Synthesis and formation mechanism of VO$_2$(A) nanoplates with intrinsic peroxidase-like activity†

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Monocrystalline VO$_2$(A) nanoplates have been synthesized via a one-pot hydrothermal process. In situ powder X-ray diffraction was used to monitor the hydrothermal synthesis and it was found that VO$_2$(A) nucleates and grows directly from solution after the complete hydrolysis of a 2.0 M VO(acac)$_2$ precursor solution, rather than involving a previously reported intermediate phase VO$_2$(B). A hydrating–exfoliating–splitting mechanism was established to explain the formation of the nanoplate architecture. The synthesized VO$_2$(A) nanoplates showed outstanding peroxidase-like activity and hence are a promising candidate for artificial peroxidase.

1. Introduction

Vanadium oxides and their metastable structures have received considerable attention because of their diverse structures and novel physico-chemical properties. Up to now, several crystalline phases of VO$_2$ and V-O hydrates with oxidation states from $+2$ to $+5$ have been reported, including monoclinic VO$_2$, VO$_2$(M), rutile VO$_2$(R), tetragonal VO$_2$(A), monoclinic VO$_2$(B), VO$_2$(C), paramontroseite VO$_2$(P), rutile-$\cdot$H$_2$O, VO$_2$-$\cdot$0.5H$_2$O, VO$_2$-$\cdot$0.25H$_2$O, haggetite V$_4$O$_6$(OH)$_4$, and VO$_2$H$_2$O$_2$ (montroseite, orthorhombic and hollandite-type phases). Among them, monoclinic VO$_2$(M) (space group $P_{2_1}c$) and tetragonal VO$_2$(R) ($P4_2/mnm$) undergo reversible phase transformation at $\sim$67 °C, accompanied by dramatic changes in electrical resistance and optical transmittance. These properties enable a wide range of applications in smart windows, gas sensors, optoelectronic switching devices, Mott field-effect transistors, and so forth. Another thermodynamically metastable polymorph VO$_2$(B) ($C2/m$) is the most common phase formed from solution synthesis. It consists of layers of distorted corner and edge-sharing VO$_6$ octahedra which form a tunnel structure. It has also attracted much interest in the last few years owing to its proper work potential as well as its high energy capacity when used as electrode materials in aqueous Li-ion batteries (LIBs). As is well known, the traditional intercalation compound VO$_2$(A) shows similar layered structure as VO$_2$(B) except for the distorted VO$_6$ octahedra in VO$_2$(B) and different stack mode between them. However, research on other metastable phases, such as layered VO$_2$(A), has been rarely reported.

Théobald first discovered the existence of VO$_2$(A) as an intermediate phase in a study of hydrothermal reaction in the V$_2$O$_5$–V$_2$O$_3$–H$_2$O system. Later, the crystal structure and phase transition were thoroughly investigated by Oka. More recently, various VO$_2$(A) nanostructures have been successfully fabricated. For example, Ji and coworkers selectively prepared VO$_2$(A) by controlling the pressure during the hydrothermal synthesis. Li and coworkers reported the ultra-long VO$_2$(A) nanobelts synthesized hydrothermally using V$_2$O$_5$ sol as precursor and polyethylene glycol as both surfactant and reducing agent. Xie et al. reported the large-scale fabrication of VO$_2$(A) nanobelts by simple hydrolysis of VO(acac)$_2$ and observed an intermediate phase VO$_2$(B). In addition, Dai et al. prepared 1D VO$_2$(A) nanostructures via a one-step hydrothermal method using VOSO$_4$ and NH$_3$·H$_2$O as precursors; the prepared material was used as a high performance cathode in LIBs.

