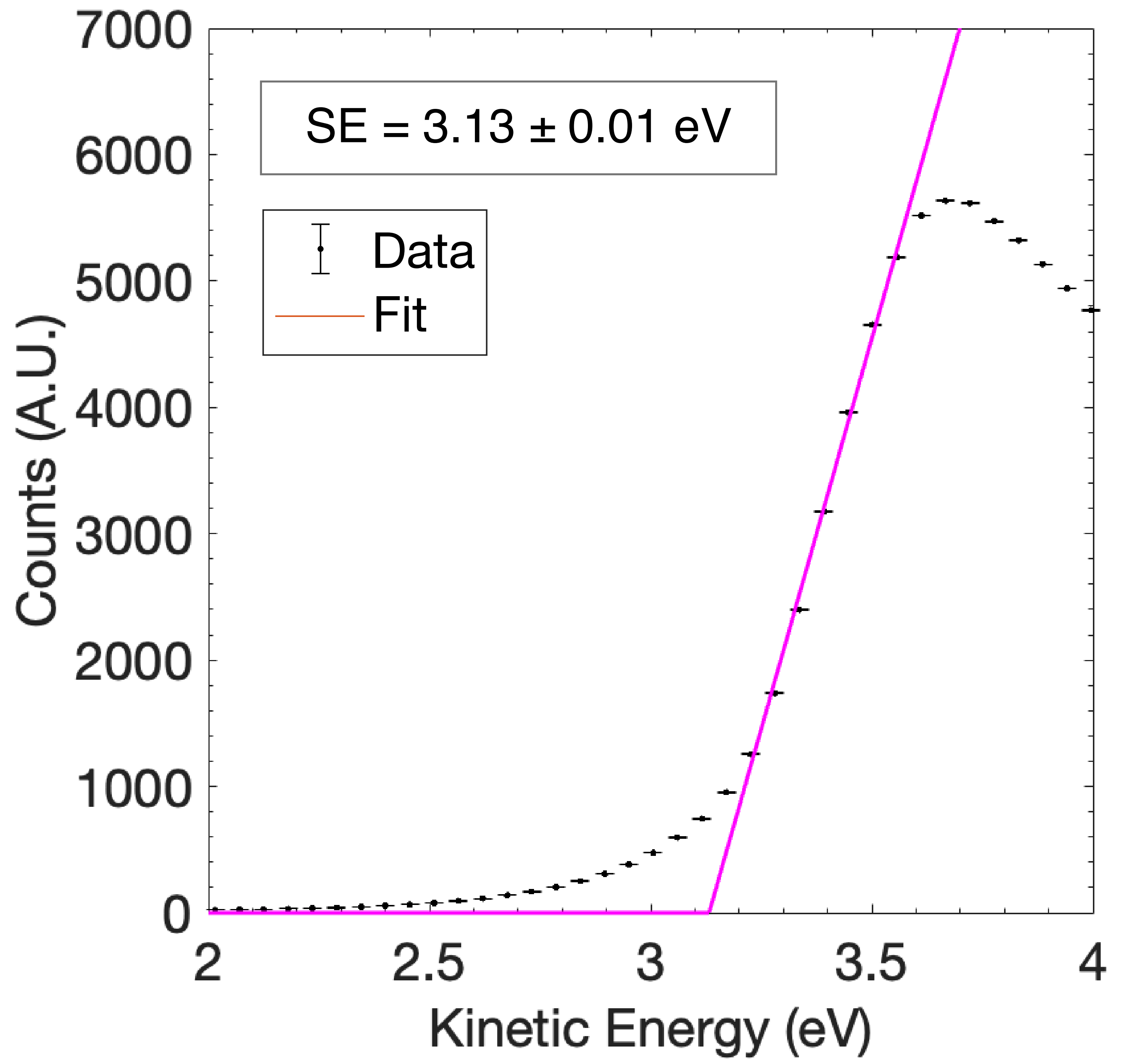
$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

kT is fixed at 25 meV (T = 293 K)

