Shape-controlled synthesis and influence of W doping and oxygen nonstoichiometry on the phase transition of VO$_2$

Ru Chen$^{1,2}$, Lei Miao$^{1,3}$, Chengyan Liu$^{1}$, Jianhua Zhou$^{3}$, Haoliang Cheng$^{1}$, Toru Asaka$^{4}$, Yuji Iwamoto$^{4}$ & Sakae Tanemura$^{1,3}$

Monoclinic VO$_2$(M) in nanostructure is a prototype material for interpreting correlation effects in solids with fully reversible phase transition and for the advanced applications to smart devices. Here, we report a facile one-step hydrothermal method for the controlled growth of single crystalline VO$_2$(M/R) nanorods. Through tuning the hydrothermal temperature, duration of the hydrothermal time and W-doped level, single crystalline VO$_2$(M/R) nanorods with controlled aspect ratio can be synthesized in large quantities, and the crucial parameter for the shape-controlled synthesis is the W-doped content. The dopant greatly promotes the preferential growth of (110) to form pure phase VO$_2$(R) nanorods with high aspect ratio for the W-doped level $= 2.0$ at% sample. The shape-controlled process of VO$_2$(M/R) nanorods upon W-doping are systematically studied. Moreover, the phase transition temperature ($T_c$) of VO$_2$ depending on oxygen nonstoichiometry is investigated in detail.

Vanadium dioxide (VO$_2$) plays a crucial role in many fundamental research and practical applications. For instance, Mott field-effect transistor, light modulator and optical storage medium are potential products based on VO$_2$.$^1$-$^3$ Moreover, VO$_2$ with a metal-insulator phase transition (MIT) is a key material for applying to thermo-chromic smart windows because it exhibits a reversible structural transformation from an infrared-transparent monoclinic phase (VO$_2$(M$_1$)) at low temperature to an infrared-reflective rutile state (VO$_2$(R)) at higher temperature than the transition, while maintaining certain visible transmittance.$^4$-$^7$ Whereas, VO$_2$ exhibits hysteresis in its phase transition properties and mechanical degradation on passing through the MIT because of stresses during the structural change.$^8$ In addition, the phase transition temperature ($T_c$) of MIT (68 °C) is always too high for the practical application of VO$_2$-based materials$^4$. Nano-materials often exhibit extraordinary physical and chemical properties compared to their bulk counterparts.$^9$ One dimensional nanostructures, for example, nanorods represent particularly attractive because they present novel characteristics owing to their small radial dimension while retaining longitudinally connected substance.$^{10}$ In confined nanoscale system, more localized electronic states as well as narrower bands are usually supposed to increase the densities of states and lead to the superior phase transition behavior of VO$_2$.$^{11}$ Using the hydration-cleavage-exfoliation solvothermal process, Banerjee and co-workers have reduced the $T_c$ of undoped VO$_2$ by synthesizing various sized nanostructures.$^{12}$ In their research, the phase transition temperature during the cooling cycle is more significantly affected than the heating cycle by nanostructuring, therefore, the hysteresis width is observed to be much wider.
for all the nanostructures. Gao and co-workers have also regulated the hysteresis width through the nano-size effect\textsuperscript{13}, which provides a key that nanoscale VO$_2$(M$_1$/R) possesses the probability of tuning hysteresis width for obtaining a sharper, more reproducible phase transition. Up to now, more than 20 compounds of vanadium oxide (VO, V$_2$O$_3$, VO$_2$, V$_6$O$_{13}$, V$_8$O$_{15}$, V$_2$O$_5$ and so on\textsuperscript{14}) and 10 polymorphs of VO$_2$ (B, A, T, M$_1$, M$_2$, R phase and so on\textsuperscript{15}) had been reported. Only the VO$_2$(M/R) (the M$_1$ phase is referred to as the M phase of VO$_2$ in this study) experiences a fully reversible MIT at the vicinity of room temperature (RT). Moreover, low temperature synthetic method has usually generated VO$_2$(B) nanobelts and subsequently can be transformed to VO$_2$(M/R) by the post-heating treatment, but the nanostructure has been nearly destroyed\textsuperscript{16–18}. So it should be a challenge to synthesize pure phase VO$_2$(M/R) with a shape controlled nanostructure.