Much effort has been put into developing synthetic strategies for the fabrication of VO$_2$ nanostructures, using methods such as sol–gel, templating, ion implantation, precursor pyrolysis, hydrothermal and solvothermal syntheses, magnetron sputtering and gas-phase deposition. These methods generally produced VO$_2$(R) or VO$_2$(B), but the metastable VO$_2$(A) was only obtained by the hydrothermal method. Therefore, hydrothermal synthesis is considered to be the most favorable and
flexible method for the synthesis of phase pure VO$_2$(A) as well as being scalable, simple in concept, and environmentally benign. However, hydrothermal synthesis can be very complex mechanistically, as several metastable and stable hydrates and non-hydrate oxides may form upon rapid heating to high temperature in a pressurized autoclave. The abundance of phases and complexity of the hydrothermal phase diagram make it difficult for the formation and stabilization of each specific phase under specified conditions. It is not surprising that VO$_2$(A) was often reported as the intermediate phase during transition from the metastable monoclinic VO$_2$(B) to the more stable tetragonal rutile VO$_2$(R) phase, with changes in temperature, pressure, and time. This leads to an ambiguous understanding of the transformation between VO$_2$ polymorphs and therefore, the formation mechanism of VO$_2$(A).\textsuperscript{25,33,34} Hence, it is still a great challenge to synthesize phase pure VO$_2$(A).

In this paper, we have investigated the facile synthesis of VO$_2$(A) monocrystalline nanoplates via a one-step hydrothermal process by the hydrolysis of a high concentrated (2.0 M) VO(acac)$_2$ solution. The formation mechanism of the nanoplates has been characterized by both \textit{ex situ} characterization and \textit{in situ} powder X-ray diffraction (PXRD). In addition, the activity of the nanoplates as a novel biomimetic catalyst for the oxidation of the substrate 3,3’,5,5’-tetramethylbenzidine dihydrochloride (TMB) in the presence of H$_2$O$_2$ has been determined.

2. Experimental section

2.1 Materials
Vanadyl acetylacetonate (VO(acac)$_2$), sodium acetate (CH$_3$COONa), H$_2$O$_2$ (30 wt%), and 3,3,5,5-tetramethylbenzidine dihydrochloride (TMB) were purchased from Aladin Ltd. (Shanghai, China). All chemicals used in this study were commercially available analytical grade and used without further purification.

2.2 Synthesis
VO$_2$(A) nanoplates were synthesized by a facile hydrothermal method using VO(acac)$_2$ as the vanadium source. In a typical synthesis, 30 mmol (7.96 g) of VO(acac)$_2$ was dispersed in 15 mL deionized water and then the mixed suspension was transferred into a 25 mL PTFE-sealed autoclave. The autoclave was heated to 220 °C and kept at that temperature for 24 h before it was cooled to room temperature in air. The resulting precipitate was filtered, washed with distilled water and ethanol three times, and finally dried at 60 °C under vacuum overnight.

2.3 \textit{Ex situ} characterization
The PXRD patterns were recorded on a Rigaku D/Max-RB X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). A small amount of products were ultrasonically dispersed in ethanol and deposited on copper grids for transmission electron microscopy (TEM, JEM-2100F, JEOL) measurements. Field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL) was employed to examine the morphology of the products. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a VG ESCALAB MK II system equipped with Al KR radiation as the X-ray source. The measurements were carried out in an ultrahigh vacuum (UHV) chamber. The carbonaceous C$_1s$ line (284.5 eV) was used as the reference for the calibration of the binding energies.

2.4 \textit{In situ} PXRD
One \textit{in situ} PXRD experiment was conducted on the powder diffraction beamline at the Australian Synchrotron and two laboratory-based \textit{in situ} PXRD experiments were carried out using an Inel EQUINOX 3000 instrument at CSIRO Mineral Resources Flagship. For the synchrotron-based \textit{in situ} PXRD experiment, the X-ray wavelength (0.6889 Å) was calibrated using a LaB$_6$ standard (NIST SRM 660b). For the laboratory-based \textit{in situ} PXRD, a Mo Kα radiation ($\lambda = 0.7093$ Å) was used. The same sample presentation setup was used in both synchrotron- and laboratory-based \textit{in situ} experiments and was described in detail elsewhere.\textsuperscript{35-37} The starting precursor (5.4 mg VO(acac)$_2$ and 10.7 μL Milli-Q water) was injected into a quartz glass capillary (1 mm in diameter, 0.1 mm in wall thickness, and 40 mm in length), which was then fitted to a custom-made stainless steel holder. The precursor-containing capillary/ stainless steel holder was then attached to the goniometer head of the diffractometer and heated to the synthesis temperature 220 °C by a hot air blower beneath the capillary. External N$_2$ pressure (3 MPa) was applied to the capillary during the synthesis to prevent vaporization of the solvent. For the synchrotron-based \textit{in situ} experiments, the heating rate was 5 °C min$^{-1}$, which is similar to the heating rate of a laboratory scale autoclave. For the lab-based \textit{in situ} experiments, faster (30 °C min$^{-1}$) and slower (1 °C min$^{-1}$) heating rates were used to study the effect of heating rate on the syntheses mechanism. The temperature was monitored by a K-type thermocouple 3.5 mm beneath the capillary. \textit{In situ} PXRD patterns were collected simultaneously during the synthesis with a time resolution of ~2 min. The capillary was oscillated continuously during the measurements, which ensured temperature homogeneity and minimized potential effects of preferred orientation. For the lab-based \textit{in situ} experiments, a surveillance camera was also used for monitoring visual appearance of the contents of the capillary reaction vessel as the synthesis reactions progressed.

