

Electronic Supplementary Information

Synthesis and Formation Mechanism of VO₂(A) Nanoplates with Intrinsic Peroxidase-like Activity

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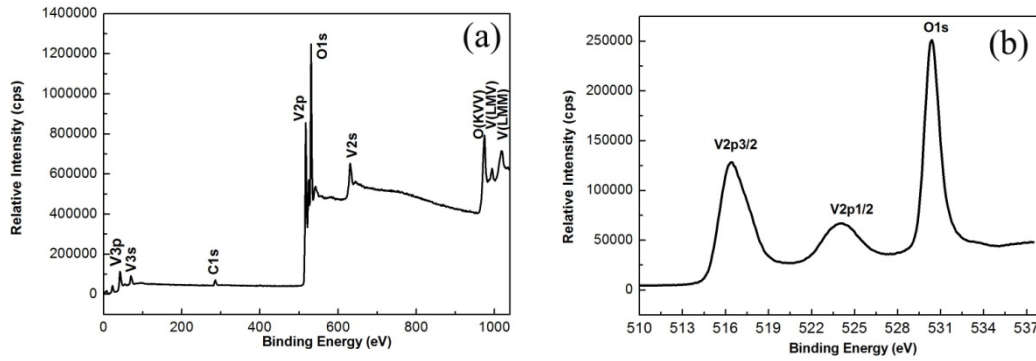


Figure S1 XPS spectra of the plate-like VO₂(A) nanostructures: (a) survey spectrum and (b) core-level spectrum of V2p and O1s.

In order to study the chemical composition and chemical state of as-synthesized plate-like VO₂(A), XPS analysis was conducted and the spectra are shown in Figure S1. The binding energies were corrected for specimen charging by referencing C_{1s} to 284.50 eV. It can be clearly seen that only peaks of elements of C, O, and V could be observed on the survey spectrum (Fig. S1a). The two main peaks centered at 516.4 and 524.0 eV can be attributed to the characteristic V2p_{3/2} and V2p_{1/2} peaks of V(IV) oxidation state, respectively (Fig. S1b).^[1] The peaks for O can be assigned to VO₂(A), or CO₂ and H₂O absorbed on the sample surface.^[2,3]

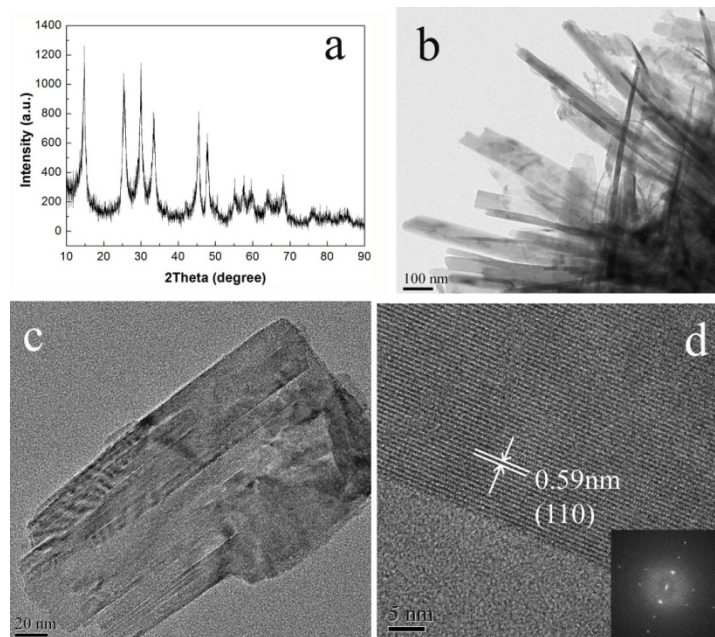


Figure S2 PXRd pattern (a) and HRTEM images (b, c, d) of the products obtained at 220 °C for 30 min. The inset is its SAED pattern.