The ongoing debate associated to the fundamental origin of the phase transition behavior in VO$_2$ involves electron-correlation-driven (Mott transition)\textsuperscript{19,20}, structure-driven (Peierls transition)\textsuperscript{21,22}, or the cooperation of both\textsuperscript{23}. W doping is known as an effective route to regulate electron density in the conduction band for decreasing T$_c$ by approx. 20–26°C/at% W for the bulk and by 50–80°C/at% W in nanostructures\textsuperscript{24–27}. Synthesis of VO$_2$(M/R) by controlling both the shape of nanostructures and the amount of W dopant could be a good strategy to narrow the hysteresis width while reducing T$_c$ for obtaining an excellent phase transition property of VO$_2$(M/R)-based materials. Of note, systematically experimental investigation of nonstoichiometric effect in VO$_2$ has been insufficient. The phase transition behavior has been demonstrated to be also sensitive to vanadium or oxygen related vacancies, even a deviation in the oxygen stoichiometry by a few percent can cause the lattice structure change and result in several orders of magnitude difference in the resistivity transition or the phase transition temperature shift\textsuperscript{28,29}. Therefore, studying on oxygen nonstoichiometry induced reduction of T$_c$ will contribute to the general understanding of the intrinsic MIT mechanism in VO$_2$.

In this study, we successfully explored a one-pot hydrothermal method to prepare VO$_2$(M/R) with desired morphology. It is inspiring to discover that the W dopant promotes the generation of pure phase VO$_2$(M/R) nanorods with high aspect ratio. Moreover, the effect of oxygen nonstoichiometry on the structural phase transition and subsequently T$_c$ of VO$_2$ is discussed in detail.

**Results**

**Shape-controlled synthesis and phase metamorphism behavior upon W doping.** Figure 1 shows the crystalline phase metamorphic behavior of W$_x$V$_{1-x}$O$_2$ with $x = 0$, 0.5, 1.0 and 2.0 at%
respectively where the temperature being kept at 280 °C but the different duration of the hydrothermal time being applied. For the undoped VO₂, pure phase VO₂(B) is obtained for the duration of the hydrothermal time for 6h. By increasing the duration of the hydrothermal time from 12 to 72h, the peak of {011} for VO₂(M) (M {011} at around 27.8°) appears and becomes more significant. However, there always exists the secondary phase VO₂(B) in the final product. Serial SEM images in Fig. 2 show the morphology transition behavior of the undoped VO₂ upon increasing the duration of the hydrothermal time. Products of the metastable VO₂(B) are the tangled nanobelts in the morphology for the 6h-sample. By increasing the duration of the hydrothermal time from 12 to 72h, VO₂(B) nanobelts always exist as partial morphology except the block or snowflake VO₂(M). In conclusion, we could not synthesize pure phase VO₂(M) without W doping.

Figure 2. SEM images of undoped VO₂ synthesized at 280 °C for different duration of hydrothermal time.
By increasing the W-doped level to 0.5 at%, VO$_2$(B) nanobelts always exist as partial morphology except the snowflake or rod-like VO$_2$(M) for the duration of the hydrothermal time $\leq$ 48 h as shown in Figs 1 and 3. Inspiringly, the peaks of VO$_2$(B) vanish and pure phase VO$_2$(M) (T$_c$ > RT) with uniformly rod-like morphology is successfully synthesized for the 72 h-sample. Meanwhile, for the hydrothermal samples prepared at 280 °C with W-doped of 1.0 and 2.0 at%, pure phase VO$_2$(R) with uniformly rod-like morphology is obtained when the duration of the hydrothermal time $\geq$ 48 h and $\geq$ 12 h respectively as shown in Figs 1, 4 and 5. The synchrotron radiation X-ray powder diffraction (SRXPD, $\lambda$ = 0.50 Å)
data confirm the pure phase VO$_2$(M/R) is exactly free from the existing of the other V-O compounds and other VO$_2$ phases, which was reported by our group in the recently study$^{30}$. As an overall comparison, the schematic illustration of the morphology metamorphic behavior of VO$_2$ is summarized in Fig. 6.
W$_x$V$_{1-x}$O$_2$ with $x$ = 4.0, 6.0 and 10.0 at% were prepared at 280°C for 72 h to investigate more W dopant on the crystalline phase metamorphic and morphology transition behavior of the as-obtained products as shown in Figs 7 and 8. Pure phase VO$_2$(R) is still obtained for the 4.0 and 6.0 at% sample. When the W-doped level increases to 10.0 at%, VO$_2$(B) nanobelts are grown again besides the main phase VO$_2$(R). The results indicate a certain doping level of W could promote VO$_2$(B) metamorphoses to pure phase VO$_2$(M/R), which agrees with the previous reports$^{14,18}$. Whereas, more excess W dopant would prevent the metamorphosis from VO$_2$(B) into VO$_2$(R) thoroughly. The intensity ratio between the XRD peaks of {110} and that of {101} of VO$_2$(R) prepared at 280°C for 72 h with different W-doped levels.

