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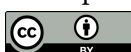
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How Does Nanomagnetite Stoichiometry (Fe(II)/Fe(III)) Influence the Surface Speciation of Trivalent Chromium?

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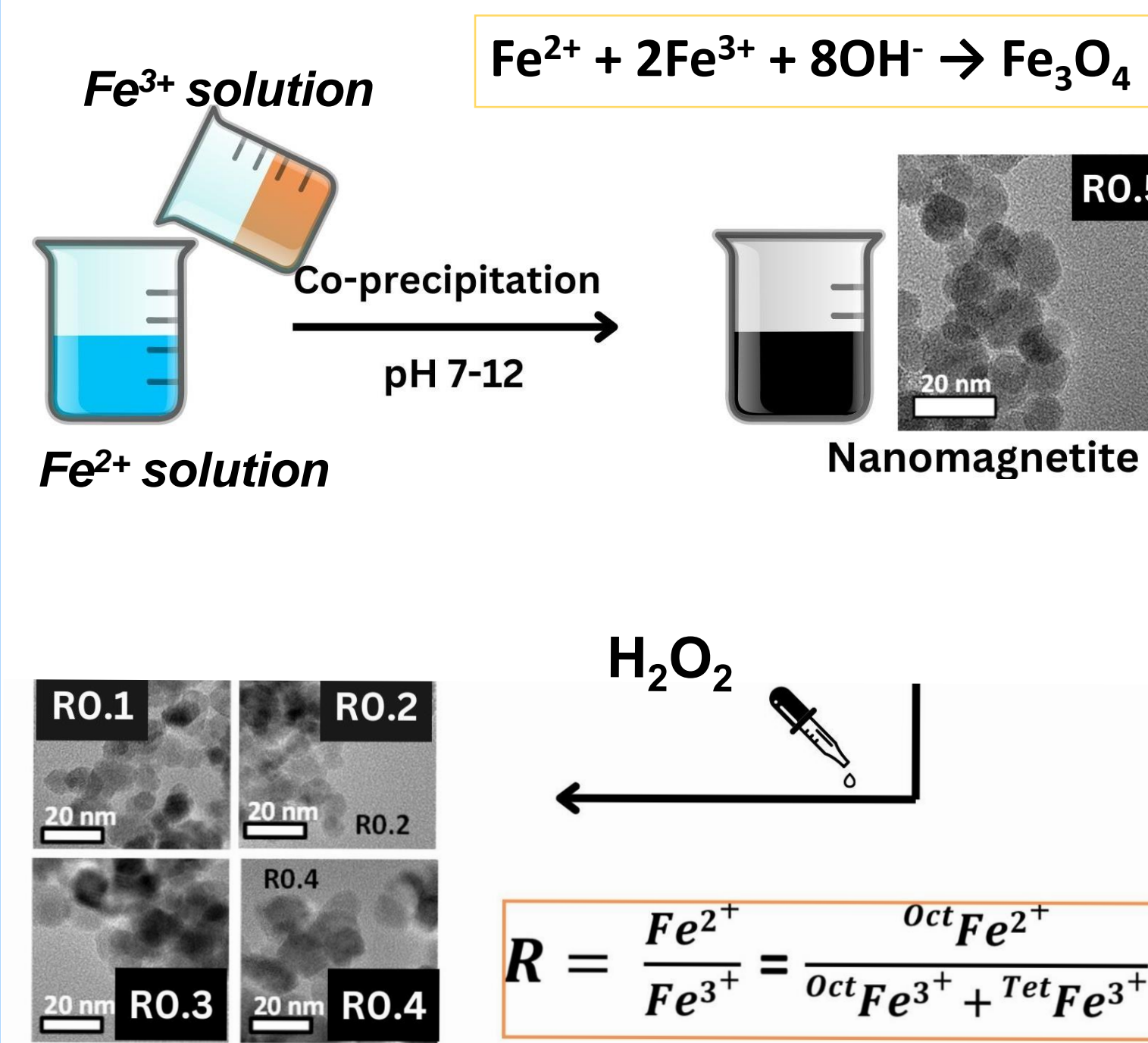


