Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Capturing local structure modulations of photoexcited $BiVO_4$ by ultrafast transient X-ray absorption fine structure spectroscopy

Yohei Uemura, Daiki Kido, Akihiro Koide, Yuki Wakisaka, Yasuhiro Niwa, Shunsuke Nozawa, Kohei Ichiyanagi, Ryo Fukaya, Shin-ichi Adachi, Tetsuo Katayama, Tadashi Togashi, Shigeki Owada, Makina Yabashi, Keisuke Hatada, Akihide Iwase, Akihiko Kudo, Satoru Takakusagi, Toshihiko Yokoyama and Kiyotaka Asakura

Index

I. Sample characterization of $BiVO_4$

The prepared sample was characterized by x-ray diffraction (XRD), UV-Vis spectrum and Scanning Electron Microscope (SEM). The prepared sample was a monoclinic phase and any other phases were not observed (Fig. S1 (A)). The bandgap was estimated as about 2.5 eV by UV-Vis spectrum (Fig. S1 (B)). The particle size of the prepared $BiVO_4$ was evaluated by SEM and its average size was 200 nm (Fig. S1 (C)). The band structure of $BiVO_4$ are displayed in Fig. S1 (D). [1, 2]

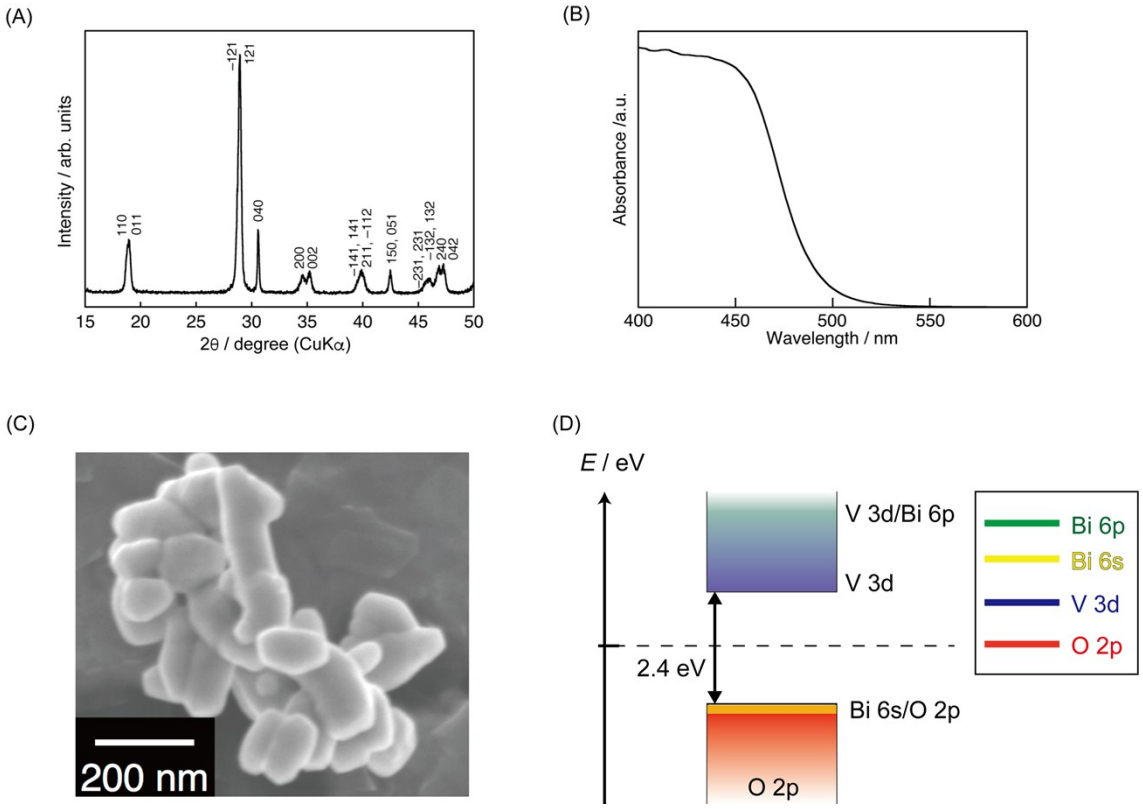

Fig. S1: X-ray diffraction (A), UV-Vis spectrum (B) and the image of $BiVO_4$ particle obtained by Scanning Electron Microscope(SEM), (D) A proposed band structure of $BiVO_4$.

