Review

Tracking the Local Structure Change during the Photoabsorption Processes of Photocatalysts by the Ultrafast Pump-Probe XAFS Method

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Received: 10 October 2020; Accepted: 2 November 2020; Published: 4 November 2020

Featured Application: Ultrafast pump-probe XAFS investigation of photocatalysts.

Abstract: The birth of synchrotron radiation (SR) facilities and X-ray free electron lasers (XFELs) has led to the development of new characterization tools that use X-rays and opened frontiers in science and technology. Ultrafast X-ray absorption fine structure (XAFS) spectroscopy for photocatalysts is one such significant research technique. Although carrier behavior in photocatalysts has been discussed in terms of the band theory and their energy levels in reciprocal space (k-space) based on optical spectroscopic results, it has rarely been discussed where photocarriers are located in real-space (r-space) based on direct observation of the excited states. XAFS provides information on the local electronic and geometrical structures around an X-ray-absorbing atom and can address photocarrier dynamics in the r-space observed from the X-ray-absorbing atom. In this article, we discuss the time dependent structure change of tungsten trioxide (WO₃) and bismuth vanadate (BiVO₄) photocatalysts studied by the ultrafast pump-probe XAFS method in the femtosecond to nanosecond time scale with the Photon Factory Advanced Ring (PF-AR) and the SPring-8 Angstrom Compact free-electron LAser (SACLA). WO₃ shows a femtosecond decay process of photoexcited electrons followed by a structural change to a metastable state with a hundred picosecond speed, which is relaxed to the ground-state structure with a nanosecond time constant. The Bi L₃ edge of BiVO₄ shows little contribution of the Bi 6s electron to the photoabsorption process; however, it is sensitive to the structural change induced by the photoexcited electron. Time-resolved XAFS measurements in a wide range time domain and with varied wavelengths of the excitation pump laser facilitate understanding of the overall details regarding the photocarrier dynamics that have a significant influence on the photocatalytic performance.

Keywords: pump-probe XAFS; XFEL; photocatalyst; arrival timing monitor

1. Introduction

The X-ray absorption fine structure (XAFS) method has been developed over the past half century according to the progress of X-ray sources. In particular, its time resolution has been improved significantly. In the early days of XAFS experiments (i.e., in the 1970s before the birth of synchrotron radiation (SR) facilities), it took a couple of days or more than a week to obtain a XAFS spectrum with a good signal-to-noise (S/N) ratio due to the low X-ray flux of standard X-ray tubes. SR facilities were the first game-changer to make the measurement time of XAFS much shorter. It became possible to measure an XAFS spectrum with a good S/N ratio in less than 1 h in the 1980s using SR facilities. Further progress was achieved by the development of fast data acquisition techniques such as quick XAFS (QXAFS) [1] and dispersive XAFS (DXAFS) [2], which improved the time resolution down to the millisecond region in the 1990s. It is presently possible to measure an XAFS spectrum with a time resolution equal to or less than millisecond order [3,4]. Although the time resolution of XAFS has been reduced by an order of approximately 10^8 compared to its early days, it is usually limited by the physical motion of X-ray optics for QXAFS or the response of data acquisition systems for QXAFS and DXAFS. Although there were transient XAFS methods to observe faster phenomena that happen within an order of milliseconds [5–7], it was difficult to reduce the time resolution below a single nanosecond. To go beyond this limitation, the pump-probe XAFS method was developed in the early 2000s, and could provide dynamics of materials in a time resolution of nanoseconds or less [8–12]. X-rays coming from an SR are pulses with finite pulse width (typically ca. 100 ps). Such a short pulse feature enables the dynamics of materials to be tracked during the photoinduced states by XAFS spectra as a function of the delay time between the pump (excitation) and the probe (detection). The time resolution in SR facilities is limited by the pulse duration of the X-ray pulse because the pulse duration of an excitation laser (100 fs) is typically much shorter than the X-ray pulse duration (ca. 100 ps). The advent of very short pulse X-ray sources such as the X-ray free electron laser (XFEL) has extended the horizon of the pump-probe XAFS to the femtosecond region [13]. The high peak intensity enables the application of XAFS techniques such as high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XAFS) [14,15] or resonant inelastic X-ray spectroscopy (RIXS) [16–18].

