

Time-resolved X-ray absorption and emission spectroscopy on ZnO nanoparticles in solution

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Abstract: We have performed time-resolved resonant X-ray emission spectroscopy after UV photoexcitation of a colloidal solution of ZnO nanoparticles. The results point to electron trapping sites located at oxygen vacancies in the lattice.

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1. Introduction

Nanoscale functional materials represent a unique hybrid of bulk crystalline structure with some degree of disorder due to their large surface area. It is this duality that has made them attractive for a broad range of applications. Among a wide variety of materials, ZnO has proven to be a highly versatile nanomaterial with applications ranging from light-emitting diodes to photocatalysis. [1] For solar energy conversion and storage, photosensitization and photocatalysis the primary aspect is the lifetime and mobility of charge carriers (electrons and holes). Understanding the mechanism by which these charges traverse the nanoparticle, become trapped and/or recombine is therefore of fundamental as well as practical importance. In order to better understand the structure-function relationship and the dynamics of the charge carriers in such devices it is important to be able to measure both electronic and structural properties simultaneously. Here we study the electron-hole dynamics within a colloidal solution of 35 nm ZnO nanoparticles photo-excited with above band-gap UV light (3.2 eV). Using pump-probe X-ray absorption spectroscopy (XAS) combined with a dispersive X-ray emission spectrometer we perform time-resolved resonant X-ray emission spectroscopy (RXES), [2,3] which yields detailed information on both the occupied and unoccupied electronic states and geometric structure after photo-excitation.

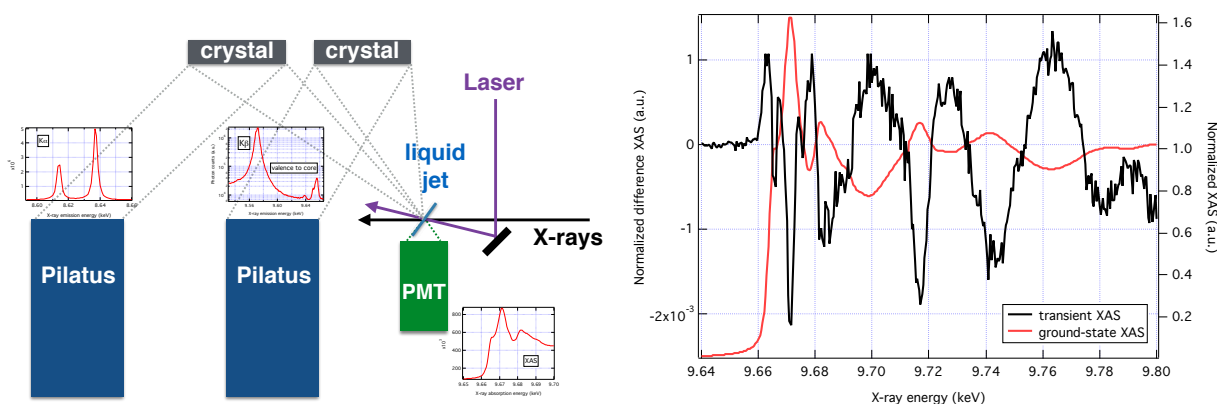


Fig. 1. Left: Top view of the setup used at the APS with the two-crystal von Hamos XES spectrometer. Right: Ground-state and pump-probe XAS of a colloidal solution of 35 nm ZnO nanoparticles measured in total fluorescence yield at a time delay of 100 ps and an average fluence of 90 mJ/cm².

2. Experiment

The experiment was performed at 7ID-D at the Advanced Photon Source, using their high-repetition rate laser and data acquisition setup. [4] The X-ray emission measurements were performed with a temporary installation of a two-crystal/two-detector setup in a von Hamos geometry to simultaneously measure the $K\alpha$ and $K\beta$ emission signals. [5] The crystals used were cylindrically bent Ge(220) and Si(111) with a 25 cm radius of curvature and the detectors used were two Pilatus 100K modules. The sample was flowed through a 100 μm jet nozzle to ensure a continuous stream of fresh sample and the total fluorescence yield signal was measured with a photomultiplier tube (PMT).

3. Results

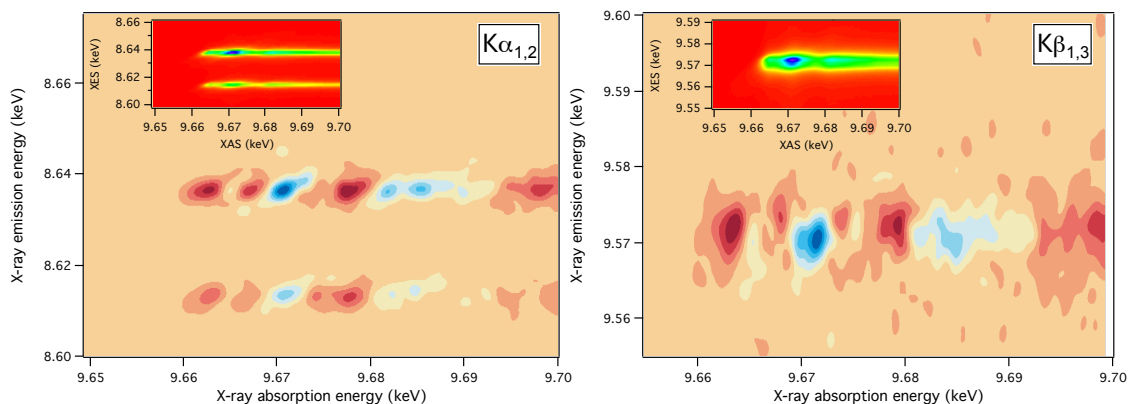


Fig. 2. Left: Pump-probe RXES measurements of the Zn $K\alpha$ emission signals. Right: Pump-probe RXES signals Zn $K\beta$ emission signal. Ground-state RXES shown as insets. Measured on a sample of 35 nm ZnO nanoparticles in water 100 ps after excitation at a fluence of 80 mJ/cm^2 .

Time-resolved XAS and RXES were measured 100 ps after photo excitation. The XAS transient signal shown in Figure 1 shows a clear signature of both electronic and structural changes in the nanoparticle. The EXAFS structural modulations above 9.7 keV are a clear signature of a change in the structural environment of the trapped electronic excitation. The transient RXES signals shown in Figure 2 demonstrate that the total fluorescence yield signals are more complicated than a simple change in fluorescence yield. Both the $K\alpha$ and $K\beta$ emission signals demonstrate simultaneous shifts in the emission energy and amplitude change in the total fluorescence yield.

4. Conclusions

We have successfully measured the transient XAS and RXES signals from a colloidal solution of ZnO nanoparticles. The signals show a combination of both structural and electronic changes indicating the likelihood of a specific localized defect being responsible for the long-lived trapped electronic state. Preliminary analysis indicates the trapping site is at an oxygen vacancy in the lattice.

References

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