Metastable Adaptive Orthorhombic Martensite in Zirconia Nanoparticles

Shaocun Liu, Wentao Hu, Yang Zhang, Jianyong Xiang , Fusheng Wen, Bo Xu, Julong He, Dongli Yu, Yongjun Tian,[*] Zhongyuan Liu[*]

State Key Laboratory of Metastable Materials Science and Technology,

Yanshan University, Qinhuangdao 066004, China

ABSTRACT: We report here the observations of isolated orthorhombic (o) ZrO_2 nanoparticles with Pbca space group under atmospheric condition. These special nanoparticles are composed of o domains separated by internal semi-coherent boundaries. They are identified to transform from the lamellar-twinned tetragonal (t) nanoparticles. In viewpoint of energy, the constraining effect of twinning boundaries impedes the direct martensitic transformation to monoclinic (m) phase, but favors the transformation to o phase. The internal boundaries are considered to evolve from the lamellar-twinning boundaries, playing an important role in stabilization of the o structure under atmospheric condition. The observed o structure should be an adaptive martensite in the t-to-m transformation process, different from the general consideration of o phase as an intermediate stage. A new lattice correspondence (LC) relationship of $(011)_o//(100)_t$ and $[100]_o //[001]_t$ is determined for the t-to-o transformation. A possible transformation path is proposed to be t ($P4_2/nmc$)-o (Pbcm or $Pbc2_1$, named as oA)-o

(Pbca, named as oB), and the LC relationship is identified to be $(100)_t//(100)_{oA}//(011)_{oB}$ and $[001]_T//[010]_{OA}//[100]_{OB}$.

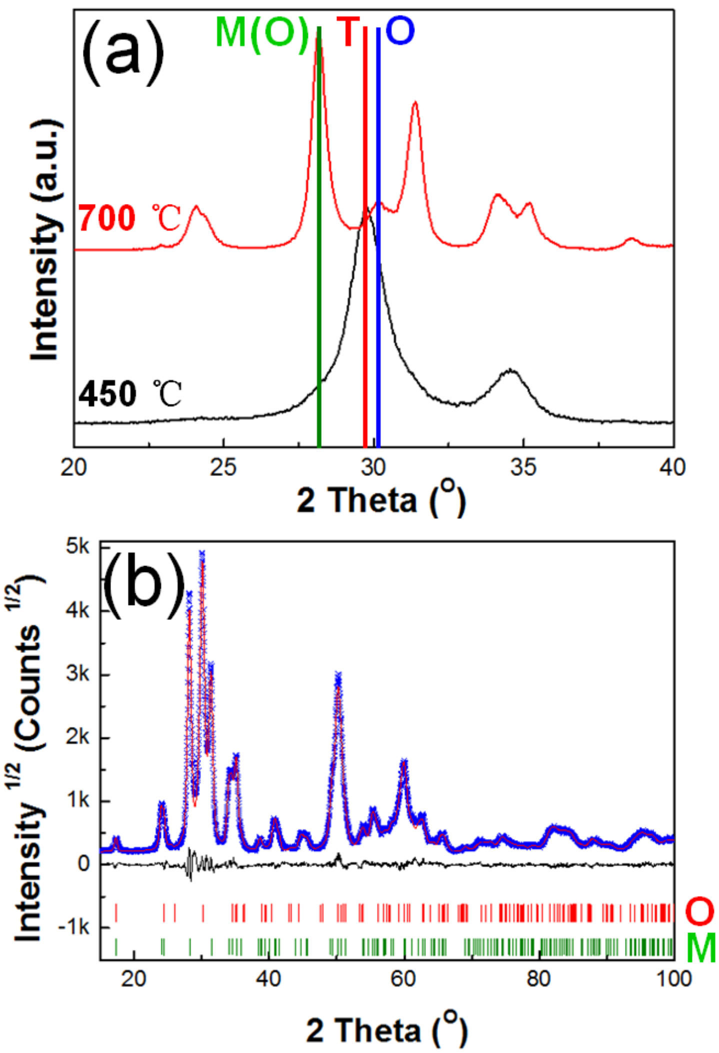

Figure S1. (a)The XRD patterns for ZrO_2 nanoparticles obtained by the oxidation of $ZrC_{0.6}$ with ordered carbon vacancies in air at 450°C and 700°C. O—Orthorhombic, T—Tetragonal, M—Monoclinic. The vertical lines label out the positions of reflection peaks corresponding to tetragonal (T) {101}, orthorhombic (O, Pbca or Pbcm) (211), and monoclinic (M) ($P2_1/c$) diffractions. (b) The experimental (x) and calculated (Solid line) XRD spectra for ZrO_2 nanoparticles produced by the oxidation at 700°C. The vertical bars represent the reflection peak positions for the M and O phases. The difference between the experimental and calculated results is displayed by the solid line between the vertical bars and the XRD spectra.