In this short review, we describe our studies on the photoexcitation processes of the tungsten trioxide (WO_3) and bismuth vanadate (BiVO_4) photocatalysts by pump-probe XAFS in SR and XFEL [19–22] over the last decade. The behavior of photocarriers in photocatalysts has been discussed in terms of band theory. The electron in the valence band mainly composed of oxygen atoms is photoexcited to the conduction band mainly composed of cations. The created photocarriers (electron in the conduction band or hole in the valence band) travel to the surface and react with substances [23–25]. Most experimental data have been obtained by optical spectroscopic techniques, which provide information regarding the energy levels of photocarriers in the reciprocal space (k-space). On the other hand, the location of photocarriers in real-space (r-space) has rarely been discussed based on the direct observation of photocatalysts after photoexcitation. XAFS provides information on the local electronic and geometrical structures around the X-ray absorbing atom. Therefore, XAFS can address photocarrier dynamics in the r-space around the X-ray absorbing atom [15,26,27]. WO_3 and BiVO_4 , to which we have applied the pump-probe XAFS, comprise a Z-scheme photocatalyst system that mimics a photosynthesis system [28–30]. In the W L_3 edge of WO_3 , we mainly followed the excited electron and the local structure of W induced by the excited electron while the Bi L_3 edge of BiVO_4 was expected to provide the behavior of the hole and the related local structure change around Bi. We discuss the photoinduced processes and demonstrate the importance of the wide time scale and the varied excitation energy measurements [19–22]. The photoexcited electron is revealed to be localized at the bottom of the conduction band, which induces distortion around the cation to stabilize itself. Finally, we discuss the future directions for pump-probe XAFS experiments.

2. Materials and Methods

WO₃ (particle size <200 nm) and BiVO₄ (particle size ca. 200 nm) were prepared as described elsewhere [28,30,31]. The nanoparticles were dispersed in distilled water. The concentrations of the suspensions were adjusted to obtain an appropriate optical length for the pump laser to pass through the suspensions. A typical concentration was ca. 1 mmol L⁻¹.

Figure 1 shows the pump-probe XAFS setup at NW14A in the Photon Factory Advanced Ring (PF-AR) [9,20]. PF-AR is a 6.5 GeV electron storage ring and its ring current is typically 50 mA. PF-AR is always operated in a single bunch mode, i.e., only a single electron bunch circulates in the storage ring. This isolated electron bunch creates an X-ray pulse of which the pulse duration is ca. 100 ps with a 1.26 μ s interval. The NW14A beamline is dedicated to the time resolved X-ray sciences. Besides pump-probe XAFS measurements [19–22,32,33], X-ray liquid scattering [34,35], X-ray diffraction [36], and X-ray single crystallography [37] techniques have been developed and have contributed to significant scientific achievements. There are two femtosecond lasers available to excite samples for pump-probe XAFS measurements. One is a Ti-sapphire laser with a regenerative amplifier that provides laser pulses up to 800 μ J/pulse at 800 nm with a repetition rate of 946 Hz. The other is a high-repetition rate laser of which the fundamental wavelength is 1030 nm. The laser can be synchronized with each X-ray pulse in the PF-AR. This laser enables high repetition data acquisition experiments to be conducted, which significantly improves the S/N ratio of transient XAFS signals [38]. This high repetition scheme is effective for the measurement of the pump-probe extended X-ray absorption fine structure (EXAFS) and transient XAFS of extremely dilute samples or samples with a small X-ray absorption cross section, such as L₁ edge XAFS.

Figure 1. Schematic illustration of the pump-probe X-ray absorption fine structure (XAFS) setups at (A) NW14, Photon Factory Advanced Ring (PF-AR), and (B) EH2, BL3 at SPring-8 Angstrom Compact free electron Laser (SALCA).

Frequency-doubled laser pulses of the Ti-sapphire laser (400 nm) were used to excite the sample in the W L₃-edge XAFS experiments. The focal size of the laser on the sample was ca. 0.6 mm and its pulse duration was approximately 1 ps, and the laser fluence was estimated to be 280 mJ·cm⁻². A photomultiplier tube with a plastic scintillator was employed as an X-ray detector and two boxcar integrators were used to separately accumulate pumped and unpumped XAFS signals. The WO₃ suspension was circulated continuously using a magnet-gear pump and produced a 500 μ m liquid

jet on the sample position where the pump laser and the probe X-ray source were overlapped with each other.

