

Phase and Morphology Evolution during the Solvothermal Synthesis of VO₂ Polymorphs

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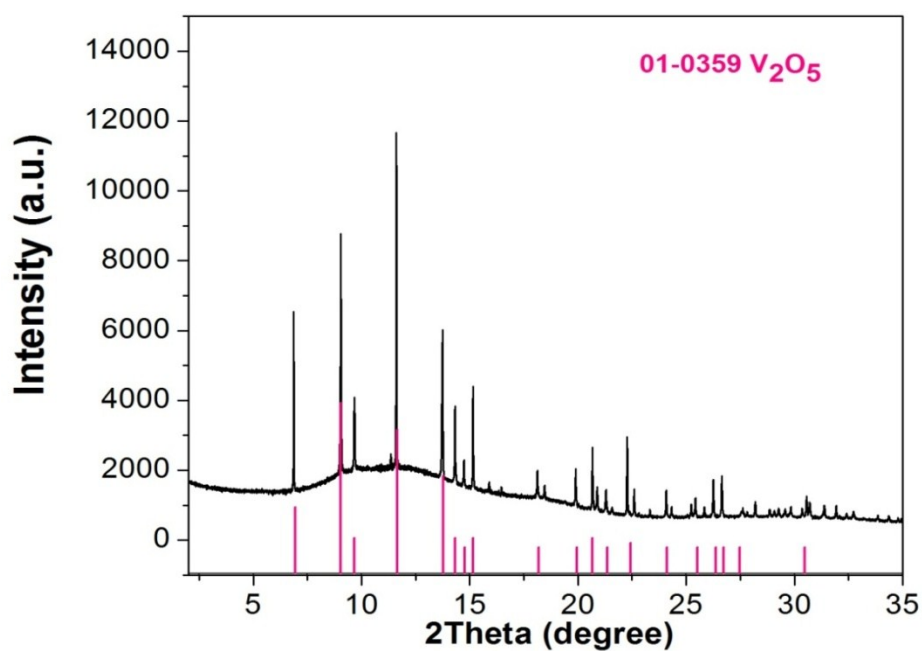


Fig. S1 *In-situ* SB-PXRD pattern of the precursor mixture with the molar ratio of EG:

$\text{V}_2\text{O}_5=1:1$, showing a single V_2O_5 phase.

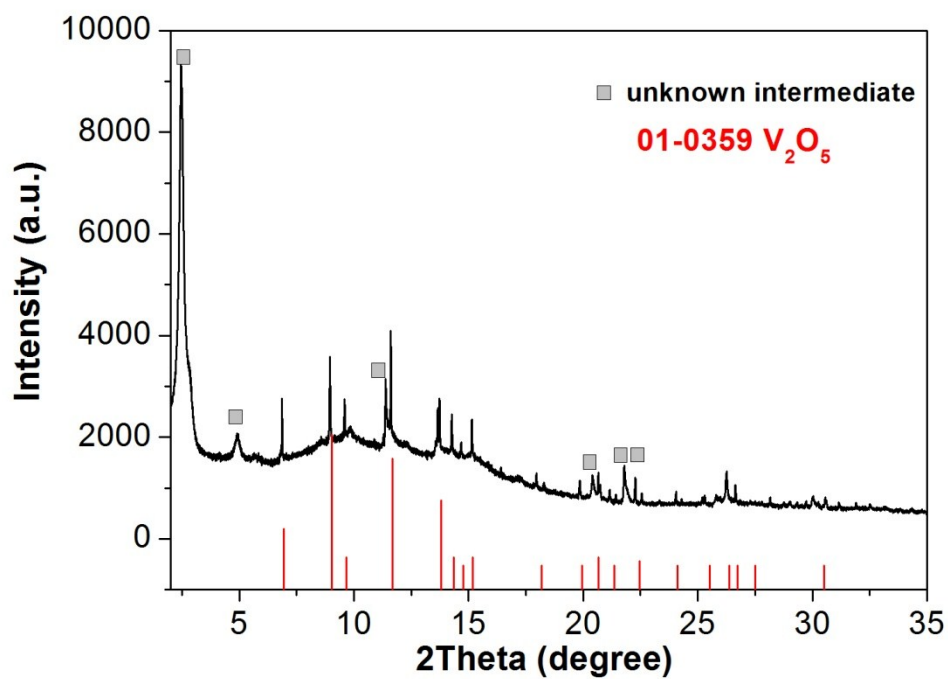


Fig. S2 *In-situ* SB-PXRD pattern of the reaction mixture during the synthesis of $\text{VO}_2(\text{B})$

