Supporting information

Investigations of Co(II) to Co(III) oxidation mechanisms at $Fe_{3-\delta}O_4$ nanoparticle surface

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The supporting information section contains 10 pages, 7 figures and 2 tables.

Table S1 Corresponding total ($[Co]_{tot}$), aqueous ($[Co]_{aq}$) and solid ($[Co]_s$) concentrations of cobalt (determination error 5%). Samples analyzed by XAS and XMCD at the L-edge are marked with a star (*) and those analyzed by XAS at the *K*-edge by a circle (°).

$[Co]_{tot}$ (mM)	$[Co]_{aq}$ (mM)	$[Co]_s$ (mM)	$[Co]_s$ (atom nm^{-2})
0.1	0.008	0.092	0.53
0.5*	0.071	0.427	2.47
1	0278	0.716	4.14
2*	0.816	1.164	6.74
3*°	1.629	1.174	6.80
4*	2.270	1.538	8.91
5	3.298	1.622	9.39
6*°	4.213	1.736	10.05
7	4.939	1.898	10.99
8	5.817	1.991	11.53
9	6.487	1.992	11.53
10	7.224	2.184	12.71
11	7.532	2.928	16.95
12*°	5.529	6.140	35.55

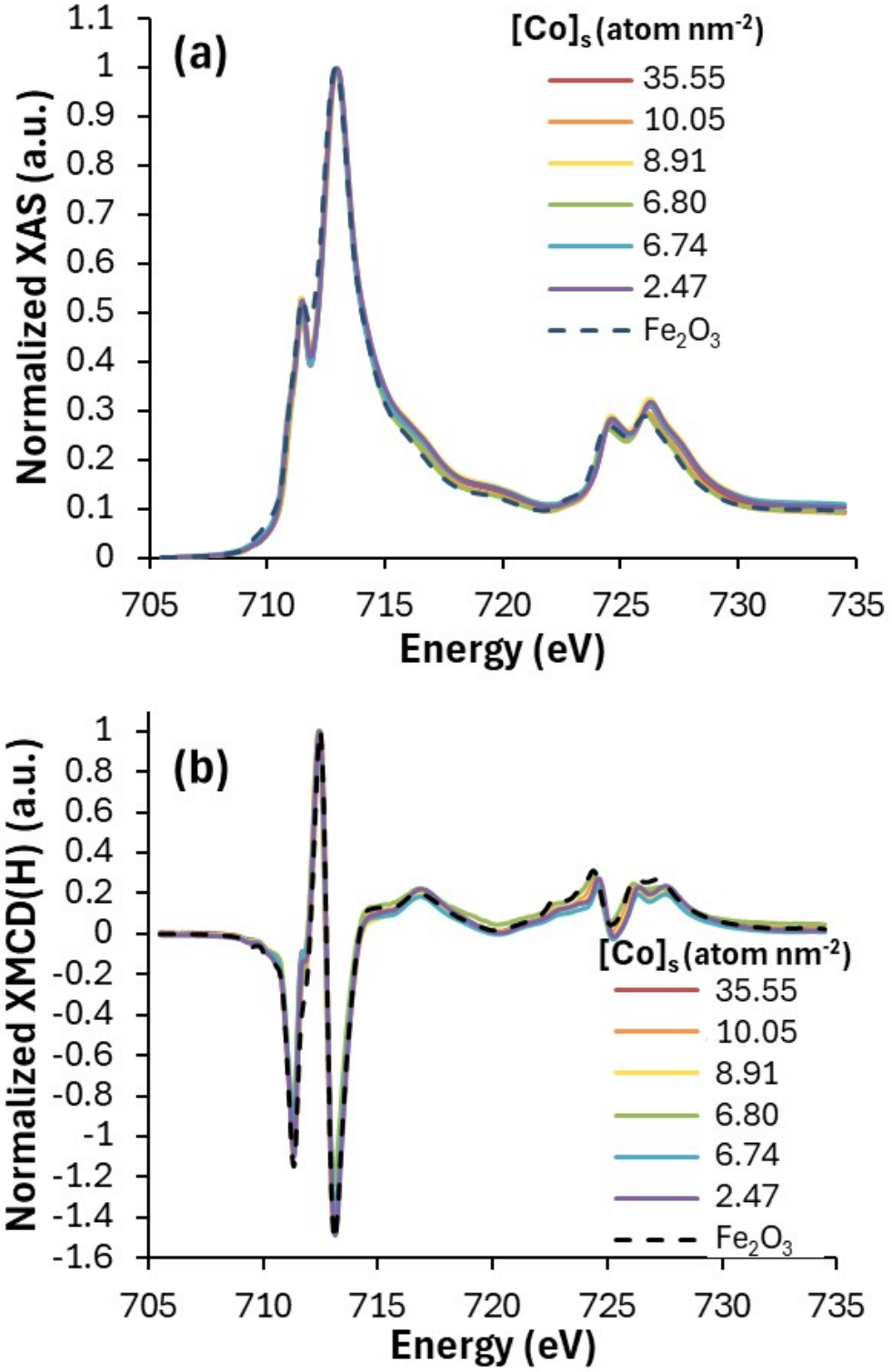

Fig. S1 Normalized XAS (a) and XMCD (b) spectra with the background at the Fe $L_{2,3}$-edges of $Fe_{3-\delta}O_4$ at pH 8 with different $[Co]_{tot}$ (from 2.47 to 35.55 atom nm^{-2}). The dashed line corresponds to the spectra of Fe_2O_3 (data from Jungcharoen *et al.* (2021)).[18]