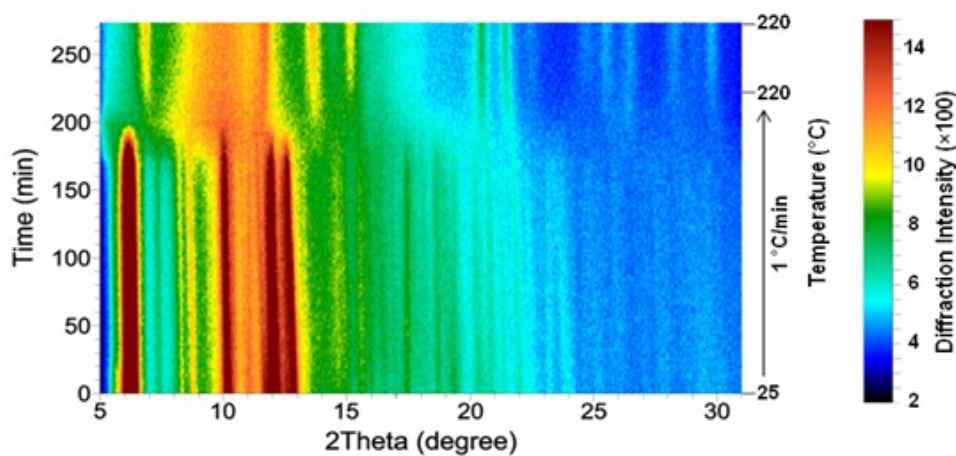


Figure S3. Accumulated time-resolved laboratory in-situ PXRd patterns (viewed down the intensity axis) collected during the synthesis of $\text{VO}_2(\text{A})$ at 220 °C with slow heating ($1\text{ }^\circ\text{C min}^{-1}$). The X-ray wavelength was 0.7093 \AA (Mo $\text{K}\alpha$).

It is clearly shown that after the hydrolysis of $\text{VO}(\text{acac})_2$ into the solution $\text{VO}_2(\text{A})$ started to grow after complete dissolution of $\text{VO}(\text{acac})_2$ at 203 °C. Whereas the starting greenish blue slurry started to turn to dark colour at 99 °C, then became

darker and finally became completely black at 205 °C (Fig. S4). This phenomenon suggests that VO₂(A) nucleation commences at a lower temperature such as 99 °C when the concentration of [VO(H₂O)₅]²⁺ coordinated cations is beyond saturation. Unfortunately, they are so few and little crystals that they were swamped by the signals of VO(acac)₂. Once the crystallization begins, the intensity of the peaks rises gradually until the end of the experiment.

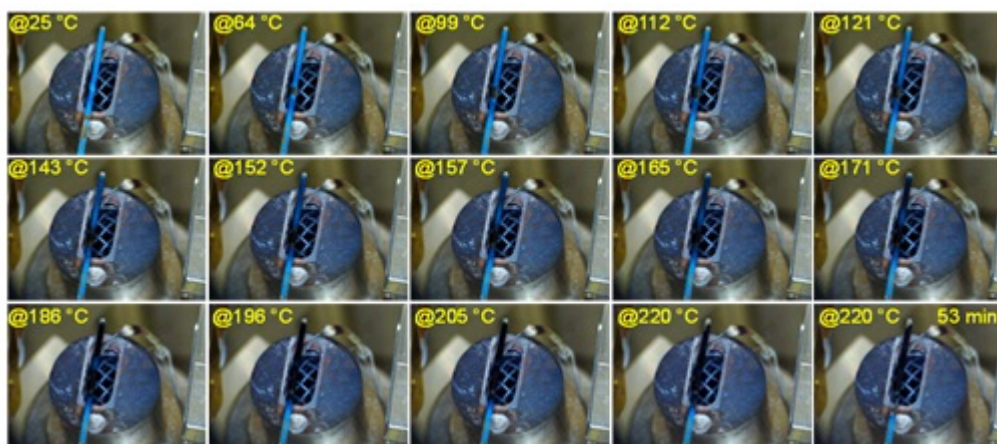


Figure S4. Images captured by the surveillance camera at different stages of laboratory-based in-situ PXRD experiment at 220 °C with slow heating (1 °C min⁻¹), showing color change inside the quartz glass capillary reactor vessel.

Figure S4 shows the images captured by the surveillance camera at different stages of synthesis. The colour change may help to clarify the pathway by which the phase transition took place under hydrothermal condition. It was observed that the starting greenish blue slurry started to turn to dark colour at 99 °C. The colour became darker with increasing temperature and finally became completely black at 205 °C. This is the temperature for complete decomposition/dissolution of VO(acac)₂ from PXRD pattern. The colour remained unchanged during the heating at 220 °C for 53 min.

