CrystEngComm



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PAPER

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Cite this: *CrystEngComm*, 2022, **24**, 6009

Received 13th June 2022, Accepted 3rd August 2022

DOI: 10.1039/d2ce00813k

rsc.li/crystengcomm

Introduction

Vanadium dioxide (VO₂) is a versatile material that can access many different crystal phases, each with its own chemical, electronic, and physical properties.¹ One phase in particular, VO₂(B), has attracted significant attention due to its potential application as an electrode in aqueous lithium ion and postlithium ion batteries.^{2,3} The structure of VO₂(B) is comprised of double layers of double chains of edge-sharing distorted VO₆ octahedra that are analogous to the V₄O₁₀ layers found in δ -M_xV₄O₁₀ materials containing intercalated metal ions.³ In VO₂(B) these layers are connected by corner-sharing linkages between VO₆ octahedra, as opposed to being separated by

Influence of water concentration on the solvothermal synthesis of VO₂(B) nanocrystals[†]

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Nanocrystals of VO₂(B) have attracted significant attention for their promising performance in electrochemical energy storage applications. Phase-purity and nanocrystal morphology are both crucial factors for the performance of these materials, but given the large number of crystal polymorphs available to VO₂, achieving simultaneous control over crystal phase and nanocrystal size is a significant synthetic challenge. This paper describes the impact of water concentration on the synthesis of VO₂(B) nanocrystals *via* solvothermal reaction of a molecular V(w) precursor in toluene. Using controlled, stoichiometric amounts of water (20 equivalents per vanadium centre) enables access to short nanorods of VO₂(B) whose lengths follow a Gaussian distribution with an average and standard deviation of 110 \pm 30 nm. Decreasing the amount of water present to two or four equivalents results in formation of VO₂(A) nanocrystals and eliminating it entirely results in no reaction. Increasing the amount of water to more than 20 equivalents increases the average length of the VO₂(B) nanorods and causes the distribution in rod lengths to evolve from Gaussian to lognormal. This evolution in the size distribution is consistent with changes in a model Gaussian distribution observed upon simulated end-to-end oriented attachment events. These results demonstrate that control over the concentration of water is a useful strategy for tuning the morphology and crystal phase of VO₂ nanocrystals.

intercalated cations. The resulting structure possesses onedimensional tunnels conducive to the facile uptake of lithium ions at potentials compatible with aqueous electrolytes.^{2,3} Previous work has demonstrated that lithium ion batteries containing an electrode fabricated from VO₂(B) nanoparticles show increased capacity correlated to decreased particle size.^{4–6} This observation suggests that optimization of the performance of this material as a battery electrode will require development of synthetic methods that provide access to phase-pure VO₂(B) nanocrystals with controlled size and shape.

Although several routes for the preparation of VO₂ nanocrystals with various crystal phases have been reported, these syntheses tend to produce either exceptionally small spherical nanocrystals ($d \sim 3-5$ nm) using high-temperature hot injection techniques,⁷ or microns-long nanorods *via* solvothermal methods.⁸⁻¹⁸ Accessing nanocrystal sizes that lie between these two extremes while maintaining selectivity for the VO₂(B) phase is a significant synthetic challenge. Nanocrystals of both VO₂(B) and a related phase, VO₂(A), are typically synthesized at elevated pressures using solvothermal methods in which water is the solvent (see Table S1 in ESI† for a summary of reported procedures). V₂O₅ is often used as a precursor in these methods in conjunction with a reducing agent (*e.g.* oxalic acid). A mononuclear V(rv) precursor,

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[†] Electronic supplementary information (ESI) available: Summary of previously reported methods for the solvothermal synthesis of VO₂(A) and VO₂(B) nanocrystals, experimental details of powder X-ray diffraction measurements, MatLAB code used to model nanorod growth *via* oriented attachment, characterization of the solid product obtained after heating in dry toluene, indexed pXRD spectra and selected area electron diffraction measurements of VO₂(A) and VO₂(B), SEM and pXRD of VO₂(B) nanocrystals synthesized in various amounts of water, electronic absorption spectra of supernatant solutions, dependence of nanorod length on reaction time in 20 and 200 equivalents of water. See DOI: https://doi.org/10.1039/d2ce00813k

namely vanadyl acetylacetonate (VO(acac)₂), enables synthesis of VO₂(B) or VO₂(A) nanocrystals without a reducing agent and provides a more straightforward pathway for nucleation of VO₂ nanocrystals by eliminating the need to decompose a bulk starting material.^{17,18} Since VO₂(A) and VO₂(B) can both be made from the same hydrothermal reaction mixture, careful control of temperature, pressure, and reaction time is required to achieve phase-pure products using these methods.