A high repetition rate measurement scheme was employed for the W L₁-edge and Bi L₃-edge XAFS experiments. The third harmonics (ca. 343 nm) of the high repetition laser was used to excite the sample with a fluence of ca. 35 mJ·cm⁻². The X-ray was focused using an X-ray capillary lens to Ø100 µm and the sample was a 300 µm liquid jet.

The pump-probe experiments in the femtosecond and picosecond regions were conducted in the EH2 unit of BL3, SPring-8 Angstrom Compact free electron LAser (SALCA) [39,40]. SACLA generates intense X-ray pulses with a pulse duration less than 10 fs at a repetition rate of 60 Hz [41]. These X-ray pulses are delivered evenly to BL2 and BL3, and consequently, the repetition rate of XFEL pulses in the pump-probe XAFS experiments is 30 Hz. The low repetition rate of the SACLA has an advantage in the use of a commercial optical parametric amplifier for the excitation light source so that the excited wavelength can be easily selected. The EH2 unit has a platform [42] designed for ultrafast liquid chemistry, which covers several complementary X-ray techniques, e.g., pump-probe XAFS [19,21,27,43,44], pump-probe X-ray emission spectroscopy (XES) [45], and pump-probe X-ray liquid scattering. The monochromatized X-ray pulses were focused with a Be compound refractive lenses (CRLs) [46] to give a beam size of 100 × 100 µm² at the sample position. Two types of X-ray detectors were utilized to measure the fluorescence X-ray intensity emitted from samples. One was a large 2-dimensional detector developed by RIKEN, Japan, which is referred to as a multi-port charge-coupled device (MPCCD) detector [47]. The other was a Si photodiode detector (Hamamatsu Photonics, S3590-09). The MPCCD can be utilized for various types of X-ray measurements. Each pixel in the MPCCD has an energy resolution (<1 keV); therefore, the MPCCD can be used as an energy-dispersive detector similar to a solid state detector (SSD) or a silicon drift detector (SDD), which are widely used in XAFS beamlines. On the other hand, the photodiode detector produces a charge pulse upon the acceptance of a fluorescence X-ray photon, which is processed by charge-sensitive and shaping amplifiers. The output signals from the amplifiers are evaluated by a waveform fitting [48].

The incident X-ray intensity was measured with a transmissive intensity monitor for the normalization of the fluorescence X-ray intensity. Inside the intensity monitor, there were photodiodes that measured X-ray intensity scattered by a polyimide or CVD film [42]. The frequency-doubled Ti-sapphire laser was employed as an excitation laser, where the pulse duration was 70 fs and the estimated fluence at the sample position was 520 mJ·cm⁻². The timing jitter between the excitation and X-ray laser pulses was typically 500 fs, which limited the time resolution. The timing jitter was corrected for the ultrafast experiment (≤100 fs) using an arrival-timing monitor (ATM) [49]. The ATM developed at the SACLA recorded the time difference between the probe X-ray and the pump laser pulses using the change of the transmittance of a gallium arsenide (GaAs) thin film by the irradiation of a short X-ray pulse. Analysis of the time difference for each X-ray pulse revealed the net delay time of the laser pulse. This post-data-processing improves the time resolution of the measurements. The time resolution using the ATM can be estimated as ca. 12 fs [27,50]. (It should be noted that the actual time resolution is dependent on other factors of the experimental setup, such as the pulse duration of the pump laser and the thickness of the sample.)

3. Results

3.1. Photoexcited States of WO₃ in Femtosecond and Nanosecond Regions

Figure 2 shows the W L₃-edge normalized XAFS spectrum of ground-state WO₃ [20]. WO₃ is known as a wide-bandgap semiconductor, of which the bandgap is ca. 2.4 eV. WO₃ can promote the oxygen evolution reaction because of its valence band position [51], and this catalytic property is applied to a visible-light sensitive photocatalyst in the Z-scheme mechanism [7,8]. The peak at the X-ray absorption edge (called the white line) could be assigned to the transition from the W