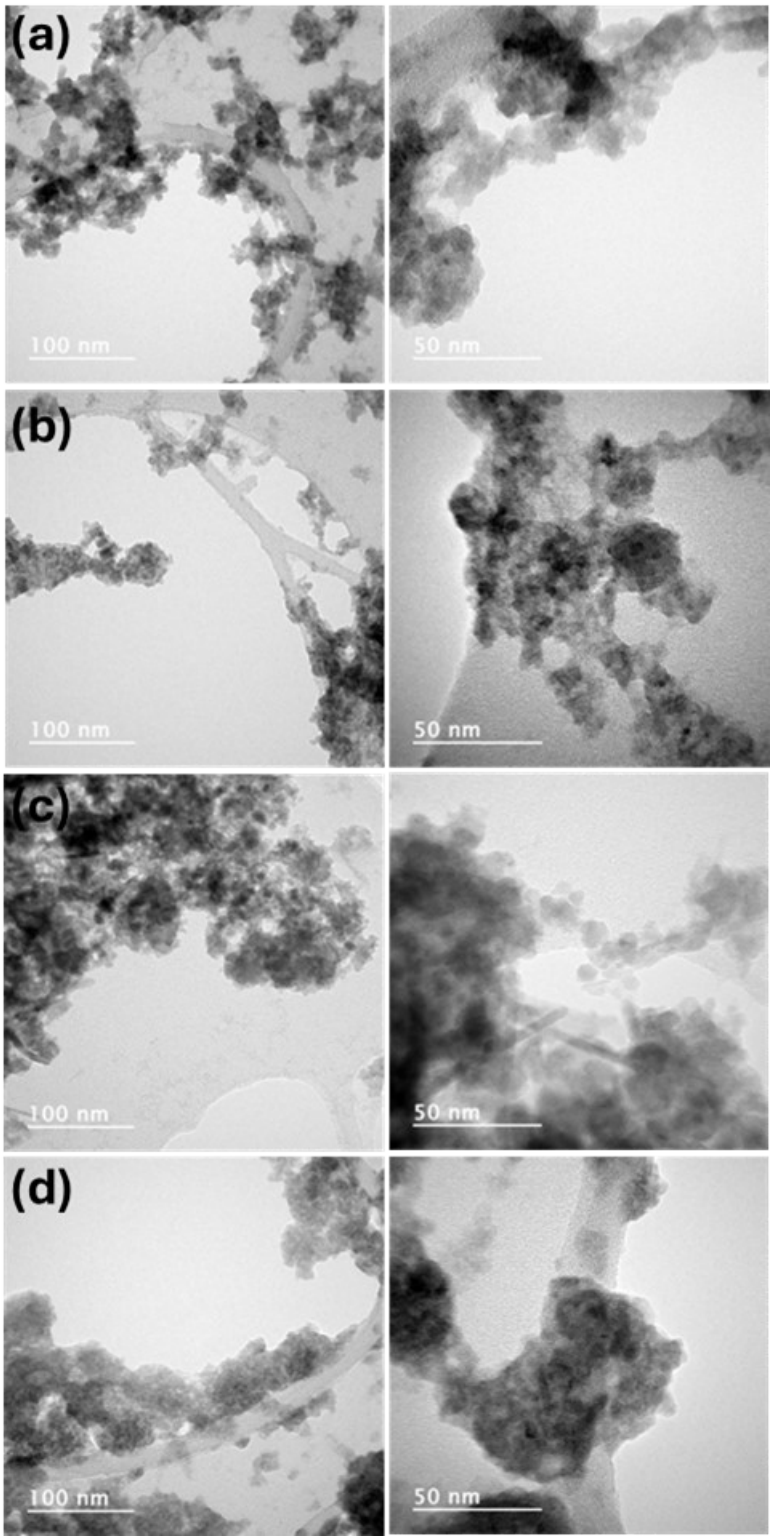

Fig. S2 TEM images of $Fe_{3-\delta}O_4$ with (a) $[Co]_s$ = 2.47 atom nm^{-2} ([Co]tot = 0.5 mM), (b) $[Co]_s$ = 6.80 atom nm^{-2} ([Co]tot = 3 mM), (c) $[Co]_s$ = 10.05 atom nm^{-2} ([Co]tot = 6 mM) and (d) $[Co]_s$ = 35.55 atom