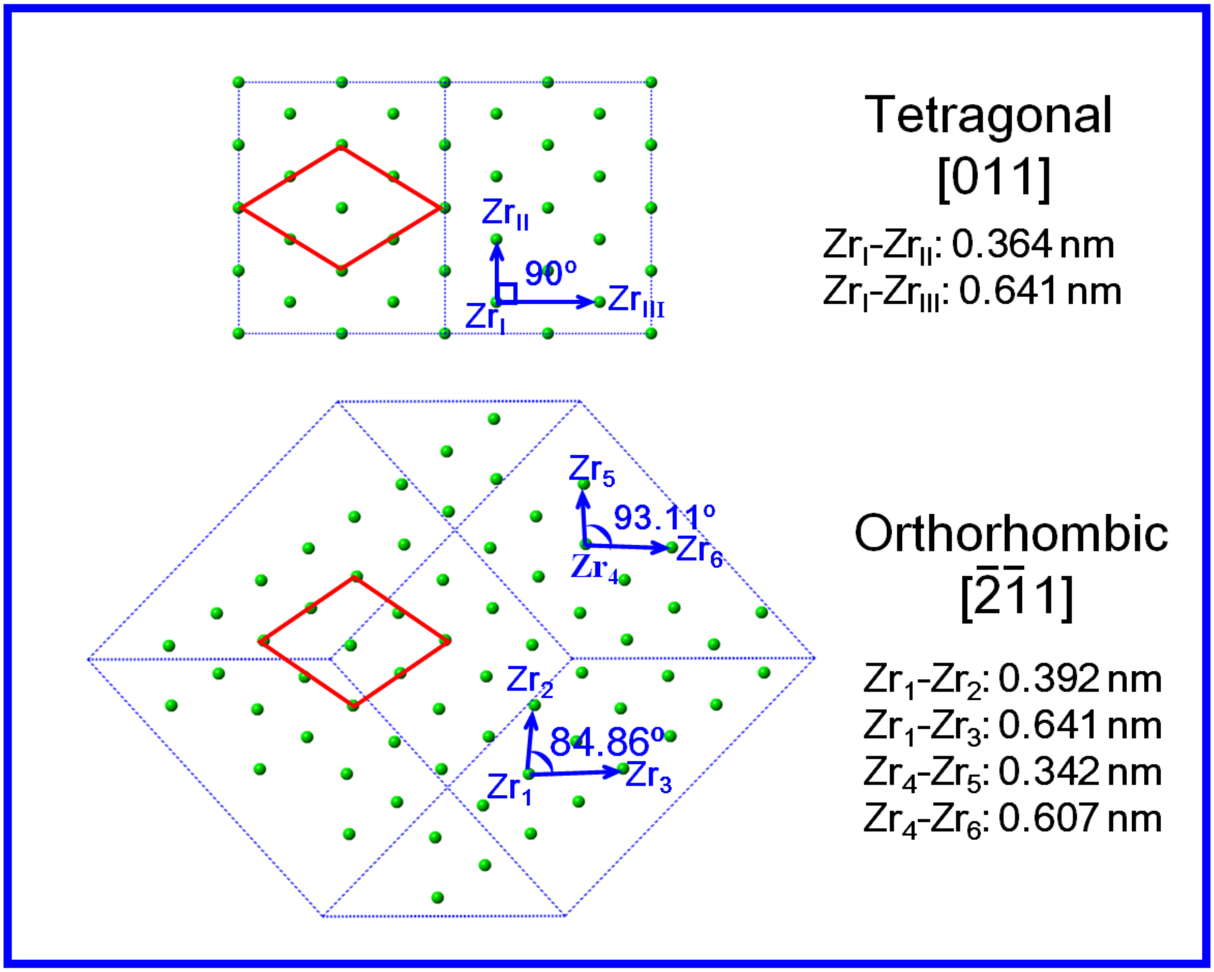

Figure S2. Constructed crystal models to display the lattice correspondence relationship of the interface between tetragonal and orthorhombic domains shown in Figure 3. The tetragonal and orthorhombic domains have the similar Zr-skeleton. Hence, the tetragonal-to-orthorhombic transformation just involves the fine adjustments of Zr atoms.