The typical morphology of VO₂(B) nanocrystals synthesized in water is microns-long nanorods or nanobelts.^{12-15,17,19-22} Although the factors driving formation of these long $VO_2(B)$ nanostructures are not clear, formation of long nanorods of other phases of VO_2 , such as $VO_2(A)$ and $VO_2(R)$, has been attributed to oriented attachment of shorter nanorods.8,9,23,24 For example, Nguyen, *et al.* studied the formation of $VO_2(R)$ nanocrystals via solvothermal reaction of a molecular V(v) peroxo precursor in mixtures of toluene and water.²⁵ They found that increasing the volume ratio of water in the solvent mixture produced nanorods of $VO_2(R)$ with increasing length and proposed that this growth was driven in part by oriented attachment in the presence of increased amounts of water. We hypothesized that if altering the water to toluene ratio could change the size of $VO_2(R)$ nanorods, then limiting the concentration of water in solvothermal reactions may be the key to producing smaller VO₂(B) nanocrystals.

Herein we report the impact of varying the solvent composition on the solvothermal synthesis of VO₂(B) nanocrystals from VO(acac)₂. We find that mixing toluene with a stoichiometric amount of water (20 equivalents per vanadium centre) produces a reaction system that consistently and reliably produces small VO₂(B) nanobelts with submicron lengths averaging 110 nm. Control over the size of the nanocrystals is accomplished by increasing the amount of water present in the reaction mixture. Statistical modelling indicates that changes in the shape of the size distribution observed upon increasing the concentration of water are consistent with promotion of end-to-end oriented attachment. Notably, decreasing the amount of water present in the reaction mixture below 20 equivalents per vanadium centre results in formation of VO₂(A) nanocrystals, demonstrating that the concentration of water influences the crystal phase as well as the morphology of VO₂ nanocrystals.

Experimental methods

General considerations

Prior to addition of water to the reaction mixtures, all manipulations were carried out in an MBraun inert atmosphere glovebox under a nitrogen atmosphere unless otherwise stated. Autoclave reactors and Teflon liners were pumped down in an evacuated antechamber overnight prior to use in the glovebox. Molecular sieves (3 Å, Fisher Scientific) were activated by heating at 200 °C under vacuum overnight. Toluene was dried over 20% by weight activated sieves for at least 24 hours, then purged with nitrogen for at

least 1 hour before being transferred *via* cannula to a Schlenk flask. The toluene was then pumped into the glove box overnight in an evacuated antechamber and stored over activated 3 Å molecular sieves. $VO(acac)_2$ purchased from Sigma-Aldrich and lauric acid purchased from Millipore were both pumped into the glove box overnight in an evacuated antechamber before use.

Solvothermal synthesis of VO₂ nanocrystals

A 25 mL Teflon-lined autoclave reactor was charged with 1 mmol (0.200 g) lauric acid, 0.25 mmol (0.068 g) $VO(acac)_2$, and 10 mL toluene. The autoclave reactor was sealed and removed from the glove box. Under ambient atmosphere, the autoclave reactor was opened and the desired amount of water was added (0.5–100 mmol). The autoclave reactor was sealed again and heated in an oven at 200 °C for 24 hours. The autoclave reactor was then allowed to cool to room temperature. The black product was collected by centrifugation under ambient atmosphere and washed with ethanol. The product was rotovapped to dryness and stored in the glove box under nitrogen.

Monitoring nanocrystal growth as a function of time

Teflon-lined autoclave reactors (25 mL volume) charged with 1 mmol (0.200 g) lauric acid, 0.25 mmol (0.068 g) VO(acac)₂, and 10 mL toluene were sealed and removed from the glove box. The autoclave reactors were opened in air and 5 or 50 mmol water was added to each. The autoclave reactors were resealed and heated in an oven at 200 °C. The autoclave reactors were removed one at a time at various time points (e.g., 0.5, 1, 2, 3, 6, 9, 12, 15, 18 hours) and cooled to room temperature. The contents of each reactor were centrifuged under ambient atmosphere and solid precipitates were collected along with the supernatants. The solid products were washed with ethanol, rotovapped to dryness, and stored in the glove box under nitrogen. The supernatants were rotovapped to dryness and any remaining solids were resuspended in 10 mL of filtered toluene via sonication. These solutions were characterized by electronic absorption spectroscopy to determine the concentration of unreacted VO(acac)₂ (see ESI[†] Fig. S8 and S9).