2.5 Peroxidase-like activity of the as-synthesized VO$_2$(A) nanoplates
The peroxidase-like activity of VO$_2$(A) nanoplates was evaluated as follows: 30 μL VO$_2$(A) dispersion (0.3 mg mL$^{-1}$) was mixed with 3 mL CH$_3$COONa buffer solution (0.1 M, pH 4.0) containing 100 μM TMB and 5 mM H$_2$O$_2$. The mixture was then measured in wavelength-scan mode or time-scan mode by monitoring the absorbance change of TMB at 652 nm for 600 s on a UH4150 UV-visible spectrophotometer at 25 °C. The peroxidase-like reaction,\textsuperscript{38} catalyzed by VO$_2$(A) nanoplates, can be described as follows:

\[
\text{TMB(aq)} + \text{H}_2\text{O}_2(aq) \xrightarrow{\text{VO}_{2}(\text{A})} \text{oxTMB(aq)} + 2\text{H}_2\text{O(l)}
\]
The kinetic data were obtained under the optimum conditions by changing the concentrations of TMB and keeping the concentrations of H2O2 constant, or vice versa. The apparent steady-state reaction rates of the VO2(A) nanoparticles were deduced according to their absorbance data and the molar absorption coefficient of TMB-derived oxidation products (ε = 39 000 M⁻¹ cm⁻¹). The dynamics parameters (Vmax and Km) were determined using the Michaelis–Menten equation and a Lineweaver–Burk plot:

\[
\frac{1}{v} = \frac{K_m}{V_{max}} \left( \frac{1}{[S]} + \frac{1}{V_{max}} \right)
\]

where v, [S], Km and Vmax stands for the initial velocity, substrate concentration, the Michaelis–Menten constant and the maximal reaction velocity, respectively.\(^\text{38.51}\)

3. Results and discussion

3.1 Structure and morphology

Single crystalline tetragonal VO2(A) phase nanoplates were synthesized on a large scale under mild hydrothermal condition by the hydrolysis of a 2.0 M VO(acac)₂ solution at 220 °C for 24 h. The phase identity of the product was confirmed by PXRD (Fig. 1), where the reflections match well with those of metastable tetragonal VO2(A) (space group: P4/nnc, ICDD database no. 70-2716). The absence of any other phases suggests the synthesis of pure VO2(A) phase. The chemical state and the crystal structures of the nanoparticles were also confirmed by XPS, as shown in Fig. S1.†

The morphology of the VO2(A) nanoplates can be observed in the TEM and SEM images shown in Fig. 2. Fig. 2a displays a representative SEM image of the high yield VO2(A) materials. The high-magnification SEM image (Fig. 2b) distinctly shows that the VO2(A) nanostructures are composed of uniformly plate-like nanoparticles with average width measuring ~30–50 nm, length of 100–200 nm and thickness of 20–30 nm, respectively. The TEM image shown in Fig. 2c also confirms the plate-like morphology which is typically 20–40 nm wide and 100–200 nm long, in agreement with SEM observation. The high-resolution TEM (HRTEM) image (Fig. 2d) demonstrates the well-resolved lattice fringes with an interlayer spacing of about 0.60 nm, corresponding to the (110) lattice plane of VO2(A). Selected-area electron diffraction (SAED) pattern (inset of Fig. 2c) further validates the single crystalline nature of a single nanoplate.