$2p_{3/2}$ to 5d orbitals. A strong white line appeared because W is in the 6-valent state, i.e., the d^0 state. After excitation, the white line intensity decreased, as shown by the red curve in Figure 2 (XAFS at a delay of 150 ps). The change in the X-ray absorption intensity was recovered at around 10 ns. This change could be simply explained by photoexcitation of the electron of O 2p at the valence band to the conduction band mainly composed of W 5d; however, this simple interpretation was rejected due to the following reason. The second derivative of W L_3 -edge XAFS spectrum gave two peaks that correspond to the crystal field d-orbital splitting. If the local structure of W in WO_3 was assumed to have an octahedral structure, then the 5d orbitals were split into t_{2g} and e_g orbitals, which appeared as two peaks in the second derivative [52]. The bottom of the conduction band was mainly constructed from the t_{2g} states. The spectral change seemed to be the occupation of the higher e_g orbitals with the photoexcited electrons because the e_g orbitals in the second derivative and the photoinduced change peak top coincided well, as shown in Figure 2. However, it was not possible to excite the electron at the valence band to the higher e_g orbital, because the energy difference between the two was much greater than the photon energy of the pump laser. We could not explain why the photoinduced electron was not located at the bottom of the conduction band but at the higher level. The transient XAFS at a delay of 150 ps should be a secondary state after the structural change and the rearrangement of the density of states. The primary process could not be observed with the time resolution of the PF-AR.

Figure 2. W L_3 edge XAFS spectra for WO_3 before (black) and after (red) photoexcitation (top panel), and difference XAFS spectrum of photoexcited WO_3 and a 2nd derivative of the XAFS of WO_3 (blue in bottom panel). (The figure is reproduced from [20] with permission of Chemical Society of Japan).

Picosecond-order pump-probe XAFS experiments were conducted with the SACLA to observe the hidden primary process. Difference spectra at several delays are shown in Figure 3. The time resolution was ca. 500 fs due to the presence of time jitter [42,50]. Three distinctive peaks were observed in the difference spectra, as shown in Figure 3a. A rise peak A at 11,206 eV and a bleach peak C at 11,211 eV appeared at a delay of 500 fs together with a smaller peak B in-between. The rise peak at A was not observed in the previous experiments conducted at the PF-AR. The rise and bleach features arose from the spectral shift to lower energy. When the pump laser excited an O 2p valence electron to the conduction band consisting of W orbitals, the W valence state should be reduced to 5+, which induces the W L_3 edge shift. The first derivative multiplied by the energy shift ($\Delta E = 0.4$ eV), $\Delta\mu = \frac{d\mu}{dE} \times \Delta E$, agreed well with the difference spectrum at the peak positions at A and C [21]. However, peak A was smaller than the peak height expected from the first derivative. The smaller intensity than that expected could be explained by filling of the t_{2g} state with the photoexcited electron which was located at the bottom of the conduction band. In the following process, the magnitude of peak A decreased

with the increase in the magnitude of peak C by 200 ps, which suggests that the structural change formed a metastable WO_3 state. Peak C gradually recovered to its initial value with a similar decay rate of nanosecond order as observed with the PF-AR.

Figure 3. (a) W L_3 edge and (b) W L_1 edge difference spectra between the photoexcited (pumped) and the ground-state (unpumped) WO_3 measured at SACLA. The upper panels of (a,b) show the raw spectra of ground-state WO_3 . (c) Theoretically calculated L_1 edge difference spectra using FPMS code with different model structures. (The figure was reproduced from [21] with permission of John Wiley and Sons and from [22] with permission of the Royal Chemical Society).

The W L_1 edge is sensitive to the structural change; therefore, an attempt was made to measure the W L_1 pump-probe XAFS, even though its X-ray cross section was low. Figure 3b shows the W L_1 -edge spectrum of the ground-state WO_3 (upper panel) and its difference spectra (lower panel) at several delays. Two peaks, denoted as (A) and (B), appeared in the difference spectra. The bottom of the difference spectra labeled as the energy shift corresponded to the calculated difference spectra between that with and without the negative 1 eV energy shift where the two peaks appeared at the corresponding positions of (A) and (B). Consequently, peaks (A) and (B) were mainly caused by the edge shift due to the photoexcited electron transfer from O^{2-} to W^{6+} . However, the intensity ratio between peak (A) and peak (B) changed significantly with time after the photoexcitation. The intensity of peak (A) became greater than that of peak (B) at 150 ps. The origin for the intensity ratio changes in peaks (A) and (B) could be attributed to the formation of the metastable state at 150 ps. Peak X in the upper panel of Figure 3b was identified as the electron transition from the 2s to the 5d orbital. Although the 2s→5d transition was dipole-forbidden, the distortion from the O_h symmetry allowed the hybridization of 5d with 6p orbitals and a strong dipole transition occurred at peak X. Peak X is a good indicator for the structural distortion around W [53]. Additionally, peak X was shifted to lower energy just after the photoabsorption and increased by the subsequent distortion; therefore, the lower energy peak (A) in the difference spectrum should increase at 150 ps.

