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Particle size, morphology and phase transitions in hydrothermally produced VO₂(D)†

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Different morphologies and sizes of VO₂(D) particles were synthesised *via* hydrothermal synthesis using ammonium metavanadate (NH₄VO₃) or vanadium pentoxide (V₂O₅) as a vanadium precursor. By adjusting the concentration of vanadium precursors and the pH of the starting solution, a variety of morphologies and sizes of VO₂(D) particles from 20 nm to 3 μm could be produced. A flower-shape morphology was obtained under strongly acidic conditions, passing through star-shape particles of 1 μm at pH 2.5 and finally obtaining homogeneous round balls of around 3 μm at pH 6.9. Nanoparticles were produced hydrothermally using V₂O₅ as a precursor and hydrazine as a reducing agent. The transition from VO₂(D) to thermochromic VO₂(R) in micron scale particles occurred at 350 °C under vacuum. However, the nanoparticles of VO₂(D) had a significantly lower VO₂(D) to thermochromic VO₂(R) transition temperature of 165 °C after annealing for only a few minutes. This is, to our knowledge, the lowest annealing temperature and time reported in the literature in order to obtain a thermochromic VO₂ material *via* another VO₂ phase. After the conversion of VO₂(D) microparticles to thermochromic VO₂(R), the metal to insulator transition temperature is 61 ± 1 °C for the heating cycle and 53 ± 1 °C for the cooling cycle. However, VO₂(R) nanoparticles showed a significantly reduced metal insulator transition temperature of 59 ± 1 °C and 42 ± 1 °C for the cooling cycle lower than that reported in the literature for bulk VO₂. This is important due to the need for having a compound with a switching temperature closer to room temperature to be used in smart window devices for energy consumption. W-VO₂(D) star shape microparticle samples were prepared using 2–7 at% of the dopant (using ammonium metavanadate as a precursor), although unexpectedly this does not seem to be a viable route to a reduced metal to insulator transition in this system.

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1. Introduction

VO₂ has been investigated for a wide range of technological applications, including optical and electrical switching devices, multifunctional spintronics,¹ IR sensors and vision equipment, as coatings to prevent detection by reducing the IR transmittance of blackbody emitters,² to missile seeker sensors, and various other applications.³ VO₂ nanorods have been used to prepare Li-ion batteries with a discharge capacity of 152 mA h g⁻¹.⁴ W-Doped VO₂(B) nanobelts are used in supercapacitors.⁵ VO₂ nano-flowers were synthesized by Kang *et al.* for energy-storage devices and supercapacitors.⁶ TiO₂/VO₂ nanofibers are reported to photocatalyze the degradation of pollutants from wastewater by Zhao *et al.*⁷ VO₂(B) nanosheets were fabricated as a cathode

electrode presenting a high initial discharge and stable cyclability compared to bulk VO₂(B) as Want *et al.* reported in their work.⁸

VO₂ has also been widely studied for architectural applications due to its thermochromic properties: VO₂ displays a reversible phase transition from a low temperature, monoclinic insulating phase, VO₂(M) to a high temperature, rutile, metallic phase, VO₂(R) at 68 °C.⁹ This metal to semiconductor phase transition (MST) is associated with an increase in reflectivity in the near infrared which has led to the use of VO₂ as a thermochromic material, able to change its optical properties with temperature. Specifically, VO₂ films coated onto windows can actively switch between a high IR transmittance state below the MST temperature to a low IR transmittance state above the MST temperature.

The transition temperature of undoped VO₂(M) is 68 °C, which is too high for solar control coating applications. The transition temperature, however, can be reduced by doping with W, Ti, Mg or other ions; W doping is the most effective dopant, with a reduction of ~25 °C per at% W incorporated. Therefore, doping is seen as an effective method to achieve

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T_c in the optimum range for thermochromic windows.^{10–12} Being able to reduce the phase transition temperature, towards room temperature, would allow for the maximum energy saving potential of solar control coatings.

Vanadium dioxide (VO₂) has a well-known range of stable phases, such as VO₂(M) and VO₂(R), as well as metastable phases, such as VO₂(A), VO₂(B) and VO₂(C).^{13,14} Most of these phases consist of octahedrally coordinated V⁴⁺ ions with different linkages of octahedra leading to different crystal structures.¹⁵ VO₂(A) has a MST temperature of 162 °C. The solid has a good thermal stability and oxidation resistance in air below 408 °C.¹⁶ VO₂(B) has been commonly used as a convenient route to achieving the VO₂(M) phase by annealing at 450 °C or above under an inert atmosphere.¹⁷

VO₂(D) is a newly discovered meta-stable phase^{17,18} that has gained attention in the VO₂ field as it allows the direct transition to VO₂(M) at relatively low temperatures (250–400 °C).^{13,18} Moreover, once the monoclinic phase is obtained from the VO₂(D) phase, the MST temperature of the resulting VO₂(M) material is lower (61 °C) than that widely reported in the literature (68 °C).¹³