II. Comparability of transient XAFS spectra of 150 ps and 306 ps

The difference spectra at 150 ps, 306 ps and 500 ps are compared in Fig. S2. Δμt at 150 ps and 500 ps were measured at PF-AR. The wavelength of the excitation laser was 343 nm and the fluence of the excitation laser was about 35 mJ/cm^2. On the other hand, Δμt at 306 ps was measured at SACLA. The wavelength of the excitation laser was 400 nm and the laser fluence was about 200 mJ/cm^2. Δμt at 150 ps and 500 ps in Fig. S2 were calculated by multiplying Δμt in Fig. 2 by 5.7 (= 200/35) to compare to each other. A normalized chi-square (χ_υ^2) was calculated to evaluate the uniformity of Δμt at 150 ps and 305 ps. χ_υ^2 was estimated as 0.6992 for 60 data points. The estimated χ_υ^2 is small enough for the two data sets to be essentially identical to each other.

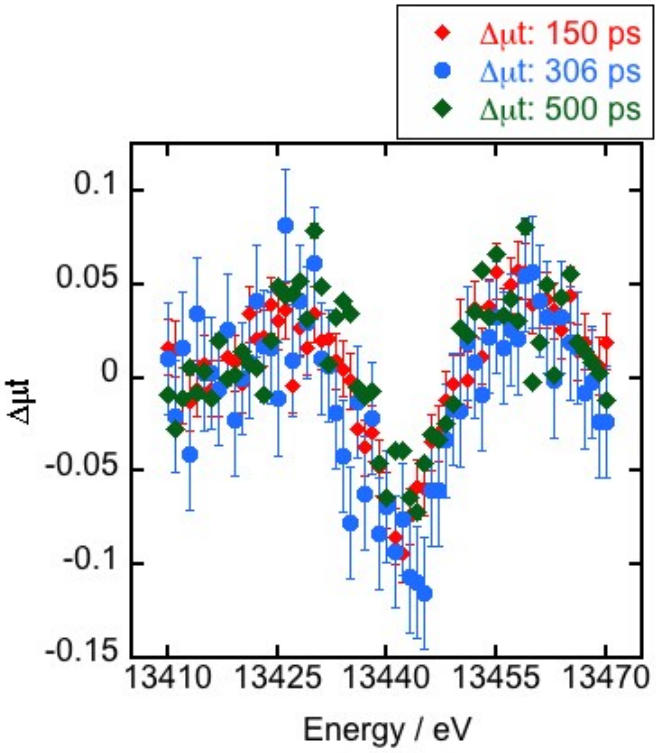

Fig. S2: The difference spectra (Δμt) at 150 ps, 306 ps and 500 ps: Δμt at 150 ps and 500 ps in the figure were calculated by multiplying Δμt in Fig. 2 and in Fig. S4 by 5.7, respectively. The value was estimated from the difference of the laser fluence between Δμt at 150 ps and 500 ps (35 mJ/cm^2) and Δμt at 306 ps (200 mJ/cm^2)

III. The change of x-ray absorbance in the vicinity of the time zero

The time resolution of our experimental setup was checked by measuring the x-ray absorption at 13443 eV. The time resolution was consistent to our previous experiments (~500 fs). [3]