Although the difference spectra in Figure 3b could be interpreted based on the knowledge of XAFS, it was difficult to elucidate how the local structure of WO_3 changes after photoexcitation. The difference in the W L_1 -edge XAFS at 150 ps was analyzed by conducting full-potential multiple scattering calculations using an FPMS code to understand more details of the local structural change of photoexcited WO_3 [54]. The position of the central W atom was moved by 0.1 Å from its original position along the three axes as shown in Figure 3c. The difference of the spectra was calculated based on the structures between distorted and original. The short bonds W-O(1) (1.756 Å) and W-O(2) (1.767 Å) were aligned along the c and b axes together with long W-O(5) (2.107 Å) and W-O(6) (2.173 Å), respectively. The +c or +b movement corresponded to the W-O(1) or W-O(2) contraction and indicated the formation of a more distorted structure, while −c or −b corresponded to a less distorted structure. Peak (A) became larger only when the W moved in the +c or +b directions, which indicates enhancement of the distortion of WO_3 as expected.

Combining the results of L_3 and L_1 edge XAFS, the bottom of the conduction band mainly composed of W d states was partially filled with photoexcited electrons at less than 1 ps. In the molecular orbital pictures, d states at the bottom of the conduction bands corresponded to the lowest antibonding π -states that were accompanied with longer bonds. The filling of the lowest antibonding π -state made the longer bond weaker and elongated them so that the shorter bond became shorter to enhance the distortion. Consequently, distorted metastable WO_3 was formed at 150 ps.

Although the initial photoexcited state of WO_3 should be formed within a shorter time scale and should have a different electronic structure compared to its later time domain, we could not address the initial photoexcitation state of WO_3 formed in the very early time (<500 fs) due to the limitation of the time resolution of the experimental setup. The change of peaks A and C was observed with ATM to understand the electronic structure of WO_3 in the early state of its photoexcited state [50]. Figure 4 shows the changes in the X-ray absorption intensity for peaks A(11,206 eV) and C(11,211 eV) in the W L_3 -edge difference spectrum. The time resolution without ATM was estimated to be ca. 700 fs from the rise of peak A and the fall of peak C. On the other hand, the time resolution with ATM in this experiment was estimated to be ca. 180 fs. Although there was no obvious difference observed in peak C, except for the different time resolution around 0 fs, a new ultra-fast process was observed in peak A less than 1ps. The peak intensity grew by ca. 300 fs and decreased by 600 fs. A time constant for this decay process was estimated as ca. 0.20(1) ps using a single exponential function. Without ATM, this fast process was smeared out because of the poor time resolution. No change in the time evolution of the peak C intensity with and without ATM meant that the electron transfer from the O to W site occurred in the very early stage of less than 180 fs. The sharp rise in peak A followed by the quick decay could be explained in terms of d-electron filling. The electrons at the very early stage may be excited not to the bottom of the conduction band but to the higher states of the conduction band, both of which are composed of W orbitals. After 180 fs, the extra energy of photoexcited electrons was released to relax to the bottom of the conduction band, which caused the reduction of peak A. A similar phenomenon was observed in hematite where the hot electron was relaxed within 200 fs to form a small polaron [17].

Figure 4. Kinetic traces of X-ray absorption intensity at peak A and C in the W L_3 edge difference spectra.

In summary, the photoexcited state of WO_3 was observed in a wide range of time domains (femtosecond, picosecond, and nanosecond). In less than the picosecond time domain, the photoexcited electron relaxed to the bottom of the conduction band mainly composed of the W d state. The electrons at the bottom of conduction band induced the structural distortion in the 100–200 ps time scale to create

the metastable state. The metastable state was then relaxed to the ground-state in the nanosecond time scale.