nm^{-2} ([Co]tot = 12 mM). (Left) scale of 100 nm and (Right) scale of 50 nm.

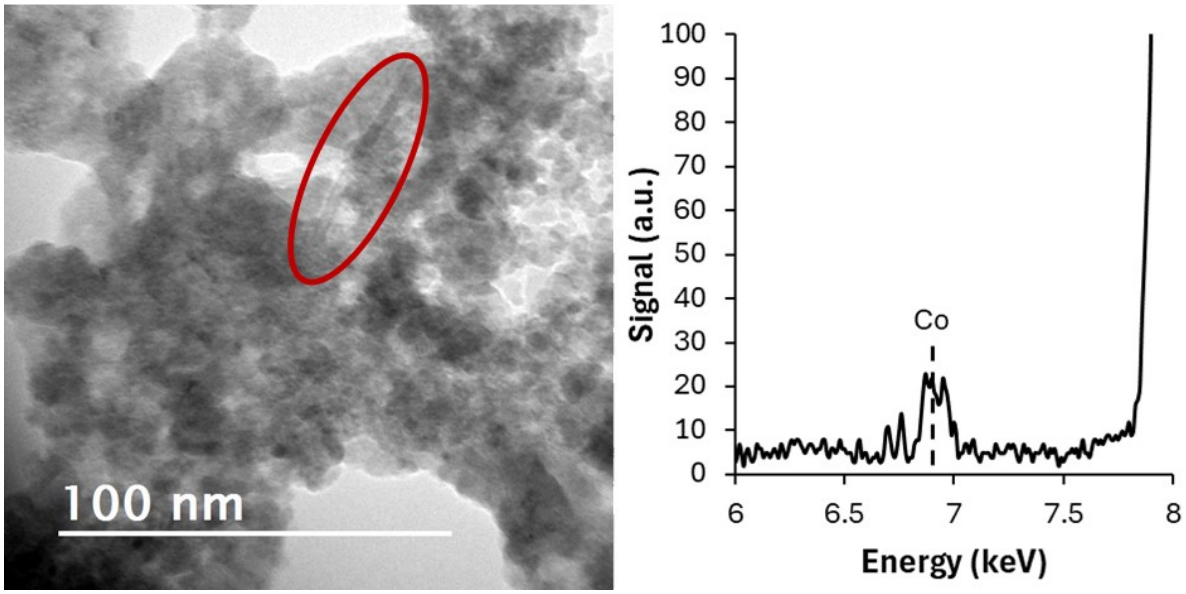

Fig. S3 TEM image of a crystallized sheet for $[Co]_s$ = 10.05 atom nm^{-2} ($[Co]_{tot}$ = 6 mM), and the corresponding energy-dispersive X-ray spectroscopy (EDXS).

