X-ray absorption spectroscopy study of electronic and structural properties of volcanic ashes and carbon nanotubes probed for the sorption of chromium

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Plan

Introduction

I-Review basics of x-ray absorption spectroscopy (XAS) theory

II-Basic notions on volcanic ash materials

III-Basic notions on carbon nanotubes materials

IV-Location of Cameroon volcano and sampling area

V-Sorption experiments for Chromium

VI.1-Electronic properties on volcanic ash

VI.2-Electronic properties on carbon nanotubes

VII.1-Structural properties on volcanic ash

VII.2-Structural properties carbon nanotubes

Conclusion

Introduction

Objective of XAS
an understanding of physical properties of materials based on knowledge of their local structure

- X-ray absorption spectroscopy (XAS) provides electronic, chemical and structural information on the material through the spectrum of x-ray absorption coefficient.
- Determination of: chemical environment and composition, number and type of its neighborhood atoms, interatomic distance, structural disorder.
- Does not require a long-range order (distance from 5 to 10 Å radius).
- Selective technique for a specific element.
- Appropriate to: amorphous and crystalline; solid, liquid and gas.

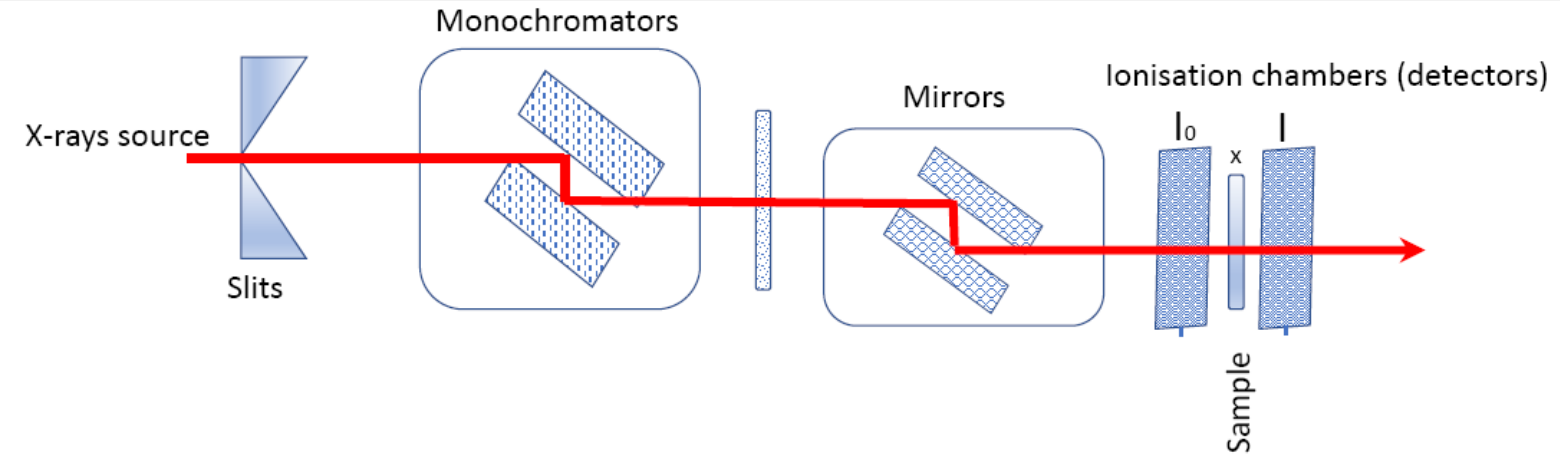
In this presentation, XAS is applied to characterize the chromium sorbed volcanic ash (VA) and carbon nanotube (CNTs) materials **with the aim to understand their electronic and structural properties**.

- The VA are from the Cameroon volcanic line collected at Djoungo in Littoral region in Cameroon.
- The CNTs are synthesized by chemical vapor deposition method.

Application in wastewater treatment.

I-X-ray absorption spectroscopy (XAS)

Beam attenuation of x-ray

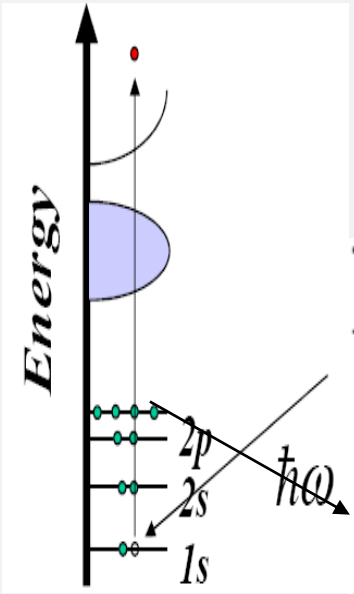


Exponential attenuation of x-ray: Beer-Lambert law $\longrightarrow$ $I = I_0 \exp(-\mu x)$

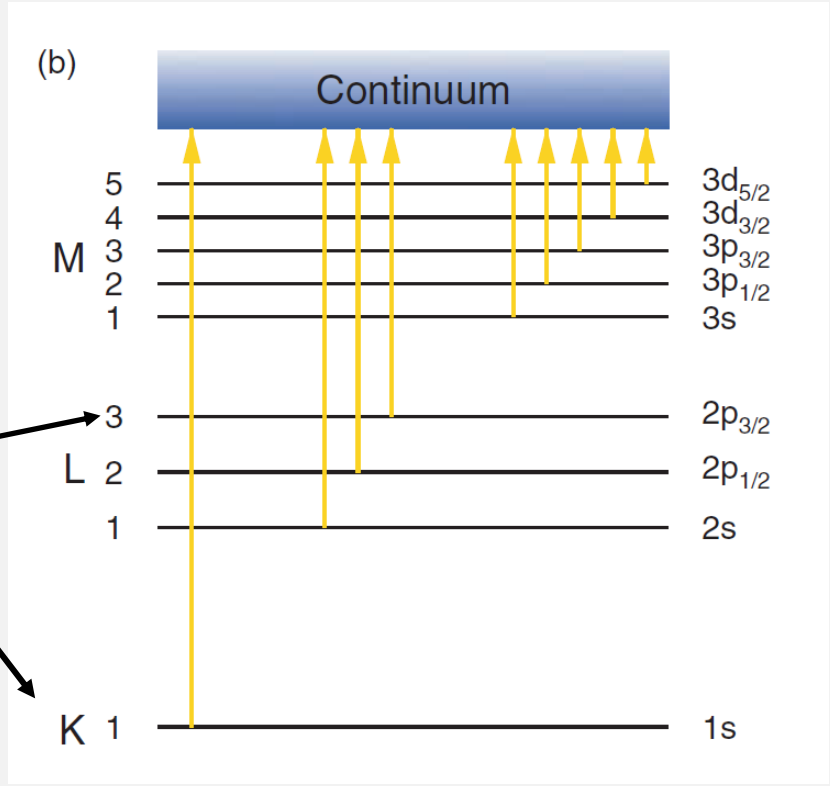
Attenuation absorption coefficient $\longrightarrow$ $\mu x = ln \frac{I_0}{I}$

I-X-ray absorption spectroscopy (XAS)

Absorption edges

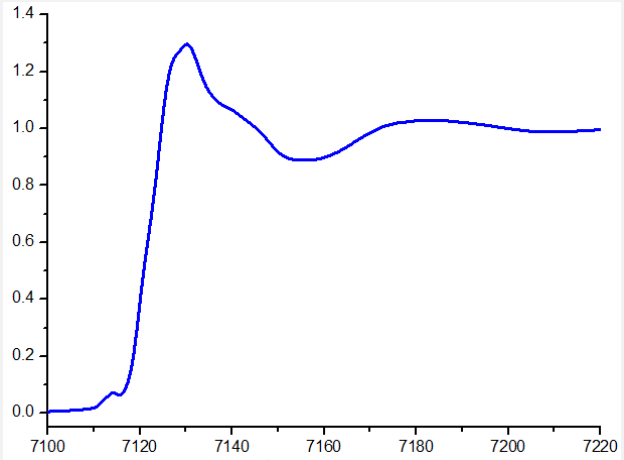


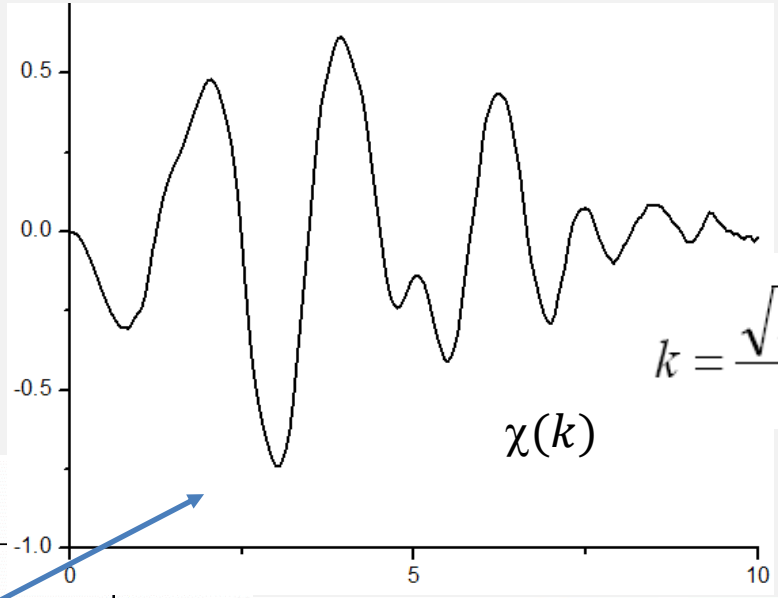
Edge	Configuration
K	$1s$
L_1	$2s$
L_2	$2p_{1/2}$
L_3	$2p_{3/2}$
M_1	$3s$
M_2	$3p_{1/2}$
M_3	$3p_{3/2}$
M_4	$3d_{3/2}$
M_5	$3d_{5/2}$



