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# Ultrafast dynamics of photoexcited states in cerium oxide investigated by pump-probe XAS at the EuXFEL

S. Pelatti[1,2], E. Spurio[1,2], J.S. Pelli Cresi[3], S. Benedetti[2], A. di Bona[2], S. D'Addato[1,2], P. Zalden[4],
Y. Jiang[4], Y. Uemura[4], H. Wang[4], D. Vinci[4], X. Huang[4], F. Lima[4], M. Biednov[4], D. Khakhulin[4],
Chris Milne[4], S. Turchini[5], G. Ammirati[5], P. O'Keeffe[6], D. Catone[5],
F. Boscherini[7] and P. Luches[2*]

[1]*Dipartimento FIM, Università degli Studi di Modena e Reggio Emilia, 41125 Modena, Italy*
[2]*Istituto Nanoscienze, CNR (NANO-CNR) ,41125 Modena, Italy*
[3]*Elettra-Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy*
[4]*European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany*
[5]*Istituto di Struttura della Materia – CNR (ISM-CNR), EFSL, Rome, Italy*
[6]*Istituto di Struttura della Materia – CNR (ISM-CNR), EFSL, Monterotondo Scalo, Italy*
[7]*Dipartimento di Fisica e Astronomia, Alma Mater Studiorum – Università di Bologna, Bologna, Italy*

*e-mail: paola.luches@nano.cnr.it

Pump-probe spectroscopies utilizing X-ray free-electron lasers (XFELs) offer element-specific insights into the processes occurring in photocatalysts following photoexcitation, which are essential for the rational optimization of these materials' efficiency. At the FXE instrument of the European XFEL facility[1] we investigated the dynamic evolution of photoexcited sates in cerium oxide, a material widely used as a catalyst or photocatalyst.

The sample was a stoichiometric $CeO_2$ film grown by reactive magnetron sputtering on a sapphire substrate. The measurements were performed at grazing 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. We employed pump-probe X-ray absorption spectroscopy (XAS) at the Ce $L_3$ edge in both the near-edge and extended energy ranges to simultaneously probe the ultrafast electronic and local atomic structure modifications following photoexcitation. The data were acquired in the total fluorescence yield within a delay time range up to 300 ps with approximately 50 fs resolution.

The results revealed a rapid de-excitation pathway occurring within the first few hundred femtoseconds, followed by the formation of a metastable excited state with a lifetime on the order of hundreds of picoseconds. The analysis of pump-probe XAS in the extended energy range identified a structural distortion consistent with the formation of a photoinduced small polaron state, that was hypothesized by a previous study done by optical pump-probe transient absorption spectroscopy.[2] The observed time correlation between the photoinduced electronic and structural changes further reinforces the hypothesis of photoinduced polaron formation.

Such transient charge localization is expected to have a positive impact on cerium oxide-based photocatalysts by weakening the bond between the cation and oxygen, thereby reducing the energy required for oxygen vacancy formation, which is crucial for the material's functionality. At the same time, it can extend the lifetime of the photoexcited carriers.

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