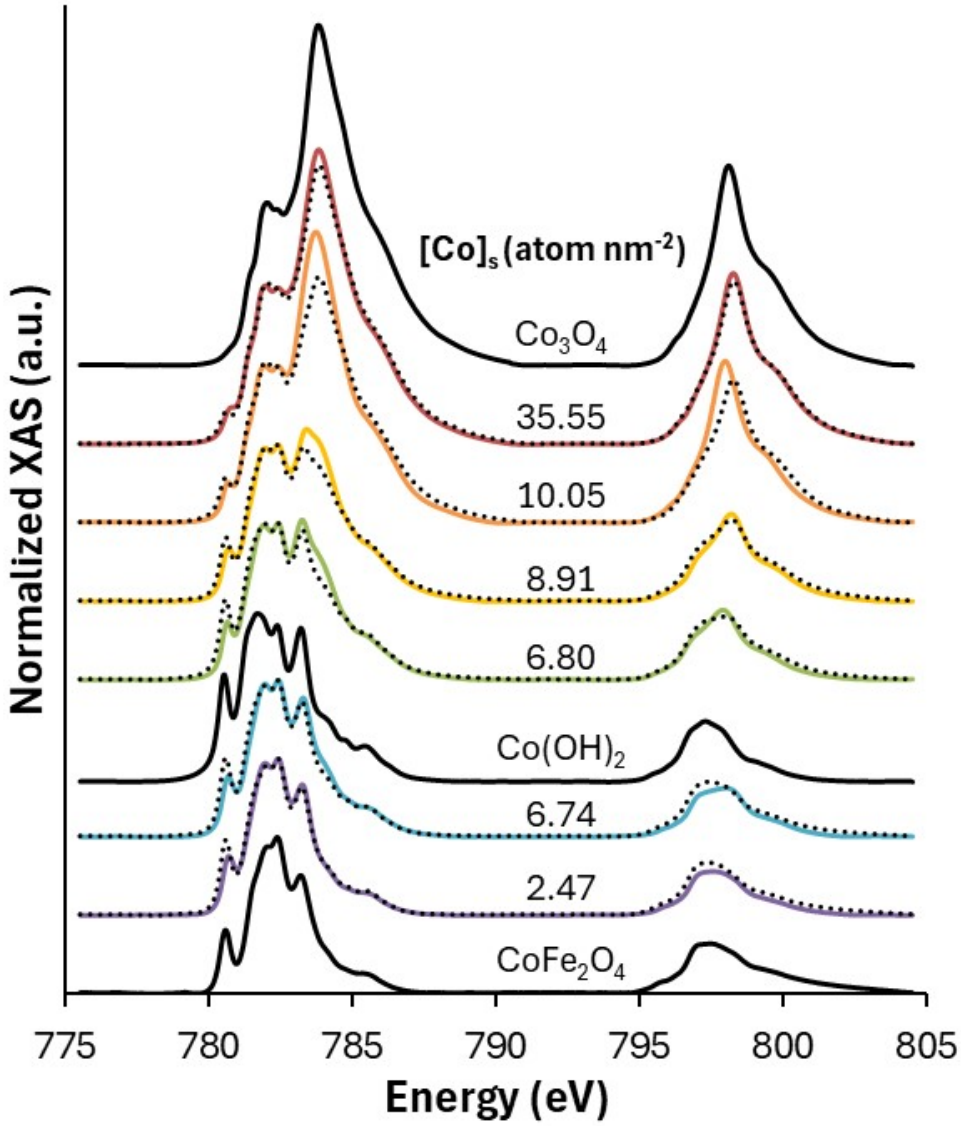

Fig. S4 Fits of linear combination analysis of normalized XAS spectra at Co $L_{2,3}$-edge for different $[Co]_s$ (from 2.47 to 35.55 atom nm^{-2}), using $Co(OH)_2$, $CoFe_2O_4$ and Co_3O_4 references. Data are represented by a solid line and models by a dotted line.