Characterization methods

Powder X-ray diffraction measurements were performed using a Rigaku XtaLAB Synergy-S Dualflex single crystal diffractometer operating in powder collection mode (See ESI† for details). An FEI Tecnai F20 G2 scanning transmission electron microscope (TEM) operated at 200 kV and equipped with a single-tilt sample holder was used to analyse the VO2 nanocrystals. TEM samples were prepared by dropcasting nanocrystals from a hexanes or toluene dispersion onto 300 mesh copper grids coated in lacey carbon (Ted Pella). Fourier transform infrared (FT-IR) spectra were recorded on a **IRAffinity-1** Fourier transform infrared Shimadzu spectrophotometer and were reported in wavenumbers

 (cm^{-1}) . Electronic absorption spectra were collected on a Cary 7000 UV-vis-NIR spectrometer.

Computational modelling of nanorod growth *via* oriented attachment

The evolution of the distribution in nanorod lengths following growth via end-to-end oriented attachment was simulated using a MatLAB script (see ESI[†] for additional information regarding the code used). Briefly, we first constructed a Gaussian distribution containing 10 000 random values of nanorod lengths with an average and standard deviation matching that of the distribution in lengths of VO₂(B) nanorods obtained after 3 hours of reaction time at 200 °C in the presence of 5 mmol of water (20 equivalents per vanadium centre). Two nanorod lengths from this distribution were chosen at random. These lengths were removed from the distribution and replaced with their sum. The process of replacing two random values with their sum was repeated many times, and each iteration decreased the total number of values in the distribution by one. After every 2000 iterations, up to a total of 8000 iterations, we plotted the distribution to illustrate its evolution from Gaussian to lognormal.

Results

We set out to develop a method to control the size and shape of VO₂(B) nanocrystals (Fig. 1). Previous reports use water as a solvent, where VO₂(A) was typically synthesized with temperatures of 220–230 °C and VO₂(B) was typically synthesized at temperatures of 180–200 °C (Table S1†). As

such, initial experiments focused on the use of hydrothermal reaction conditions in which the solvent is composed entirely of water.

Heating VO(acac)₂ and lauric acid (added to promote colloidal stability of the resultant nanoparticles) in water to 200 °C in an autoclave for 24 h produces nanorods of VO₂ that are several microns long (Fig. 1A). Notably, we found that the phase of the VO₂ nanocrystals synthesized under these conditions varies between VO₂(A) and VO₂(B) on a batch-to-batch basis. This observation is perhaps not surprising, as previous reports obtain VO₂(B) and VO₂(A) under similar reaction conditions, with slight variation in reaction pressure, temperature, or time.¹⁷ In an effort to obtain reproducible results, we focused on attempting the formation of VO₂ nanoparticles under rigorously non-aqueous conditions.

Given previous reports that have demonstrated control over the size of VO₂(R) nanoparticles synthesized using a molecular V(v) diperoxo complex as a precursor in toluene,²⁵ we opted to study similar effects using a vanadium(rv) starting material. A typical reaction involved heating a mixture of anhydrous toluene, VO(acac)₂, and lauric acid in a sealed autoclave reactor at 200 °C for 24 hours. Analysis of the resulting crude reaction mixture by powder X-ray diffraction and FTIR spectroscopy revealed that only the starting materials, lauric acid and VO(acac)₂, were present (see Fig. S1 and S2 in the ESI†). This observation suggests that water is required for the nucleation and growth of VO₂ nanocrystals.