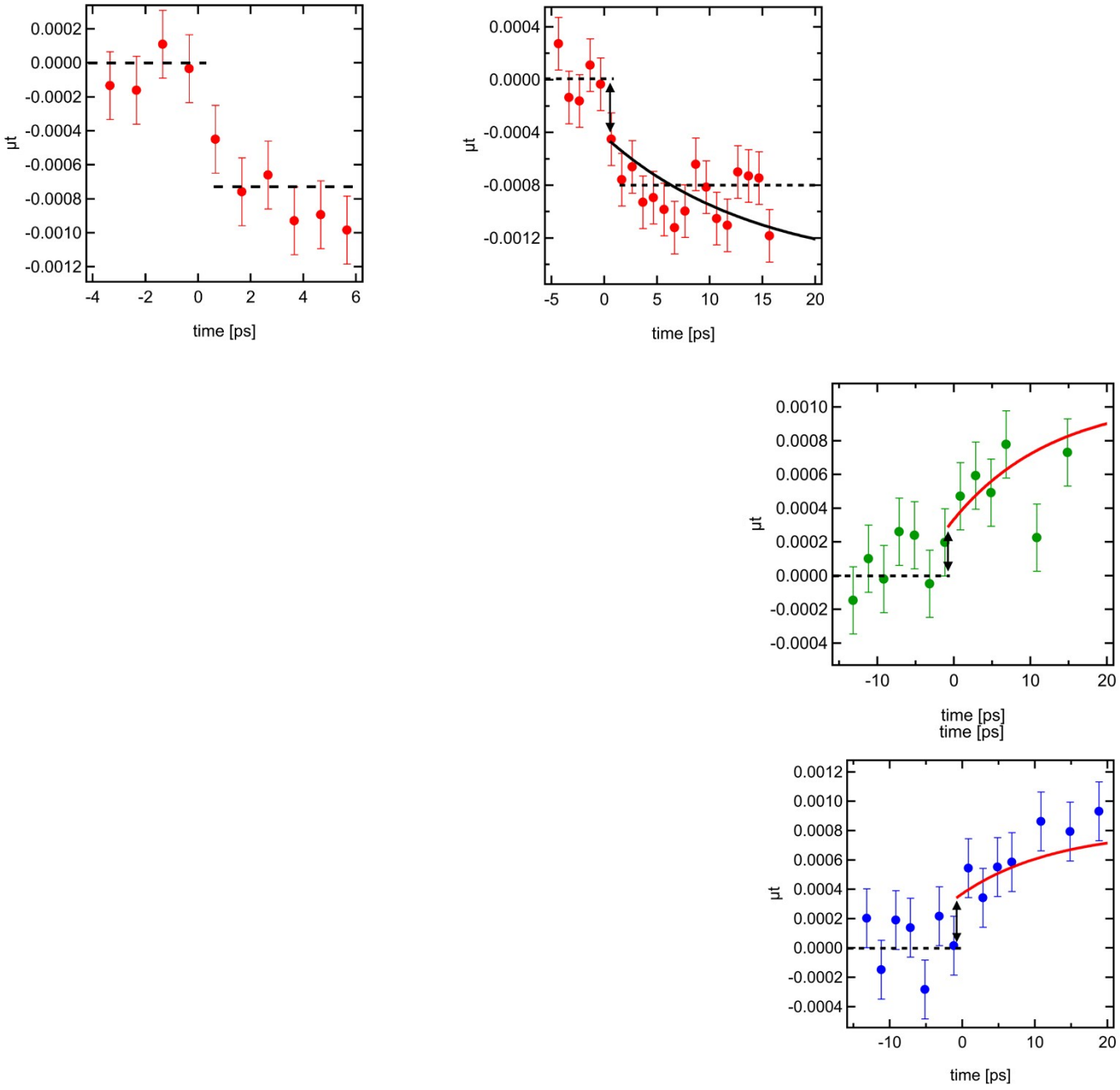

Fig. S3: The change of x-ray absorption around the delay time 0 ps: (A) and (B) are at 13443 eV with 1-ps steps. (C), (D) and (E) are the change of the x-ray absorption at 13430 eV, 13443 eV and 13460 eV, respectively which are shown in Figure 1. Solid lines in (B), (C), (D) and (E) are fitting lines.

IV. Transient XAFS spectra in the nanosecond range

Transient XAFS spectra in nanosecond range were measured at PF-AR and the difference spectra are displayed in Fig S4. Peak A and C monotonously decayed similarly to peak B.

