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MOLECULAR STRUCTURE DETERMINATION FOR PHOTOGENERATED INTERMEDIATES IN PHOTOINDUCED ELECTRON TRANSFER REACTIONS USING STEADY-STATE AND TRANSIENT XAFS

Lin X. Chen
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA.
Phone:(630)252-3533; Fax:(630)252-9289; e-mail:lchen@anlchm.chm.anl.gov

Michael R. Wasielewski
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA.
Phone:(630)252-3538; Fax:(630)252-9289; e-mail:wasielewski@anlchm.chm.anl.gov

Tijana Rajh
Chemistry Division Argonne National Laboratory, Argonne, Illinois 60439, USA.
Phone:(630)252-3542; Fax:(630)252-9289; e-mail:rajh@anlchm.chm.anl.gov

Peter L. Lee
Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
Phone:(516)344-5706; Fax:(516)344-5934; e-mail:lee@anlsrs.msd.anl.gov

Marion C. Thurnauer
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA.
Phone:(630)252-3570; Fax:(630)252-9289; e-mail:thurnauer@anlchm.chm.anl.gov

Pedro A. Montano
Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
Phone:(630)252-6239; Fax:(630)252-0365; e-mail:pedro_montano@qmgate.anl.gov

Abstract Many photoinduced electron transfer reactions are accompanied by nuclear rearrangements of the molecules involved. In order to understand the reactivities of the molecules and the reaction mechanisms, precise information on the molecular structural changes accompanying the electron transfer is often required. We present here conventional XAFS and transient energy dispersive XAFS studies on (1) the structures of excited and photoinduced charge separated states of porphyrin and porphyrin based supermolecules, and (2) structures of TiO_2 colloid and the heavy metal ions that bind to the colloid surfaces during photocatalytic reductions.

Running header: Molecular Structure Studies by Time-resolved XAFS

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Lin X. Chen[1a], Michael R. Wasielewski[a], Tijana Rajh[a], Peter Lee[b], Marion C. Thurnauer[a], Pedro A. Montano[b]

[a]Chemistry Division and [b]Material Science Division
Argonne National Laboratory
Argonne, Illinois 60439

Abstract Many photoinduced electron transfer reactions are accompanied by nuclear rearrangements of the molecules involved. In order to understand the reactivities of the molecules and the reaction mechanisms, precise information on the molecular structural changes accompanying the electron transfer is often required. We present here conventional XAFS and transient energy dispersive XAFS studies on (1) the structures of excited and photoinduced charge separated states of porphyrin and porphyrin based supermolecules, and (2) structures of TiO_2 colloid and the heavy metal ions that bind to the colloid surfaces during photocatalytic reductions.

1. Introduction

Photoinduced inter- and intra-molecular electron transfer processes occur in many chemical reactions[1,2], such as those in solar energy conversion and storage, molecular devices and environmental clean up processes. Many reactions are accompanied by nuclear rearrangements of the molecules involved. Most of the photoinduced charge separation processes are achieved via excited states or a series of intermediate states having electronic structures distinctively different from those of the ground state molecules. The determination of the structures of these transient species is the key to understanding the fundamental chemistry of photoinduced charge separation. However, most of the lifetimes of these transient species are very short, ranging from 10^{-6}--10^{-12} seconds. Thus, determining transient molecular structures on that time scale should be feasible as the third generation synchrotron X-ray sources become available.

In the past several years, we have been working on structural determination of photoinduced charge-separated meta-stable states with relatively long lifetimes on second generation synchrotron beamlines[3-5]. The experiments were conducted at cryogenic temperatures at which the metastable species can be trapped for a relatively long time. Although these studies are on a time scale that is much longer than most of the photoinduced charge separation reaction, the XAFS studies already offer new information on reaction mechanisms and identities of intermediates that was not known from other studies.