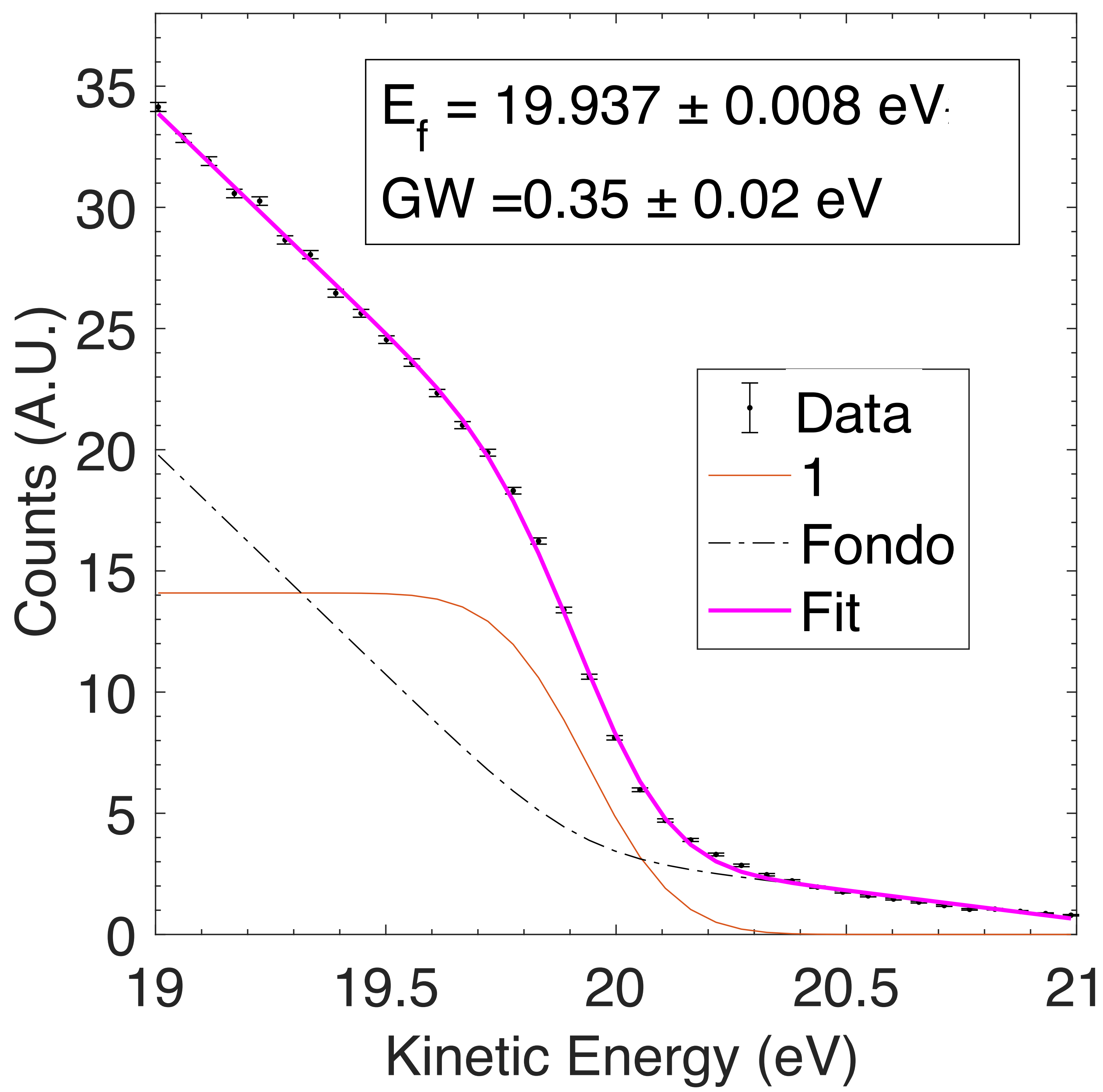
$$\phi_{sample} = h\nu - \Delta E_k = h\nu - (E_f - SE)$$

Uncertainty treatment

Secondary onset



Fermi Level



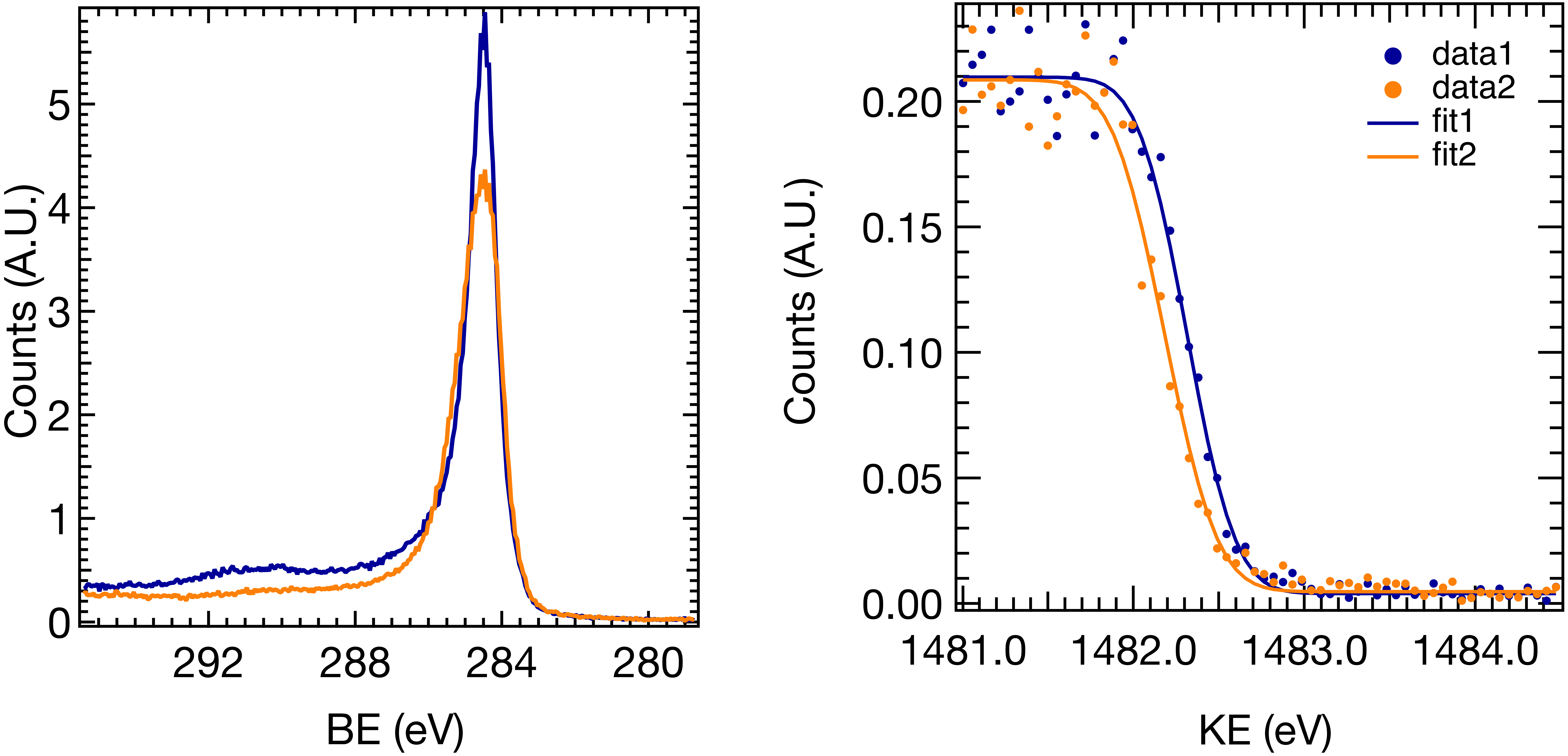
ϕ_{sample} = hν - ΔE_k = hν- (E_f - SE) = 21.22 - (19.937-3.13) = **4.41** eV

What about the uncertainty?