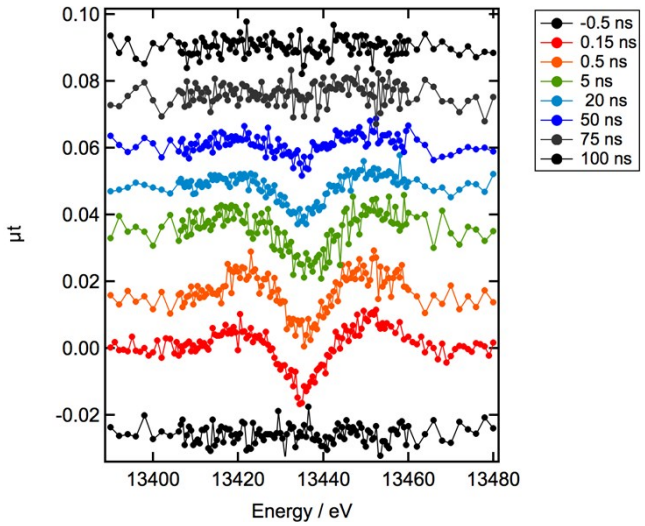

Fig. S4: The difference XANES spectra of $BiVO_4$ at the delay of nanoseconds. (The spectra are shifted arbitrarily for clarity.)

V. The comparison of the transient $BiVO_4$ spectrum and the calculated difference spectra

Difference spectra between the Bi XANES spectra positively or negatively shifted and the ground state are displayed in Fig. S4. The energies shifted from 1 eV to 5 eV. Any shifted spectra do not reproduce the feature of the difference spectra at 2 ps

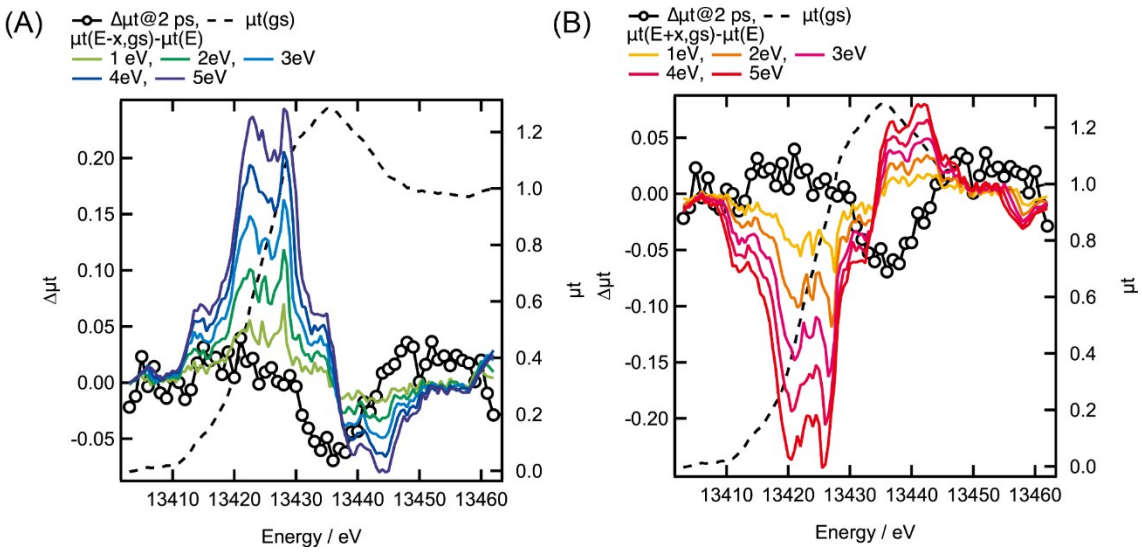

Fig. S5: Bi L3 XAFS spectrum (μt(gs)) and difference spectra: Δμt is a difference between the excited XAFS spectrum (μt(ex)) at 2 ps and the ground state spectrum (μt(gs)). "μt(E+x,gs) - μt(gs)" is a difference between the μt(gs) which is shifted positively by x eV ($1 \leqq x \leqq 5$) and the original μt(gs). "μt(E-x,gs) - μt(gs)" is a difference between the μt(gs) which is the μt(gs) which is shifted negatively by x eV ($1 \leqq x \leqq 5$) and the original μt(gs).

VI. Bi L3 XANES and difference spectra calculated by FEFF

The difference spectra of Bi L3 XANES were calculated by FEFF to understand how structural changes affect Bi L3 XANES features. The structures where the position of the Bi atom shifts to a VO4 unit represent the feature of the difference spectrum between the excited state and the ground state.

