

# Charge-carrier dynamics of photoexcited 4d metal oxides using pump-probe XAS

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X-ray spectroscopies are sensitive to the electronic and structural changes around the absorbing element, and have been used to study photoexcited states of materials at synchrotron radiations (SR) and X-ray free electron lasers (XFELs). There have been pioneering studies on photocatalysts based on 3d or 5d elements using X-ray absorption spectroscopy (XAS). However, far fewer studies have been conducted on photocatalysts consisting of 4d elements, whose absorption edges occur either on hard (> 18 keV, K-edge) X-rays, which are difficult to access. NW14A could deliver the high photon energy X-ray pulses and provide established pump-probe XAS setup. Using these capabilities, we have recently succeeded in performing transient Nb K-edge (19 keV) X-ray absorption spectroscopy on a colloidal suspension of Nb<sub>2</sub>O<sub>5</sub> nanoparticles with ~100 ps resolution. Following the ps time resolution studies, we succeed in collecting the ~100 fs resolution transient XAS signals at FXE instrument of European XFEL. It is found that the local structural change is decoupled from the photoexcitation in short time scale below 1 picosecond, and grows until few picoseconds.

## 1 Introduction

Photocatalysis is one of the most promising solutions to tackle global challenges such as energy production and environment sustainability. Semiconductor materials based on transition metal oxides offer great advantages and are currently the most widely used systems [1]. The photocatalytic efficiency strongly depends on the dynamics of charge carriers, namely the excitation and recombination processes. For instance, the localization of electrons/holes due to the extra structural distortion after photoexcitation limits the mobility of free carriers but improve their lifetime, which in turn affect the photocatalytic efficiency. Therefore, direct tracking the photoexcited state relaxations and structural evolutions would allow a deep understanding of the photocatalysis processes and inspire new photocatalyst design. Standard ultrafast optical characterization techniques are not element-specific and do not provide direct information on structures. Time-resolved (tr-) X-ray probes, e.g., X-ray absorption and emission spectroscopies (XAS and XES, respectively), have the advantage of being sensitive to the electronic configurations and local structures around the absorbing element. These techniques can be applied to numerous systems, e.g., solid-state materials or molecules in solution, etc., and has routinely been employed to study photoexcited states of materials at synchrotron radiation (SR) and X-ray Free Electron Laser (XFEL) large-scale facilities [2].

XAS has become one of the essential techniques for characterization of materials in photoexcited state, as it provides rich complementary information to the standard ultrafast all-optical spectroscopic methods. There have been pioneering studies on photocatalysts based on 3d or 5d elements using XAS/XES [2]. However, far fewer studies have been conducted on photocatalysts consisting of 4d elements. Their absorption edges occur either on hard

(> 18 keV, K-edge) or tender X-rays (< 3 keV, L-edges), and special conditions are required to measure the respective XAS/XES spectra with sufficient quality and spectral resolution. Interestingly, 4d elements and their oxides exhibit unique competition between fundamental interactions, e.g., the dominant role of electron correlations and spin-orbital coupling may be inverted in 3d and 4d metal oxides. 4d elements' physical behaviours could be differ from their 3d counterparts [3] and offer wide-ranging opportunities for the discovery of new functionalities. Hence, implementing efficient XAS/XES methodology in the upper hard X-ray will allow addressing questions related to the photoexcitation dynamics of the 4d systems. For that, FXE instrument at European XFEL provides unique capabilities of delivering high photon energies with high X-ray pulse intensity.

Nb<sub>2</sub>O<sub>5</sub>, which is one of the popular 4d metal oxide photosensitizers for catalysis, exhibiting strong redox ability and unique Lewis's acid sites, and strong absorption in the blue region of the spectrum. It shows relevant applications in conversion of photodegradation of pollutants, activation of hydrocarbon, photoreduction of CO<sub>2</sub>, and selective transformation of amines and alcohols [4]. Recent optical transient absorption measurements of Nb<sub>2</sub>O<sub>5</sub>-based heterojunctions claimed that the accelerating charge transfer could boost the photocatalytic H<sub>2</sub> evolution of the material, however the mechanism governing photoexcitation dynamics is currently lacking [5, 6]. Complexity of the transient dynamics combined with the lack of element specificity on the measurements make it challenging to accurately assign the states involved. In this work, we investigate ultrafast dynamics of niobium oxides nanoparticles in solution by means of picosecond (ps) and femtosecond (fs) tr-XAS.

## 2 Experiment

Tr-XAS with  $\sim 100$  ps resolution was collected at the NW14A beamline of Photon Factory Advance Ring (PF-AR) synchrotron at KEK, Japan and with  $\sim 100$  fs resolution at the FXE Instrument (Figure 1). The transient XAS signals after excitation show a rich temporal evolution, in particular in the first 10 ps. Figure 1(a) shows the transient X-ray absorption near edge structure (XANES) of  $\text{Nb}_2\text{O}_5$  nanoparticles in water solution at 200 ps. Figure 1(b) shows the XANES spectrum for different time delays collected at FXE. The incoming energy resolution differs slightly in those measurements due to difference in beam divergence. The tr-XAS at short time scales below  $\sim 10$  ps are remarkably different from the ones at long time scales, e.g., 200 ps. The transient peak at  $E_2$  is due to a shift on the

main edge energy, probing changes in the valence band (consisting mainly of O  $2p$  orbitals) to the conduction band (mostly Nb  $4d$  orbitals). A shift towards lower energies is consistent with more reduced Nb centers. The pre-edge transitions ( $E_1$ ) are mainly due to quadrupole transitions from Nb  $1s$  to the mixed niobium  $4d$  and oxygen  $2p$  states and are, in general, sensitive to the local structure changes (more or less distortion) around the Nb and the specific details of its electronic configuration. Feature  $E_3$  is the white line overlapped with the beginning of the extended X-ray absorption fine structure (EXAFS), and normally provides a fingerprint for local structure changes.