Fig. 1 A and B) Representative TEM images of VO₂ nanocrystals obtained upon reaction of VO(acac)₂ in pure water (A) and in toluene containing 20 equivalents of water per vanadium centre (B). C) Powder X-ray diffraction spectra of nanocrystals obtained from solvothermal reaction of VO(acac)₂ in toluene with various amounts of added water: 2 (green), 4 (blue), 12 (orange), and 20 (purple) equivalents per vanadium centre. Reference peaks for VO₂(A) (JCPDS 00-042-0876) are shown as vertical red bars and reference peaks for VO₂(B) (JCPDS 01-081-2392) are shown as vertical black bars. The dashed black boxes highlight regions where the diffraction pattern for VO₂(A) contains one peak but the diffraction pattern for VO₂(B) contains multiple peaks. D and E) Crystal structures of VO₂(B) (space group *C2/m*) (D) and VO₂(A) (space group *P4/ncc*) (E) oriented to show side views of the stacked layers of zig-zag chains of edge-sharing distorted VO₆ octahedra that comprise these structures. For VO₂(A), these layers form along the (110) plane whereas these layers are parallel to the (001) plane for VO₂(B). These structures were generated using X-ray diffraction data reported in ref. 22 (VO₂(B)) and 9 (VO₂(A)).

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To probe this hypothesis, the synthesis of VO₂ nanocrystals was attempted in the presence of stoichiometric amounts of water (*e.g.* 2–20 equiv. per vanadium centre). Fig. 1C contains powder X-ray diffraction data obtained for these experiments. Addition of two (0.5 mmol) or four (1 mmol) equivalents of water per vanadium centre to the reaction mixture results in the formation of phase-pure VO₂(A) nanocrystals. Increasing the concentration of water to 20 equivalents per vanadium centre consistently produces VO₂(B) nanorods with an average length of 110 nm. Fig. 1B contains a representative TEM image and the ESI† contains complete TEM analyses of multiple batches of VO₂(B) nanocrystals synthesized in the presenece of 20 equivalents of water per vanadium centre.

Table 1 compiles crystal structure information for $VO_2(A)$ and $VO_2(B)$. Both of these structures contain layers of zig-zag double chains of edge-sharing distorted VO₆ octahedra, but these structures differ in how the layers are arranged and stacked (Fig. 1D and E). In VO₂(B), the stacked layers result in a crystal structure with the monoclinic space group C2/min which the layers are parallel to the (001) plane (Fig. 1D). For $VO_2(A)$, the stacking produces a structure with the tetragonal space group of P4/ncc in which the layers are parallel to the (110) plane (Fig. 1E). The similarities in their crystal structures lead to similar X-ray powder diffraction patterns. However, the lower symmetry of the $VO_2(B)$ structure results in multiple distinct diffraction peaks in some areas where the VO₂(A) pattern has only one peak. These areas are highlighted by dashed black boxes in Fig. 1C. For example, the (110) peak that occurs at $2\theta = 14.9^{\circ}$ in $VO_2(A)$ becomes two peaks corresponding to the (001) (2 θ = 14.4°) and (200) ($2\theta = 15.3^\circ$) planes in VO₂(B). Similarly, the (220) peak at $2\theta = 30^{\circ}$ in VO₂(A) splits into multiple peaks in the VO₂(B) structure, the most prominent of which are the (002) $(2\theta = 29^\circ)$ and (401) $(2\theta = 30.2^\circ)$ reflections. The ESI⁺ contains a complete indexing of the diffraction patterns shown in Fig. 1C.

Fig. 1C also contains a powder X-ray diffraction spectrum collected for nanocrystals produced from a solvothermal reaction mixture that contained 12 equivalents of water per vanadium centre. In this pattern, the "splitting" of the peak at $2\theta \sim 30^{\circ}$ associated with VO₂(B) is apparent, but only one peak is discernible at $2\theta \sim 15^{\circ}$. Peaks at $2\theta = 47^{\circ}$ and $2\theta = 49^{\circ}$ that are associated with VO₂(A) and VO₂(B), respectively, are also both present in this spectrum. We therefore

 Table 1
 Crystal structure information for VO₂(A) and VO₂(B)

	$\mathrm{VO}_2(\mathrm{A})^a$	$\mathrm{VO}_2(\mathrm{B})^b$
Space group	P4/ncc	C2/m
Bravais lattice type	Tetragonal	Monoclinic
Unit cell parameters	a = b = 8.4347 Å	a = 12.0417 Å
	c = 7.6722 Å	b = 3.6892 Å
	$\alpha = \beta = \gamma = 90^{\circ}$	c = 6.4312 Å
		$\alpha = \gamma = 90^{\circ}$
		$\beta = 106.965^{\circ}$

^{*a*} From ref. 9. ^{*b*} From ref. 22.