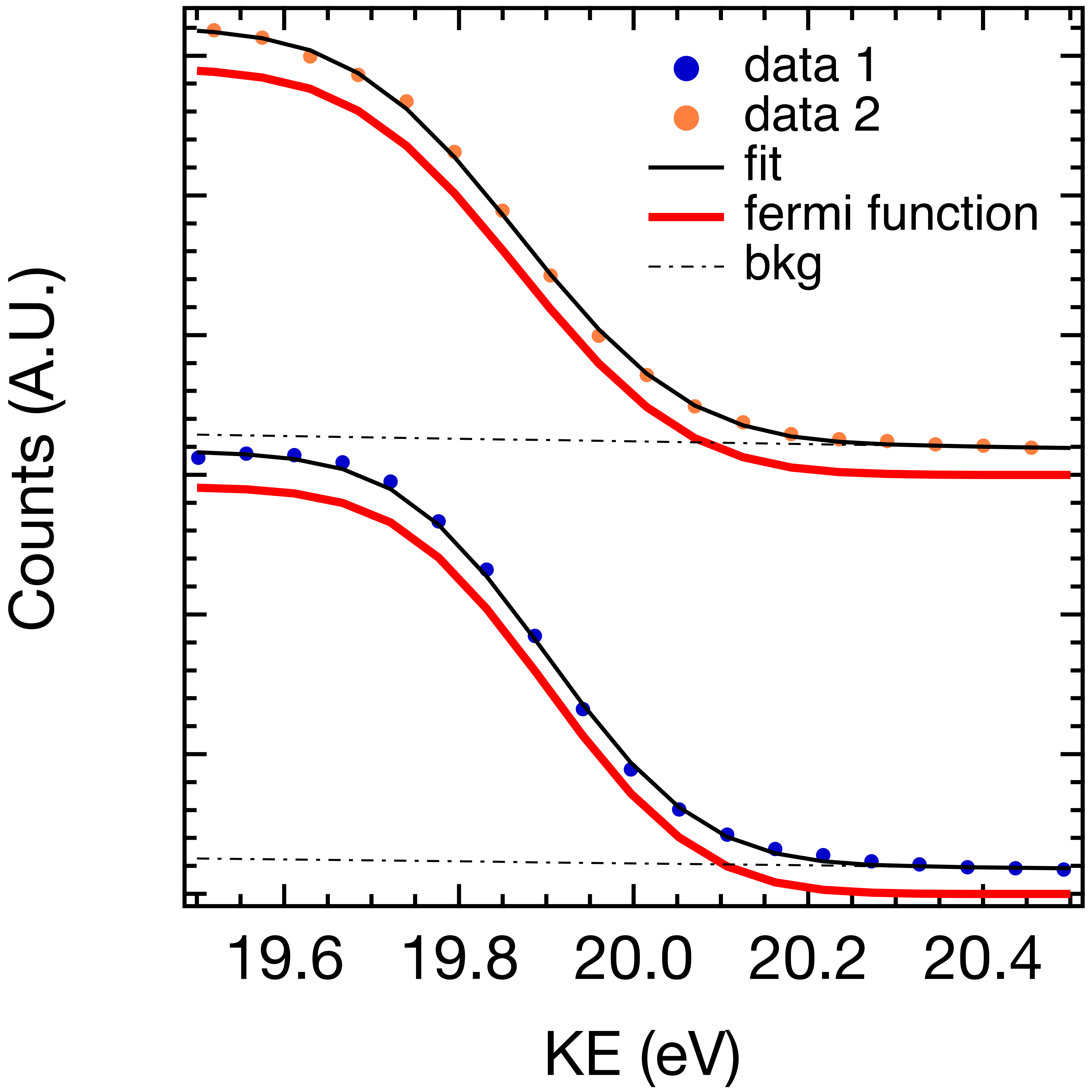
the **SE onset strongly depends on how the data points for the fit are selected**

choosing different “windows” of data points in the linear rising region **± 0.05 eV should be a reasonable value**

