Time-resolved XAS to study molecular photocatalytic H_2 evolving systems

Grigory Smolentsev,[1] Mikhail Soldatov,[2] Benjamin Probst,[3] Cyril Bachmann,[3] Johannes Windisch,[3] Arno Schneider,[4] Alexander Guda,[2] Nicolo Azzaroli,[1] Roger Alberto,[3] Maarten Nachtegaal,[1] Jeroen A. van Bokhoven[1,4]

(1)Paul Scherrer Institute, Villigen, 5232, Switzerland; (2) Southern Federal University, Rostov-on-Don, 344090, Russia; (3) University of Zurich, Zurich, 8057, Switzerland (4)ETH Zurich, Zurich 8093, Switzerland

grigory.smolentsev@psi.ch

Recent developments and applications of time-resolved X-ray absorption spectroscopy (XAS) at SLS synchrotron will be presented. The main focus of our efforts is the time range 20ns - 500μs which is relevant to study photocatalytic reactions [1]. Two principal components of photocatalytic systems are photosensitizer and catalyst. We have investigated cobalt complex with pentadentate pyridine-based ligand which are promising molecular catalyst evolving H_2 from water [3] and recently developed Cu-based photosensitizer with long excited state lifetime which can work in combination with Co-based catalyst. The recent review article summarizes our time-resolved XAS results in the field of artificial photosynthesis for other systems [1].

Time-resolved XAS measurements in the 30 nanoseconds -100 microseconds time range have been performed using pump-sequential-probes setup that we have developed at the SuperXAS beamline of SLS [2]. To investigate metal complexes in solution during reactions, we use the pulsed laser for photoexcitation and continuous synchrotron X-ray beam for probing. Transient XANES spectra have been analyzed using combination of DFT prediction of possible structural models, calculation of XANES spectra using Finite Difference Method (FDMNES code) and structure refinement based on XANES fitting (FitIt code).

The structure of Co(I) intermediate of this catalyst has been determined based on Co K-edge XANES analysis. Similar approach we have demonstrated previously [4]. We have found that one pyridine ligand dissociates from Co and the metal center remains 4-coordinated without any strong bonds with the solvent. The protonation of both metal center and pyridyl is possible which opens perspectives for rational design of more efficient catalyst. The structure of Cu phenanthroline-based photosensitizers in the triplet excited state has been also determined with time-resolved XAS. Bulky sec-butyl groups at 2,9 positions of phenanthroline block the access of solvent to the metal in the excited state, reduce the flattening distortions and increase the excited state lifetime.

Pump-sequential-probes XAS method is efficient technique to study molecular photocatalytic systems relevant for energy-related applications. Quantitative analysis of time-resolved XAS provides the structure of intermediates of catalysts and excited photosensitizers.

References

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