3.2 Ex situ characterization of the samples synthesized under different conditions

In order to investigate the growth processes of VO2(A) tetragonal crystalline nanoparticles, a series of experiments were conducted to track the evolution of morphologies and phases as a function of temperature and time by FESEM and PXRD. Temperature played an important role in controlling the size, shape, and crystal structures of the nanoparticles. By varying the hydrothermal synthesis temperature, the nanoparticles exhibited distinctly different shapes and morphologies, which is consistent with the evolution of crystalline structures. The PXRD patterns collected for the samples hydrothermally treated at 140 °C match well with pure V2O4·2H2O\(^\text{39}\) (ICDD database no. 13-0346) (Fig. 3a). All the peaks were the characteristic structures of layered hydrates of V2O4·2H2O particles.\(^\text{40}\) This phase was found to be stable when temperature was increased to 160 °C. Their solution synthesis and thermal stability have been previously fully analyzed by our group.\(^\text{39}\) Bunches of microrods (1–8 μm in length and 0.5–1 μm in diameter) consisting of tiny nanoparticle nuclei have been observed at 140 and 160 °C, as shown in the insets of Fig. 4a and b, respectively. As the temperature increased to 170 °C, the PXRD pattern shows the coexistence of V2O4·2H2O and VO2(A) (Fig. 3c). Correspondingly, some sheet-like VO2(A) nanoparticles were produced by consuming surrounding V2O4·2H2O microrods (Fig. 4c). However, when the
The temperature was further increased up to 180 °C, VO₂(A) started to form slowly (Fig. 3d). The intensities of the VO₂(A) phase reflections increase continuously with elevated reaction temperatures in Fig. 3. The crystalline sizes were estimated from the (110) diffraction peak at 2θ = 14.7° using the Scherrer formula. They were calculated to be 15.0 nm for 180 °C-24 h sample, 13.2 nm for 200 °C-10 h sample, 14.8 nm for 200 °C-24 h sample and 19.2 nm for the reactions carried out for 1, 3, 6, 10, 18 and 24 h, respectively. At the same time, irregular nanosheets stacked randomly and exhibited a well-dispersed morphology (Fig. 4d–f).

VO₂(A) ordered nanoplates formed only when the temperature was raised to 220 °C (Fig. 4g), indicating that higher reaction temperature is beneficial for increasing crystallization rate and for uniformity of morphology of the particles.

To elucidate in depth the formation mechanism of the plate-like VO₂(A) architecture, time-dependent hydrothermal synthesis experiments were carried out at 220 °C. The ex situ PXRD patterns of the phase evolution of the nanocrystals as a function of time are presented in Fig. 5 and S2a. All of the reflections match well with the ICDD pattern for pure VO₂(A) with tetragonal symmetry (no. 70-2716), and no intermediate phases or impurities were observed. The absence of intermediate phases will be further verified by in situ PXRD experiments (to be discussed later). We also observed that the phase abundance and crystallite size increase with increasing synthesis time from 1 to 24 h, as the peaks became higher and narrower with time. The crystallite sizes estimated from the (110) diffraction peak are 9.5 nm, 12.5 nm, 14.3 nm, 14.5 nm, 16.2 nm and 19.2 nm for the reactions carried out for 1, 3, 6, 10, 18 and 24 h, respectively.

When the synthesis time exceeds 30 min, single phase of VO₂(A) nanosheets assembled from nanowires were obtained (as shown in Fig. S2†). After synthesis for 1 h and 3 h, 3D urchin-like microspheres having a diameter of ~2–5 µm were formed (Fig. 6a and c). The hierarchical urchin-like super-structures are composed of radially aligned nanobelts having a thickness of ~30 nm, width in the range of 100–200 nm and length up to 100 nm (Fig. 6b and d). More interestingly, exfoliation from the surface of the layer associated with splitting to narrow plates can be clearly observed (highlighted by red circles in Fig. 6b). It is likely that the existence of intrinsic stress and surface energy caused the rolling up of the nanosheets and subsequent exfoliation and splitting. When the reaction time was prolonged to 10 h and above, the sheets were cleaved into well-aligned plate-shaped building blocks, as demonstrated in Fig. 6f–h.