XPS C 1s plot + FL

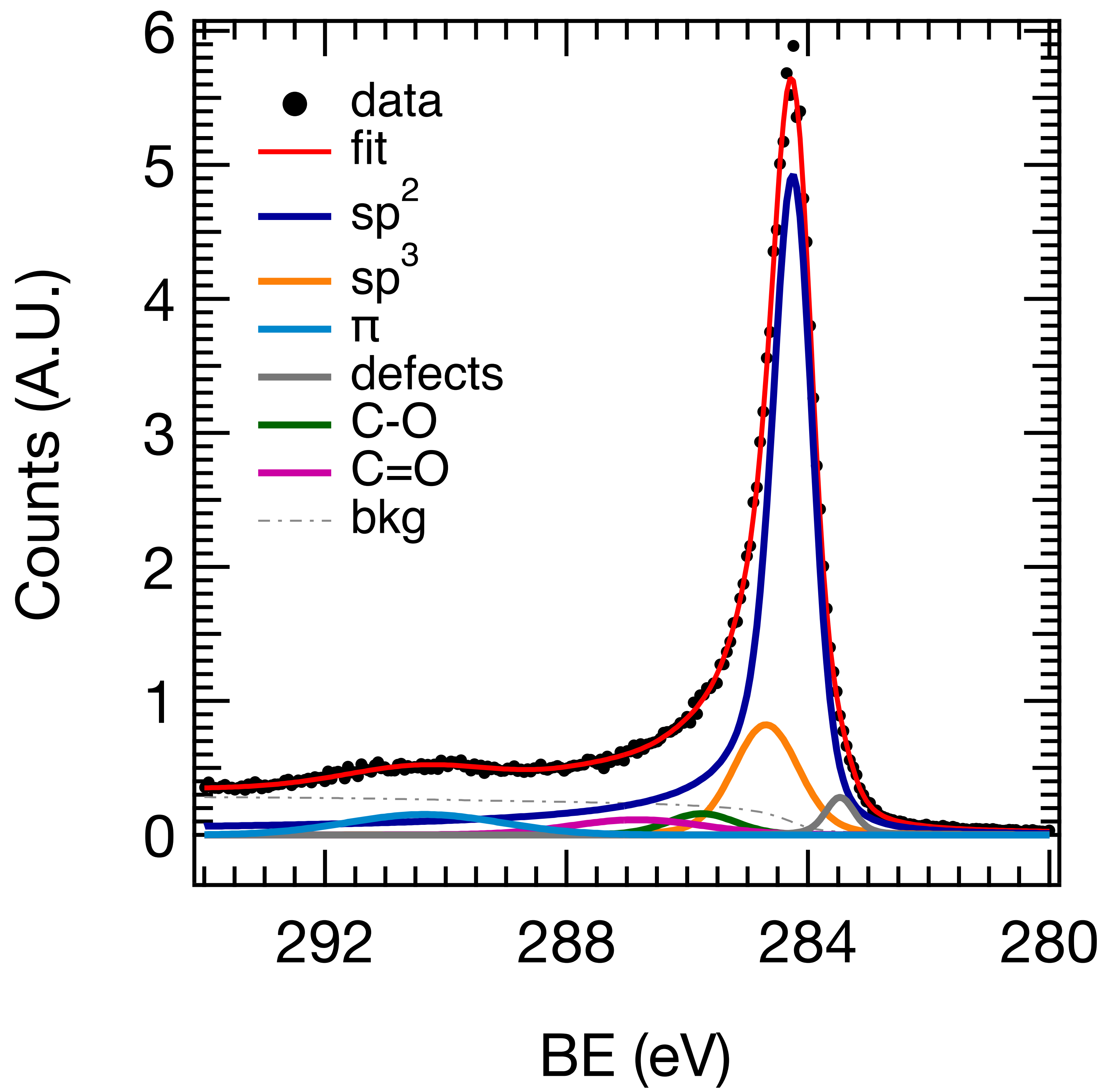


UPS FL



data 1
data 2
fit
fermi function
bkg
Counts (A.U.)
19.6
19.8
20.0
20.2
20.4
KE (eV)

