Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Atomic scale observation of defect-mediated first-order phase transition in VO_2(A)

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Contents of Supporting Information:

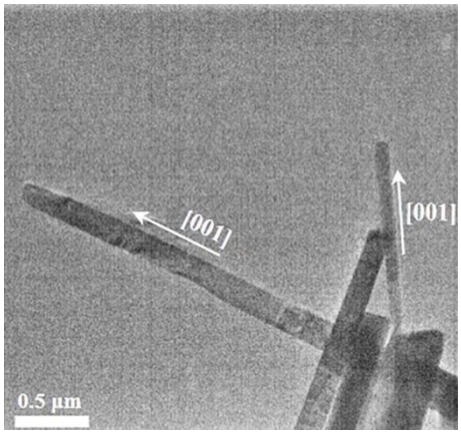

Fig. S1 TEM image of VO_2(A) nanowires. Same as Ji's work [1-3], VO_2 powders were synthesized by hydrothermal method using V_2O_5 as the source of vanadium and dihydrate oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) as a reducing agent. By optimizing the hydrothermal treatment temperature and time, VO_2 nanowires with diameter of about 200 nm growing along [001] direction were successfully fabricated.

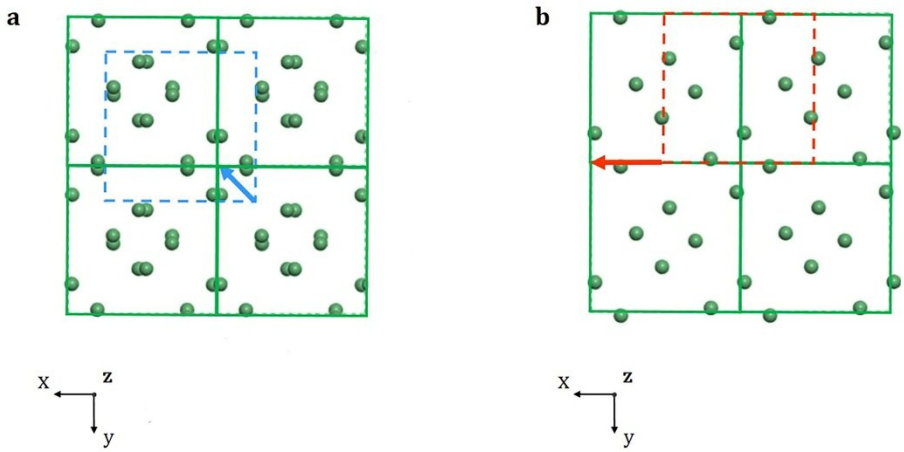

Fig. S2 Structures of VO_2(A) projected along Z axis. **(a)** low temperature phase (LTP); **(b)** high temperature phase (HTP). Green spheres represent V atoms.

Considering that the crystal models in ICSD cannot conveniently describe the relationship between low temperature phase (LTP) and high temperature phase (HTP) of VO_2(A), we redefine the unit cell of LTP and HTP. By translating the origin of the

LTP unit cell (ICSD code-51213, marked with blue dashed rectangle in Fig. S2a) by a vector $(+\vec{a}/4-\vec{b}/4)$ (marked with blue arrow in Fig. S2a), we redefine the unit cell of LTP (marked with green rectangle in Fig. S2a). We also redefine the unit cell of HTP (marked with green rectangle in Fig. S2b) by translating the origin of the HTP unit cell (ICSD code-51214, marked with orange dashed rectangle) by a vector $(+\vec{a}/2)$(marked with orange arrow in Fig. S2b). With the redefined crystal models of LTP and HTP, we can easily found that the V atoms are not on the X or Y axis but a slight deflection both in LTP and HTP, which would be discussed in the main text.