The VO₂(B) nanorods produced in reactions containing 20 equivalents of water per vanadium centre are much shorter than those obtained from reactions carried out in pure water (Fig. 1A and B). Furthermore, scanning electron microscopy reveals that the nanorods obtained from a reaction containing 20 equivalents of water form spherical aggregates, but the nanorods obtained from reaction in pure water do not (see ESI† Fig. S5). We also observe that addition of any amount of water between 5 and 100 mmol (20–400 equivalents per vanadium centre) results in phase-pure VO₂(B) nanocrystals (see ESI† Fig. S6).

In order to characterize the mechanism of nanocrystal formation in these reactions, we measured the consumption of the VO(acac)₂ precursor as a function of reaction time in the presence of 20 equivalents (5 mmol) of water per vanadium centre *via* electronic absorption spectroscopy (Fig. 2 and S7 and S8 in ESI†). Fig. 2A depicts a plot of the percent of VO(acac)₂ remaining in the supernatant collected after the first round of centrifugation *versus* reaction time. This data indicates that the VO(acac)₂ is not completely consumed until approximately nine hours into the reaction. Powder X-ray diffraction spectra of the products obtained during early time points indicate that VO₂(B) does not form as a crystalline product until three hours into the reaction



Fig. 2 A) Plot of the percent of VO(acac)₂ remaining in the reaction mixture *versus* reaction time for the solvothermal reaction of VO(acac)₂ in toluene in the presence of lauric acid and 20 equivalents of water. B) Powder X-ray diffraction spectra of solid products collected upon centrifugation of the reaction mixtures obtained after reaction times of 30 minutes, 1 hour, 2 hours, and 3 hours. The complete diffraction pattern of VO₂(B) does not emerge until 3 hours into the reaction. C) Representative TEM images and corresponding histograms tabulating the lengths of VO₂(B) nanorods obtained after reaction times ranging from 3 to 24 hours in the presence of 20 equivalents of water per vanadium centre.

(Fig. 2B). Additionally, analysis of the morphology of $VO_2(B)$ nanocrystals collected at various time points reveals that no significant changes in the average length of nanorods occur after three hours of reaction time (Fig. 2C and S11 in ESI⁺), despite the fact that 16% of the initial $VO(acac)_2$ remains present in solution at the three hour mark.

The lack of observable growth in the presence of remaining precursor suggests that nucleation of new particles continues to occur throughout the reaction. The lack of significant change in the morphology of the nanocrystals with additional reaction time after the precursor is consumed (*i.e.*, for reaction times longer than 6 hours) indicates that additional growth in the absence of precursor via mechanisms such as dissolution and recrystallization or oriented attachment does not occur under these reaction conditions (i.e., with 20 equivalents of water per vanadium centre). Instead, these observations are consistent with a continuous nucleation mechanism, in which nucleation of new particles occurs continuously and simultaneously with nanocrystal growth. This mechanism has been observed previously for Pd, Ir, InP, and CdSe nanocrystals synthesized under ambient pressure and is characterized by a rapid increase in the average nanocrystal size followed by a plateau in average size with continued reaction time.^{26–29} Indeed, the average length of the VO₂(B) nanocrystals does not increase from when the first crystalline particles are observed at a reaction time of three hours through completion of the reaction at 24 hours (Fig. 2B and C).



Fig. 3 TEM images and corresponding histograms tabulating the length of VO₂(B) nanobelts obtained (left) after reaction times ranging from 3 to 24 hours in the presence of 200 equivalents (50 mmol) of water per vanadium centre and (right) upon reaction for 24 hours in the presence of various concentrations of water ranging from 20 to 400 equivalents per vanadium centre. The red dashed and blue solid lines plot Gaussian and lognormal fits, respectively, to the size distributions.