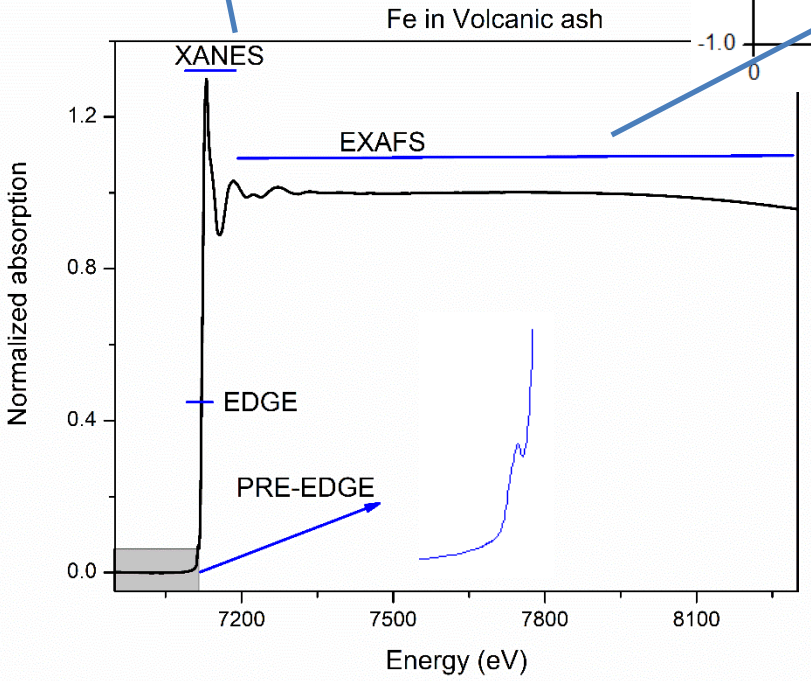
I-X-ray absorption spectroscopy (XAS)

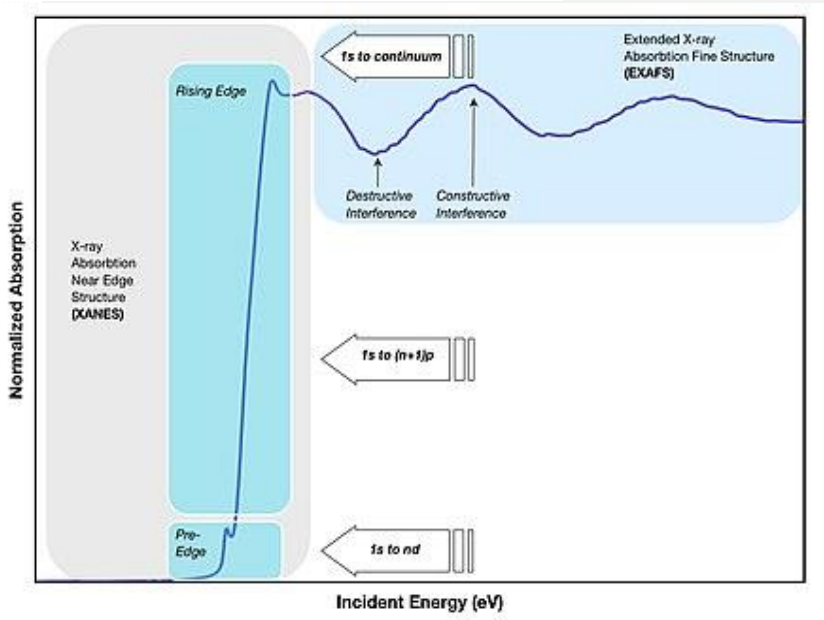
Regions of x-rays absorption spectrum





$$k = \frac{\sqrt{2m(\hbar\omega - E_B)}}{\hbar}$$





I-X-ray absorption spectroscopy (XAS)

EXAFS equation

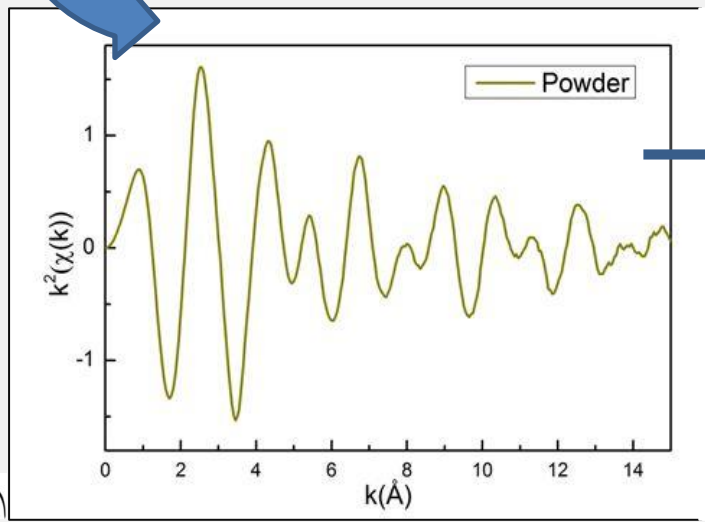
From *ab-initio* calculations or from reference compounds

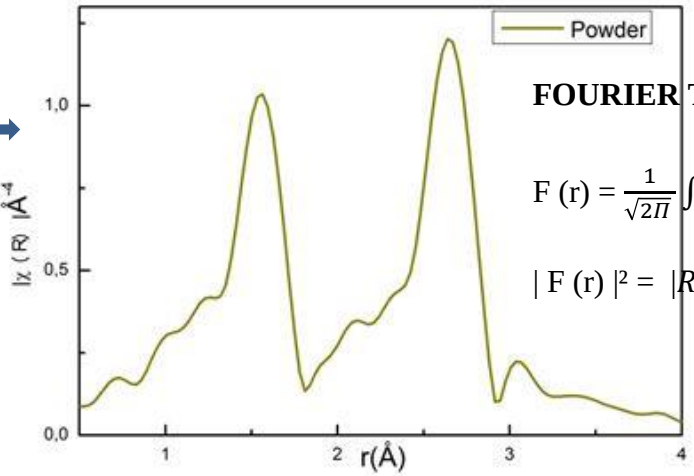
$$\chi(k) = S_0^2 \sum_{j=shells} N_j A_j(k) Sin[2kr_j + \varphi_j + 2\delta_1] e^{-2k^2\sigma_j^2}$$