3.3 In situ characterization of the formation of VO₂(A) phase

The poor understanding of most hydrothermal syntheses is largely due to the challenge of carrying out in situ and real time characterization, because the high temperature and high pressure autoclave condition is not accessible to most characterization techniques. By application of the in situ PXRD technique for tracking hydrothermal and solvothermal syntheses, we have the opportunity of unveiling the ‘black box’ of hydrothermal syntheses and elucidating unambiguous
synthesis mechanisms, similar to which has been achieved in recent studies. Fig. 7 shows the results of the synchrotron-based *in situ* PXRD experiments, with the accumulated time-resolved PXRD patterns viewed down the intensity axis. In this synthesis, a heating rate of 5 °C min⁻¹ was used, very close to the heating scheme of laboratory autoclaves. It is clearly shown that hydrolysis of VO(acac)₂ occurred at around 170 °C as all diffraction peaks of VO(acac)₂ disappeared. Immediately following this, diffraction peaks of this phase appear at the same time there was a sharp increase in the intensity of small angle X-ray scattering (SAXS) tail at low angle below 1.5°. The appearance of the SAXS tail was most likely due to the formation of a great number of nuclei of VO₂(A). Subsequently, the intensity of the VO₂(A) diffraction peaks increased with time while the intensity of the SAXS tail dropped. The dropping of the SAXS tail suggests the moving of scattering to lower angles which means the formation of larger crystals. This is in agreement with the increasing sharpness of the diffraction peaks. However, a complete understanding of the SAXS feature requires a separate study using a dedicated high resolution SAXS instrument which is capable of covering of much wider q range. No other phases were observed. Hence, the synthesis of VO₂(A) follows a direct crystallization mechanism, in which VO₂(A) nucleates and subsequent grows from a supersaturated solution formed by hydrolysis of VO(acac)₂.

To study the effect of heating rate on the synthesis mechanism, another two laboratory-based *in situ* PXRD experiments...
were carried out using a heating rate of 1 °C min⁻¹ (slow heating) and 30 °C min⁻¹ (fast heating). The results are shown in Fig. S3–S5.† It was found that varying heating rate had no effect on the synthesis mechanism. VO₂(A) nucleated and grew directly from solution following the complete hydrolysis of VO(acac)₂ with no other intermediate phases observed. However, the laboratory in situ PXRD experiments provided more information from the colour change of the reaction mixture observed by the surveillance camera (Fig. S4†). For the slow heating experiment, the starting greenish blue precursor started to turn dark at 99 °C, becoming darker until turning black at 205 °C (Fig. S4†). This phenomenon suggests that VO₂(A) nucleation may commence below 170 °C with the minor amount and poor crystalline nature of the nuclei possibly explaining why they were not detected using PXRD. These nucleation events were not detected by in situ PXRD though possibly due to the minor amount and poor crystalline nature of the nuclei.

In previous studies, VO₂(B) was regarded as the inevitable intermediate product in the initial stage of hydrolysis of VO(acac)₂ under mild hydrothermal condition. Usually, its formation was assigned to the condensation of [VO(H₂O)₅]²⁺ complex ions and subsequent formation of vertex and edge sharing VO₆ octahedra. However, this intermediate VO₂(B) phase was not observed in the in situ PXRD experiments performed here. This may be because the precursor concentration (2.0 M) used here was dozens of times higher than the precursors used in previous studies. The hydrolysis of the higher concentration precursor resulted in a very high concentration of dissolved vanadium species (e.g., [VO(H₂O)₅]²⁺) that directly triggered nucleation and subsequent growth of the thermodynamically more stable phase VO₂(A) rather than the metastable VO₂(B) phase. This is in agreement with the selective formation of VO₂ polymorphs being greatly dependent on synthesis parameters including pressure, temperature, pH value, and precursor concentrations.

Based on the above results, the formation mechanism of plate-shaped VO₂(A) can be described as follows: (a) VO(acac)₂ hydrolyzes to form [VO(H₂O)₅]²⁺ complex ions and then condenses to vertex and edge sharing VO₆ octahedra; (b) direct nucleation of VO₂(A) and growth of nanosheets with a layered structure; (c) plate-like nanostructures formation due to the exfoliation and splitting of the nanosheets in order to reduce system energy. Scheme 1 summarizes the hydrating–exfoliation–splitting process during the formation of the nanosheets. This mechanism was also proposed to elucidate the formation of other nanostructures. For example, it is observed in diverse cases such as the exfoliation formation of vanadium oxide (VO₂(B), V₂O₅·2H₂O, V₂O₅·0.25H₂O, V₂O₅·3H₂O, TiO₂, MnO₂, and Ag nanowires.†