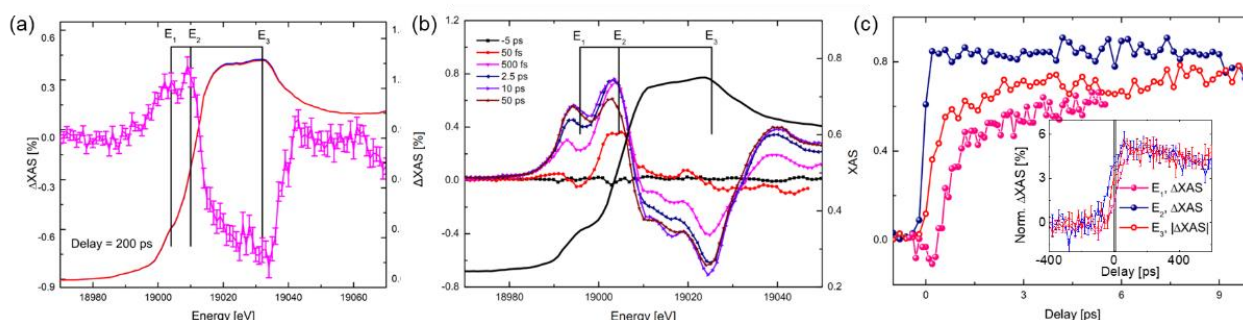


Figure 1. (a) X-ray absorption near edge structure (XANES) and transient signal collected using  $\sim 100$  time-resolution XAS setup at Photon Factory, delay is fixed to 200 ps, wavelength of pump laser is 343 nm. And (b) shows the XANES scans and transient signals at different time delays, which are collected using  $\sim 150$  fs time-resolution XAS setup at FXE, wavelength of pump laser is 267 nm. (c). The time traces of transient X-ray absorption signal at different X-ray energies,  $E_1$  is around the pre-edge, and  $E_2$  is around the main edge of Nb K-edge,  $E_3$  is around one of the white line peaks. The inset shows the ps-resolution data. Different energy resolutions were noted in the measurements at Photon Factory and FXE.

### 3 Results and Discussion

The rich dynamics of  $\text{Nb}_2\text{O}_5$  can be seen on the time traces at different incident X-ray energies  $E_1$ ,  $E_2$  and  $E_3$  (Fig. 1(c)). For example, the transient XAS at energy  $E_1$  shows interesting features after photoexcitation: firstly, it reaches to negative values in early times ( $< 0.3$  ps), then grows quickly until  $\sim 1.3$  ps and continue with a slow increase in intensity until  $\sim 6$  ps. The transient XAS at  $E_2$  appears instantaneously within our temporal resolution and arises from the energy shift of the main edge. It can then be ascribed to the first photoexcitation processes being a reduction in the Nb centers. This signal decays with  $\sim$ ns lifetime. The time trace at  $E_3$  raises later and slower than compared to the  $E_1$ . It is very weak in the early times, growing slowly until few tens of ps and finally decaying until  $\sim 600$  ps. This rich behaviors after ultrafast photoexcitation observed in the time traces indicate that the local structural change reported by the  $E_3$  feature is decoupled from the photoexcitation in short time scale  $< 1$  ps, and keeps growing until few ps. This complexity of photoexcited dynamics may be aggravated by specific aspects of each  $4d$  metal that can introduce additional complexity to the local structure. Specifically,  $\text{Nb}_2\text{O}_5$  has various polymorphic forms, where the Nb ions exist in different coordination (tetrahedral, octahedral or/and

pentagonal bipyramids), which is more complex than its counterpart  $\text{V}_2\text{O}_5$ . In  $\text{V}_2\text{O}_5$ , the vanadium ions only adopt tetragonal coordination (the stable form of  $\text{V}_2\text{O}_5$  is orthorhombic). In our case, despite also having an orthorhombic structure, the  $\text{Nb}_2\text{O}_5$  nanoparticles exhibits two distinct Nb sites for coordination (tetrahedral and octahedral). Thus, the dynamics of photocarriers in  $\text{Nb}_2\text{O}_5$  can potentially induce additional local structural changes. Singular value decomposition (SVD) analysis and TD-DFT calculations are ongoing to provide additional details on the photo-physics of  $\text{Nb}_2\text{O}_5$  after photoexcitation.

The femtosecond-resolved XAS data shown here demonstrate the ability to perform tr-XAS at energies above 18 keV opening new opportunities for investigating materials with  $4d$  metals. Direct tracking the photoexcited state relaxations and the associated structural evolution would allow a fundamental understanding of the photocatalysis processes in transition metal oxides and inspire new photocatalyst design, especially with respect to comparing the similarities and particularities between  $3d/5d$  and  $4d$  metal oxides. Further efforts in order to improve the energy resolution by using high-resolution spectrometers are ongoing.

### Acknowledgement

We gratefully acknowledge the beamtime at NW14A of photon factory advanced ring and at FXE instrument of European XFEL. This work is supported by the research and development project at European XFEL (R&D project HELIOS: High-Energy Laue X-ray emission Spectrometer at FXE).

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#### Research Achievements

1. The manuscript is under preparation.

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