In contrast, reactions containing 200 equivalents of water exhibit significant evolution in the nanocrystal size distribution for reaction times longer than three hours (Fig. 3). Analysis of supernatants obtained from these reactions reveal that the VO(acac)₂ precursor is consumed within the first three hours of reaction time (see ESI⁺), indicating that increasing the concentration of water increases the rate of precursor conversion. The left-hand side of Fig. 3 shows representative TEM images and histograms of VO₂(B) nanocrystals obtained after various reaction times in the presence of 200 equivalents of water. After three hours of reaction time, the size distribution is Gaussian with an average length longer than that obtained after a three-hour reaction with 20 equivalents of water (400 nm vs. 110 nm, see Fig. S11 in ESI⁺). As the reaction progresses, we observe an increase in the average length of the nanorods along with evolution of the shape of the size distribution from Gaussian to lognormal. We observe a similar evolution in the size distribution of nanorods obtained from reactions run for 24 hours in the presence of various amounts of water (right-hand side of Fig. 3). As the concentration of water increases from 20 to 400 equivalents per vanadium centre, the average nanorod length increases and the distribution evolves from Gaussian to lognormal.

Fig. 4 shows high-resolution transmission electron micrographs (TEM) obtained from $VO_2(B)$ nanorods synthesized *via* reaction of $VO(acac)_2$ with 200 equivalents of water for 24 hours. Selected area electron diffraction



Fig. 4 A and B) High-resolution TEM images of VO₂(B) nanorods obtained upon reaction of VO(acac)₂ with 200 equivalents of water per vanadium centre for 24 hours in which the *d*-spacings for the (001), (110), and ($\overline{3}$ 10) planes are resolved. Scale bars correspond to 5 nm. C and D) Crystal structures of VO₂(B) oriented to illustrate the relationship between the lattice spacings observed in parts A and B and the morphology of the nanorods. The horizontal direction coincides with the length of the nanorods.

Paper

indicates that the nanoparticles in this sample are highly crystalline (see Fig. S12 in ESI[†]). In Fig. 4A and B, three *d*-spacings corresponding to the (001), (110), and ($\bar{3}10$) planes of VO₂(B) are clearly visible. The (001) and ($\bar{3}10$) planes are parallel to the length of the nanorods whereas the (110) plane is roughly parallel to the cross-section of the rods. Fig. 4C and D depict the crystal structure of VO₂(B) in two different orientations to illustrate how the crystallographic directions map onto the nanorod morphology. These data indicate that preferential growth parallel to the (001) and ($\bar{3}10$) planes, possibly due preferential addition of monomer species to faces terminated by (110) planes, drives formation of VO₂(B) nanorods.

We hypothesize that the evolution in the size distribution from Gaussian to lognormal with increasing reaction time in the presence of 200 equivalents of water and increasing concentration of water is due to increased end-to-end oriented attachment of preformed nanorods at the (110) faces. Growth of VO₂(A) nanorods has previously been proposed to occur *via* oriented attachment,^{8,9,23,24} however no sizing data has been previously used to support this growth mechanism for VO₂(B). The suppression of oriented attachment may explain why the nanocrystals obtained upon reaction with only 20 equivalents of water are shorter than those obtained upon reaction in 100% water (Fig. 1A and B).



Fig. 5 A) Histograms depicting the initial distribution (blue) used to simulate oriented attachment and the distributions obtained after 2000 (red), 4000 (orange), 6000 (purple), and 8000 (green) iterations. The insets zoom in on the initial distribution containing a total of $N = 10\,000$ entries fit to a Gaussian distribution and the distribution obtained after 8000 iterations (N = 2000) fit to a lognormal distribution. B) Plot of the mean values of the simulated distributions shown in (A) *versus* the number of iterations. C) Histograms tabulating the distributions of VO₂(B) nanorod lengths obtained from reactions containing 20 (blue), 40 (red), 120 (orange), 200 (purple), and 400 (green) equivalents of water per vanadium centre. The insets plot the distributions obtained from the reactions containing 20 equivalents of water (fit to a Gaussian distribution) and 400 equivalents of water (fit to a lognormal distribution). D) Plot of the mean values of the distributions shown in (C) *versus* equivalents of water present in the reaction.