Figure 7. XRD patterns of the W$_x$V$_{1-x}$O$_2$ prepared at 280°C for 72 h with W doping levels ranging from 4.0 to 10.0 at%. The filled dark blue diamond is characteristic peaks for B phase of VO$_2$. The black column belongs to standard pattern in JCPDS card No. 76–0677 for VO$_2$(R).

Figure 8. SEM images of the W$_x$V$_{1-x}$O$_2$ prepared at 280°C for 72 h with different W doping levels. (a) 4.0 at.% (b) 6.0 at.% (c) 10.0 at.%.
is listed in Table 1. It increases significantly from 2.1 to 5.7 with increasing the W-doped level from 1.0 to 2.0 at%. The strong intensity of the [110] reflections points to the strongly preferential growth direction of the structures, as has also been noted previously for VO$_2$ nanowires prepared at high temperatures by vapor transport$^{31-33}$. Simultaneously, the aspect ratio of the VO$_2$(R) nanorods increases from nearly 5 to 10 with the increased dopant. Whereas, if the W-doped level increases from 4.0 to 10.0 at%, the intensity ratio [110]/[101] decreases from 2.5 to 1.1. Meanwhile, the aspect ratio of nanorods decreases with the increased W dopant as shown in Fig. 8. Finally, the bulk crystal of VO$_2$(R) is grown for the 10.0 at% sample. The results indicate a certain doping level of W can promote the preferential growth of R [110] and the increased aspect ratio of VO$_2$(R) nanorods, whereas the excess W would restrain.

Table 1. Intensity ratio between the XRD peaks of [110] and that of [101] of W$_x$V$_{1-x}$O$_2$ prepared at 280°C for 72 h with different W-doped levels.

| W-doped level (at. %) | Intensity ratio [110]/[101] |
|-----------------------|-----------------------------|
| 1.0                   | 2.1                         |
| 2.0                   | 5.7                         |
| 4.0                   | 2.5                         |
| 6.0                   | 1.9                         |
| 10.0                  | 1.1                         |

**The shape-controlled mechanism revealed by TEM.** The length of W-doped 4.0 at% VO$_2$ nanorods (synthesized at 280°C for 72h) is about 2.5 μm with 600 nm in diameter as shown in the low magnification TEM image in Fig. 9A. The single-crystalline nanorods is confirmed by the lattice images of HRTEM and the inset SAED pattern as shown in Fig. 9. The lattice constants observed in Fig. 9B are 0.3236 and 0.2430 nm respectively, which can be indexed to the spacing of R [110] and R [101], and the angle between the two lattice images is 67.9° in arc and this corresponds to the angle between the designated crystal planes of R (110) and R (101). In addition, the (001) plane orientation is just perpendicular to the nanorod growth direction R (110), and revealing the preferential growth direction of the VO$_2$(R) nanorods is along [001]. The results demonstrate that the preferential growth of nanorod growth direction R (110) is responsible for the increased aspect ratio of VO$_2$(R) nanorods. It is generally known that the greater the d-spacing, the atom arrange more closely on the crystal plane. For the body-centered tetragonal VO$_2$(R), (110) with the largest d-spacing contributes to the lowest surface energy for the preferential growth of VO$_2$ grains. According to the SAED pattern shown in the inset of Fig. 9A, the bright diffraction spots reveal the good crystallinity of the sample. Based on the Bragg equation, the diffraction spots can be ascribed to different crystal planes of VO$_2$(R). The three Bravais lattice points shown in the SAED of the inset of Fig. 9A correspond to crystal planes of R (110), R (101) and R (211) respectively as indexed therein. This definitely demonstrates the nanorods belong to VO$_2$(R). Moreover, no fringe
Spacing belongs to tungsten oxides or their derivatives are detected by HRTEM, which confirms the capture of W atoms into the crystal lattice of VO₂ as mother matrix and the formation of homogeneous solid-solution of WₓV₁₋ₓO₂.

