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Ultrafast dynamics of electronic and structural modifications induced by pho-toexcitation in cerium oxide

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The electronic and structural modifications occurring in photocatalysts after photoexcitation largely determine the light-induced functionality of such materials. Cerium oxide is a relevant catalyst with enhanced redox properties, due to its ability to easily and reversibly release oxygen atoms from its lattice.

In a pump-probe optical spectroscopy experiment on cerium oxide films we recently identified aphotoinduced blueshift of the band-gap absorption feature ascribed to photoinduced absorption, that was tentatively ascribed to the coupling between photo-excited charge and the structural distortions into a so-called photoinduced small-polaron state [1].
The availability of ultra-short and ultra-intense X-ray pulses from a free electron laser (FEL), tunable in energy, has allowed us to obtain a detailed picture of the modifications occurring in cerium oxide upon photoexcitation. In particular pump-probe X-ray absorption spectroscopy (XAS) has provided element-specific information on the ultrafast dynamics of the local electronic and atomic structure induced by photoexcitation above the band gap.

We report here the results of pump-probe XAS experiments performed at the FXE instrument of the European XFEL on cerium oxide films. The measurements were performed at 10 degrees incidence, to minimize sample damage and maximize the sensitivity of the method to the thin film investigated. The sample was excited using a laser pump pulse with energy above the band gap and probed by XFEL pulses at the Ce L3 edge. We successfully measured pump-probe Ce L3-edge XAS spectra in the total fluorescence yield acquisition mode by acquiring X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectra with time resolution of approximately 100 fs and up to 10 ps delay time. In the XANES region we observed a dynamic evolution of both the intensity and the shape of the pump-probe signal, reflecting the changes in the 5d states from which the various features originate. The analysis of the pump-probe EXAFS spectra has demonstrated the presence of photoinduced structural distortions with a comparable lifetime as the electronic modifications. The obtained results allow to have previously unavailable details on photoinduced small-polaron states, that possibly determine a long-living transient increase of the redox functionality of the material.

References

[1] J. S. Pelli Cresi et al., J. Phys. Chem. Lett. 11, 5686 (2020).

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