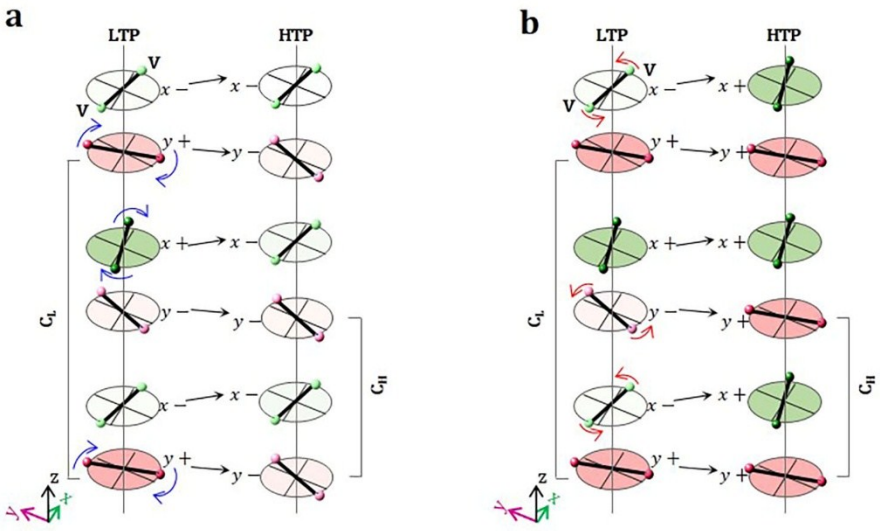

Fig. S3 Mechanism of phase transition between LTP and HTP represented by V-V pairs (marked with black solid lines, colored spheres represent V atoms) stacking along Z axis (reference). Directions of atomic movements through the transitions are indicated by arrows. **(a)** Phase transition from LTP to HTP is (x-, y-, x+, y+) to (x-, y-, x-, y-) when increasing the temperature. **(b)** Phase transition from LTP to HTP is (x-, y-, x+, y+) to (x+, y+, x+, y+) when increasing the temperature.

According to the transition mechanism proposed by Oka *et al.* [4] based on theoretical models, the transition between LTP and HTP is accomplished by the deflections of V-V pairs from X axis and Y axis in the (001) planes and a slight movements of V-V pairs along the [001] axis. So there are two types of phase transition from LTP to HTP. One case is from (x-, y-, x+, y+) to (x-, y-, x-, y-), in which the V-V pairs in x+ and y+ atomic layers will deflect clockwise around Z axis (marked with blue arrows in Fig. S3a), resulting in the transformation from LTP to HTP. As a result, the lattice parameter of HTP c_H becomes approximately half of c_L of HTP ($c_H \approx c_L/2$). The layers in HAADF image of HTP along [210] zone axis shown in small dots/lines, which is the same as that of LTP's x- and y- layers. The other case is from (x-, y-, x+, y+) to (x+, y+, x+, y+), in which V-V pairs in x- and y- atomic layers will rotate anticlockwise around Z axis (marked with red arrows in Fig. S3b). The layers in HAADF image shown in large dots, which is the same as LTP's x+ and y+ layers. So according to the HAADF images we can distinguish the type of the phase transition [from (x-, y-, x+, y+) to (x-, y-, x-, y-) or from (x-, y-, x+, y+) to (x+, y+, x+, y+)].

