Supporting Information

From VO_2 (B) to VO_2 (A) Nanobelts: First Hydrothermal Transformation, Spectroscopic Study and First Principles Calculation

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S1. Methods for XAS calculation

We have not simulated the XAS directly, because the HSE06 methods have not been include in other packages which can give a XAS result. Instead, the oxygen excited PDOS of the VO_2 (A) and VO_2 (B) have been calculated. Many calculations found that the excited PDOS is comparable with the experimental XAS spectra [S1]. The core-hole effect is considered with the method of changing the occupation of core level. One core hole has been introduced at an oxygen 1s orbital. To reduced the core interactions among the core holes between the periodic boundary conditions calculations, the VO_2 (B) are replicated 2 x √2 x √2. The core-hole has been separated with a distance of 7.7 Å and 7.2 Å in VO_2 (A) and VO_2 (B), respectively. For both of VO_2 (A) and VO_2 (B), 48 atoms are included in the calculations, which are the limits of our calculation resources with the methods of HSE06. The binding energy of O 1s orbit is calculated as the energy difference between the ground state and the core-excited state with one core electron removed. For each kind of crystal, two types of oxygen core-hole sites have been produced. The PDOSs are added together in the same crystal with the equal weighting.

S2. The phase transformation process from VO_2 (B) to VO_2 (A) nanobelts

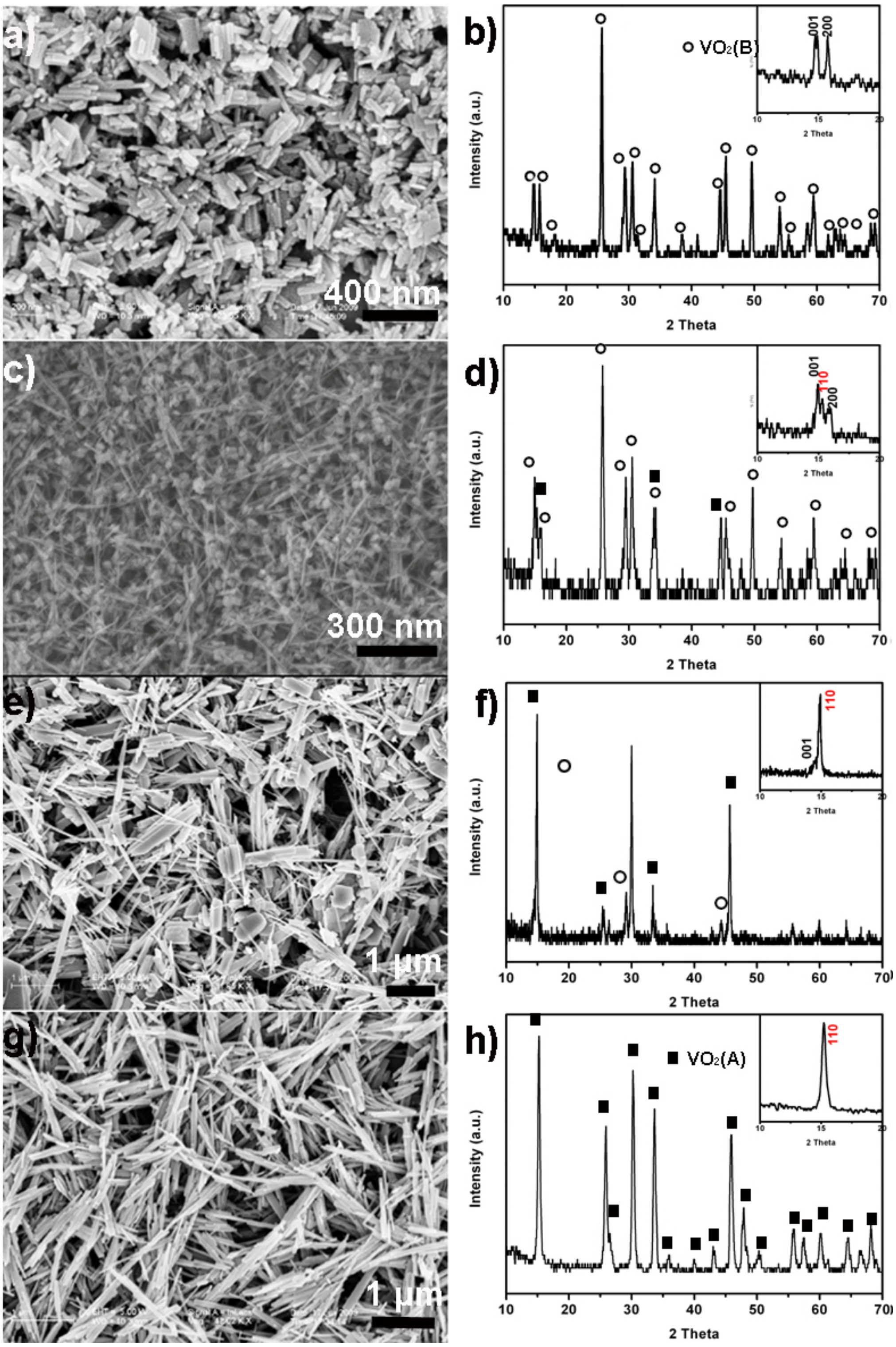