To test this hypothesis, we performed a simple simulation of the impact oriented attachment would have on the distribution in nanorod lengths (Fig. 5). We start with a Gaussian distribution of 10 000 randomly generated nanorod lengths with an average and standard deviation equal to that measured for the product of the reaction run for three hours in 20 equivalents of water. Upon each iteration of the simulation, two entries within this distribution are chosen at random, removed from the distribution, and replaced with their sum. Thus, each iteration represents the end-to-end oriented attachment of two nanorods to produce one longer nanorod. Fig. 5A plots the distributions obtained from this simulation after 2000, 4000, 6000, and 8000 iterations. From this plot, it is apparent that both the mean value and the width of the distribution increase as the number of iterations increase. Fig. 5B plots the mean value versus the number of iterations and shows that it does indeed increase monotonically as the simulation progresses. Closer inspection of the distribution obtained after 8000 iterations reveals that it follows a lognormal distribution (Fig. 5A inset). For comparison, Fig. 5C plots the distributions of measured lengths of VO₂(B) nanorods produced from reactions with various amounts of water. These data show a similar evolution with increasing water concentration as the modelled data show with increasing iterations of the simulation. Namely, the mean value (Fig. 5D) and width of the distribution both increase with increasing water concentration. Notably, the smallest concentration of water (20 equivalents) produces a Gaussian distribution whereas the largest concentration of water (400 equivalents) produces a distribution that more closely resembles a lognormal distribution (Fig. 5C insets). The similarity in the evolution of the modelled distributions with increased number of oriented attachment events and the experimentally measured distributions with increased water concentration supports our hypothesis that water promotes end-to-end oriented attachment of VO₂(B) nanobelts under solvothermal reaction conditions.

We note that the simulated results shown in Fig. 5A and B are based on a purely mathematical model that describes the evolution of a Gaussian distribution as a function of the number of oriented attachment events, but does not account for factors such as thermodynamics, kinetics, diffusion, or chemical reactivity that may impact the rate or relative probabilities with which these oriented attachment events occur. For example, the dependence of the mean value of the modelled distributions on the number of oriented attachment events appears to be exponential (Fig. 5B) whereas the experimental mean values increase more linearly with increasing concentration of water (Fig. 5D). This discrepancy could arise from a nonlinear increase in the frequency of oriented attachment events with the concentration of water or to a length-dependent probability for certain rods to attach to each other over others. Our model assumes that any two rods are equally likely to attach to each other. Accounting for such subtleties will require a more sophisticated model than that presented here; one that

explicitly incorporates one or more of the chemical factors mentioned above.

Discussion

The results presented here demonstrate that the concentration of water impacts both the crystal phase of VO_2 nanocrystals formed during solvothermal reaction of $VO(acac)_2$ and the morphology of these species. These observations combined with the observation that rigorous exclusion of water results in no conversion of the starting material indicate that water is involved in all phases of the nanocrystal reaction – precursor conversion, nucleation, and growth. In this section, we discuss the implications of these observations for the mechanisms by which $VO_2(B)$ nanocrystals form under these solvothermal conditions.

First, we consider possible mechanisms by which increasing the concentration of water in the reaction promotes formation of VO₂(B) over VO₂(A). Previous reports indicate that VO₂(A) is a more thermodynamically stable polymorph than VO₂(B); however, under hydrothermal reaction conditions where water is the reaction solvent, VO₂(B) is the kinetically favored product.^{11,17} VO₂(B) is typically produced at lower reaction temperatures and shorter reaction times than VO₂(A). VO₂(B) can be converted to VO₂(A) under hydrothermal conditions in the presence of excess water and sufficient temperatures,^{17,30} however, reaction of VO₂(B) under conditions where the concentration of water is limited does not induce a phase transformation to VO₂(A) (see Fig. S13 in ESI†).

The lack of transformation of $VO_2(B)$ nanocrystals to $VO_2(A)$ nanocrystals observed under reaction conditions that produce $VO_2(A)$ nanocrystals from the $VO(acac)_2$ precursor (*i.e.* 2 equivalents of water per vanadium centre) indicates that the reactions that form VO_2 nanocrystals operate under kinetic control, and that the final crystal structure of the product is determined during the nucleation step. Consequently, our results imply that the relative heights of



Reaction Coordinate

Fig. 6 Qualitative illustration of the proposed reaction coordinate diagrams showing the change in kinetic barriers for nucleation of VO₂(A) and VO₂(B) from VO(acac)₂ as the concentration of water present in the reaction increases.

the kinetic barriers to nucleation of $VO_2(A)$ and $VO_2(B)$ depend on the concentration of water present in the reaction. As illustrated in Fig. 6, when only two or four equivalents of water per vanadium centre are present in the reaction, the barrier to nucleate $VO_2(A)$ is lower than the barrier to nucleate $VO_2(B)$. When 20 or more equivalents of water are present, the barrier to nucleate $VO_2(B)$ is lower than the barrier to nucleate $VO_2(A)$. Determining whether the absolute heights of only one or both barriers change with the concentration of water is beyond the scope of this study.