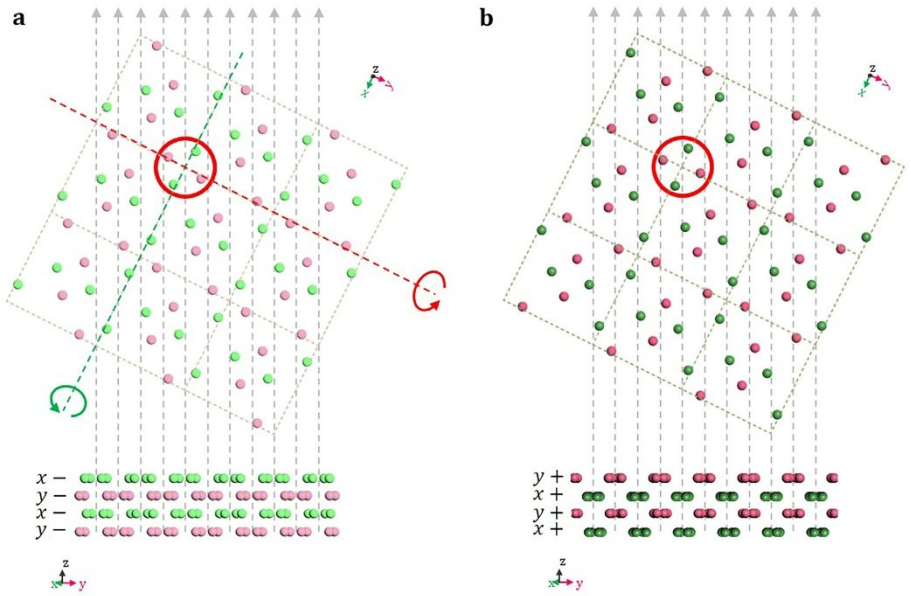

Fig. S4 Schematic diagram of two HTP structures (domains) under the same coordinate. **(a)** Crystal model diagrams of the HTP in Fig. 2c. The upper panel is top view of (001) planes along the negative direction of Z axis. The lower panel is side view of (001) planes along [210] zone axis. The V-V pairs (marked with red solid circle, colored spheres represent V atoms) deflect clockwise from X and Y axes, which makes the (001) planes of HTP can be labeled as (x-, y-, x-, y-) according to the definition mentioned in Fig. 2a. **(b)** Crystal model diagrams when rotating the (001) planes shown in (a) by 180 ° along X axis or Y axis (marked with green and red arrow respectively in Fig. S4a). It should be noted that we still use the coordinate in Fig. S4a to index Fig. S4b for description convenience since the structures (domains) we studied are in the same image (Fig. 3a). In this case, the V-V pairs (marked with red solid circle) deflect anticlockwise from X and Y axes, which makes the (001) planes can be labeled as (y+, x+, y+, x+) according to the definition mentioned in Fig. 2a.

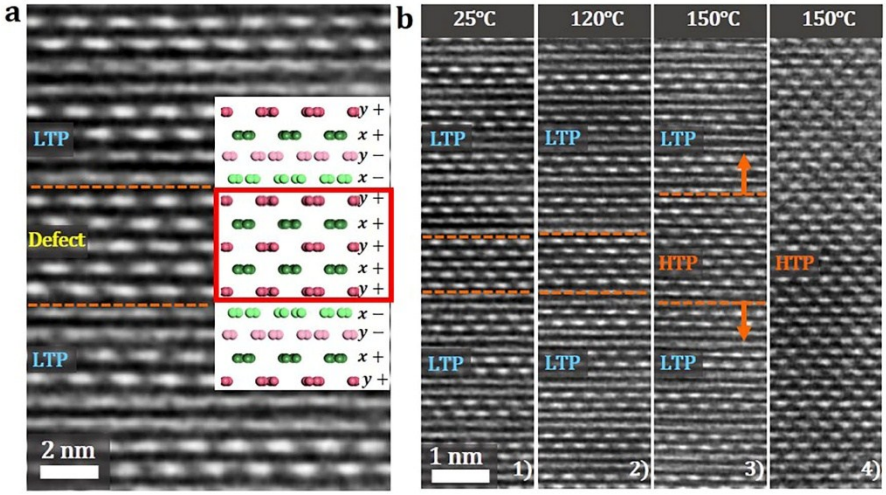

Fig. S5 An odd-atomic-layer defect in LTP. **(a)** High resolution HAADF image of a five-atomic-layer defect in LTP along [210] direction. The defect is labeled with orange dashed lines. The inset is the atom model diagram. **(b)** Sequential *in-situ* HAADF images at 25, 120, 150 and 150 ˚C show the dynamic of phase transition.