### 3.4 Peroxidase-like activity

To investigate the peroxidase-like activity of the as-prepared VO₂(A) nanosheets, experiments of catalytic oxidation of chromogenic substrate TMB were conducted in the presence or absence of H₂O₂. The peroxidase-like activity was evaluated based on the intensity of the absorbance peak centered at 652 nm produced by the blue oxidation product (oxTMB). In the control experiments, mixtures of TMB + VO₂ and H₂O₂ + VO₂ only showed negligible adsorption, and mixture of TMB + H₂O₂ showed no absorptions in the scan range 400–800 nm (Fig. 8a). By contrast, after adding VO₂(A) into the TMB + H₂O₂ solution, the clear solution turned to blue and meanwhile a strong absorption peak at 652 nm were observed (Fig. 8a). These observations clearly confirm the outstanding peroxidase-like catalytic activity of VO₂(A) nanosheets toward the oxidation reaction between TMB and H₂O₂. Similar to the natural enzyme (horseradish peroxidase, HRP) and most artificial nanozymes, catalytic oxidation of TMB by VO₂(A) nanosheets is highly dependent on the concentration of VO₂(A) and pH, as shown in Fig. 8b–d. Therefore, the subsequent experiments were performed at the optimal VO₂ concentration of 3.0 μg mL⁻¹ and at pH 4.0.

The apparent kinetic parameters (the Michaelis constant Kₘ and the maximal reaction velocity Vₘₐₓ) were calculated based on a series of experiments carried out at 25 °C by varying one substrate concentration each time and keeping the other constant. Typical Michaelis–Menten curves were obtained as shown in Fig. S6†. The Kₘ and Vₘₐₓ parameters were obtained using Lineweaver–Burk double reciprocal plot and their
comparison with other nano-inorganic peroxidase mimics is
given in Table 1. Remarkably, the $K_{m}$ value (0.058 mM) of VO$_2$(A)
nanoplates with H$_2$O$_2$ as substrate is signi-

cantly lower than that of HRP (3.7 mM), and even much lower than other nano-

enzyme mimics, suggesting that VO$_2$(A) nanoplates has a higher

affinity to H$_2$O$_2$ than HRP and other peroxidase mimics. The

higher performance of VO$_2$(A) may be attributed to the more

"active site" on the surface of the VO$_2$(A) nanoarchitecture when

compared with HRP. In addition, $K_{m}$ of VO$_2$(A) nanoplates

with TMB as the substrate was about 50% lower than that of

HRP, while being larger relative to some other nanoparticles

enzyme mimics. This result indicates that a higher TMB

concentration is required to achieve maximum activity of

VO$_2$(A) nanoparticles.

Table 1  Comparison of apparent kinetic parameters among natural and artificial enzymes

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<th>Catalyst</th>
<th>$K_{m}$ (mM)</th>
<th>$V_{max}$ ($\times 10^{-8}$ M s$^{-1}$)</th>
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<tr>
<td></td>
<td>TMB</td>
<td>H$_2$O$_2$</td>
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<td>VO$_2$(A) nanoplates</td>
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<td>0.058</td>
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<tr>
<td>HRP</td>
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<td>NiO NFs</td>
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<td>TiO$_2$@CeO$_2$</td>
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<tr>
<td>rGO–CFs</td>
<td>0.046 ± 0.001</td>
<td>14.72 ± 2.332</td>
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4. Conclusions

In summary, plate-like VO$_2$(A) nanostructures were successfully synthesized by a facile, template-free and scalable hydrothermal synthesis. The VO$_2$(A) nanoparticles consist of uniform nanoplates of 30–50 nm in width, 100–200 nm in length, and 20–30 nm in thickness. The formation of VO$_2$(A) follows a direct crystallization mechanism as no intermediate phases were observed in both ex situ and in situ PXRD-based characterization. Based on the time-dependent experimental results, a hydrating–exfoliating–splitting model was proposed to describe the formation mechanism of the nanoplate structure. The produced VO$_2$(A) materials showed outstanding peroxidase-like activity and may find potential applications in biotechnology.
Acknowledgements

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Notes and references