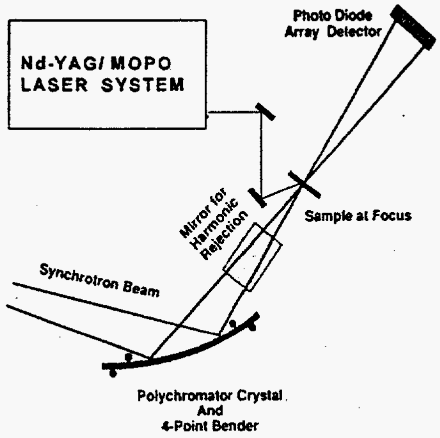

Figure 1. EDXAS setup at X6A, NSLS with a Nd-YAG pumped OPO system synchronized with photodiode detector.

2. Molecular Structure Determination of Photo-excited States and Photoinduced Electron Transfer Intermediates Using Energy Dispersive XAFS

We have started real time resolved XAFS studies with millisecond time resolution on excited triplet state structures of zinc tetraphenylporphyrin (ZnTPP) and zinc

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[1] To whom the correspondence should be addressed.

octaethylporphyrin(ZnOEP) using energy dispersive XAFS at beamline X6A[6,7], NSLS, Brookhaven National Laboratory. The experimental setup is shown in Figure 1. A Nd-YAG laser pumped optical parametric oscillator (OPO) operating at 10 Hz is synchronized with the read-out frequency of a linear photodiode detector. The laser pulse width (FWHM) is 6 ns, thus the time resolution is currently limited to the detector read-out time of 5ms. Twenty read-outs from the detector can be made between laser pulses. This restriction makes the selection of the molecular systems, which can be studied using such energy dispersive XAFS system, very critical. Several factors are important to the experiment: (1) the lifetime of the metastable state must be longer than 5 ms and must return to the ground state within 100 ms; (2) the laser pulse energy must be high enough for a high yield conversion from the ground state to the excited state; (3) the excitation must have a high quantum yield; (4) there must be enough molecules in the X-ray path for the transmission XAFS detection, yet the concentration of the sample must be low enough to prevent bimolecular processes, such as excitation annihilation; (5) the detector dark current must be small and have minimum fluctuation allowing small changes in the spectra between the ground state and the metastable state to be detected. In the experiment on ZnTPP and ZnOEP, the first four conditions are fulfilled with a solution cell that provides a much longer pathlength for the X-rays than for the laser light. We are working on improving the stability of the dark current during the experiment. Meanwhile, we have synthesized an electron donor-acceptor supermolecule which could have significant structural changes due to photoinduced electron transfer from the excited triplet state. We are currently carrying out optical spectroscopic characterization of the molecule by fast optical transient absorption.