There are five atomic layers showing in large dots (labeled with orange dashed lines) at the defect area as shown in Fig. S5. The structure of this defect can be indexed as (y+, x+, y+, x+, y+) (marked with red rectangle in Fig. S5a) which is exactly same with the structure of HTP in Fig. 2d. It should be easily found that the crystal is a twin crystal with the central layer of the defect being the twinning plane. Phase transition from LTP to HTP starting at the defect area was observed when heating the sample from 25 ˚C to 150 ˚C (Fig. S5b), which means the defect plays the role of HTP nuclei in LTP. As shown in image 3 of Fig. S5b, just a few atomic layers have transformed from LTP to HTP, which indicates the very beginning of the phase transition has been observed. The portion of HTP would increase with the transformation of x- and y-planes adhering to the phase boundary into x+ and y+ respectively during the phase transition from LTP to HTP.

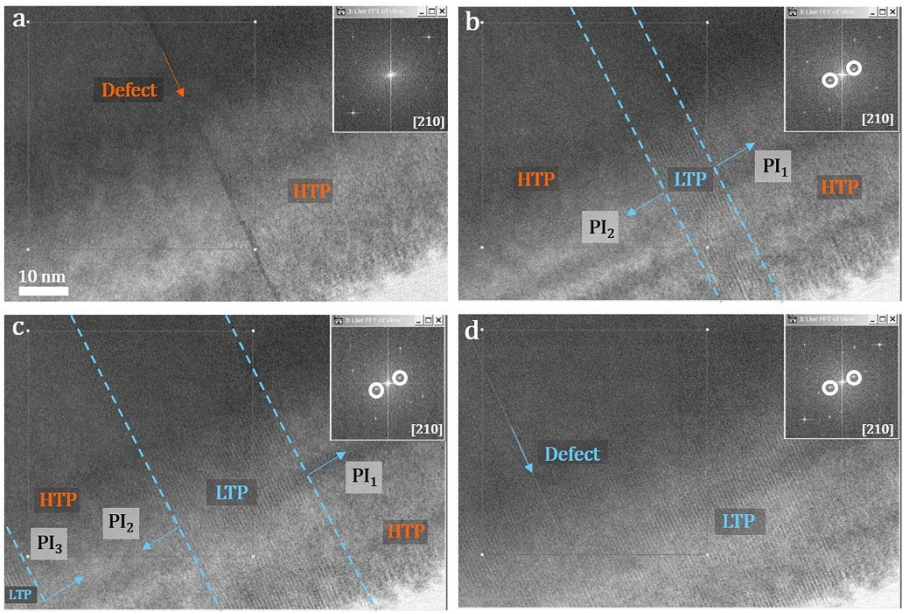

Fig. S6 *In-situ* HRTEM images of defects generations in LTP at the temperature of 220 **(a)**, 90 **(b)**, 90 **(c)** and 90 ˚C **(d).** Fig. S6a displays the HRTEM image of HTP of VO_2 with a corresponding fast Fourier transformation (FFT) pattern along [210] zone axis. We notice that there is a defect appearing in the nanowire, as indicated in Fig. S6a. When cooling the sample below the phase transition point, phase transition started at the defect with the migration of phase interfaces (PI_1 and PI_2) along two opposite directions as indicated by blue arrows in Fig. S6b. The frequencies marked with white circles (Fig. S6b) in FFT pattern shows the existence of LTP. As shown in Fig. S6c, another phase interface (PI_3) appeared and would like to encounter PI_2. With the continuous growth of new phase (LTP), the PI_2 and PI_3 encountered which resulted in the formation of a defect in LTP (marked with blue arrow in Fig. S6d).