INTRODUCTION

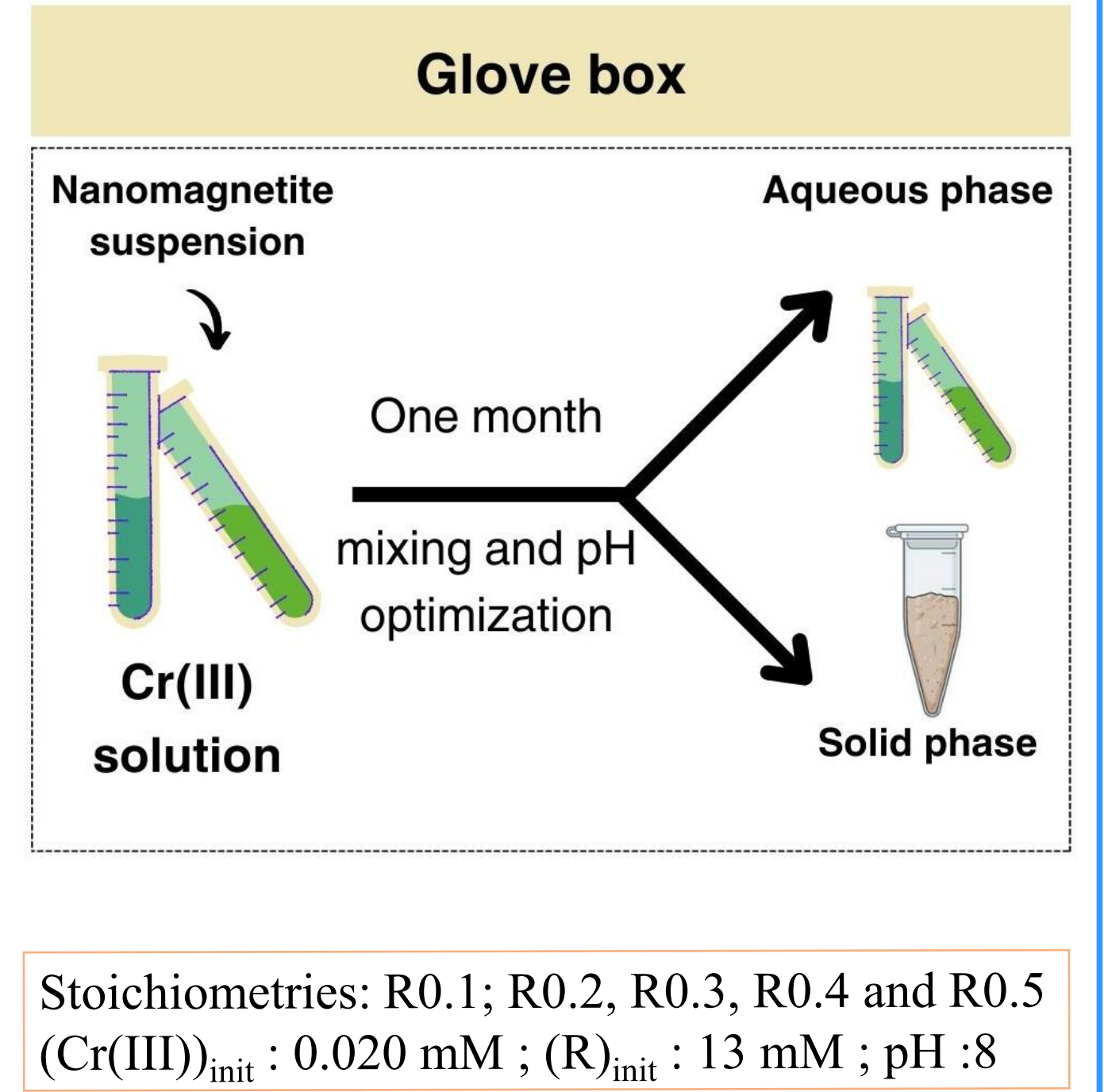
- **Chromium (Cr)** is a prevalent metal pollutant in soils and groundwater. This study examines the interaction of 10 nm-sized nanomagnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$) with Cr(III).
- **The stoichiometry of magnetite** (i.e., R ratio = Fe(II)/Fe(III)) can vary from 0 to 0.5 in natural environment, where R=0 indicates the oxidised magnetite or maghemite, whereas R=0.5 indicates the stoichiometric magnetite.
- **These studies are useful in** predicting the fate and transport of chromium, as well as in developing magnetite-based chromium remediation processes.
- **The effect of magnetite stoichiometry** (R0.1, R0.2, R0.3, R0.4 and R0.5) were investigated under anoxic condition.
- **The Cr speciation at mineral-water interface** was examined using X-Ray absorption spectroscopy (XAS) at Cr K-edge on LUCIA beamline at SOLEIL Synchrotron (France).