starting with the precursor molar ratio of $\text{EG}:\text{V}_2\text{O}_5=1:1$. This pattern was recorded

when temperature just reached $250\text{ }^\circ\text{C}$, at $t = 22\text{ min}$.

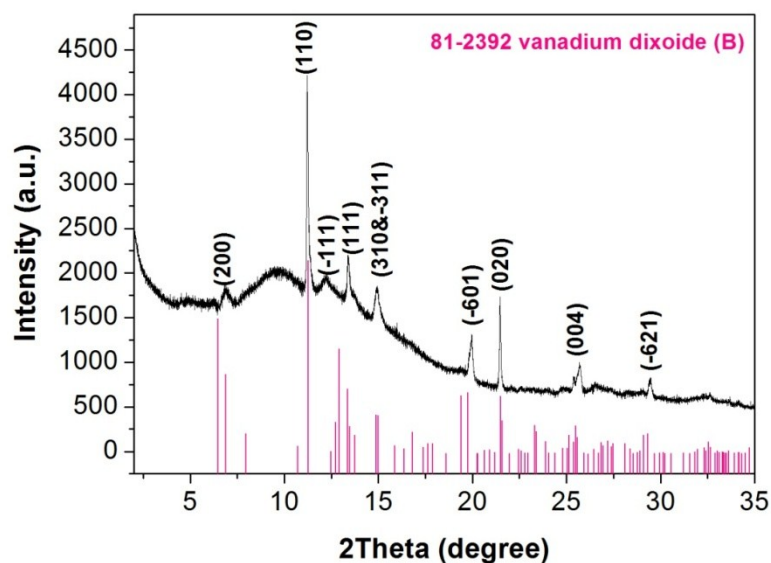


Fig. S3 *In-situ* SBR-PXRD pattern of the reaction mixture during the synthesis of $\text{VO}_2(\text{B})$ starting with the precursor molar ratio of $\text{EG}:\text{V}_2\text{O}_5=1:1$. This pattern was recorded after reaching 250 °C for 3 min at $t = 28$ min.