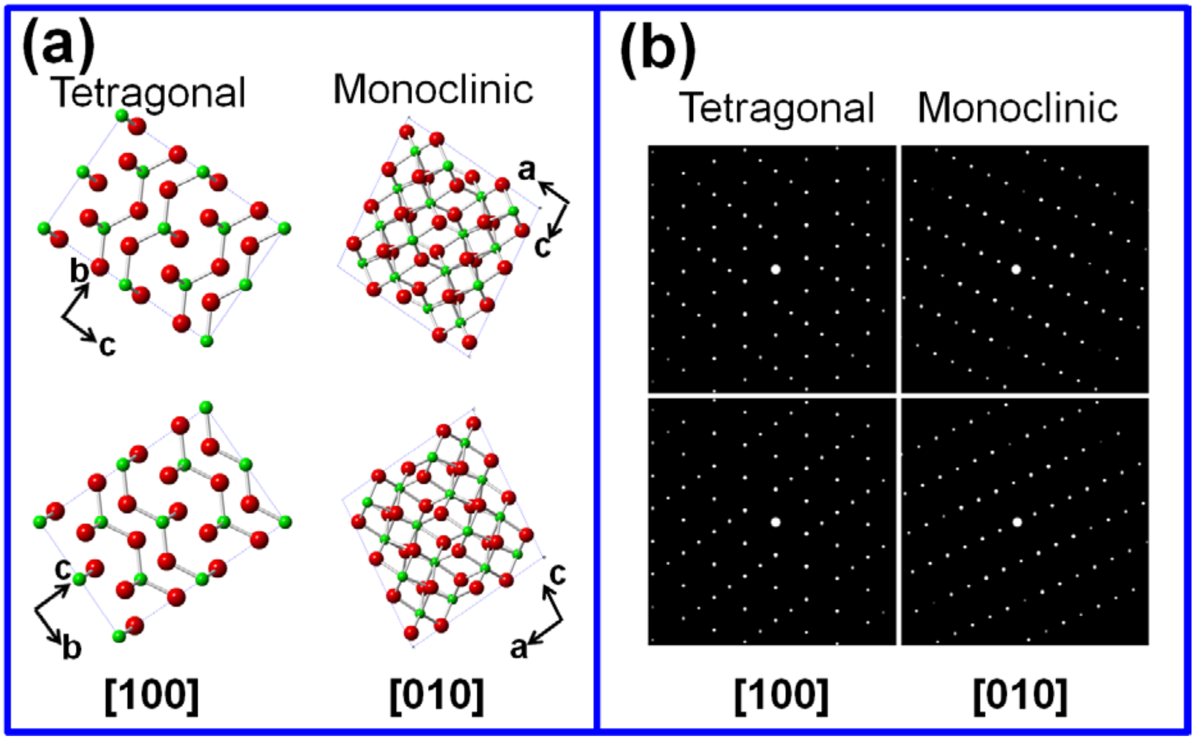

Figure S3. **(a)** The illustrative crystal models of lamellar-twinned tetragonal and transformed monoclinic ZrO_2 via a LC relationship of $(001)_t//(100)_m$, $[100]_t//[010]_m$. **(b)** The simulated SAED pattern corresponding to (a).