METHODOLOGY

Material synthesis

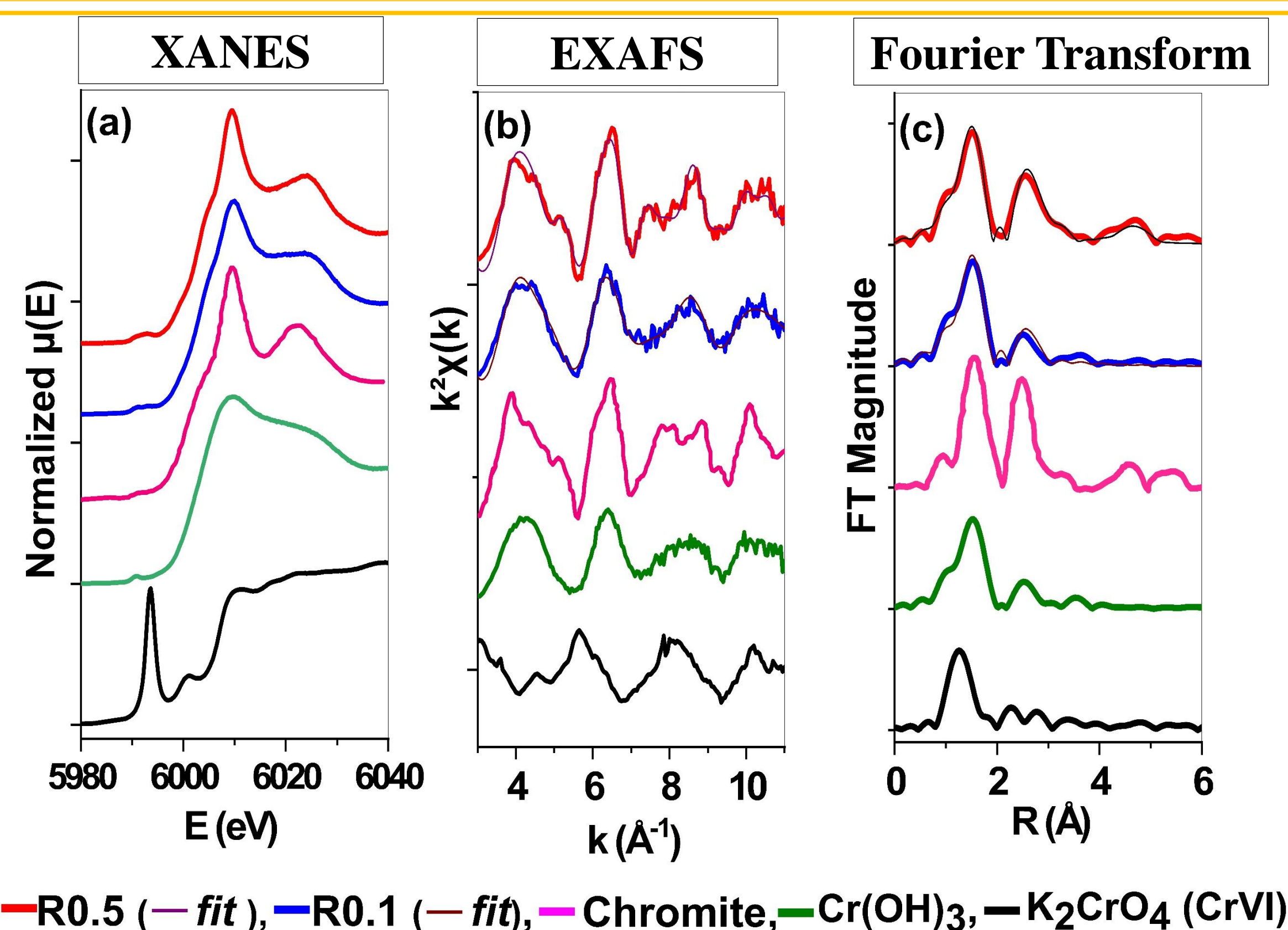


Adsorption experiments



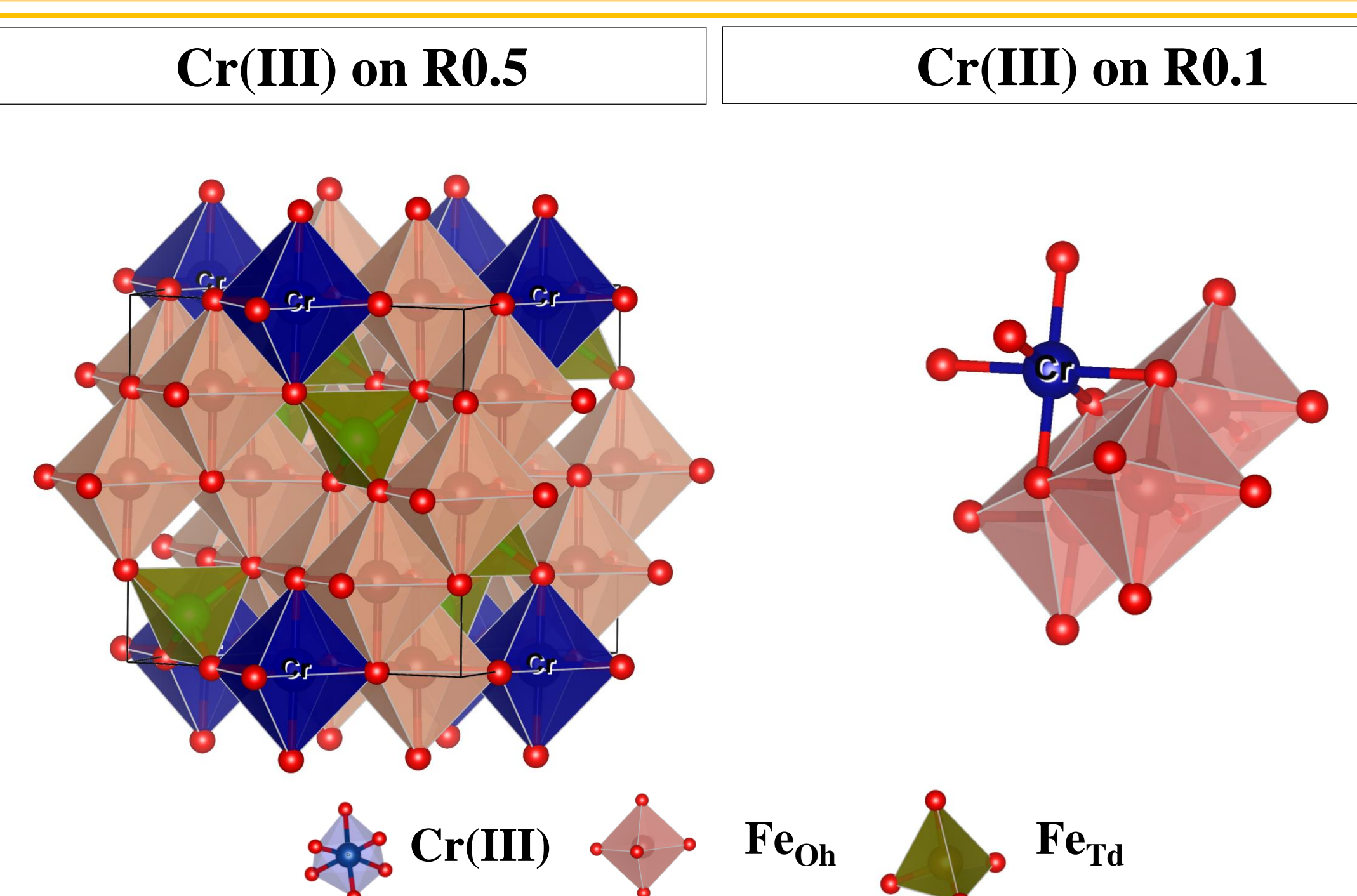
RESULTS

Cr(III) - magnetite /maghemite nanoparticles interaction



- The Cr(III) sorption mode on R0.1 and R0.5 may be as a chromite phase.
- The presence of other Cr(III) phases such as Cr oxyhydroxide precipitation may be ruled out.