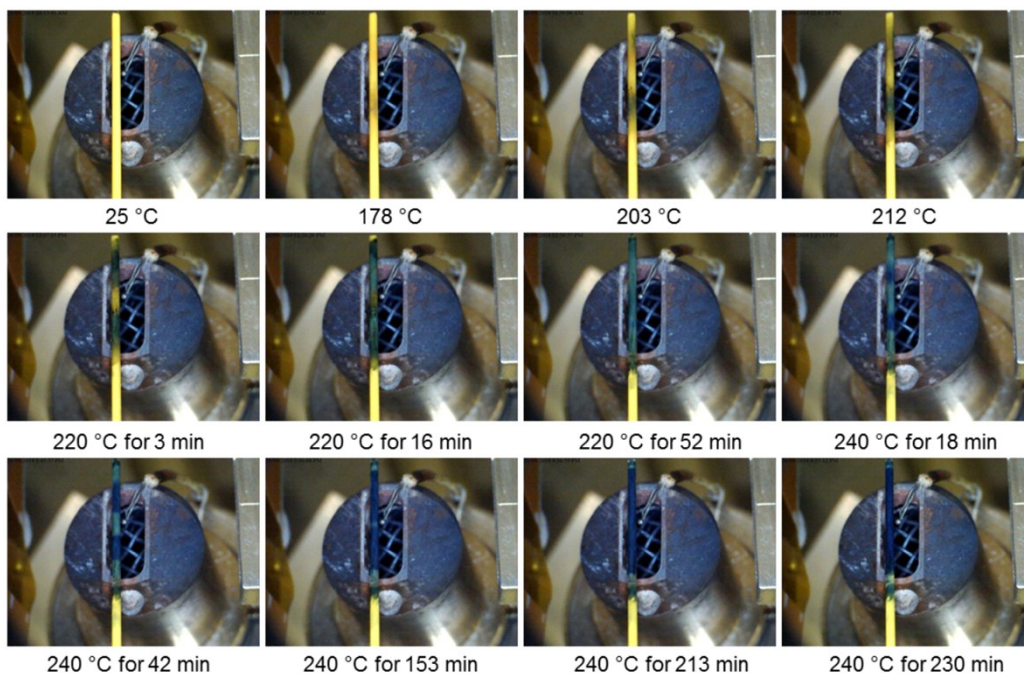


Fig. S4 Selected images captured by the surveillance camera at different stages of laboratory-based *in-situ* PXRD experiment at 240 °C with slow heating (2 °C min⁻¹), showing color change of the reaction mixture inside the quartz glass capillary reactor over 6.6 h of synthesis.

The colour change may help to clarify the pathway by which the phase transition took place under hydrothermal condition. Figure S4 shows the images captured by the surveillance camera at different stages of synthesis. It illustrates that the starting orange slurry started to turn to prussian blue colour at 220 °C. The colour became darker with increasing temperature and finally became deep blue at 240 °C. This is the temperature for the formation of VO₂(B) from PXRD pattern. The colour remained unchanged during the heating at 240 °C for 230 min. Interestingly, 395 images captured by the surveillance camera can make a video (shown in SI-2). This is the first time that such video was made from this in situ PXRD instrument. It fast plays the 6.5 h experiment in 13 seconds.

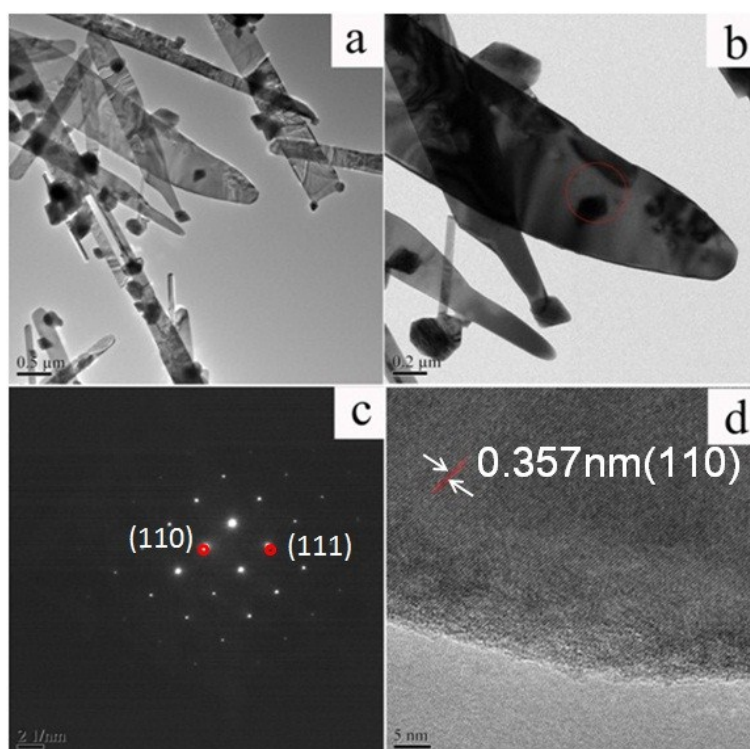


Fig. S5 TEM images of samples prepared at 250 °C for 12h. (c) HRTEM image and (d) its corresponding SAED pattern of the same sample.