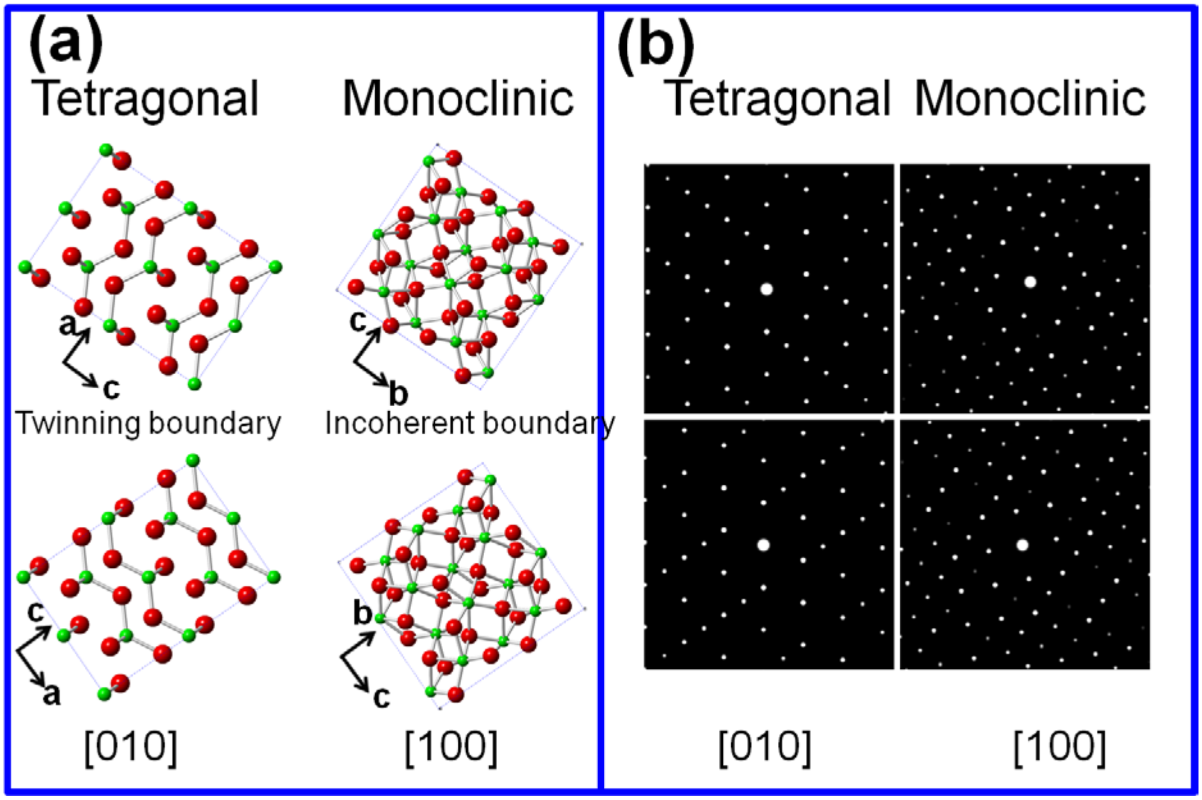

Figure S4. **(a)** The illustrative crystal models of lamellar-twinned tetragonal and transformed monoclinic ZrO_2 via a LC relationship of $(001)_t//(010)_m$, $[010]_t//[100]_m$. **(b)** The simulated SAED pattern corresponding to (a).