**Influence of oxygen nonstoichiometry on the phase transition behavior.** Figure 10A shows the DSC curve of the hydrothermally undoped sample treated at 280 °C for 72 h (HTh₁). The endothermic and exothermal transition temperature is 62.3 and 49.3 °C during heating and cooling cycles respectively. Thus, the phase transition temperature (defined as \(T_c = \frac{\left(T_{c,h} + T_{c,c}\right)}{2}\)) of the undoped micron-sized block and snowflake-like sample is about 55.8 °C, which is much lower than the transition temperature of undoped bulk VO₂ (about 68 °C) reported by Morin⁴ and undoped nanobelts VO₂ (64 °C) reported by Whittaker²⁴. The hysteresis width (\(\Delta T = T_{c,h} - T_{c,c}\)) of the undoped sample is about 13.0 °C.

To study the unusual low \(T_c\) for the HTh₁ synthesized undoped sample, we directly compare the DSC for this sample by the after annealing (HTh₁ + Annealing) with that for the hydrothermal undoped one treated at 160 °C for 72 h and after annealing (HTh₂ + Annealing) (hydrothermal treated at 160 °C for 72 h) process respectively. The red column belongs to standard pattern in JCPDS card No. 65–2358 for VO₂(M). (D) SEM images of the undoped samples synthesized by the designated two fabrication processes.
synthesized undoped sample as shown in Fig. 10D. Whereas, nanostructure is grown by the (HTh₂ + Annealing) fabrication process. Thanks to the formation energies of oxygen vacancies in rutile oxides are very high, the high hydrothermal temperature (280 °C) and reductive hydrothermal atmosphere for the (HTh₁ + Annealing) method may contribute to the generation of oxygen vacancies to form non-stoichiometric VO₂₋δ compared to the (HTh₂ + Annealing) process (160 °C), and this would promote the lattice structural transition 35,36.

Discussion. To determine the oxygen stoichiometry, the thermogravimetric analysis of the samples was conducted as shown in Fig. 11. According to the TG curves, it can be found there exists one stage for the complete oxidization of the samples in the range of 300–600 °C. The weight gain (ΔTG) is about 10.4%, 10.5% and 9.6% for the HTh₁ synthesized undoped VOₓ, (HTh₁ + annealing) undoped VOᵧ and (HTh₂ + annealing) undoped VO₂₀₀ respectively. The reaction equations for the oxidization of the samples can be given as follows (1):

\[
\text{VO}_x + \frac{2.5-x}{2} \text{O}_2 \xrightarrow{\Delta} \text{VO}_{2.5}
\]

Thus, \( \Delta_{\text{TG}} = (2.5 - x) \times M_O/M_{\text{VO}_x} \) (2)

Where \( M_O \) and \( M_{\text{VO}_x} \) represent molar mass of oxygen and VOₓ respectively. When combining the above formulas (2) and experimental results, we can work out \( x = 1.96 \), \( y = 1.95 \) and \( z = 2.00 \) respectively. The fact demonstrates that oxygen deficiency is formed in the HTh₁ synthesized undoped VOₓ, and (HTh₁ + annealing) undoped VOₓ and (HTh₂ + annealing) undoped VO₂₀₀ respectively. The phase transition temperature of the synthesized VOₓ micron- and nanocrystals by optimizing the hydrothermal conditions 37. In their research, the phase transition temperature of the synthesized VOₓ micronrods is around 68 °C. Usually, the \( T_c \) of MIT for VO₂ is affected by doping, nanosizing, nonstoichiometry, strain and etc12,30,38,39. For the HTh₁ synthesized undoped micron-sized VO₁.96, the reason for the unusual low \( T_c \) may be due to the oxygen nonstoichiometry. The nano-size effect may be responsible for the relative lower \( T_c \) (63 °C) of the (HTh₂ + Annealing) synthesized stoichiometric VO₂₀₀ nanostructure.