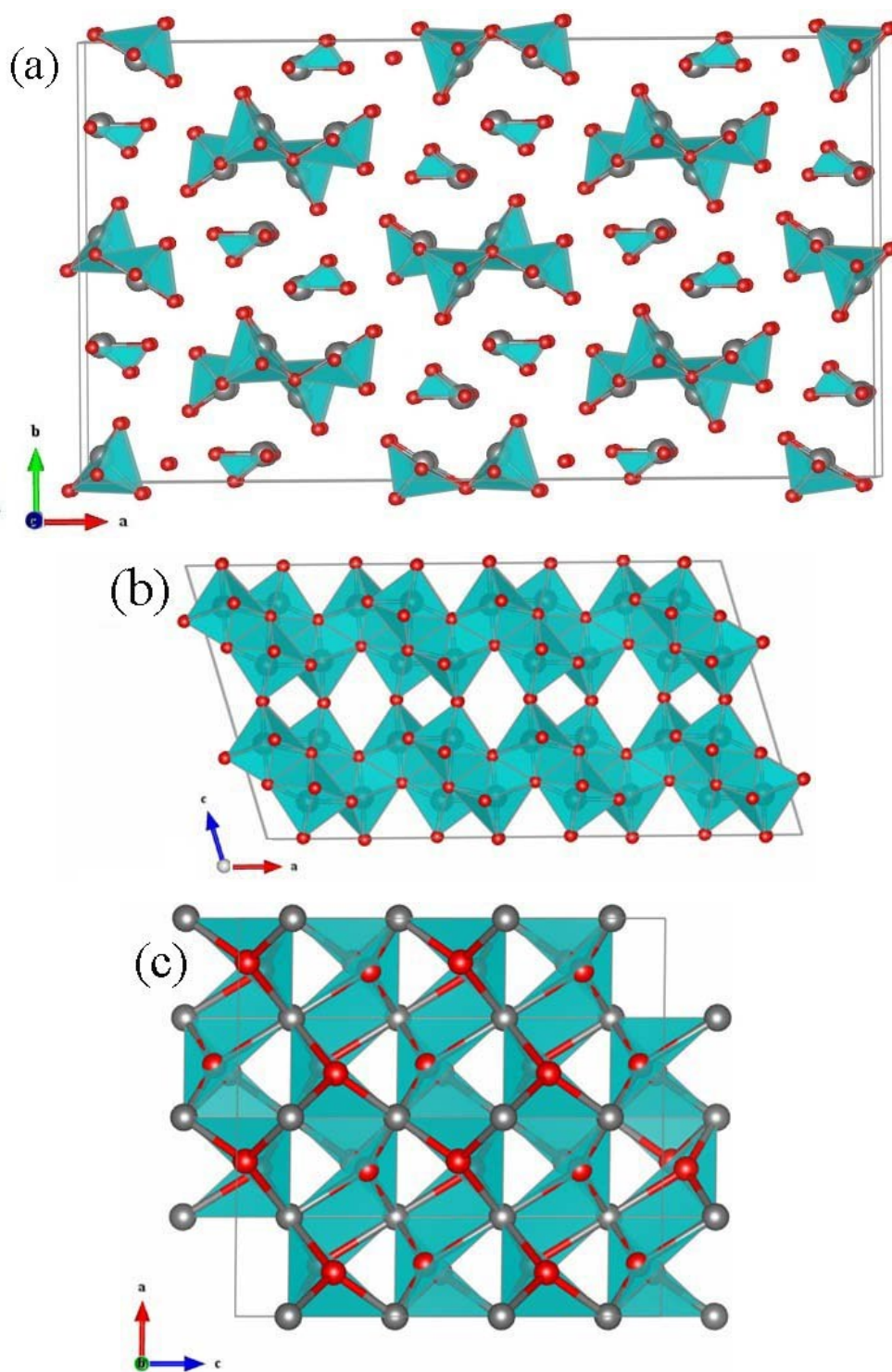


Fig.S6 The Crystal structure models of (a) V_3O_7 , (b) $VO_2(B)$ and (c) $VO_2(D)$.