Measure → Coordination number

Interatomic distance

Debye Waller factor
-Thermal vibration
- Static disorder





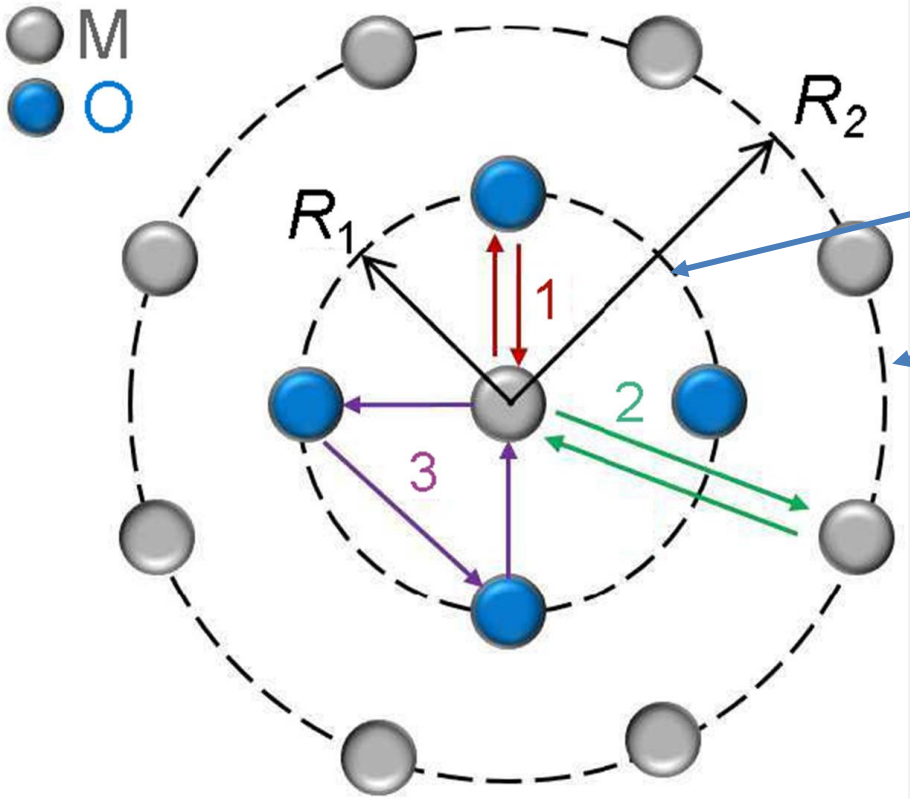
FOURIER Transform function

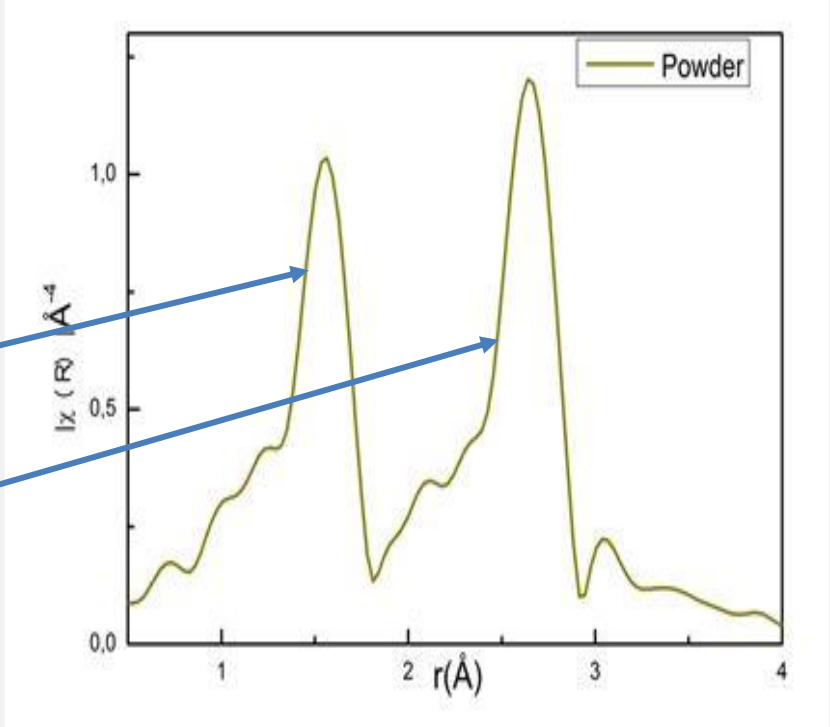
$$F(r) = \frac{1}{\sqrt{2\Pi}} \int_{k_{min}}^{k_{max}} \chi'(k)\, e^{2ikr}\, dr$$

$$|F(r)|^2 = |R_e(F(r))|^2 + |I_m(F(r))|^2 = |\chi(r)|$$

I-X-ray absorption spectroscopy (XAS)

EXAFS equation





- A central absorbing atom surrounded by two coordination shells of four atoms at distance R_1 and eight atoms at distance R_2.
- Two direct scattering paths 1 and 2, multiple scattering paths such as 3 are possible.

II-Basic notions on volcanic ash materials

- Volcanic ash (VA) is a mixture of rock, mineral, and glass particles expelled from a volcano during a volcanic eruption.
- The particles that make up VA can travel long distances, carried by winds.

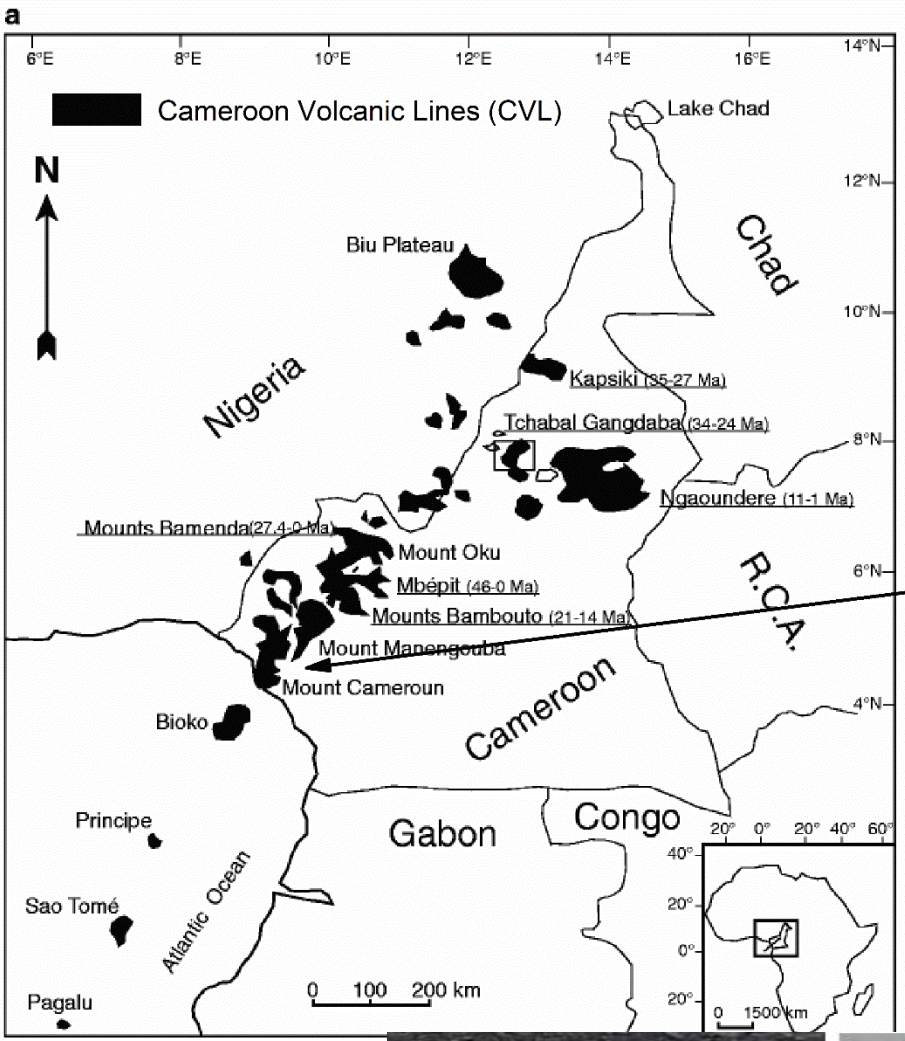
VA can be dangerous.

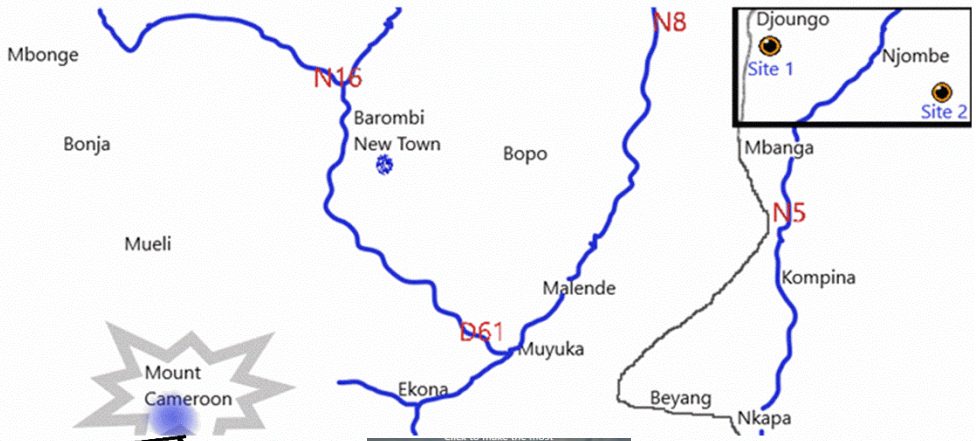
- It can cause eye, asthma, nose, lung irritation, and cardiopulmonary problems to human and animals.

Despite its dangerous character, VA is also useful.

- The soils cover by the VA are fertile leading to the production of abundant food.
- It can also be used for skincare, paste and hand soaps.
- It is used for producing cement for construction.
- It can be used as water filter resulting to a natural occurring filtration process during the rain.
- Thus, It can be used as adsorbent for the removal of some toxic element from aqueous solutions.