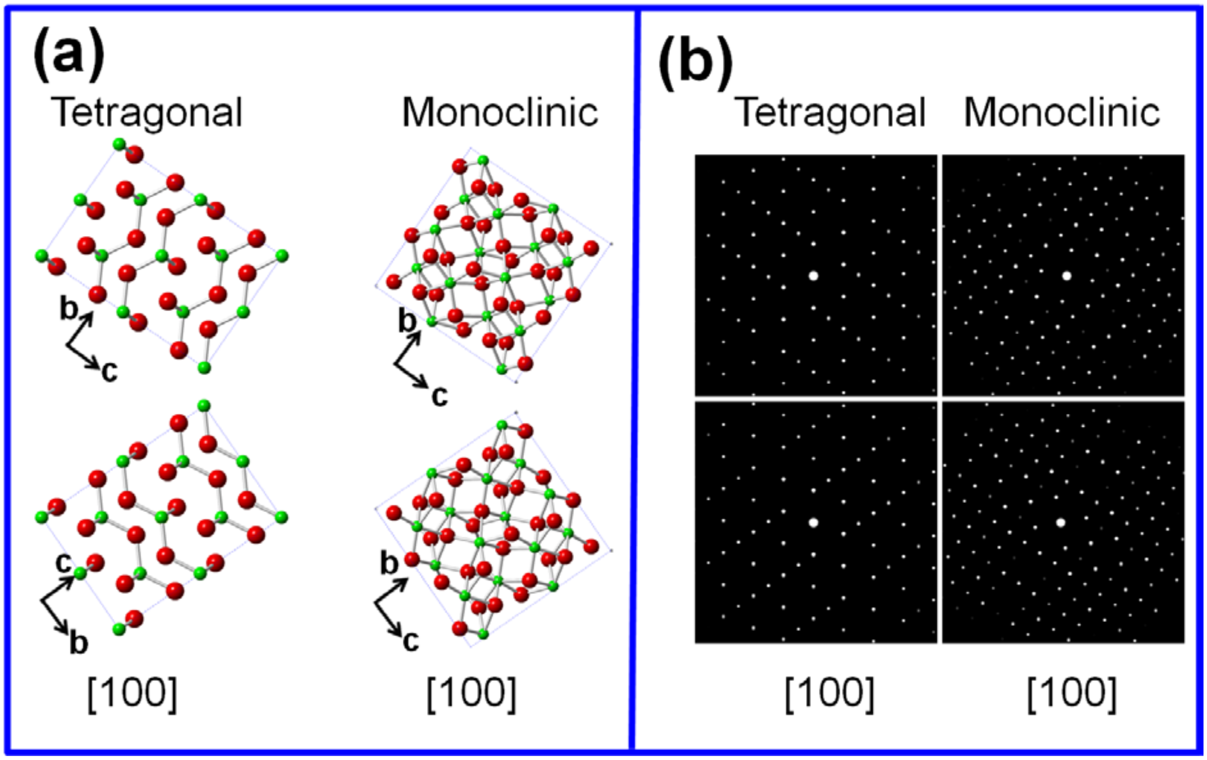

Figure S5. **(a)** The illustrative crystal models of lamellar-twinned tetragonal and transformed monoclinic ZrO_2 via a LC relationship of $\{010\}_t//\{010\}_m$, $[100]_t//[100]_m$. **(b)** The simulated SAED pattern corresponding to (a).

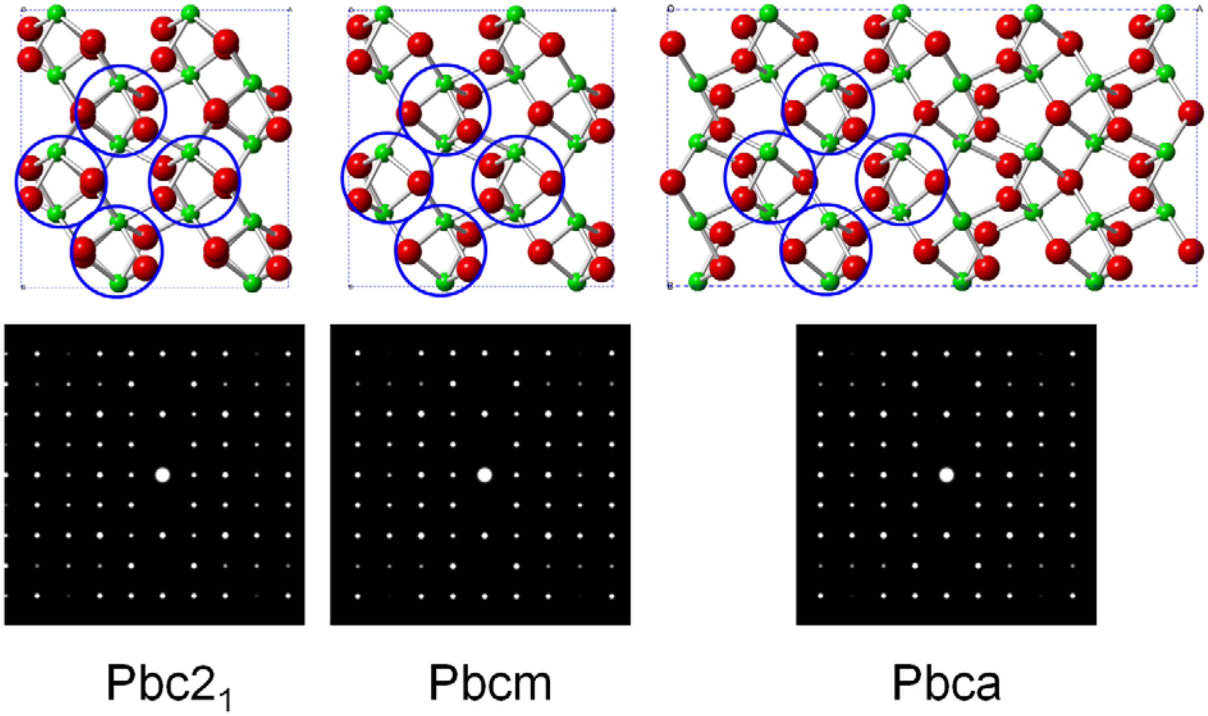

Figure S6. The crystal models (top row) and simulated SAED patterns (bottom row) for three types of orthorhombic ZrO_2 viewed along the [001] zone axis, showing the similar atomic arrangement and SAED patterns.