| Sample                  | Phase transition temperature | Hysteresis width |  
|-------------------------|------------------------------|------------------|
|                         | Heating cycle  | Cooling cycle | \( \Delta T \) |  
| HTh₁ undoped VO₁.₉₆    | 62.3°C | 49.3°C | 13.0°C | 55.8°C |  
| HTh₁ + Annealing undoped VO₁.₉₅ | 59.7°C | 47.2°C | 12.5°C | 53.5°C |  
| HTh₂ + Annealing undoped VO₂.₀₀ | 67.3°C | 58.7°C | 8.6°C | 63.0°C |  

Table 2. DSC parameters of the HTh₁ synthesized sample with W-doped at 0.0 at% and of the undoped samples synthesized by the (HTh₁ + Annealing) method and the (HTh₂ + Annealing) process respectively.

Figure 11. The thermogravimetric analysis of the samples.
Figure 12A,B shows the Raman spectra of the samples depending on dopant level and fabrication processes. The peaks in the Raman spectra are all identified as 144 (B\textsubscript{1g}), 191 (A\textsubscript{g}), 223 (A\textsubscript{g}), 260 (A\textsubscript{g}), 308 (A\textsubscript{g}), 338 (A\textsubscript{g}), 388 (A\textsubscript{g}), 437 (E\textsubscript{g}), 499 (A\textsubscript{g}), 617 (A\textsubscript{1g}), and 826 (B\textsubscript{2g}) cm\textsuperscript{-1} respectively, and these Raman-active modes are the clear evidence of the existing of VO\textsubscript{2}(M) belonging to space group C\textsubscript{2h}\textsuperscript{5}, which agrees with the identified Raman peaks by other researchers\textsuperscript{40–43}. The intensity ratio between the peak of 191 and that of 223 cm\textsuperscript{-1} (191/223) of the HTh\textsubscript{1} synthesized undoped VO\textsubscript{1.96} is 1.6. When comparing the (HTh\textsubscript{2} + Annealing) synthesized undoped VO\textsubscript{2.00} with those by the (HTh\textsubscript{1} + Annealing) synthesized undoped VO\textsubscript{1.95}, the intensity ratio decreases from 2.3 to 1.3. H. T. Kim and co-workers have studied Raman spectra for the MIT of the undoped VO\textsubscript{2} in detail and deduced the conclusion that the Raman-active A\textsubscript{g} modes at 191 and 223 cm\textsuperscript{-1} were explained by the pairing and the tilting of V cations respectively\textsuperscript{43}. Hence, the decreased relative intensity of 191 cm\textsuperscript{-1} peak suggests the depairing of V cations and the occurring of the localized structural phase transition (SPT, induced possibly by oxygen nonstoichiometry for the HTh\textsubscript{1} synthesized undoped VO\textsubscript{1.96} and (HTh\textsubscript{1} + annealing) undoped VO\textsubscript{1.95}), and this might cause the transformation from the intrinsic structure of the matrix of VO\textsubscript{2}(M) to the localized rutile structure. In addition, the local rutile structure is the structure-guided domain, which will act as the initial nucleation site for the whole SPT\textsuperscript{44}. This process might promote MIT for the origin of the lowering T\textsubscript{c}. However, this origin is still under the debate among the concerned experts as cited in the literature by Y. Xie \textit{et al.} for an example, who pointed out that the atomic structure of isolated W dopant play a role in driving the nearby symmetric monoclinic VO\textsubscript{2} lattice towards rutile phase, resulting in the depression of T\textsubscript{c}\textsuperscript{45,46}. Hence the exact mechanism for the observed unusual phenomena requires our further investigation.