III-Location of Cameroon volcano and sampling area



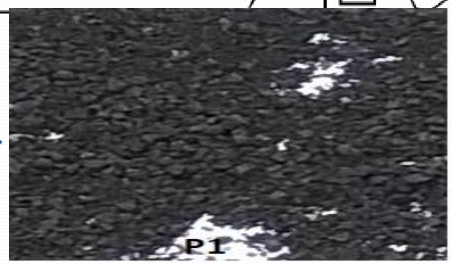


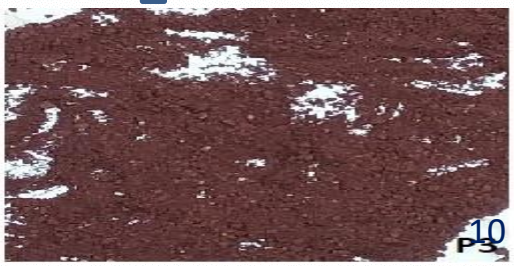
Eruption 2012

N. 04°35’12’’
E. 09°37’37’’
A. 140 ± 3 m

N. 04°35’33’’
E. 09°37’32’’
A. 147 ± 3 m

N. 04°35’09’’
E. 09°37’37’’
A. 134 ± 3 m

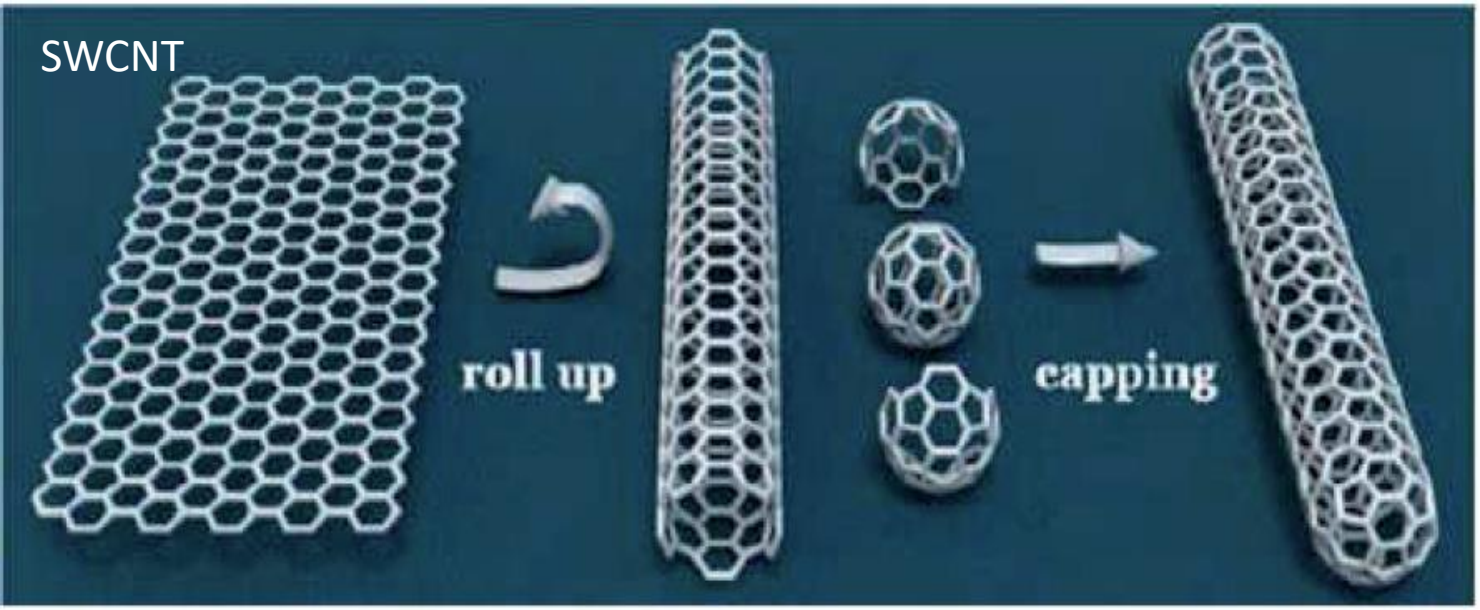


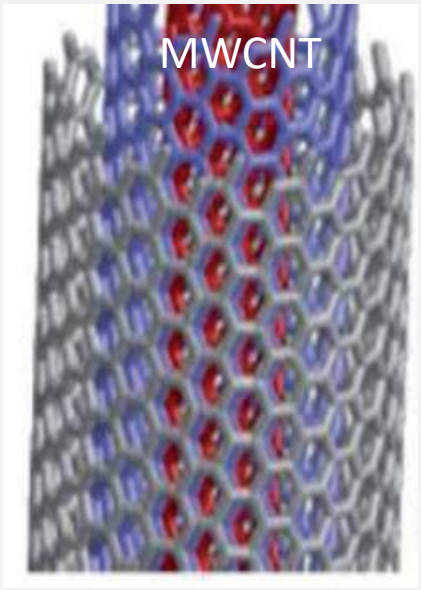


IV-Basic notions on Carbon nanotubes

Definitions

- CNTs were discovered in 1991 by Sumio Iijima.
- They can be described as cylindrically shaped molecules formed of rolled up single or multilayer sheets of graphitic planes.
- Two types are known: the single SWCNTs and multi MWCNTs



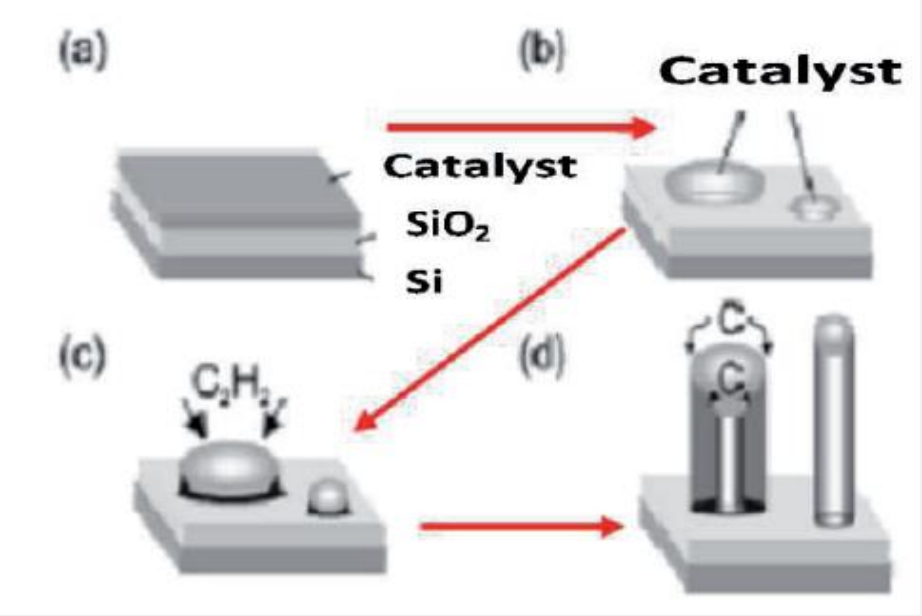


IV-Basic notions on Carbon nanotubes

CVD Synthesis

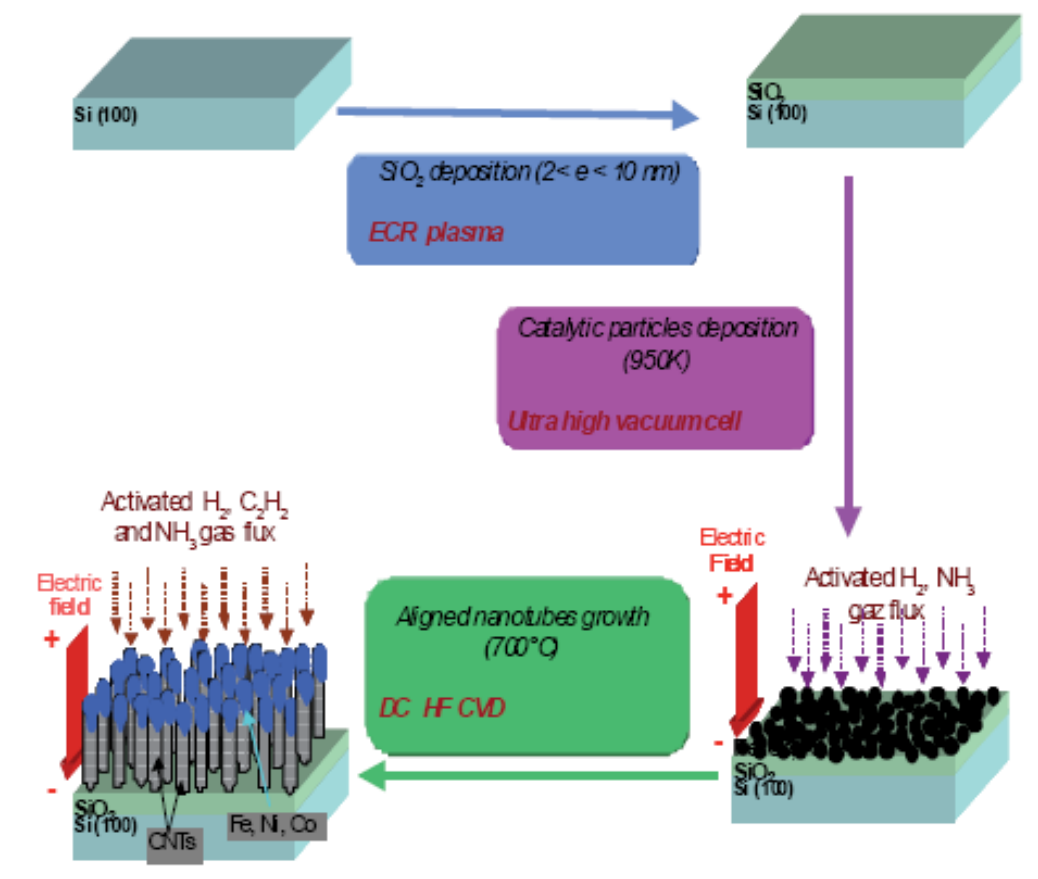
The growth mechanism of CNTs by CVD method are resumed in three steps:

- Adsorption and decomposition of hydrocarbon species (CH4, C2H4, C2H2)
- Diffusion of carbon through metallic particles
- Extrusion for obtaining graphitic walls.