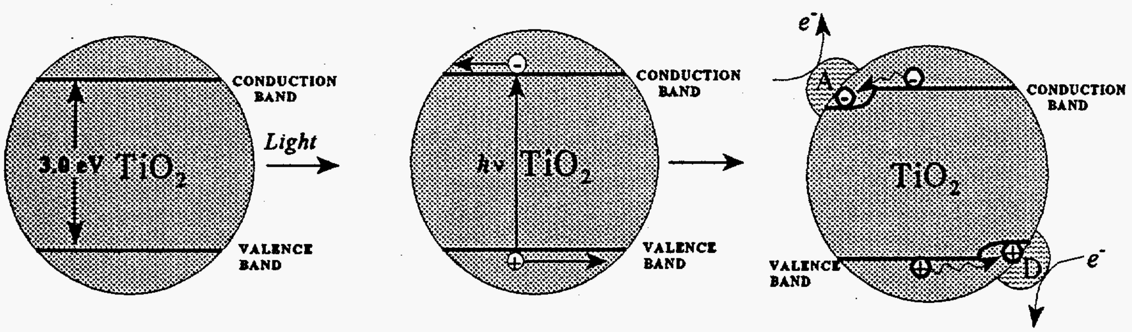

Figure 2. Photocatalytic reduction/oxidation reaction on TiO_2 colloid surfaces

We have been studying photoreduction of heavy metal ions on modified TiO_2 colloid surfaces [8]. The photocatalytic reduction/oxidation on semiconductor surfaces, such as TiO_2 can be illustrated in Figure 2. After light illumination of TiO_2 colloid particles, electrons are excited to the conduction band, resulting in charge separation between the electrons and remaining holes. The holes and electrons diffuse to the surface of the particle if they do not recombine rapidly. When an electron donor or acceptor is also in the vicinity of the surface, a redox reaction can occur. In our laboratory, we have synthesized TiO_2 colloid particles (anatase) of different sizes, ranging from 30 - 200 Å. Considering one of the dimensions of an anatase unit cell is 9.37Å, a TiO_2 colloid particle with 30Å diameter only contains 3-4 unit cells in one dimension. Important questions regarding these small TiO_2 colloid particles are whether the small particles still maintain a lattice structure such as that found in bulk TiO_2, and how the surface Ti-O bonds differ from those in the interior of the particle. In addition, we have modified the TiO_2 surface by amino acids and other organic thiol compounds. An EPR study [9] shows that the charge separation time on TiO_2 colloid surfaces is increased and the reaction efficiency is greatly enhanced upon such modifications. Some heavy metal ions which could not be easily reduced or reduced at all were photoreduced by modified TiO_2. The XAFS technique is a useful tool to examine three different local structures in these systems: surface structure of TiO_2 at the Ti K-edge, the surroundings of the heavy metal ions at the K- or L-edge of transition metals, and thiol bonding at the S K-edge. The first two XAFS studies will be presented here.

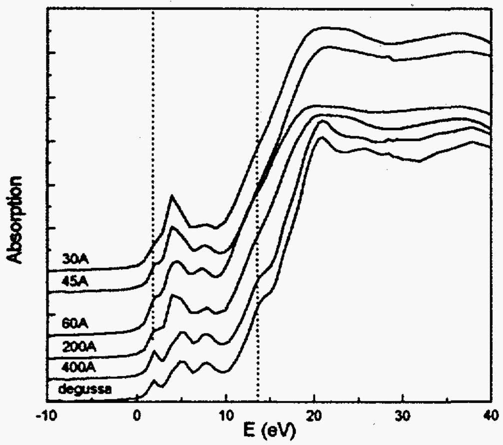

Figure 3. Systematic changes observed in XANES for TiO_2 particles with different sizes(shown as diameter). The three pre-edge peaks represent the transitions from 1s to t_{2g} and e_g in an octahedral field. The intensity of the second peak is related to distortion of the field in colloid particles.

Figure 3 shows XANES structures of TiO_2 with different particle sizes. A significant difference is observed comparing the spectrum of TiO_2 with 400Å diameter to that of 30Å diameter. The second pre-edge peak is significantly enhanced in the latter due to the distortion of an octahedral field around Ti. Other differences between the bulk and the colloid are the fine structures in the XANES region. As the particle sizes decrease, the fine structures across the spectra diminish. For example, the sharp white light peak is flattened in the spectra of smaller particles. A "shoulder" at the rising edge in the spectra of the bulk and 400Å particles also disappears in the spectra of smaller particles. The distortion can also be observed in the Fourier Transform spectra (not shown) of TiO_2 colloid particles with different sizes. The first shell Ti-O distances in 30Å diameter particles cannot be described by a single distance as in the 400Å diameter particles, rather, two Ti-O distances are formulated. The shorter Ti-O distance may be attributed to the Ti-O bond length in surface Ti-OH (about 30% TiO_2 are exposed to the solution in 30Å diameter TiO_2 particles), and the longer Ti-O bondlength, to a distorted lattice in the interior of 30Å diameter particles. These observed distortions could be the source of enhanced catalytic capability of TiO_2 due to very energetic sites on the surface.

The XAFS measurements on surroundings of the heavy metal ions can be used to identify the species produced in photocatalytic reaction, i. e., whether the reduced species is pure metal, or a precipitate of the metal salt. The measurements can also monitor the time evolution of the reaction, and the reaction yield. The photocatalytic reactions were carried out under nitrogen, and a xenon lamp was used for illuminating the sample. In a system containing only Cu^{2+} and TiO_2 particles, photoillumination did not produce a detectable amount of Cu^0 by XAFS. However, attaching alanine to the TiO_2 surface greatly enhanced the reaction rate and yield of Cu^0. Changes of Fourier transformed XAFS spectra in Figure 4 as a function of illumination time clearly demonstrated the photocatalytic reduction of Cu^{2+}. The amount of Cu^{2+} reduced is up to 50% of total copper in the system. The peaks in the high R region indicated that the reduced Cu forms large particles after 40-60 minutes illumination. The Cu particles initially formed from photoillumination are likely to have a lattice structure that is different from the Cu foil, because the

