ESRF	**Experiment title:** Monitoring bio-inspired cuboidal Co4O4 water oxidation catalysts at work with XAS techniques	**Experiment number**: 01-01-961
Beamline: BM01b	**Date of experiment**: from: Oct 29th 2014 to: Nov 3rd 2014	**Date of report**: 25.02.2015
Shifts: 12	**Local contact(s)**: Dr. Hermann Emerich	

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Report:

Photocatalytic watersplitting is an elegant way to feed the growing global energy demand with green and sustainable fuels. [1] However, the water oxidation half-reaction remains as a four electron process the bottleneck in the overall catalytic cycle. We investigated biometric cuboidal water oxidation catalyst (**Co_4O_4**, $[Co_4(hmp)_4(OAc)_4(H_2O)_2]$, hmp = 2-Methylhdroxypyridine, OAc = acetyl) (Fig 1.). [2]

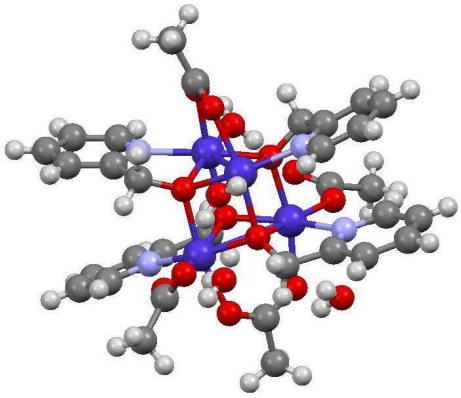

Fig. 1. Molecular structure of the water oxidation catalyst **Co_4O_4**.

An average valance state of +2 could be estimated for **Co_4O_4** in the catalytic solution based on the edge position in respect to known reference standards. The comparison of the XANES region of **Co_4O_4** in catalytic solution before and after photocatalysis displays no of the shift edge position and no significant change in the difference spectra (Fig. 2 right). Therefore, any kind of irreversible oxidation of **Co_4O_4** during photocatalyst can be excluded.

In line with the nearly identical EXAFS region of **Co_4O_4** before and after catalysis (Fig. 2 left), changes in the coordination enviroment of the Co can be negleted.

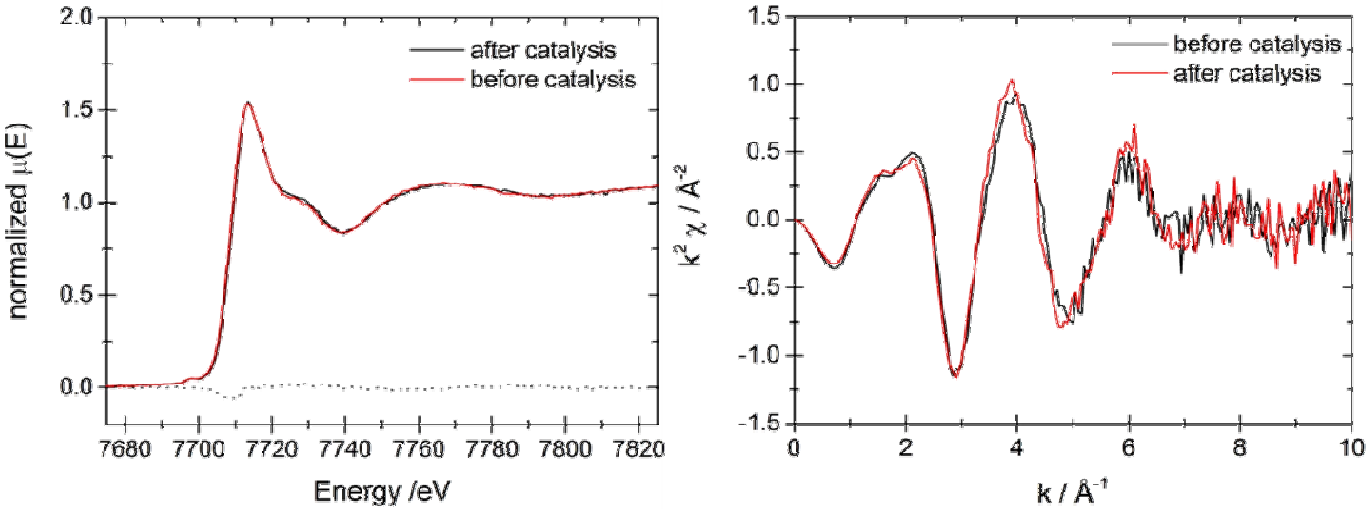

Fig. 2. Left: XANES region and difference spectrum of **Co_4O_4** before and after catalysis. Right: EXAFS region of 1 before and after catalysis plotted in K-space.

References:

[1] H. Lv, Y. Geletii, C. Zhao, J. W. Vickers, G. Zhu, Z. Luo, J. Song, T. Lian, D. G. Musaev, C. L. Hill, *Chem. Soc. Rev., 2012*, **41**, 7572.

[2] F. Evangelisti, R. Güttinger, R. Moré, S. Luber, G.R. Patzke, *J Am. Chem. Soc., 2013*, **135**, 18734.