C 1s plot

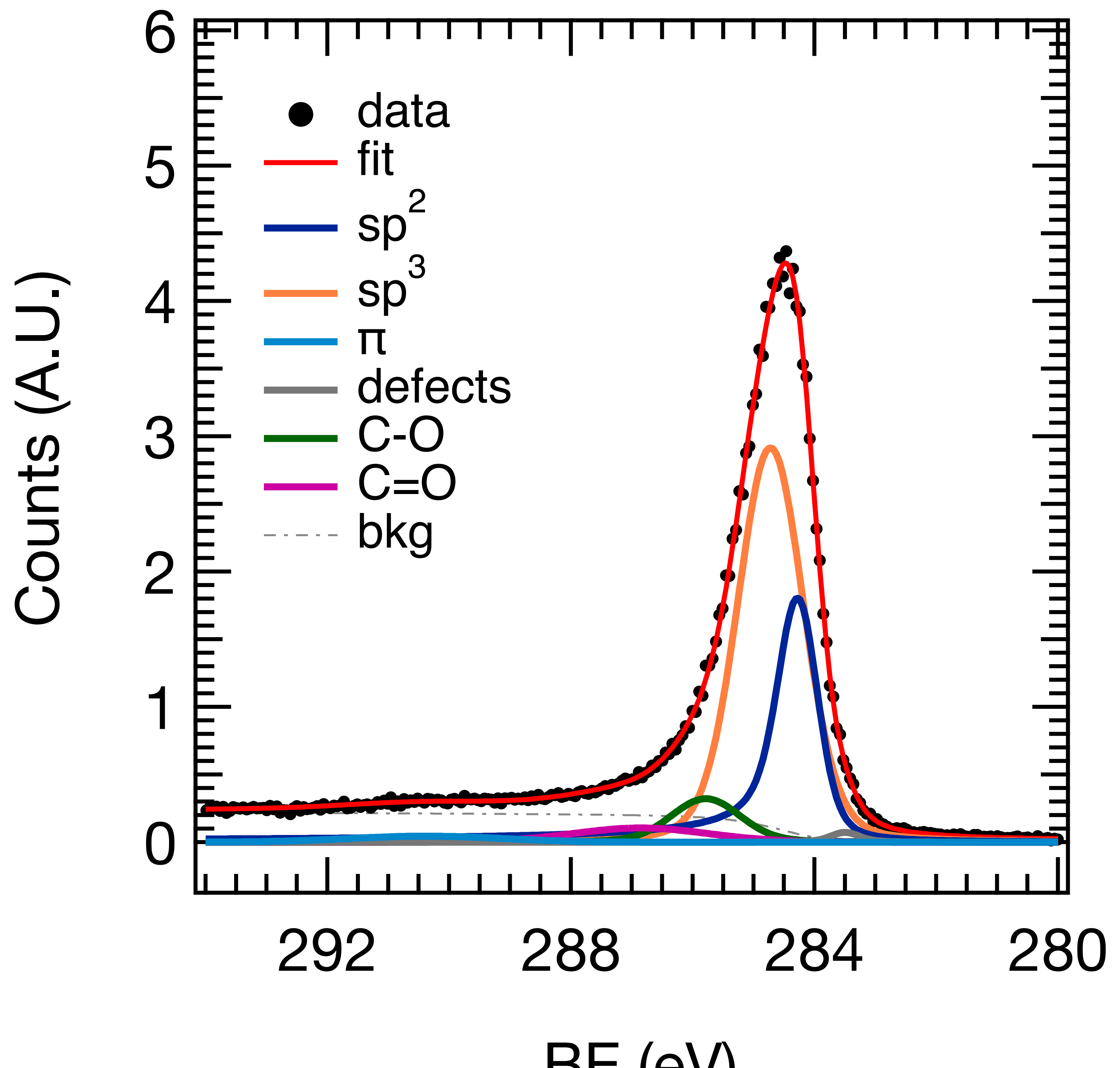


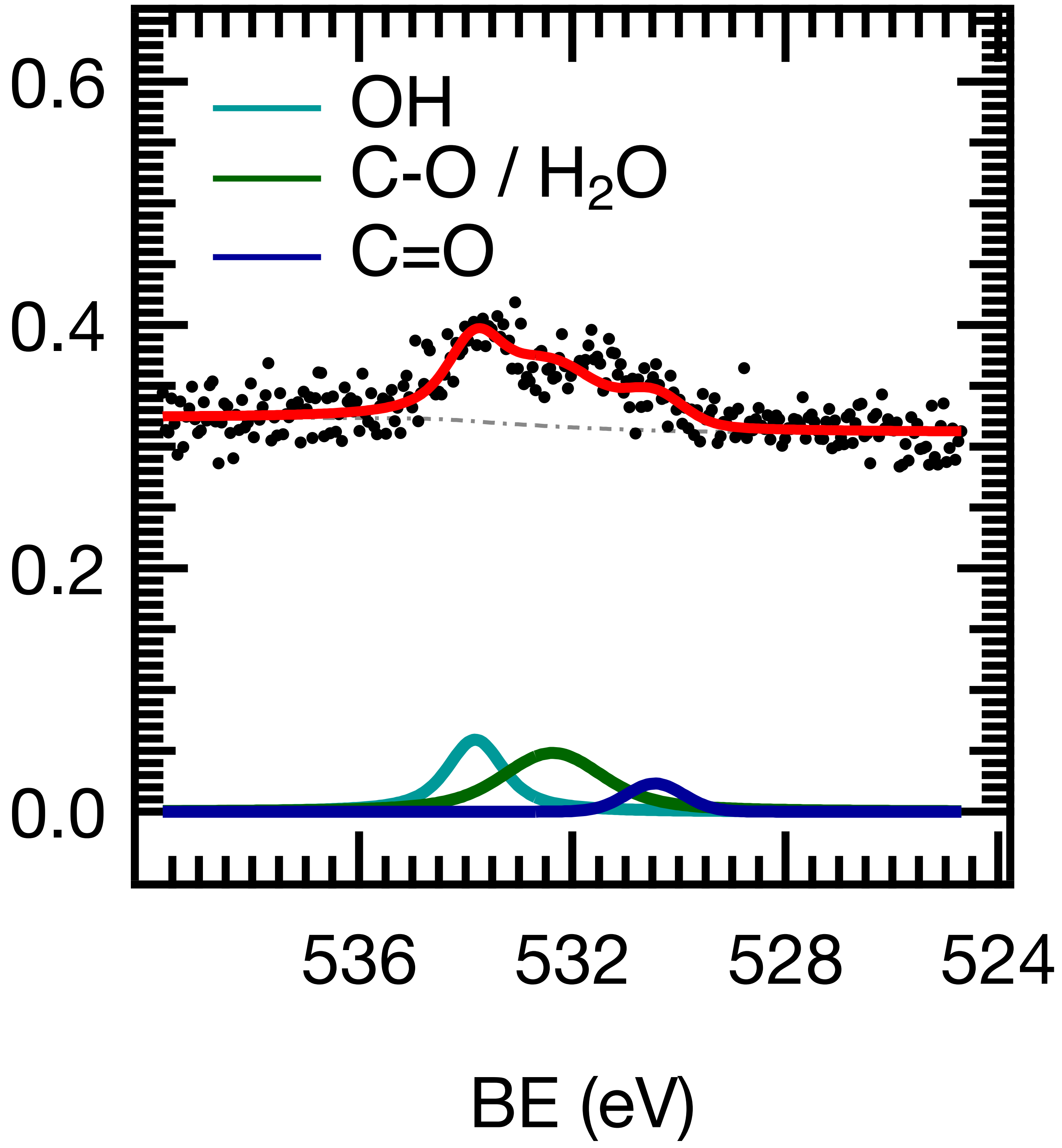
CNT_clean	8.64 ± 0.02

Asymmetry	Amp	Ek (eV)	GW	LW
0.100	5.73 ± 0.18	284.38 ± 0.02	0.62 ± 0.01	0.23 ± 0.01
0.00	1.19 ± 0.21	-0.48 ± 0.04	1.15 ± 0.06	
0.00	0.49 ± 0.23	-6.14 ± 0.07	3.00 ± 1.00	
0.00	0.20 ± 0.03	0.74 ± 0.03	0.44 ± 0.07	
0.00	0.24 ± 0.14	-1.55 ± 0.20	1.21 ± 0.27	
0.00	0.32 ± 0.16	-2.62 ± 0.55	2.50 ± 0.75	