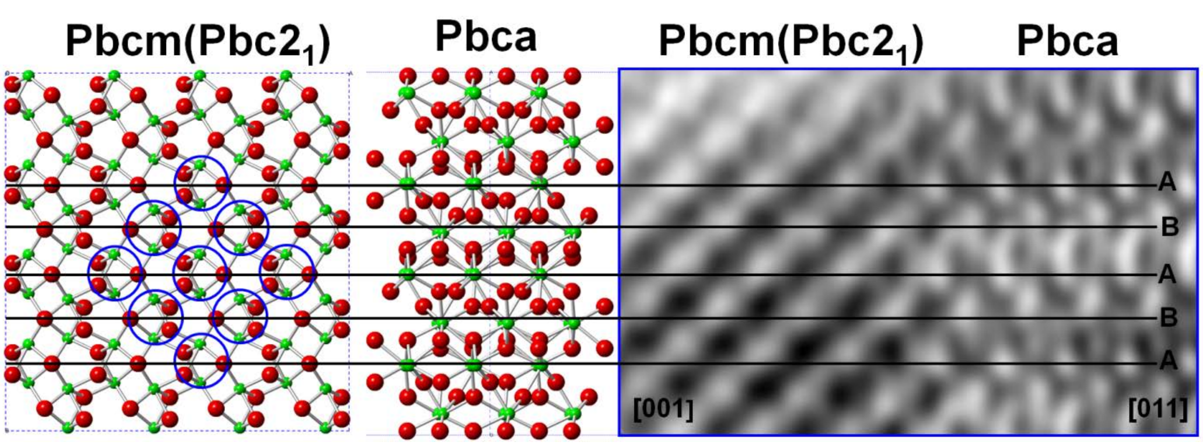

Figure S7. The structural corresponding relationship between Pbcm (Pbc2$_1$) and Pbca orthorhombic domains in Figure 5a and 6a, indicating that the Pbca orthorhombic structure is formed owing to the ordering of stacking faults in (010) planes of Pbcm (Pbc2$_1$) orthorhombic structure.

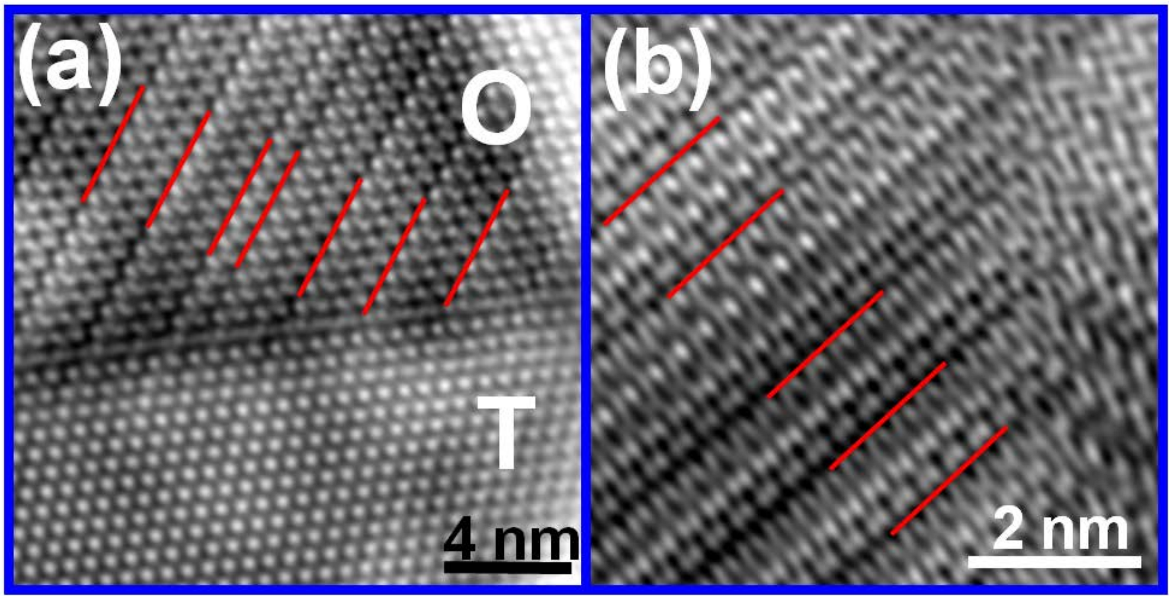

Figure S8. The enlarged HRTEM images of Figure 3a (a) and Figure 6a (b). O—Orthorhombic, T—Tetragonal. As marked with red lines, the orthorhombic domains exhibit the disturbed periodic structures.