3.2. Photoexcited States of BiVO_4

Bismuth vanadate (BiVO_4) is a potential candidate for the fabrication of useful Z-scheme photocatalysts and/or photoelectrode systems due to the band gap of 2.4–2.6 eV and the valence band position [30,31,55–59]. Apart from improving the performance of BiVO_4 by the development of novel synthetic methods [30,31,55–58], the nature of its photocatalytic activity has been investigated [60–66]. For example, density functional theory (DFT) calculations have been performed to gain insight into the ground-state electronic structure of BiVO_4 and to elucidate the properties of excited-state photocarriers [60,61] and the behavior of photocarriers in femtosecond–microsecond time scales was investigated by transient spectroscopic methods [62–66]. However, there is still an open question of the electronic structure of BiVO_4 , in particular, the contribution of Bi atoms. It has been considered that Bi atoms contribute to the top of the valence band, which makes the bandgap narrower and results in higher photocatalytic efficiency. However, there has been no direct evidence that indicates the contribution of Bi atoms. XAFS can be used to elucidate the dynamics of Bi atoms in BiVO_4 after photoexcitation because it monitors the Bi atoms selectively. In this context, pump-probe XAFS experiments on the photoexcited state of BiVO_4 were performed with the PF-AR and SACLA.

Figure 5 shows Bi L_3 edge XANES of the ground-state BiVO_4 (upper panel) and its difference spectra after photoexcitation. The main change at a delay of 2 ps appeared around 13,443 eV, denoted as B in Figure 5, which subsequently exhibited gradual growth to achieve a maximum at 60 ps (Figure 5b). The changes around 13,430 and 13,460 eV (denoted as peaks A and C, respectively) increased afterwards with some delay from the change of peak B and reached a maximum around a delay of 60 ps, i.e., a fast X-ray absorption change was observed with a delay time of 1 ps at peak B, while little change was evident in peaks A and C. The photoexcitation of BiVO_4 comprises at least two distinct processes, i.e., the fast depletion at peak B followed by slow magnitude growth of all peaks A, B, and C up to 60 ps. Figure 5b shows kinetic traces of the X-ray absorption coefficients for the A, B, and C peaks. The second slow processes were fitted with a single exponential function, $y = \alpha \cdot \exp(-t/\tau) + \beta$.

The time constants τ , for peaks A, B, and C were estimated to be 13 ± 5 ps, 14 ± 2 ps, and 13 ± 7 ps, respectively. The excited state was relaxed to the ground-state with a time constant of 40 ns, which was measured at the PF-AR. According to a previous report [60,61], Bi 6s electrons are assumed to be excited to the conduction band by photoabsorption. If this were the case, then the Bi L_3 edge XANES should have been shifted to higher energy. However, the difference XAFS at 2 ps could not be reproduced using the difference spectrum ($\delta\mu_{\text{Eshift}}$) between Bi L_3 -edge XAFS spectrum of the ground-state BiVO_4 shifted to higher energy by ΔE , $\mu^{\text{gs}}_{L_3}(E + \Delta E)$, and the original one, $\mu^{\text{gs}}_{L_3}(E)$, $\delta\mu_{\text{Eshift}} = \mu^{\text{gs}}_{L_3}(E + \Delta E) - \mu^{\text{gs}}_{L_3}(E)$ [22].

This indicates that the electron density on Bi atoms is not varied to a significant extent after the primary photoabsorption process. In previous papers, coherent oscillations were observed in the early stage (<1 ps) of the photoexcitation of BiVO_4 by optical spectroscopic measurements [62,63], which induced a dynamic local structural change around Bi atoms [59,62–64]. Therefore, it was inferred that the coherent oscillations could create peak B in the Bi L_3 edge difference XAFS spectrum. Peaks A and C, which gradually appeared, could be due to static distortion of the Bi structure because the Bi L_3 edge feature is dominantly affected by the Bi–O bond distance, as pointed out by Nan and John [67]. XANES calculations were conducted using FEFF [22] for different Bi local configurations and the movement of Bi atoms toward VO_4 units by 0.05 Å was able to reproduce peaks A, B, and C in the difference spectra at a delay of 40 ps. Therefore, the slower process lasting by a delay of 40 ps could be ascribed to a structural change of Bi–O bond contraction.

Figure 5. (a) Bi L₃ X-ray absorption near edge structure (XANES) spectrum of the ground-state and difference XANES spectra (Δ XAS) of the excited (XAS_{ex}) and ground-states (XAS_{gs}), with the corresponding delay time displayed beside each spectrum. (b) X-ray absorption intensities at points A, B, and C shown in (a) as a function of time (excited at 400 nm). The figure was reproduced from [19] with permission of the Royal Chemical Society.