CNT_H	7.48 ± 0.02

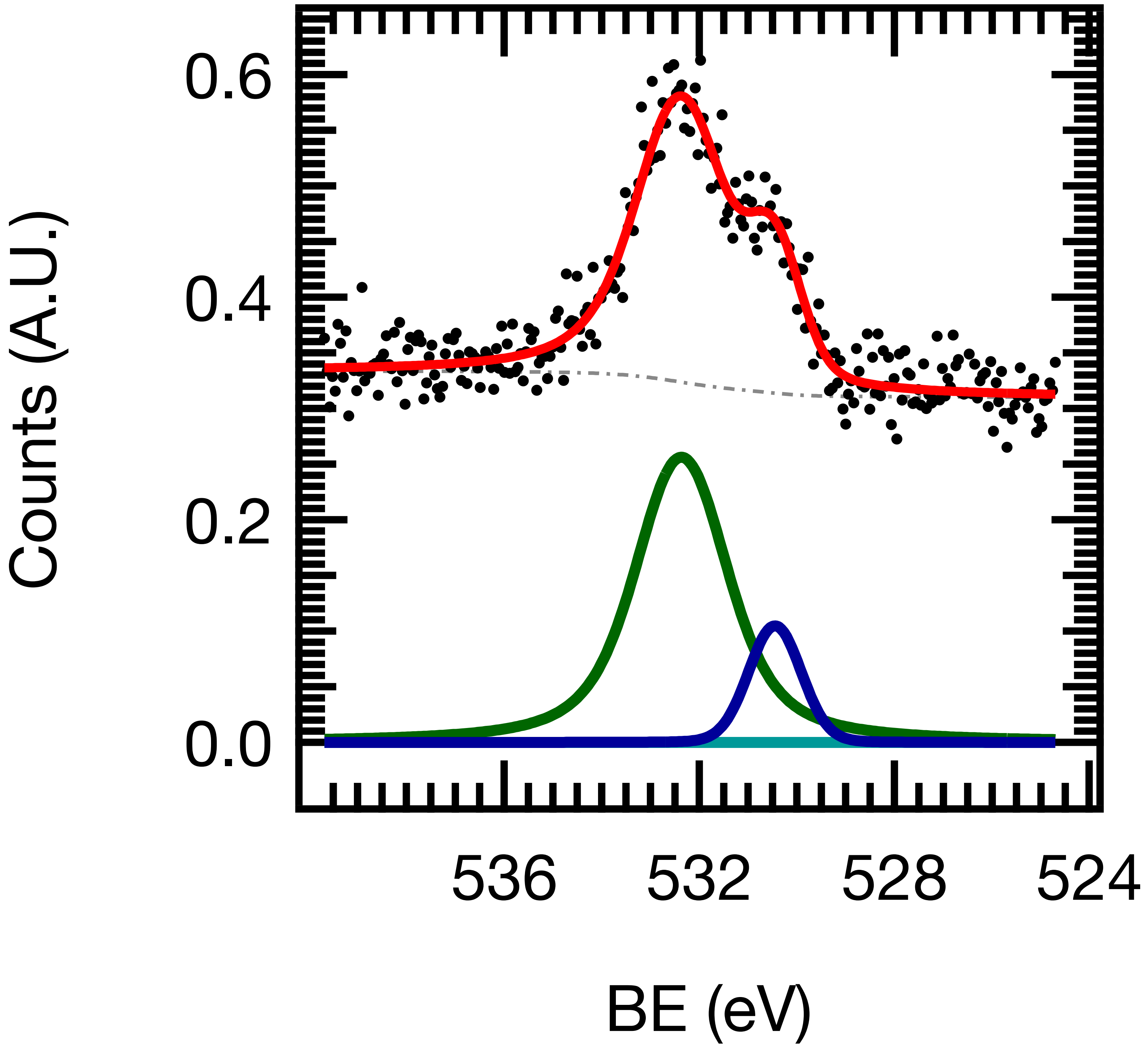
	Asymmetry	Amp	Ek (eV)	GW	LW
0.28	0.100	2.09 ± 0.23	284.27 ± 0.02	0.62 ± 0.01	0.23 ± 0.01
0.56	0.00	4.20 ± 0.33	-0.48 ± 0.04	1.15 ± 0.06	
0.02	0.00	0.14 ± 0.07	-6.14 ± 0.07	3.00 ± 1.00	
0.01	0.00	0.05 ± 0.03	0.74 ± 0.03	0.44 ± 0.07	
0.06	0.00	0.48 ± 0.25	-1.55 ± 0.20	1.21 ± 0.27	
0.04	0.00	0.30 ± 0.16	-2.62 ± 0.55	2.50 ± 0.75	