Figure S2. VO_2 samples treated at 200 °C for different hydrothermal periods. The left part shows the SEM images for the intermediate products for the morphology evolution from VO_2 (B) samples (a), VO_2 (B)+VO_2(A) (c, e), and VO_2(A) (g) during the formation process of VO_2. The right part shows the corresponding XRD patterns for the intermediate products reacting after 10 h (b), 30 h (d), 36 h (f), and 40 h (h).

As shown in Figure S2, as the reaction proceeding, two-dimensional rectangular nanoflakes gradually change to nanobelts with a length of several micrometres. On the basis of the corresponding XRD pattern, the final nanobelt products in this reaction have been confirmed to be VO_2 (A). The intermediate products were collected at different stages, whose morphologies and structural information were subjected to SEM and XRD investigation, respectively. As shown in Figure S2a, at the initial stage, the products are two-dimensional nanoplates with a width of about 150 nm and an average length of about 300 nm and the samples can be indexed as VO_2 (B) (Figure S2b). After 12 ~ 30 h of hydrothermal treatment, a mixed product made of VO_2 (B) and VO_2 (A) phases is obtained (Figure S2c). The SEM image (Figure S2c) shows that the final product includes not only two-dimensional nanoplates, but also nanoribbons. Finally, when the reaction time extends to 40h, the XRD pattern (Figure S2d) clearly reveals that the well-crystallized VO_2 (A) phase was formed. The corresponding SEM image shows VO_2 (A) nanoribbons can be successfully synthesized on a large scale (Figure S2d). In summary, VO_2 (A) phase was evolved through a gradual hydrothermal process from VO_2 (B) phase, to a mixed phase of VO_2 (B) and VO_2 (A), and finally to the well-crystallized VO_2 (A) phase.