Table S2 Results on the fits of linear combination fitting analysis for XAS data

Samples	$Co(OH)_2$ (%)	$CoFe_2O_4$ (%)	Co_3O_4 (%)	χ^2
$[Co]_s$ = 2.47 atom nm^{-2}	21.5	78.5	0.0	0.005
$[Co]_s$ = 6.74 atom nm^{-2}	32.4	63.6	4.0	0.006
$[Co]_s$ = 6.80 atom nm^{-2}	44.0	42.5	13.6	0.010
$[Co]_{tot}$ = 8.91 atom nm^{-2}	28.1	46.2	25.7	0.008
$[Co]_{tot}$ = 10.05 atom nm^{-2}	40.1	0.2	59.7	0.014
$[Co]_{tot}$ = 35.55 atom nm^{-2}	22.1	0.7	77.2	0.004

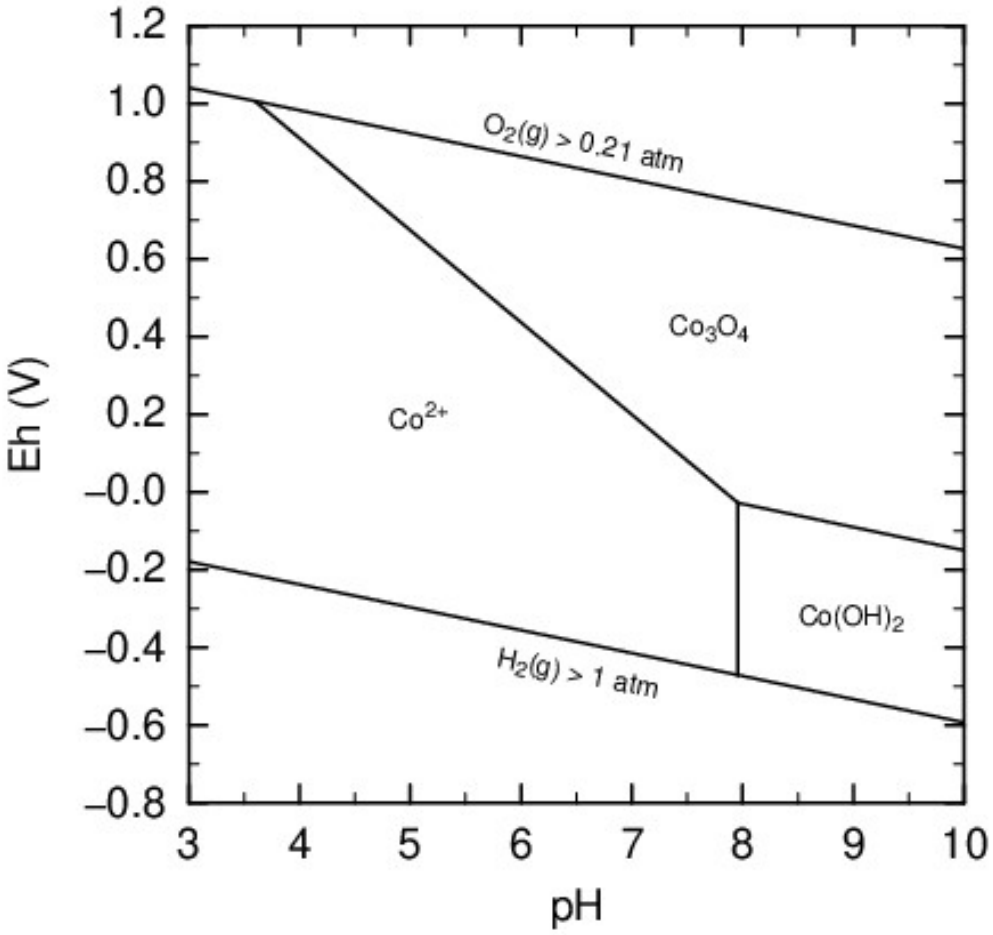

Fig. S5 pH-EH predominance diagram of Co (12 mM) in 10 mM NaCl.