We suspect that the molecular mechanism underlying this change in relative barrier heights is driven by the relative rates of precursor conversion *via* hydrolysis and the condensation reactions that drive nucleation. Previous work on the hydrothermal synthesis of VO₂ nanocrystals suggests that VO(acac)₂ undergoes hydrolysis in the presence of water to form $[V(O)(H_2O)_5]^{2+}$ or its neutral deprotonated form $V(O)(OH)_2(H_2-O)_3$.^{18,31} Self-condensation of this species forms VO₂ nuclei. We hypothesize that (i) the rate of this hydrolysis step slows down as the concentration of water decreases such that partially hydrolysed species start to participate in the condensation reactions that lead to nucleation, and (ii) condensation of these partially hydrolysed monomers favors nucleation of VO₂(A) over VO₂(B).

Our data indicates that the relative rates of nucleation and growth also depend on the concentration of water present in the reaction mixture. In the moderate concentration regime, where there is sufficient water present to promote formation of $VO_2(B)$ but not enough to induce oriented attachment (e.g., 20 equivalents of water per vanadium centre), we observe an overlap of nanocrystal nucleation and growth evidenced by the presence of VO(acac)₂ in the supernatants collected at reaction times that coincide with when the average size of the nanocrystal products has already reached its maximum. This observation implies that nucleation continues throughout the reaction as the remaining $VO(acac)_2$ does not contribute to growth. For reactions with high concentrations of water (e.g., 200 equivalents per vanadium centre), the average length of the VO₂(B) nanorods is longer than that of VO₂(B) nanorods obtained at similar reaction times with lower concentrations of water, and the average length of the nanorods continues to increase at longer reaction times. These results imply that the ratio of the rate constant for growth to the rate constant for nucleation increases with increasing water concentration.26,27

Finally, our data indicates that there are two phases of growth in reactions that contain more than 20 equivalents of water per vanadium centre. In the first phase, growth occurs primarily *via* addition of hydrolysed monomer species to $VO_2(B)$ nuclei. This addition occurs preferentially to a particularly reactive crystal face to form nanorods with a Gaussian distribution in length. The HRTEM data in Fig. 4 suggests that the reactive face forming the ends of the nanorods could coincide with a (110) plane. Once the vanadium monomer has been consumed, excess water continues to interact with the nanorods, most likely primarily on the reactive faces that form the ends of the rods. These

interactions likely form reactive hydroxylated surfaces that can react with each other, resulting in longer rods *via* oriented attachment. Water promoted oriented attachment has also been observed for VO₂(R) nanorods synthesized *via* solvothermal reaction of vanadium(v) peroxo complexes.²⁵

Conclusions

Our work demonstrates that both the crystal phase and morphology of VO₂ nanocrystals made via solvothermal synthesis are sensitive to the concentration of water present in the reaction. Phase-pure $VO_2(B)$ is obtained from reactions containing 20 or more equivalents of water per vanadium centre and phase-pure VO₂(A) is obtained from reactions containing 4 or fewer equivalents of water per vanadium centre. For the reactions that produce $VO_2(B)$, lower concentrations of water result in a continuous nucleation formation mechanism, where the nucleation and growth phases overlap in time. Additionally, increasing the concentration of water present in the reaction promotes a second phase of nanorod growth via end-to-end oriented attachment. Altogether, these results reveal that, as with other metal oxide nanocrystals,^{32,33} tuning the solvent composition, and specifically the water content, in a solvothermal reaction is a useful strategy for controlling the morphology and crystal phase of VO₂ nanocrystals.

Author contributions

E. M. M. and K. E. K. conceived of and supervised this work. B. A. B., E. M. M. and K. E. K. designed the experiments. B. A. B., X. Z., and A. V. S. carried out the solvothermal reactions and characterized the products. K. R. S.-L. collected and analysed the high-resolution TEM data. K. E. K. wrote the code for the simulations of oriented attachment growth. B. A. B., E. M. M. and K. E. K. wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by a University Research Award from the University of Rochester and a Negative Emissions Sciences Scialog grant funded by the Alfred P. Sloan Foundation. E. M. M. is the recipient of a Camille Dreyfus Teacher-Scholar Award, which has also supported this work.

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CrystEngComm

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