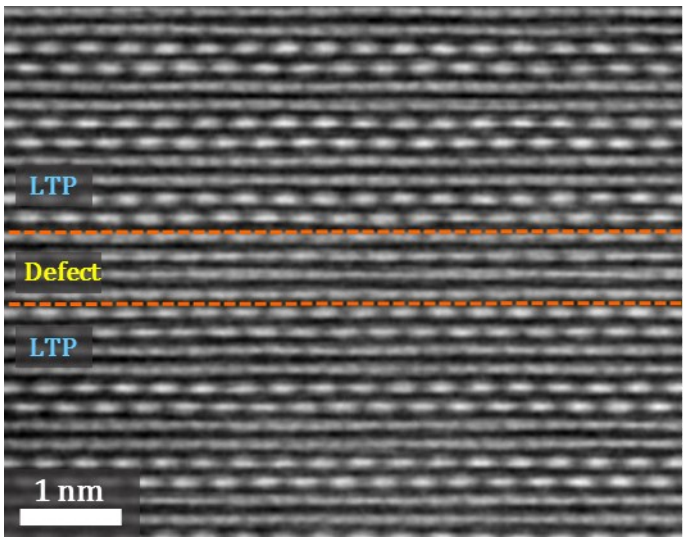

Fig. S7 High resolution HAADF image of a defect in LTP. There are four atomic layers in lines/small dots (labelled with orange dashed lines) at the defect area, showing a x- y- x- y- defect in LTP.

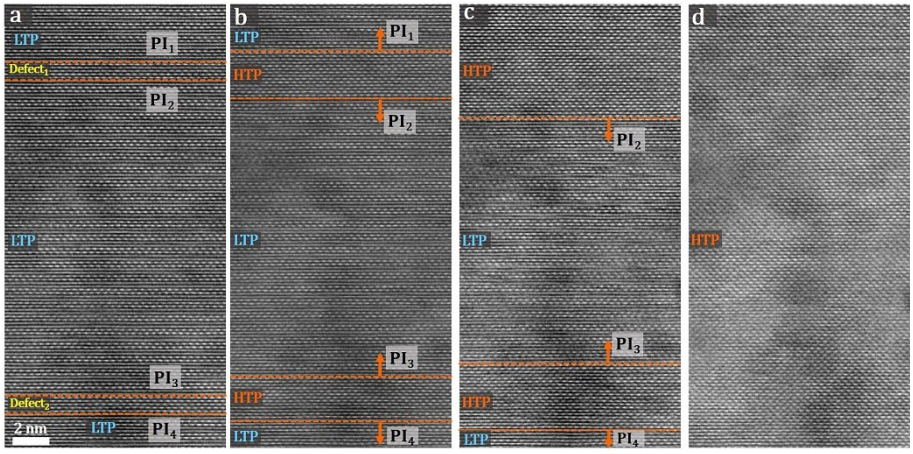

Fig. S8 *In-situ* high resolution HAADF images of process that no defect generated in HTP at the temperature of 25 (a), 150 (b), 150 (c) and 150 ˚C (d)**.** There are two five-atomic-layer defects ($Defect_1$ and $Defect_2$ marked with orange dashed lines) showing in large dots in **(a)**. $Defect_1$ and $Defect_2$ can be indexed as (x+, y+, x+, y+, x+) and (y+, x+, y+, x+, y+) respectively, which is same with the structure of HTP in Fig. 2d. Phase transition beginning at the defects was observed, together with the migration of four

phase interfaces (PI_1, PI_2, PI_3, PI_4) along the directions as indicated by orange arrows in **(b, c)**. With the growth of HTP (x+, y+), PI_2 and PI_3 would encounter and no defect was formed at their meeting site (as shown in Fig. S8d).

Reference:

1. S. Ji, F. Zhang and P. Jin, *J. Phys. Chem. Solids*, 2012, **73**, 762-769.
2. S. Ji, Y. Zhao, F. Zhang and P. Jin, J. Ceram. Soc. Jpn., 2010, 118, 867-871.
3. S. Ji, F. Zhang and P. Jin, *J. Solid State Chem.*, 2011, **184**, 2285-2292.
4. Y. Oka, S. Sato, T. Yao and N. Yamamoto, *J. Solid State Chem.*, 1998, **141**, 594-598.

Caption for Movies

Movie 1：The *in-situ* observation of phase transition from LTP to HTP when heating the sample from 140 °C to 160 °C.

Movie 2: The inverse process (HTP to LTP) took place when cooling the sample from 110 °C to 90 °C.

Movie 3: A defect in LTP was formed at the phase interfaces encountering site on the phase transition from HTP to LTP when cooling the sample from 110 °C to 90 °C.

Movie 4: No defect in HTP was formed at the phase interfaces encountering site on the phase transition from LTP to HTP at 150 °C.