It would be interesting to observe the photocarrier behavior upon excitation with a 480 nm laser, of which the energy is close to the photoabsorption threshold of BiVO₄, to understand the energy dependence of the photoexcitation dynamics of BiVO₄. Figure 6a shows Bi L₃ edge difference spectra between the photoexcited state and the ground-state of BiVO₄. The three peaks (A, B, and C) appeared, as in the 400 nm excitation experiment. Note that peaks A and C appeared clearly at 2 ps in addition to peak B. Figure 6b shows the kinetic traces of the Peaks A, B, and C. Kinetic constants were estimated using a single exponential function to be 4 ± 1 ps, 6 ± 2 ps, and 5 ± 1 ps for peaks A, B, and C, respectively. These values were shorter than those obtained from the 400 nm excitation spectra. This difference in the time constant could be understood in terms of the extra energy difference of the photoexcited electrons. The 400 nm laser could excite electrons from the valence band (mainly oxygen) to the higher energy level in the conduction band (mainly V orbitals). The photoexcited electron relaxed to the bottom of the conduction band (composed of mainly V d orbitals), releasing extra energy through the excitation of coherent vibrations or other lattice excitations. The electrons at the bottoms of V d bands induced structural change around V which was monitored by the change of the Bi L₃ edge. In the case of excitation at 480 nm, the extra energy of the photoexcited electrons was small and easily released to reach the bottom of the V conduction band to induce the structural change at the earlier stage.

Figure 6. Bi L₃ XANES spectrum of the ground-state and difference XANES spectra (Δ XAS) of the excited (XAS_{ex}) and ground-states (XAS_{gs}), with the corresponding delay time displayed beside each spectrum. (b) X-ray absorption intensities at points A, B, and C displayed in (a) as a function of time (excited at 480 nm).

4. Summary and Perspective

4.1. Photoexcited States of Photocatalysts

The photoexcited states of WO₃ and BiVO₄ photocatalysts were observed using the pump-probe XAFS method. The stage of the photoexcitation process earlier than 500 fs was successfully observed using ATM. The photoexcited electrons in a higher energy level than the bottom of the conduction level induced a shift of the W L₃ edge to the negative side. The photoexcited electrons then reached the bottom of the conduction band around 700 fs where the lowest-lying W d orbitals were present. The electrons at the bottom of conduction band induced an anisotropic structural distortion to produce the metastable state up to 150 ps, as demonstrated by theoretical calculations of the W L₁ edge XANES. On the other hand, in the photoexcited state of BiVO₄, there was no edge shift observed in the Bi L₃-edge XAFS, which indicates that not the Bi 6s, but rather, the O 2p orbitals dominantly contributed to the valence band top and the photoabsorption. However, the Bi L₃ edge could be used to monitor the structural changes. At several tens of picoseconds, the BiVO₄ reached the metastable state to stabilize the photoexcited electrons at V 3d. The time constants were dependent on the excitation wavelength, which reflected the different rate of release of the extra energy. In both systems, electron transfer from O to the cation and dynamic phonon processes (coherent vibration) occurred in less than 1 ps, followed by the structural changes in the 10–100 ps region to produce a metastable state and to stabilize the photoexcited electrons. These electrons may still have mobility and could contribute to photocatalytic reactions [68].

Structural changes around the photocarriers have previously been reported from the pump-probe XAFS methods [15,26,27,69,70]. Milne, Chergui, and colleagues reported structural changes around carrier trap sites in TiO₂ [26] and Penfold et al. reported those in ZnO [15] by pump-probe XAFS using SRs. Obara et al. studied TiO₂ by the ultrafast pump-probe XAFS and observed the absorption edge shift at 170 fs by electron trapping in TiO₂ followed by structural distortion near the surface at ca. 400 fs after the photoexcitation in the SACLA [27]. It has been assumed that the photocarriers are localized at the trap sites (defects and/or surface). We consider that photocarriers can be located at the crystal lattice sites accompanied by local structure distortion such as a polaron. A structural distortion

in α -Fe₂O₃ was observed by Katz et al., which was related to polaron formation [69], and pump-probe Fe 3p absorption spectroscopy revealed that the polaron formation in α -Fe₂O₃ occurred within 1 ps after the photoexcitation [70].