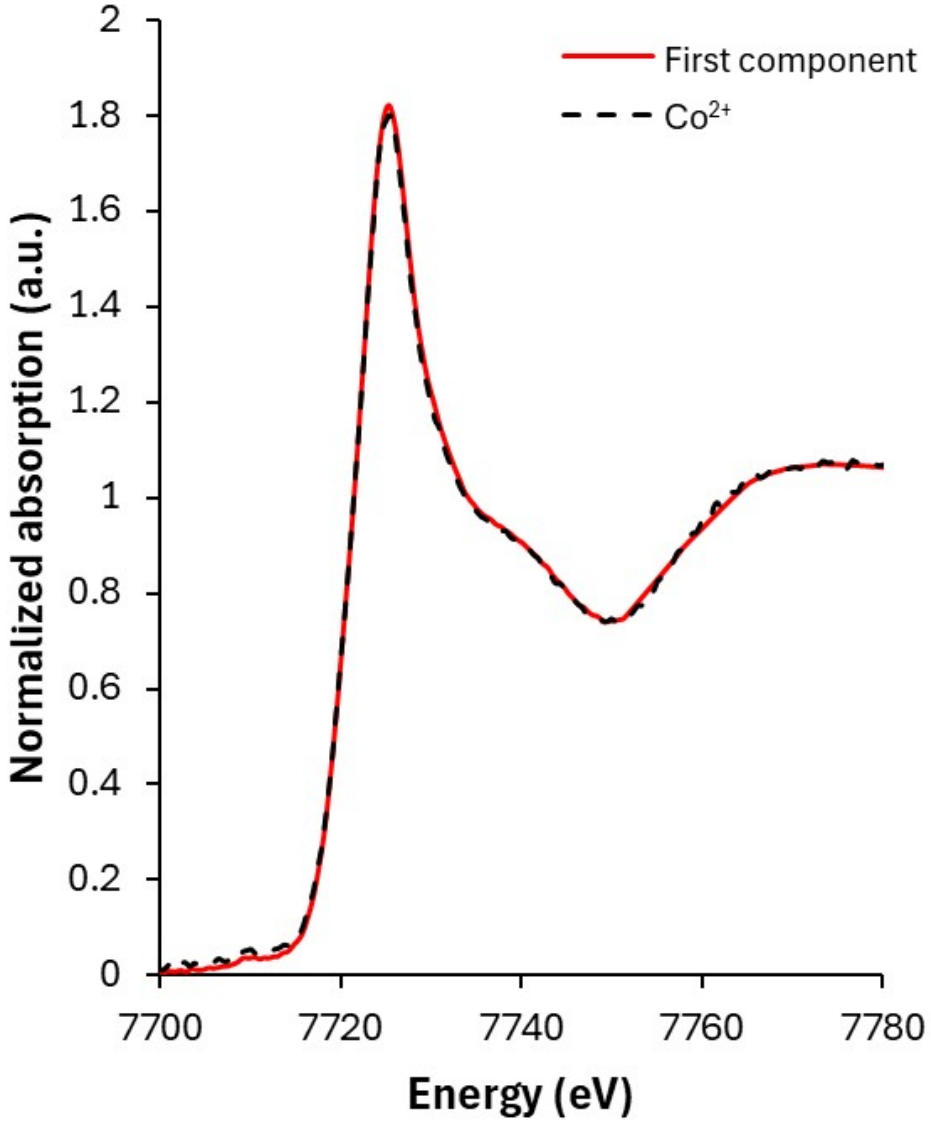

Fig. S6 Comparison between the XANES spectra of the fisrt component and of the Co^2 solution.