S3. XPS spectra of VO_2 (A) nanobelts

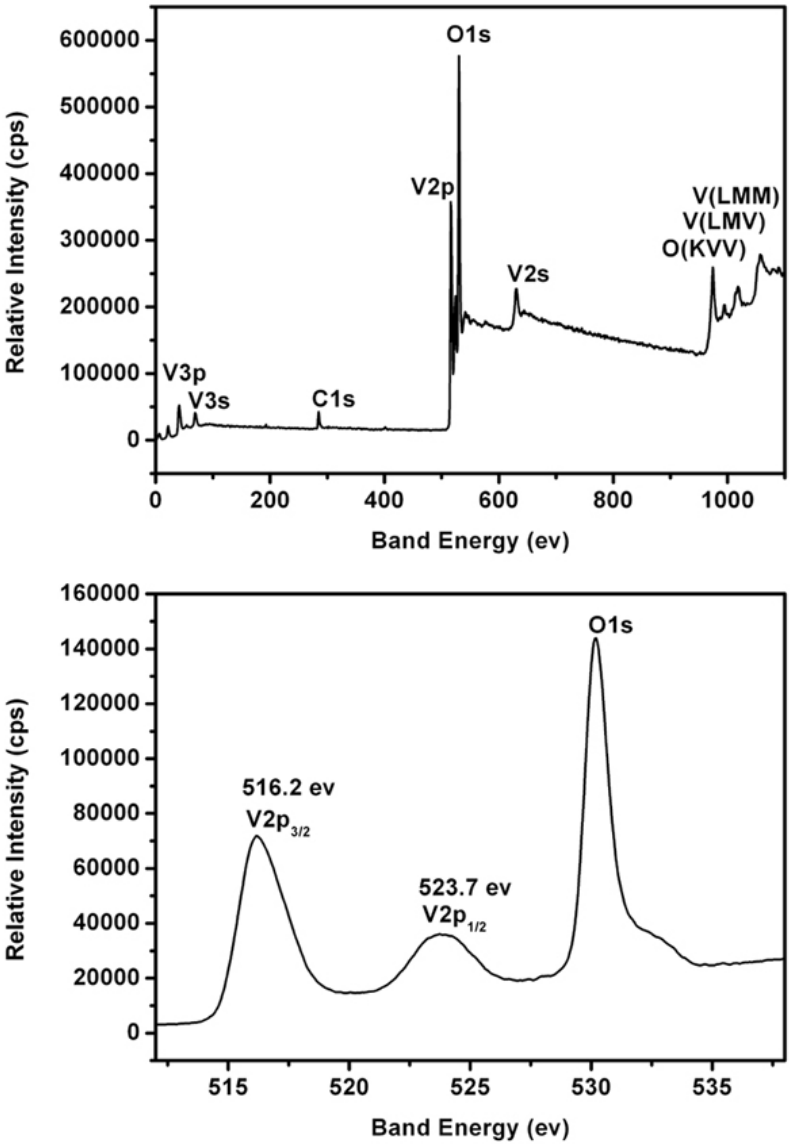

Figure S3. XPS spectra of VO_2 (A) nanobelts: (a) survey spectrum and (b) core-level spectra of V 2p and O 1s.

It is well-known that XPS is a very useful method in determination of the chemical compositions and their chemical states of material surfaces. In our case, the XPS is applied to analysize the sample compositions and chemical state of the as-prepared belt-like VO_2 (A), and the results are shown in Figure S3. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing C 1s to 284.50

eV. The V 2p core-level spectra for VO_2 are shown in Figure S3. These spectra were recorded at room temperature and they show a typical two-peak structure ($2p_{3/2}$ and $2p_{1/2}$) due to the spin–orbit splitting. The V $2p_{3/2}$ and $V2p_{1/2}$ peaks (Figure 10b) of the sample appeared at ca.516.2 and ca. 523.7 eV, respectively, which corresponded to V(IV) according to the previous results.[S2-S6] The peaks for O can be attributed to the O_2, CO_2, H_2O, or VO_2 (A). Consequently, the as-synthesized products could be determined as pure tetragonal VO_2 (A) on the basis of the results of XRD and XPS measurements.

S4. V-O bond distances (Å) in VO_2

Table S1 V-O bond distances (Å) in VO_2

VO_2 (B)		VO_2 (A)	
V-O	1.652	V-O	1.949
V-O	2.175	V-O	1.980
V-O	1.991	V-O	1.981
V-O	1.953	V-O	2.269
V-O	1.985	V-O	1.645
V-O	1.913	V-O	1.976
V-O	2.153		
V-O	1.903		
V-O	1.823		

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