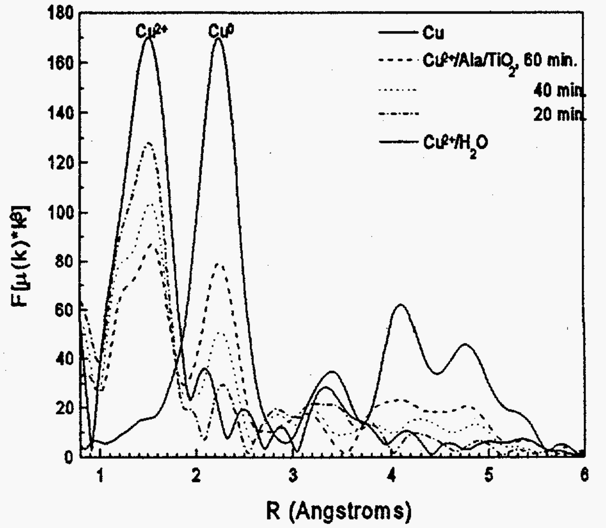

Figure 4. FT-EXAFS spectra of Cu on 60 diameter TiO_2 particle surface at diferenct illumination times. Cu foil and neat Cu^{2+} spectra were plotted for comparison.

higher shell peaks are not as sharp and regular as those in Cu foil. A better time resolution experiment is needed in order to clarify this. A similar photocatalytic reaction was carried out with Hg^{2+} and TiO_2 colloid with and without surface modification (not shown). XAFS spectra positively identified the formation of Hg metal, rather than any of dark colored Hg salts. Adding the TiO_2 surface modifier, thiolactic acid, does not increase the reaction efficiency for Hg photoreduction. However, the initial structure of Hg with thiolactic acid and TiO_2 before the illumination differs from that without thiolactic acid, indicating a direct bonding between the metal ion and the thiolactic acid. In contrast, the structurally well-defined complex of Cu and alanine did not remain intact when TiO_2 is added. Further study is in progress to understand the correlation between the bonding of metal ions to the surface modifiers and the reaction efficiency. The metastable state metal ion structure during the photoillumination remains a question that will be answered in our future time-domain XAFS experiments using energy dispersive XAFS or pump-probe XAFS using third generation synchrotron sources.

3. Future Time-resolved XAFS Studies

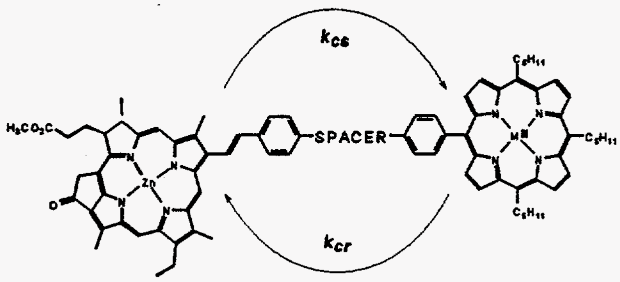

Figure 5. A general structural description for one of the many electron donor-acceptor supermolecules. k_{cs} and k_{cr} are rate constants for photoinduced charge separation and charge recombination. Electron will be transferred from the donor on the left to the acceptor on the right upon laser excitation.

Our current focus is on time-resolved "pump-probe" X-ray absorption spectroscopy at the Advanced Photon Source (APS) at Argonne, where a short laser pulse is used as a "pump" for creation of photoinduced intermediates, and an X-ray pulse, as a "probe" for monitoring the structural changes. The XAFS spectra of a particular intermediate state of molecules will be collected at a certain delay time from the laser "pump" pulse according to the kinetic information obtained from other measurements. One of the molecular systems[10] that will be studied is illustrated in Figure 5 where the structure around metal ion M (e.g. oxidation states, bondlength and coordination numbers) is expected to change when photoinduced electron transfer occurs. The information on structural changes of the electron donor/acceptor molecules following photoinduced electron transfer will reveal new insight into the correlation of the nuclear movements with electron transfer and will answer a series of fundamental questions on photoinduced electron transfer mechanism.

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