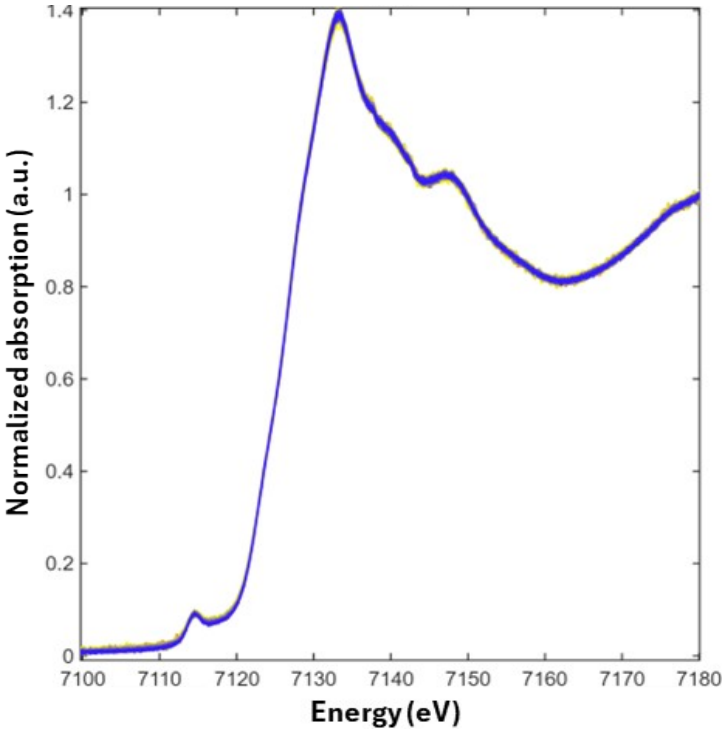

Fig. S7 XANES spectra evolution at the Fe *K*-edge as a function of time (120 min) during the oxidation kinetics in aerobic conditions, for $[Co]_{tot}$ = 12 mM.

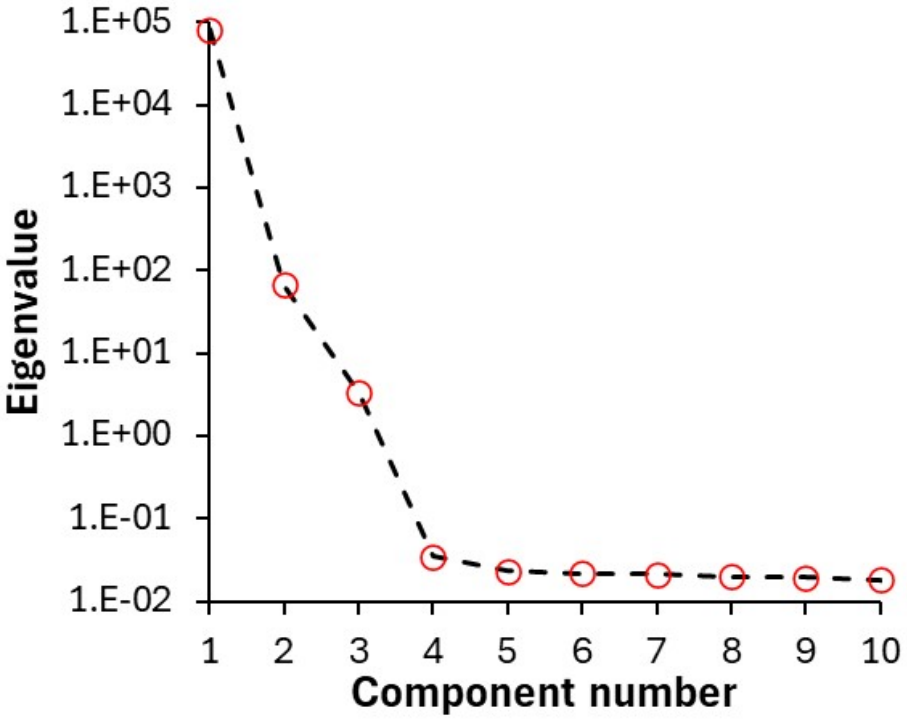

Fig. S8 Principal component analysis (PCA) on XAS data. A logarithmic scale is used.