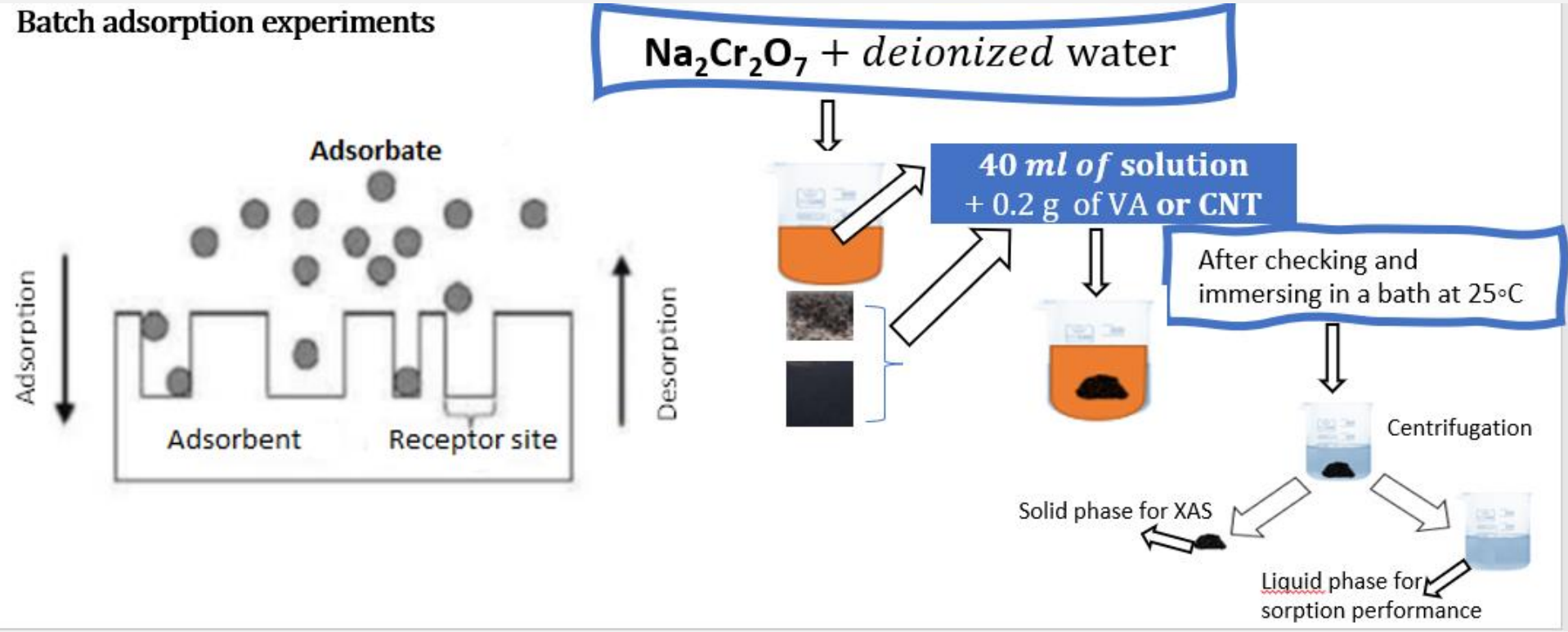
IV-Basic notions on Carbon nanotubes

CVD Synthesis



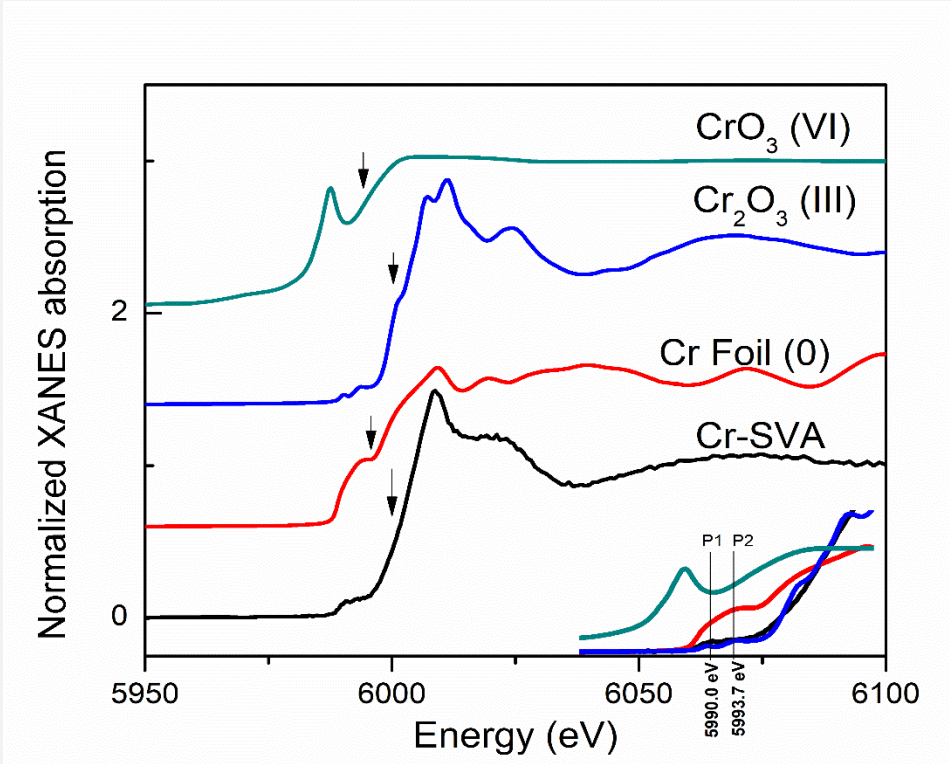
Sketch of the different steps of substrate preparation and growth of CNTs by CVD Synthesis

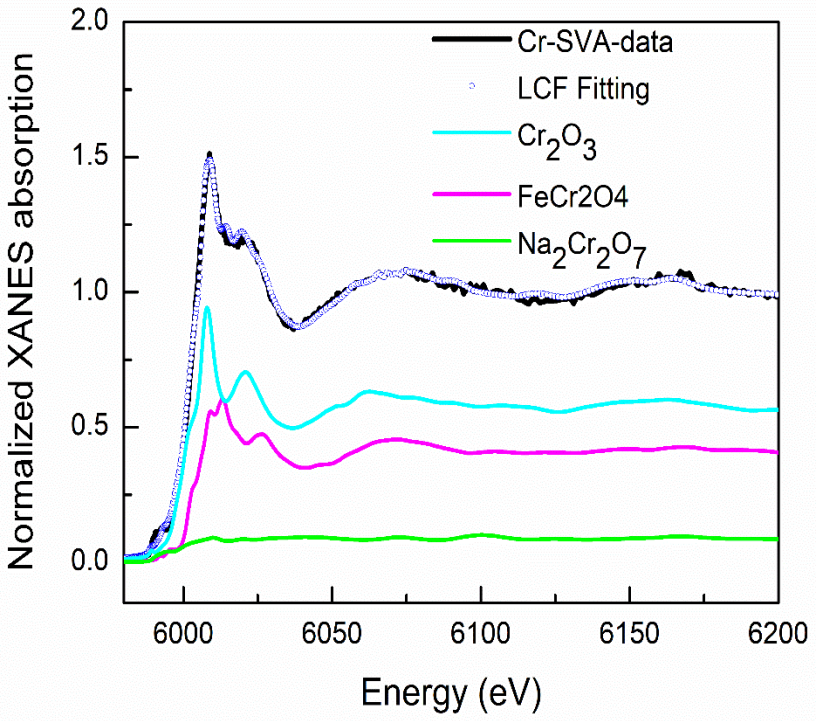
V-Sorption experiments for Cr



VI.1. Electronic properties of Cr-VA by XANES

Chromium sorbed VA





Oxidation state

Oxidation state of VA is +3

Changes from +6 to +3

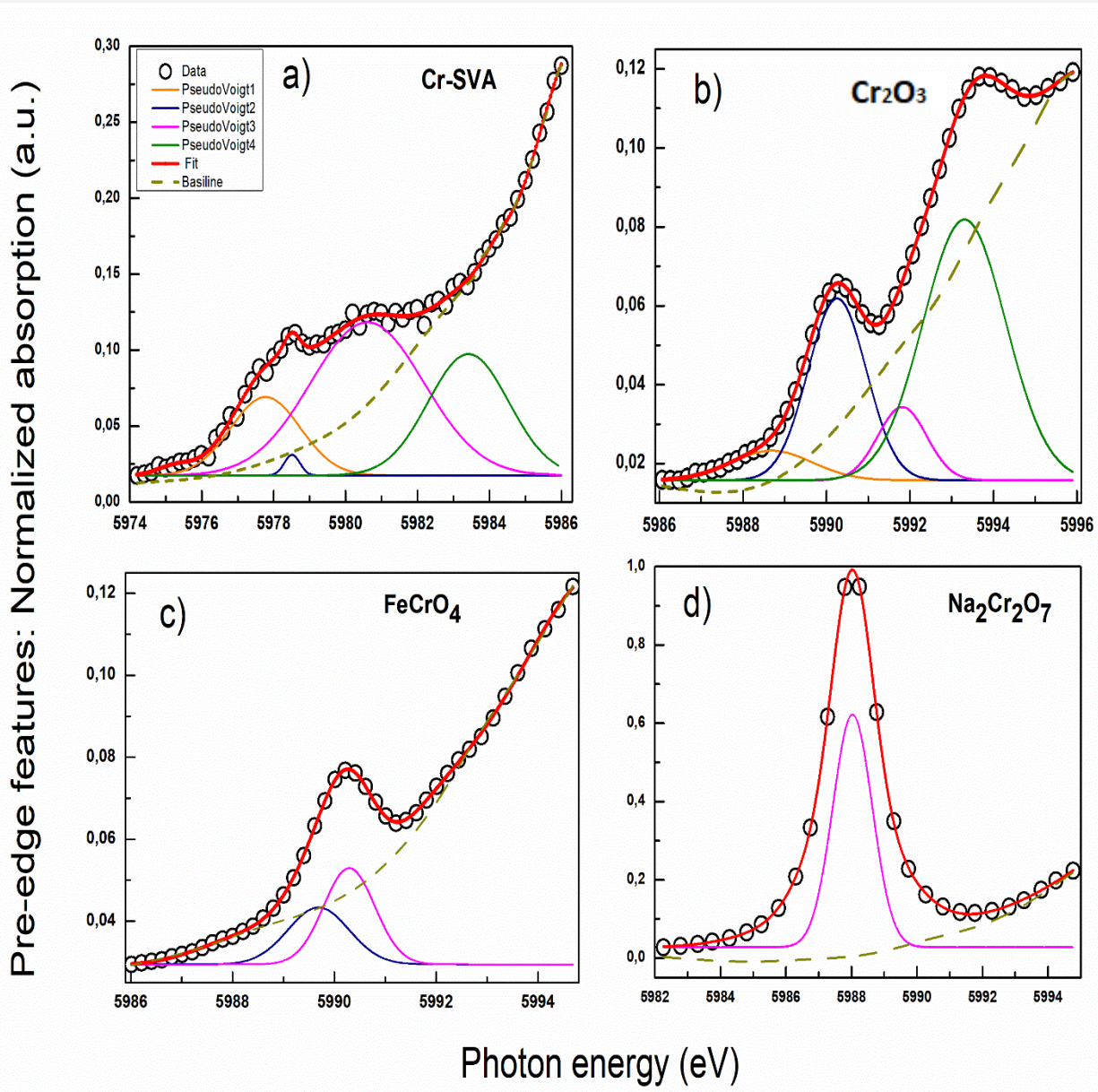
Main components: R_{factor}=0.002

- Chromium(III) oxide (Cr2O3)-wt 47.9(3%),
- Iron(II) chromite (FeCr2O4)-wt 45.2(3%),
- Sodium dichromate (Na2Cr2O7)-wt 6.9(5%)

VI.1. Electronic properties of Cr-VA by XANES

- For the electronic properties, the pre-peak features were fitted.
- The pre-peaks P1 and P2 in Cr-SVA, and those of Cr_2O_3, $FeCr_2O_4$, and $Na_2Cr_2O_7$ were also considered.