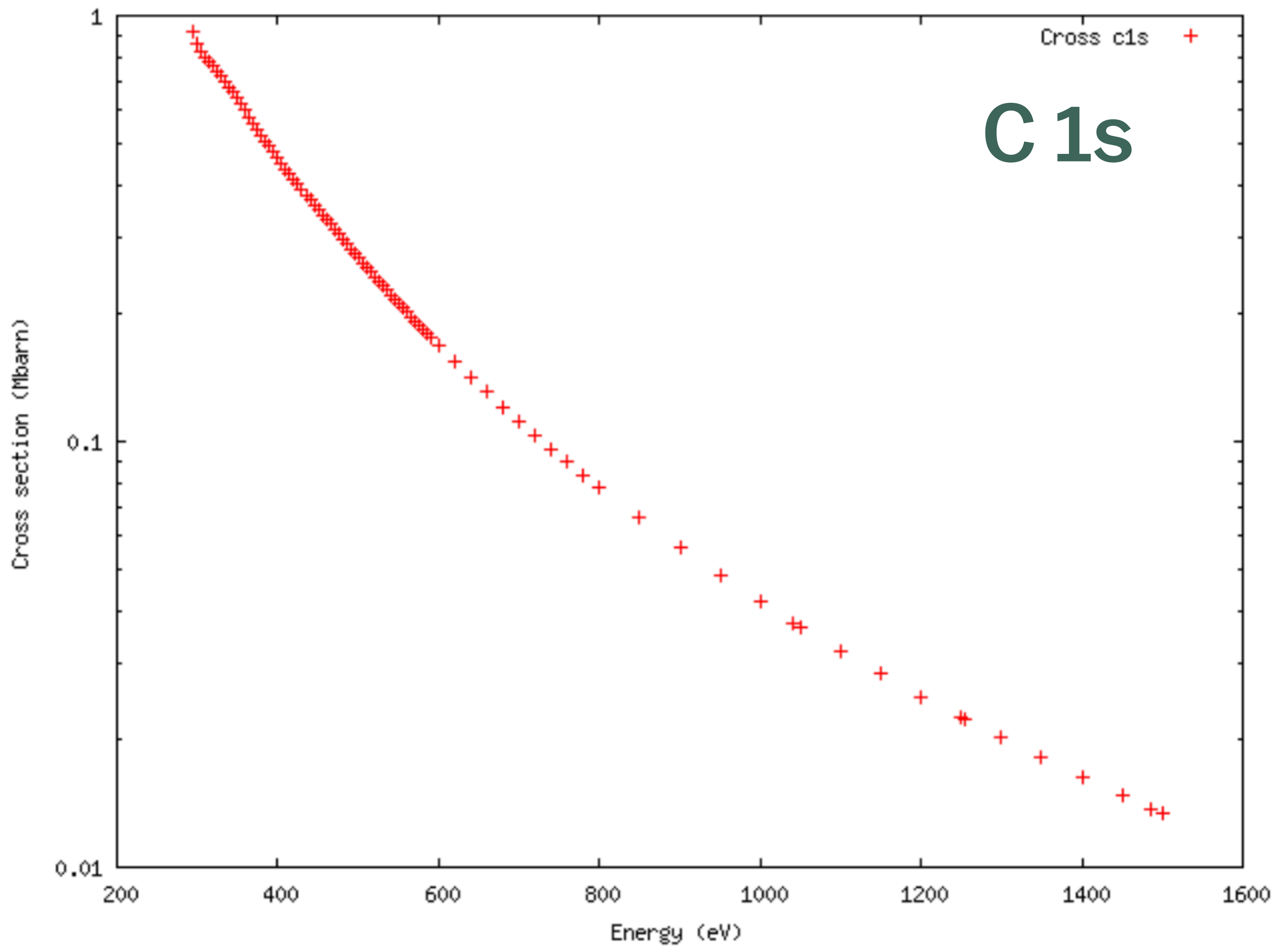


Asymmetry	Amp	Ek (eV)	GW	LW
0.00	0.10 ± 0.03	0.00	0.00	0.00
0.00	0.13 ± 0.03	0.00	0.00	0.00
0.00	0.03 ± 0.01	0.00	0.00	0.00

Asymmetry	Amp	Ek (eV)	GW	LW
0.00	0.00 ± 0.04	948.38 ± 0.07	0.65 ± 0.84	0.92 ± 0.82
0.00	0.71 ± 0.10	949.83 ± 0.05	1.51 ± 0.38	1.22 ± 0.47
0.00	0.14 ± 0.05	951.75 ± 0.08	1.23 ± 0.41	0.08 ± 0.71



XPS cross sections



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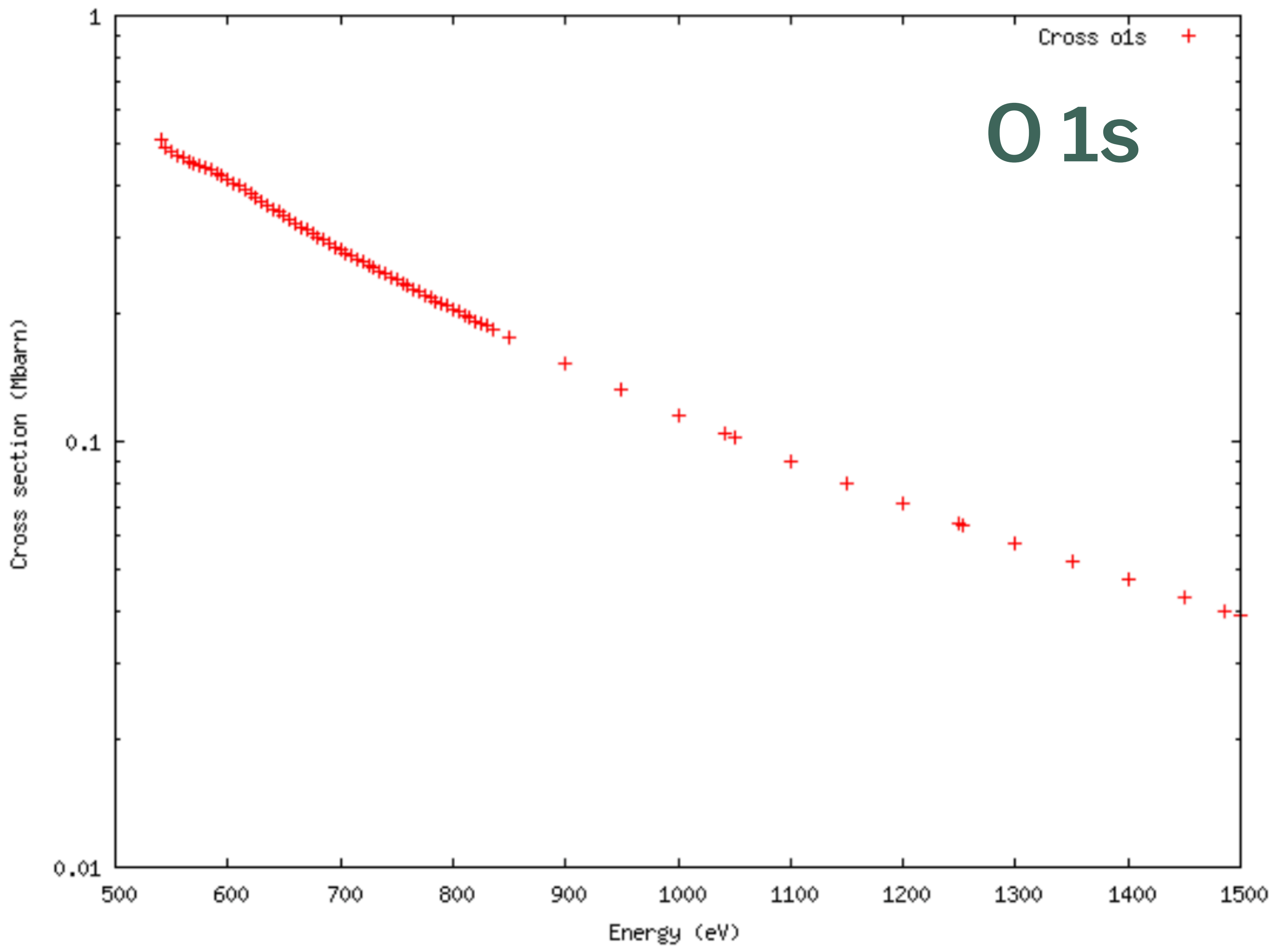