4.2. Advantage of Pump-Probe XAFS Techniques and Perspectives

The pump-probe XAFS technique is unique compared to the other pump-probe methods in that XAFS can give a local picture of a specific element. Optical pump-probe methods typically provide information such as the life-time of photocarriers in the conduction and valence bands in k-space based on their absorption kinetics [71–73]. It is also possible to obtain transient lattice behavior from vibrational information [62]. On the other hand, XAFS can reveal the behavior of photoexcited materials in r-space. This can give local information around an X-ray absorbing atom with regard to the photoinduced changes of the structure and the electronic state. The absorbing atom can be regarded as an atomic-scale detector of photocarriers embedded in the material. It is thus possible that multi-edge measurements could be used to identify the roles and functions of each component. Although we measured only XAFS of heavy elements in this paper, it is feasible to observe transient XAS of light elements such as oxygen with a time resolution of 100–200 fs using soft XFELs [17,18,74]. Oxygen atoms mainly contribute to the valence band of photocatalysts, and it is possible to capture the transient hole behavior by O K-edge XAS. Although it was difficult to measure XAFS under the ambient conditions because of the large absorption of the soft X-rays by gas or liquid, recent instrumental developments have enabled even the in situ/operando measurement of O K-edge XAS [75]. In addition to soft XFELs, X-ray Raman is another candidate to observe the light element XAFS using hard X-rays [76,77]. Multi atom resonance X-ray Raman (MARX-Raman) is a new and potential candidate to selectively observe the light elements directly bound to a photoactive metal center, even in the presence of the same elements [78]. Developments of pump-probe XAFS techniques, not only in terms of simple absorption spectra for multi-elements, but also in RIXS and Raman, will uncover the nature of photocatalysts thoroughly in the r-space through the local structures and electronic states around photocarriers, which will provide a deeper understanding of photocatalysis and accelerate the development of novel photocatalysts.

Author Contributions: Y.U. is a main contributor of the paper. Y.U., T.Y. and K.A. conceived and planned the experiments and they interpret the results. T.K.: set up the SACLA experiments and Y.U. and T.K. conducted the experiment there. S.N. set up the PF-AR experiments and S.N. and Y.U. performed the experiments. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Japan Society for the Promotion of Science (JSPS) through a Grant-in- Aid for Exploratory Research (No. 26620110), a Grant-in-Aid for Scientific Research (A) (No. 15H02173), a Grant-in-Aid for JSPS Research Fellow (No. 15J07459), grants for collaborative research in the Institute for Catalysis, Hokkaido University (Nos. 15A1004 and 18A1005) and a polymer membrane fuel cell project from the New Energy and Industrial Technology Development Organization (NEDO), Japan. This work is financially supported by Innovative Catalysis of CREST—JST program. This work was partially supported by the “X-ray Free Electron Laser Priority Strategic Program” and the “Photon and Quantum Basic Research Coordinated Development Program” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Acknowledgments: The authors appreciate all the collaborators who contributed to this work: Daiki Kido, Yuki Wakisaka, Satoru Takakusagi, Bunsho Ohtani (Hokkaido University), Akihiro Koide (Institute for Molecular Science), Yasuhiro Niwa, Kohei Ichianagi, Ryo Fukaya, Shin-ichi Adachi (Photon Factory, Institute for Materials Structure Science), Tadashi Togashi, Shigeki Owada, Yusaku Yamamoto, Misaki Katayama, Makina Yabashi (Spring-8, JASRI and SACLA, Riken), Keisuke Hatada (Toyama University), Akihiko Iwase, Akihiko Kudo (Tokyo University of Science). We also appreciate Hebatalla Elnaggar (Utrecht University) for valuable comments and suggestions. The PF-AR experiments were carried out under the approval of PF-PAC (Photon Factory Advisory Committee; Proposal No. 2013G166 and 2015G542). The XFEL experiments were performed at the BL3 beamline of SACLA with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2017B8020, 2017A8058, 2015A8039, 2016B8007, 2015A8039, and 2014B8044). Reproduced from Ref. [22] with permission from the Royal Society of Chemistry. Reproduced from Ref. [19] with permission from the Phys. Chem. Chem. Phys. CP Owner Societies.

Conflicts of Interest: The authors declare no conflict of interest.

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