- The similarity between Cr-SVA and Cr2O3 suggests that the Cr-SVA sample can adopt the electronic properties of Cr2O3.



VI.1. Electronic properties of Cr-VA by XANES

In general, the pre-peak features observed in the XANES pre-edge region of the metal element with d^n (n =1….9) electronic configuration are characteristic of the transition to bound states quadrupolar 1*s*→ 3*d* and/or dipolar 1*s*→4*p*

Thus, it can be understood that the VA sample comprises the pre-edge region, and the quadrupolar transition 1*s*→3*d*, corresponding respectively to the energy states of t_{2g} (5990 eV) and e_g (5993.7 eV) orbitals.

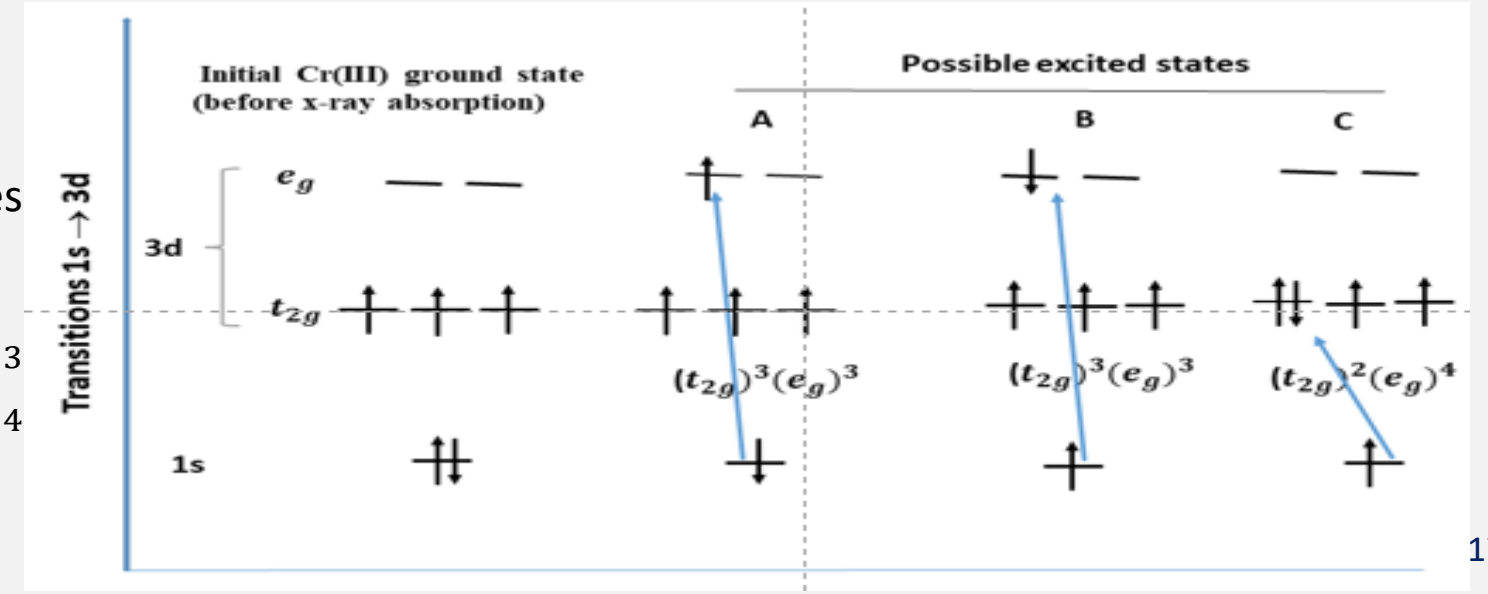
Since the Cr-VA can adopt the Cr_2O_3 structure, we attempted to assign the electronic transitions with respect to the rule used in the Cr (III) structure.

We sketch the XAS experimental process in Cr-SVA when a core electron is excited as shown below.