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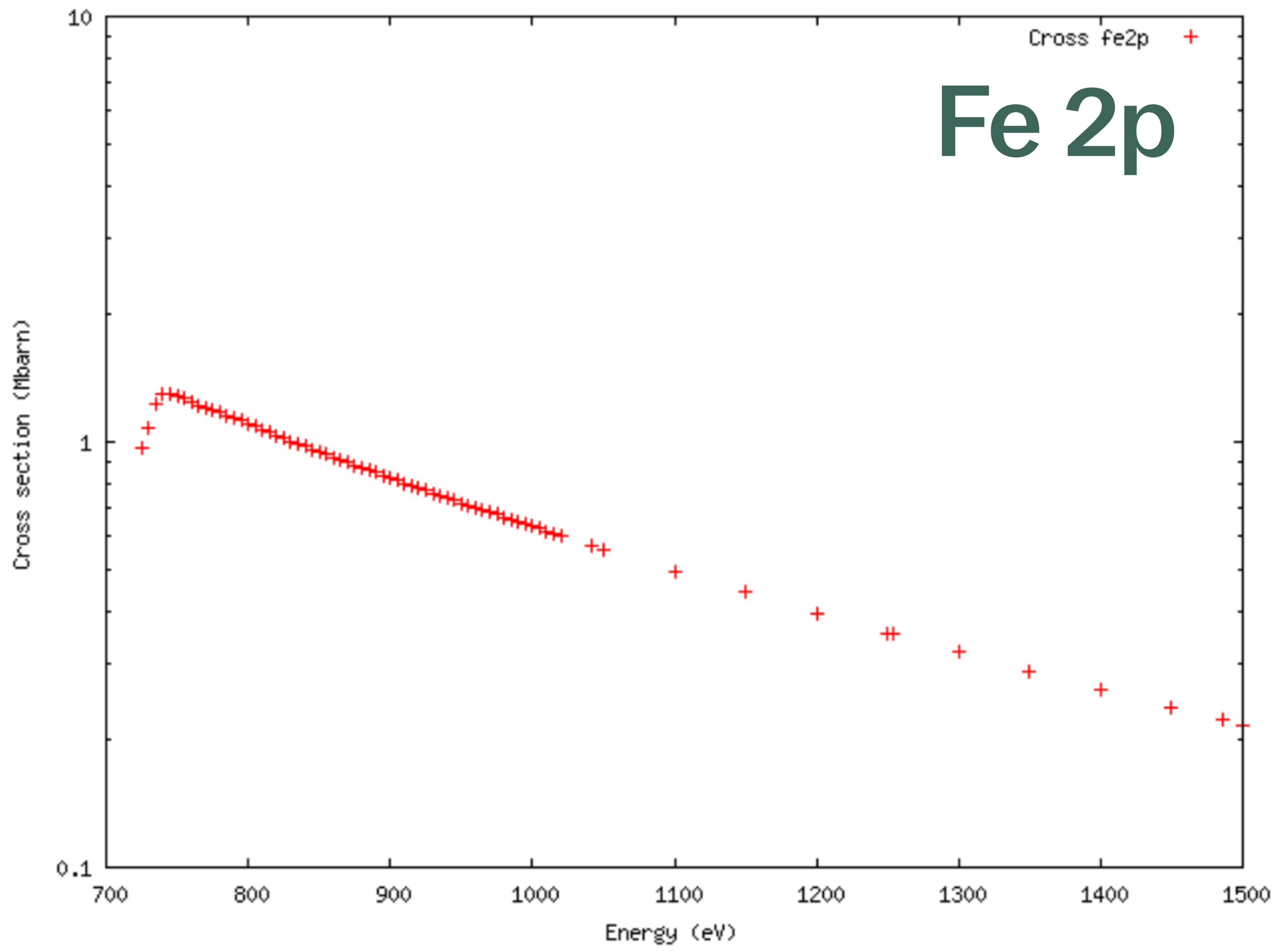

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