

# ELECTRONIC SURFACE RECONSTRUCTION IN TiO<sub>2</sub> NANO PARTICLES REVEALED BY RESONANT INELASTIC X-RAY SCATTERING

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Titanium dioxide (TiO<sub>2</sub>) is one of the photoactive semiconductors studied most frequently in the literature due to its great chemical stability, inexpensive, and nontoxic nature;<sup>[1]</sup> in addition to nanoparticles (NPs) synthesis, the quantum states provide the high surface-to-volume ratio, fast charge transport, suitable band-gap energy levels, and photochemical efficiency for variable applications.<sup>[2-4]</sup> However, TiO<sub>2</sub> NPs in tens of nanometers scale are in favor of oxygen vacancy and structural defect formation, such as Ti<sup>3+</sup> site facilitates the self-doping effect within the bandgap, but the mechanism is still under debated. Also the disorder-engineered nanophase is still unknown for the nature of 3d<sup>1</sup> electron correlation, the insulator-metal transition, and ferromagnetism.<sup>[5-7]</sup> Indeed, the individual and correlated contribution in Ti and O sites are hardly evaluated for how the Ti<sup>3+</sup> defect state plays the important role in the electronic and lattice structure of NP TiO<sub>2</sub>. Herein we describe the fundamental study of electronic reconstruction of TiO<sub>2</sub> NPs to explore the interaction of 3d orbitals, charge transfer, and lattice with the element resolvability using resonant inelastic soft X-ray scattering (RIXS) which is supported by the Synchrotron Radiation Laboratory, ISSP, University of Tokyo. The inelastic energy- and momentum-loss between incident and emitted X-ray are corresponding to the inter- and intra-coupling between electron, spin, orbital, and lattice owing to the dynamical absorption and relaxation process occurred at the intermediate state in RIXS.<sup>[8]</sup> Increasing the core hole lifetime by the resonant process, the scattering interaction is of distinct in between electronic coupling around Ti<sup>3+</sup> defect state.<sup>[9]</sup> In our study, we have investigated the role of Ti<sup>3+</sup> defect state as a new decay channel accessible to the separable Ti and O site through the strongly electron-electron and electron-phonon interactions.

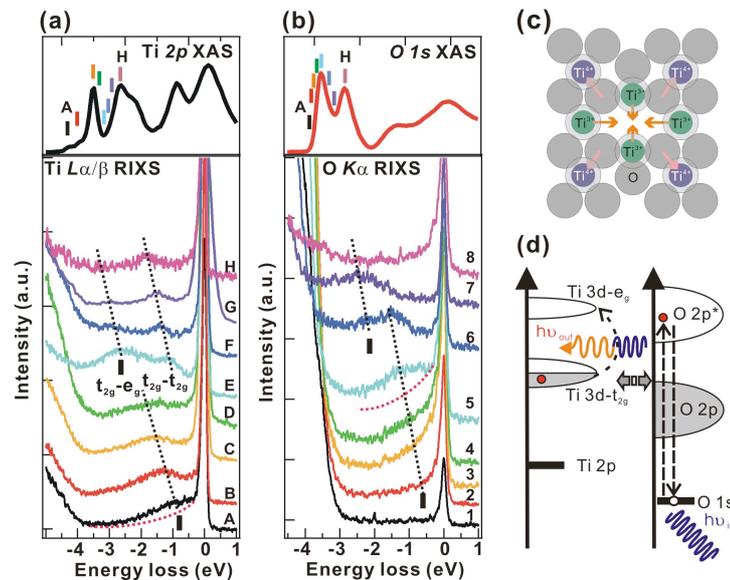


Figure 1: (a) and (b) The energy-loss representation of Ti L<sub>α/β</sub> and O K<sub>α</sub> emission spectra of NP TiO<sub>2</sub> varied with the energy-dependence probing. The electron-phonon coupling near the elastic peak is manifested as red curves to enhance the delocalized d-d excitations. (c) Oxygen vacancy and its lattice distortion in TiO<sub>2</sub> NPs. (d) Scheme of the d-d excitations models probed by the elastic scattering from O site.

The RIXS spectra recorded at different X-ray excitation energies (A-H), marked in the upper panel of Fig. 1(a)(b), exhibits the RIXS features using the energy-loss representation for the specific energy-loss channels. Figure 1(a) shows the asymmetric shape with a long tail independent of  $h\nu_{in}$  energies (A-H), which is assigned to the phonon damping while the lifetime of core-level hole state is longer than the vibrational intermediate state.<sup>[10,11]</sup> The d-d excitations (black-color dot-line) turn to grow among the phonon decay background (red-color dot-line). For example, a peak at -0.9 eV behind the phonon sideband (A) shifts to -1.5 eV (C), as probing along the Ti- $t_{2g}$  absorption peak. At the valley between  $t_{2g}$  and  $e_g$  state (E), the double-structure peak excitations show up at an energy-loss difference of -2.6 and -1.1 eV for the inter-transition ( $t_{2g}$ - $t_{2g}$ ) and intra-transition ( $t_{2g}$ - $e_g$ ).<sup>[12]</sup> Actually, the anatase and rutile TiO<sub>2</sub> show an absence of d-d excitation in the RIXS profile owing to 3d<sup>0</sup> configuration.<sup>[13]</sup> Figure 1(b) shows the O K<sub>α</sub> RIXS profiles varied with different photon energies (1-8). The asymmetric sideband is increased from the symmetric elastic peak among the resonant state of O-2p to Ti-3d  $t_{2g}$  state. At the on-resonant point (5), the additional feature at -1.4 eV emerges from the side band of elastic peak (red-color dot-line). Furthermore, move over the peak (6), two features grows up at -1.5 eV and -2.2 eV on the background level of electron-phonon relaxation. At the off-resonant points (7 and 8), the energy-loss profile shows one broadened bump centered at -2.5 eV and the symmetric-shaped elastic peak due to the lower electron-phonon coupling.

The oxygen vacancy introduces a lattice distortion and 3d election redistribution into the Ti<sup>4+</sup> state of TiO<sub>6</sub> cluster, as exhibited in Fig. 1(c). Thus, the unstable and asymmetric properties imply the phonon relaxation extensively in the lattice structure of Ti<sup>3+</sup> and O atoms. The on-resonant emission profile at the Ti L<sub>β</sub>(C) is analogous to that of O K<sub>α</sub> emission (5) mostly because of the strong correlation of O-2p and Ti- $t_{2g}$  coupling. Figure 1(d) describes that the elastic scattering process delivers the emission energy into the inter/intra d-d transition of Ti 3d orbitals by the strong charge transfer coupling of TiO<sub>6</sub><sup>8-</sup> ligand field. The electron-phonon coupling of the core exciton state is sensitive to the lattice distortion around the excited Ti atom and O atom. Our investigation provides the new understanding for the correlated 3d electrons generated by the oxygen vacancy of NP dimension and enhanced by the strong charge transfer between Ti and O.

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