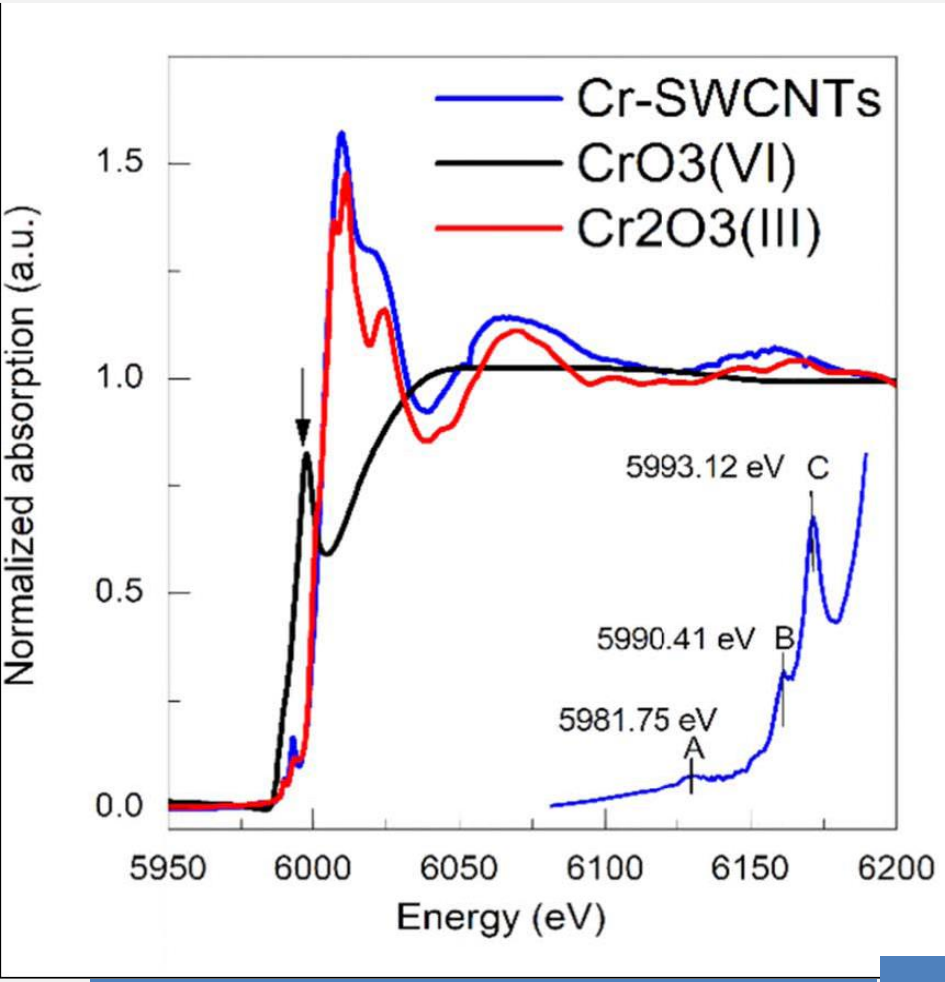
Final excited states of the 3d orbitals

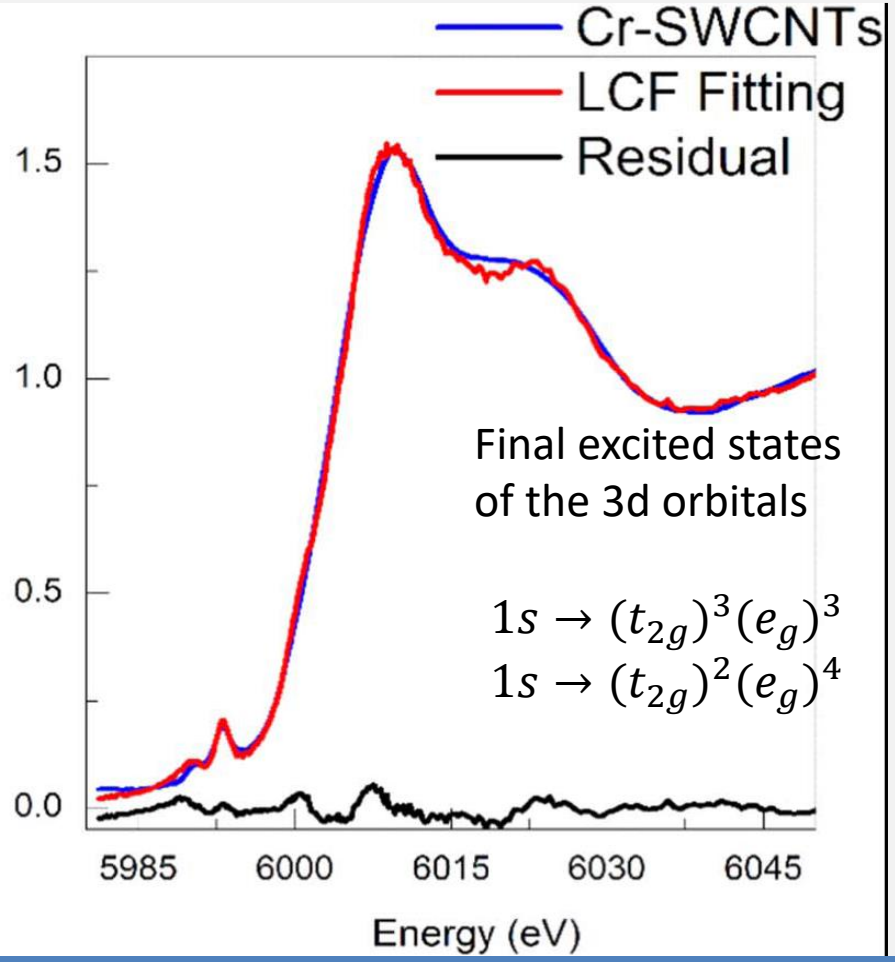
$1s \rightarrow (t_{2g})^3(e_g)^3$

$1s \rightarrow (t_{2g})^2(e_g)^4$



VI.2. Electronic properties of Cr-SWCNTs





Oxidation state

Oxidation state of VA is +3

Changes from +6 to +3

Main components: R_{factor}=0.004

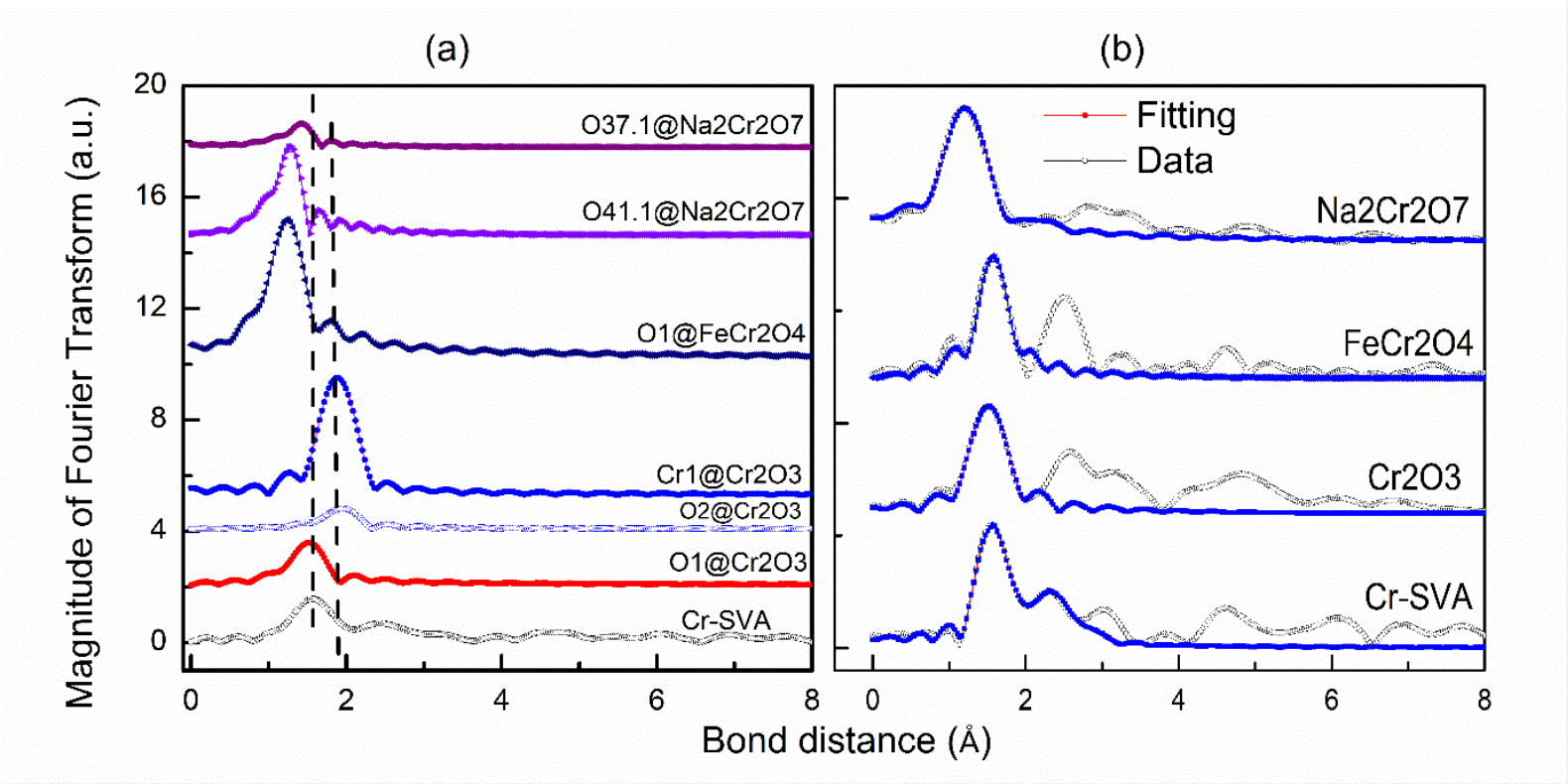
Chromium(III) oxide (Cr2O3)-wt 75(4%),

- Iron(II) chromite (FeCr2O4)-wt 30(4%),
- Sodium dichromate (CrO3)-wt 4(0.08%)

EXAFS data analysis

- For the EXAFS modelling, least-square fitting based on multiple scattering approximation was employed.
- Single and multiple paths were used.
- The EXAFS theoretical signals for all samples were generated using the FEFF6 code from the backscattering amplitudes and phase shift parameters.
- Knowledge of the space group and crystal structure of the compound to be modelled is required to generate EXAFS theoretical signals. We used the Cr2O3 for our modelling.
- Artemis program was used to fit the Fourier transform spectra.
- The R_{factor} parameter which evaluates the difference between the experimental and modelled functions, describes the reliability of the best fit.

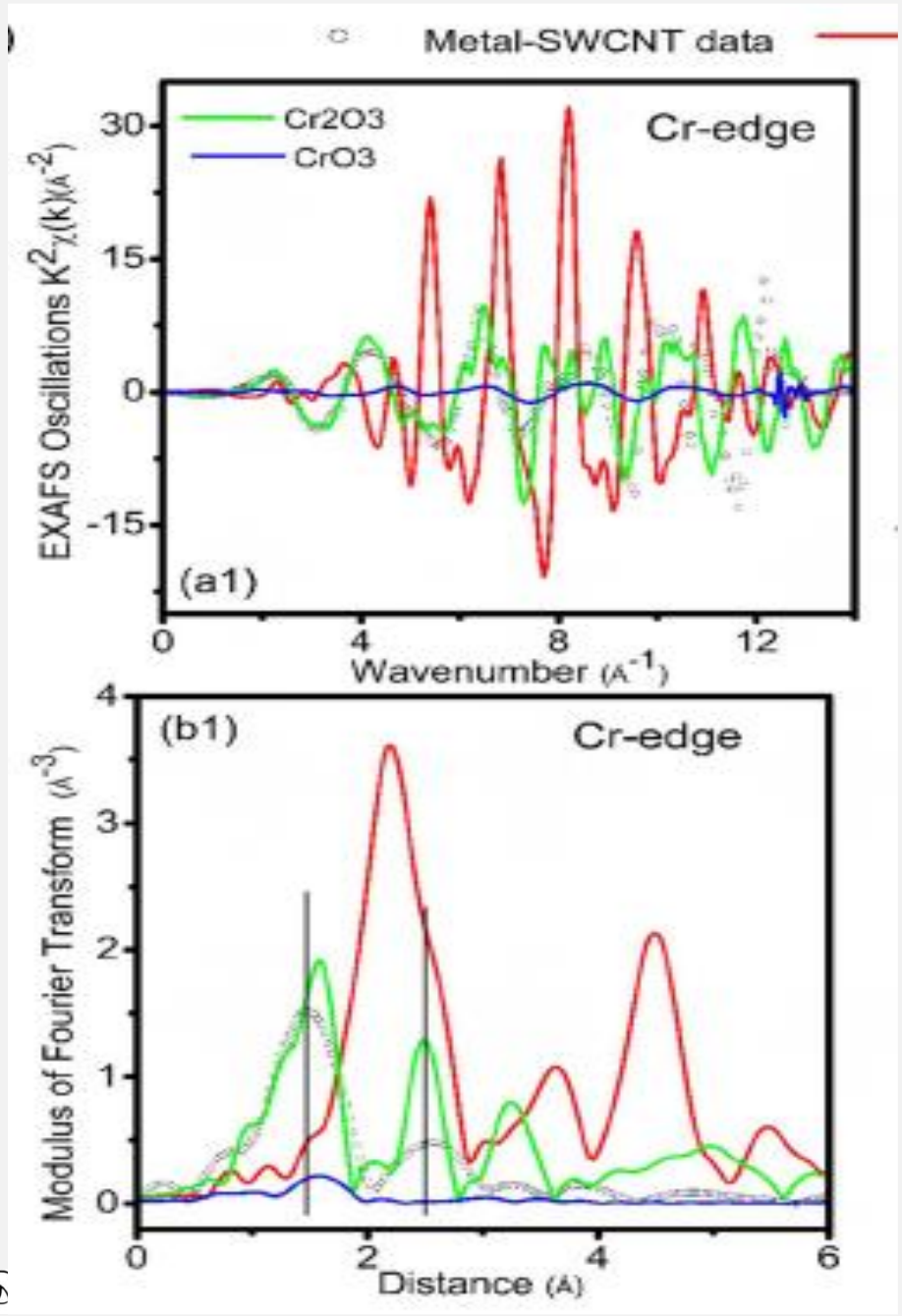
VII.1.-Structural characterization of Cr-VA by EXAFS