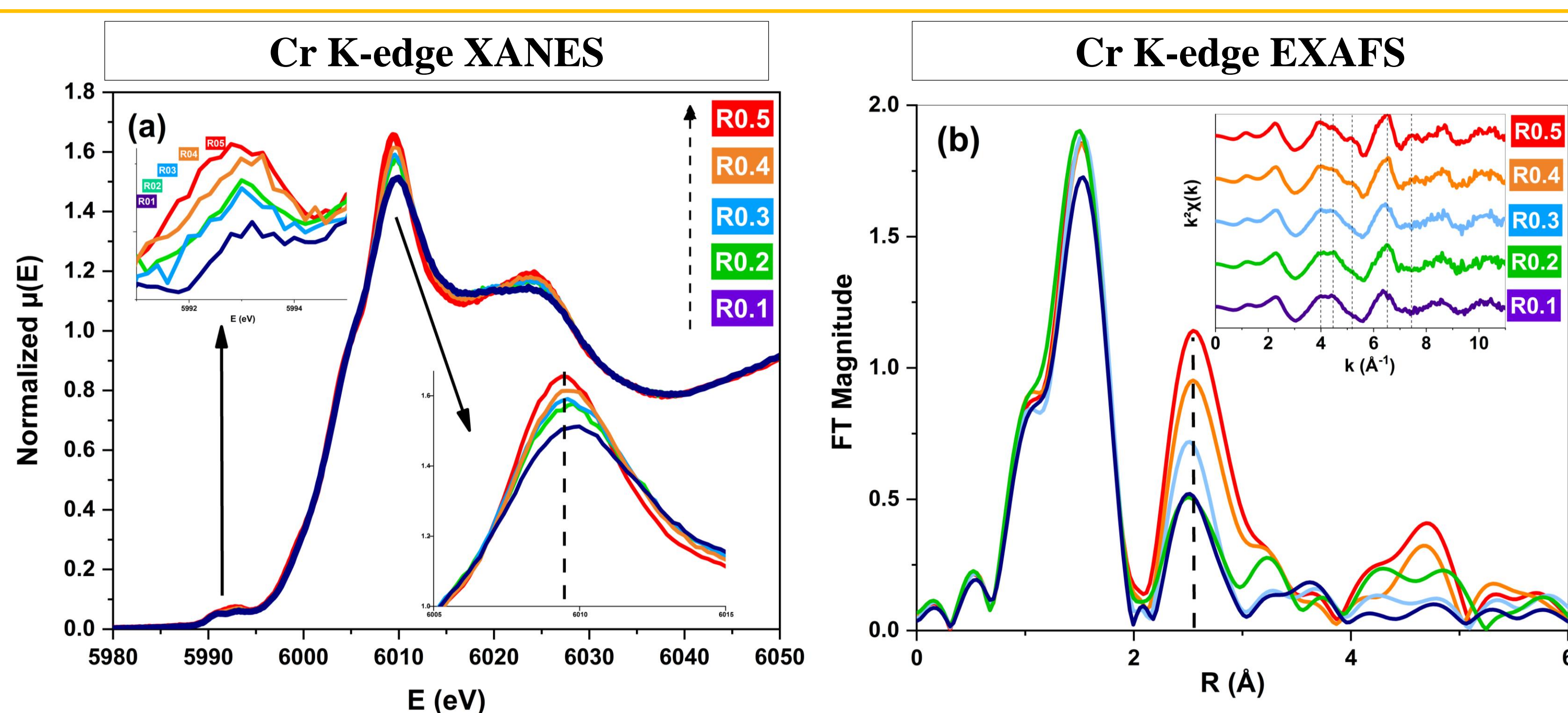
EXAFS Fitting



Interaction	Model	Shell	R (Å)	CN	σ²(Å²)
Cr(III) partially substitute Fe(III) _{Oh}	Cr(III)-R0.5	Cr-O	1.96 ± 0.01	5.62 ± 20%	0.003 ± 10%
		Cr-Cr/Fe	3.00 ± 0.03	3.24 ± 20%	0.002 ± 30%
		Cr-Cr/Fe	3.44 ± 0.03	1.95 ± 20%	0.002 ± 30%
Tridentate edge sharing	Cr(III)-R0.1	Cr-O	1.97 ± 0.01	6 ± 20%	0.003 ± 10%
		Cr-Cr/Fe	3.02 ± 0.03	3 ± 20%	0.003 ± 30%

Table 1: Fitting results of the EXAFS analysis
R (interatomic distance), N (coordination number) and σ² (Debye-Waller factor)

Effect of stoichiometry



- A gradual increase in μE intensity with increasing R value as;
R0.5 > R0.4 > R0.3 ≈ R0.2 > R0.1
- The stoichiometries in between R0.1 and R0.5 shares the two surface complexes in ratios respect to R

CONCLUSIONS

- A strong **interrelation of chromium surface complexation and magnetite stoichiometry**.
- Cr(III) adsorbs as a **tridentate inner sphere species** on the surface of maghemite (R0.1), whereas Cr(III) adsorb as **solid solution** in which Cr(III) takes the place of Fe(III)_{Oh} onto the surface of magnetite (R0.5).
- The stoichiometries in between (R0.2, R0.3, R0.4) possess the combination of the tridentate inner sphere and solid solution in ratios with **progressive evolution with R**.

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ACKNOWLEDGEMENTS