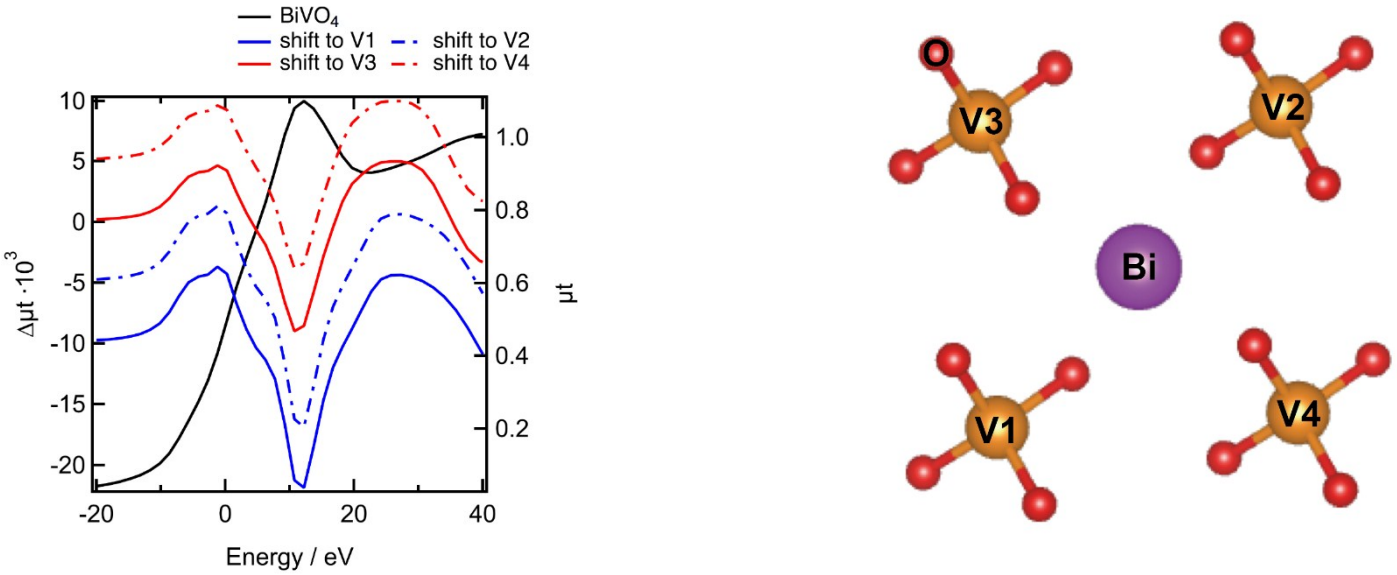

Fig. S6: FEFF calculations of Bi L3 edge XAFS. A Bi atom moved towards each V atom (V1,.V2, V3 or V4). The difference spectra are shifted arbitrarily for clarity.

The distances between the Bi atom and each O atom are: Bi-O(V1, V2): 2.373 Å, Bi-O(V3, V4) : 2592 Å.

References

1. J. K. Cooper, S. Gul, F. M. Toma, L. Chen, P.-A. Glans, J. Guo, J. W. Ager, J. Yano and I. D. Sharp, *Chem. Mater.*, 2014, **26**, 5365-5373.
2. A. Walsh, Y. Yan, M. N. Huda, M. M. Al-Jassim and S.-H. Wei, *Chem. Mater.*, 2009, **21**, 547-551.
3. Y. Uemura, D. Kido, Y. Wakisaka, H. Uehara, T. Ohba, Y. Niwa, S. Nozawa, T. Sato, K. Ichiyanagi, R. Fukaya, S.-i. Adachi, T. Katayama, T. Togashi, S. Owada, K. Ogawa, M. Yabashi, K. Hatada, S. Takakusagi, T. Yokoyama, B. Ohtani and K. Asakura, *Angew. Chem. Int. Ed.*, 2016, **55**, 1364-1367.

Fig. S5: Solid lines are Bi L3 edge XAFS spectra modulated with Debye-Waller factors ($\sigma(k)$). The modulated spectrum were calculated as $\mu t*\exp(-2k^2\sigma^2(T))$ where k is $(0.2626*(E-E_0))\text{^}(1/2)$ (E_0 = 13410 eV). Bi L_3 XANES spectrum ($\mu t(gs)$) and the difference spectra at the time delay of 2 ps and 306 ps ($\Delta\mu t$).