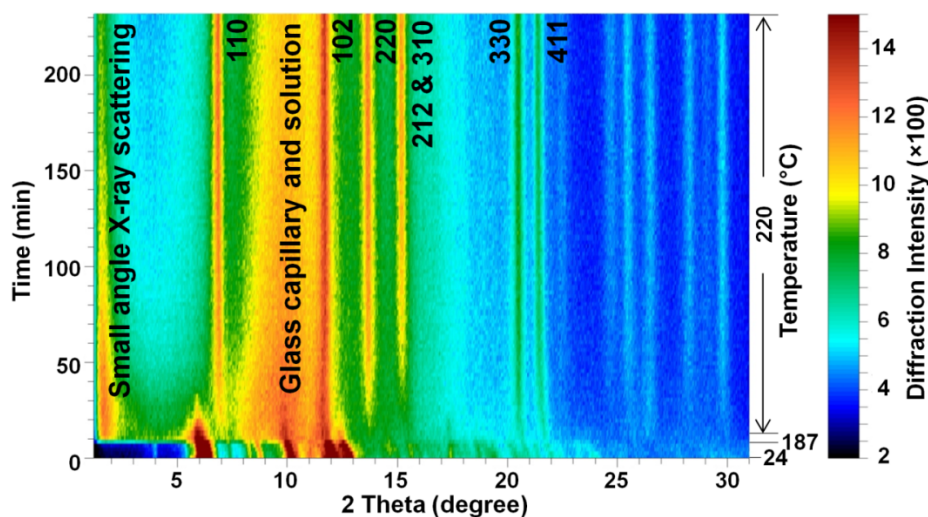


Figure S5 Accumulated time-resolved laboratory in-situ PXRD patterns (viewed down the intensity axis) collected during the synthesis of VO₂(A) at 220 °C with fast heating (30 °C min⁻¹). The X-ray wavelength was 0.7093 Å (Mo K α).

Upon heating, the diffraction peaks of VO(acac)₂ (ICDD No: 23-1965) first decreased in intensity slowly until 187 °C, and then rapidly lost intensity at 187 °C accompanied by (1) an increase in background, (2) the formation of VO₂(A) (ICDD No: 70-2716), and (3) the appearance of a small angle scattering tail at 2 theta range <2°. The increase of background at 187 °C is most likely due to the compositional change of the liquid phase as a result of the addition of the soluble decomposition by-products of VO(acac)₂. The formation of VO₂ was triggered by the rapid decomposition of VO(acac)₂ at 187 °C and after that VO₂ grew at the expense of VO(acac)₂. Complete decomposition of VO(acac)₂ occurred after heating at 220 °C for 17 min. VO₂ was the only product phase detected by PXRD and its intensity increased with time after complete decomposition of VO(acac)₂. The decreasing intensity of the small angle scattering tail is in agreement with the increasing size of VO₂ as a function of time. The peak intensities were still increasing slowly after

heating at 220 °C for 225 min.

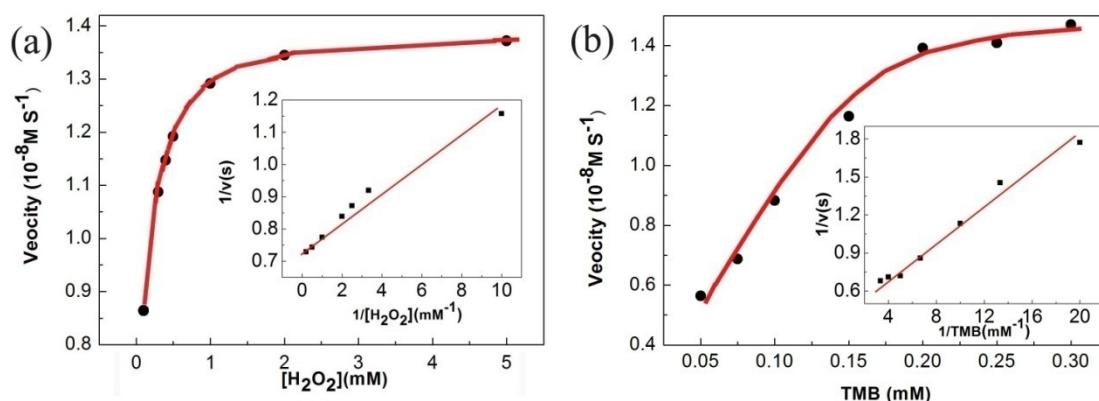


Figure S6 Reaction rate of VO₂(A) nanoplates in TMB-H₂O₂ reaction system as a function of different concentrations of (a) H₂O₂ ([TMB]=0.15 mM) and (b) TMB ([H₂O₂]=0.5 mM). The insert image is the double-reciprocal plots of VO₂(A). The catalyst concentration was fixed at 3 μg mL⁻¹ in 3 mL of acetate buffer solution (0.1 M, pH = 4.0).

Reference:

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2. S. D. Zhang, Y. M. Li, C. Z. Wu, F. Zheng, and Y. Xie, *J. Phys. Chem. C*, 2009, **113**, 15058-15067.
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