Samples	Interaction	CN	R(Å)	σ^2(Å^2)
Cr-SVA	Cr-O1	3.26(42)	1.69(2)	0.0014(3)
	Cr-O2	2.30(71)	2.59(2)	0.0009(1)
	Cr-Cr1	1*	2.54(2)	0.0023(6)
Cr_2O_3	Cr-O1	4.02(21)	1.79(2)	0.0017(8)
$FeCr_2O_4$	Cr-O1	5.73(58)	1.99(0.7)	0.0004(0.1)
$Na2Cr_2O_7$	Cr-O41.1	3.15(52)	1.67 (3)	0.0065(1)
	Cr-O37.1	1*	1.82(4)	0.0110(3)

Cr is coordinated to:
- oxygen atoms in the first coordination shell,
- Chromium atoms in the second coordination shell,
of Cr-VA materials

VII.2.-Structural characterization of Cr-SWCNTs by EXAFS

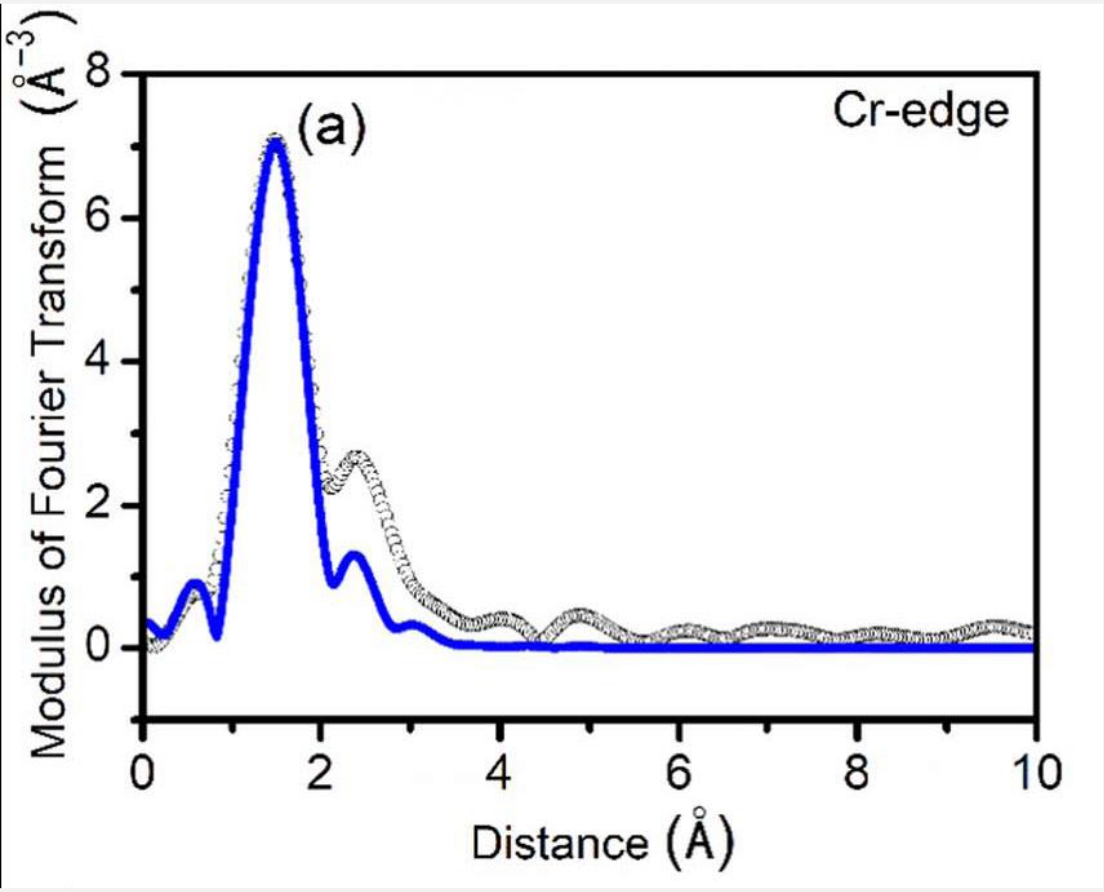


The scattering paths resulting from the theoretical structure showed bond distance values between the absorber and the oxygen scatter atom not far (<2 Å) from the values given in the FT functions, proposing oxygen atoms in their nearest neighbor.

However, the values of the distances between the absorber and the carbon atoms were too high (>3 Å), suggesting that carbon atoms cannot be in the nearest neighbor around the Cr with respect to the FT functions.

Cr is coordinated to oxygen atoms in the first coordination shell of Cr-SWCNT materials.

VII.2.-Structural characterization of Cr-SWCNTs by EXAFS



The overall results demonstrated that the first coordination shells of the Cr sorbed-SWCNT materials contain oxygen atoms with the coordination number and the interatomic distance slightly equal to the corresponding values in the model compounds.

Materials	Standards	CN_{th}	CN_{exp}	Reff(Å)	R(Å)	σ^2(Å^2)	ΔE_0(eV)	R_{factor}
Cr-SWCNTs	Cr_2O_3	3	3.8(7)	1.74	1.97(7)	0.0030(8)	−3.44	0.004

Related published papers

1) ***X-ray absorption spectroscopy study of the electronic and structural properties of hexavalent chromium adsorbed by volcanic ashes,*** Gristianho Lontin Lontin, Bridinette Thiodjio Sendja, Duclair Tchana Kamgne, Giuliana Aquilanti, Germain Ben-Bolie, *Journal of Molecular Structure 1294 (2023) 136453*

2) ***Sorption of metal elements by single-walled carbon nanotubes and x-ray absorption spectroscopy analysis,*** Cetrigue Tchienkoua, Bridinette Thiodjio Sendja, Camile Rodolphe Tchenguem Kamto, Duclair Tchana Kamgne, Nahum Andres Medellin-Castillo, Gladis Judith Labrada-Delgado and Jean Marie Ndjaka, *Physica Scripta 98 (2023) 085901*.

Conclusion

XAS has been used to characterize the chromium sorbed onto volcanic ash and carbon nanotube materials for water treatment application.

The investigation of the electronic properties demonstrate that the final excited states of the 3d orbitals in chromium sorbed VA and SWCNTs materials are:
$1s \rightarrow (t_{2g})^3(e_g)^3$ and $1s \rightarrow (t_{2g})^2(e_g)^4$

The structural characterization shows that Cr is coordinated to:
- oxygen atoms in the first coordination shell in both materials,
- Chromium atoms in the second coordination shell in Cr-VA,
However, Cr is not coordinated to carbon atoms in the Cr-SWCNT materials.

XAS might appear as a powerful characterization tool for adsorbent material containing heavy elements. Since it allows determining for the unknown materials:

1-Oxidation state
2-Chemical composition
3-Electronic properties
4-Structural characterization

Acknowledgements

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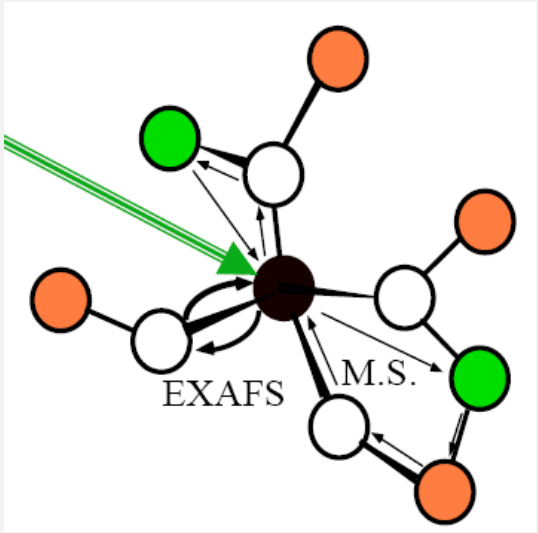
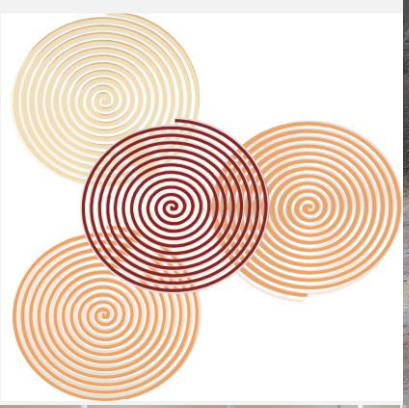
ICTP + ELETTRA: ICTP-ELETTRA users support



LAAAMP Program + ELETTRA

Staff of XAFS beamline ELETTRA

Dr Giuliana Aquilanti, XAFS and XRF beamline scientist



THANK FOR YOUR KIND ATTENTION