**Conclusions**

In this study, pure phase VO\textsubscript{2}(M/R) with controlled morphology were successfully prepared via one-step hydrothermal method. The addition of a certain level of W (0.5–2.0 at%) is vital to synthesize the pure phase VO\textsubscript{2}(M/R) nanorods. The assured level of W doping can promote the preferential growth of [110] to form VO\textsubscript{2}(M/R) nanorods with high aspect ratio. It must be emphasized that the unusual low T\textsubscript{c} equals to 55.8 and 53.5°C is observed for the nonstoichiometric VO\textsubscript{1.96} and VO\textsubscript{1.95} in the bulk respectively, and the T\textsubscript{c} is 63.0°C for the precisely stoichiometric VO\textsubscript{2.00} nanostructure. The present study demonstrates an improvement of the phase transition behavior and reduces the hindrances for the advanced applications of VO\textsubscript{2}-based materials.

| Sample                        | Intensity ratio 191/223 |
|-------------------------------|-------------------------|
| HTh\textsubscript{1} undoped VO\textsubscript{1.96} | 1.6                     |
| HTh\textsubscript{1} + Annealing undoped VO\textsubscript{1.95} | 1.3                     |
| HTh\textsubscript{2} + Annealing undoped VO\textsubscript{2.00} | 2.3                     |
Materials. Oxalic acid (H₂C₂O₄·2H₂O, AR) and vanadium pentoxide (V₂O₅, AR) were used as source material to prepare the vanadium precursor solution. Deionized water (μ = 18.2 MΩ cm) was used to prepare all aqueous solutions. Ammonium tungstate hydrate ((NH₄)₄H₂[H₂(WO₄)₃]·H₂O, AR) was chosen as the W dopant. All of these reagents were used without further purification.

The preparation process. The detail of this part has been described in previous report[20]. Briefly, V₂O₅ and oxalic acid (1: (1–3) in molar ratio) were directly added to 75 ml deionized water at RT. Then, a certain amount of W dopant was dispersed into the above solution with magnetic stirring. After mixing for 1 h, the resulting precursor was transferred into a 100 mL stainless steel autoclave with polyphenylene cup, then being sealed and maintained at 280°C for 6–72 h. After the autoclave cooling to RT, a dark blue precipitate was obtained. The product was washed with deionized water and acetone for several times, then centrifuged at 8000 rpm for 8 min and dried in vacuum at 60°C for 6 h.

In this study, (NH₄)₄H₂[H₂(WO₄)₃]·H₂O was used as the W dopant, and the reported W-doped content here is based on the quantity of W atoms added in the feed. The sample synthesized by the duration of the hydrothermal time for 6 or 72 h is simplified to the 6 or 72 h-sample.

Characterization techniques. The phase purity of the products was examined by an X-ray diffractometer (XRD, PANalytical X’pert Pro MPD) in the 2θ range of 5–80° with the step of 0.0083° using Cu-Kα radiation (λ = 1.54178 Å). The operating voltage and current were kept at 40 kV and 40 mA, respectively. The morphology and dimensions of the products were investigated using a field emission scanning electron microscope (FESEM, S-4800, Hitachi Japan) under the operating voltage of 2 kV. A JEOL-2100F instrument operated at 200 kV was used to acquire high-resolution transmission-electron-microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns. Raman scattering spectra of the samples were recorded on a LabRAM HR800 micro-Raman spectrometer using a 532 nm wavelength YAG laser. The phase transition properties depending on the surrounding temperature of the as-prepared VO₂ were studied by differential scanning calorimetry (HDSC, PT500LT/1600) under the temperature range from 25 to 100°C under the circulatory heating/cooling cycles. The thermogravimetric analysis (TG) of the samples was conducted on a Nicolet 6700-Q50 thermal analyzer under dry air flow in the range of 50–650°C with a heating rate of 5°C min⁻¹.

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Author Contributions
M.L. proposed and organized the overall project. C.R. performed the sample synthesis, TEM and phase transition behavior analysis. C.R. prepared the manuscript with discussion from M.L., L.C.Y., Z.J.H., C.H.L. and T.S. A.T. and I.Y. accomplished TEM sample preparation and observation. All the authors discussed the results.

Additional Information
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