VO₂ can be produced from a wide range of methods, including atmospheric pressure chemical vapour deposition (APCVD),^{10,19} sputtering and spin coating²⁰ and, continuous hydrothermal flow synthesis²¹ (CHFS) and hydrothermal synthesis²² among others. Nevertheless, the challenge to find an easy, scalable and affordable process to produce VO₂(M) at low temperatures remains. A new approach to obtain VO₂(M) in one step *via* hydrothermal synthesis has been reported recently,^{11,22} however the process is not easily reproducible due to the strict control required over experimental conditions such as temperature, pressure, time, pH, *etc.*

Here we report the synthesis of the VO₂(D) phase. A range of particle sizes, from nano- to micro-particles, were observed. The particle size and shape could be easily tailored by varying the pH; furthermore, when in the form of nanoparticles, the VO₂(D) to (M) phase transition could be achieved at annealing temperatures as low as 165 °C, significantly lower than previous reports on the VO₂(D) to (M) phase transformation (*ca.* 400 °C). Moreover, the VO₂(R) particles thus produced show a lower thermochromic transition temperature than expected for bulk vanadium dioxide. Finally we highlight the importance of particle size in controlling the phase behaviour of this important material. The advantages of producing nanoparticles of VO₂ are that they can give superior luminous transmittance and solar energy transmittance modulation compared to VO₂ films, as is reported in the literature by S.-Y. Li *et al.*²³

2. Experimental section

2.1 Synthesis of VO₂(D) microparticles

All reagents were obtained from Sigma Aldrich except for sodium hydroxide which was purchased from Alfa Aesar and were used without any further purification. In a typical reaction 0.625 g [0.0024 mol] of ammonium metavanadate (NH₄VO₃), 2.52 g of oxalic acid (C₂H₂O₄) used as a reducing agent, and 0.5 g of polyvinylpyrrolidone (PVP) were mixed into 50 mL of

Table 1 Sample names and descriptions for VO₂ powders synthesized by the reaction between NH₄VO₃ and C₂H₂O₄ in water. NaOH was used to adjust the pH of the starting solution. All samples were synthesized *via* hydrothermal treatment for 24 hours at 220 °C

Sample	pH of the starting solution
S01	0.65
S02	0.98
S03	1.05
S04	1.52
S05	2.5
S06	3.51
S07	4.6
S08	5.5
S09	6.91

deionized water under continuous stirring until a green solution was obtained, indicating the presence of V³⁺ in the solution. The pH of the solution was adjusted using NaOH (1 M) (Table 1). Hydrothermal treatment was carried out using 27 mL of the resultant solution into a 45 mL Teflon lined autoclave and heated at 220 °C for 24 hours. Further studies were carried out using W-doped VO₂(D) microparticles synthesised using 2–7 at% of WCl₄ (relative to the vanadium precursor) added to the initial solution. The reaction conditions were the same as used for the undoped samples. After hydrothermal synthesis, particles were filtered and washed with deionized water and ethanol.

2.2 Synthesis of VO₂(D) nanoparticles

To prepare VO₂(D) nanoparticles, 0.45 g [0.0024 mol] of vanadium pentoxide (V₂O₅), 0.75 mL of sulfuric acid (H₂SO₄) and 0.25 mL of hydrazine hydrate were added to 10 mL of deionized water and stirred for 3–5 minutes. The pH of the solution was adjusted to 6.6–6.9 using NaOH (1 M) and finally the solution was centrifuged to obtain a grey paste. The grey paste was dissolved in 19 mL of DI water and poured into a 45 mL teflon lined autoclave and heated to 240 °C for 48 hours. The product was isolated by centrifugation and washed with deionized water and ethanol.

In Table 2 the conditions used to prepare the VO₂(D) nanoparticles are stated. The pH range must be controlled within a narrow range to avoid an undesired phase. Three samples are presented here to show the pH range that can be used.

Table 2 Sample names and descriptions for VO₂ powders synthesized by the reaction between V₂O₅ and H₂SO₄ in water. NaOH was used to adjust the pH of the solution. Samples were synthesized *via* hydrothermal synthesis for 48 hours at 240 °C

Sample	pH of the starting solution
S16	6.62
S17	6.75
S18	6.84

2.3 Materials characterisation

X-ray diffraction studies were carried out using a D8 GADDS Bruker diffractometer, utilising Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) between 10 and 60, 2θ . Field Emission Scanning Electron



Microscopy (FESEM) analysis was performed using a JEOL JSM-6700Ff instrument with an accelerating voltage of 5 keV and Transmission Electron Microscopy (TEM) analysis was performed using a Phillips CM300 FEG TEM, operated at 300 kV. Differential scanning calorimetry (DSC) analysis was obtained on a DSC 1 instrument from Mettler Toledo. These experiments were carried out between 0 and 300 °C under a controlled nitrogen atmosphere with a heating ramp of 5 °C min⁻¹. Raman spectroscopy was performed using a Renishaw 1000 spectrometer with a 633 nm laser. The equipment was calibrated using a silicon reference.

3. Results and discussion

3.1 VO₂ powder characterization

VO₂ microparticles were produced through the hydrothermal reaction of ammonium metavanadate with oxalic acid in the presence of polyvinylpyrrolidone (PVP). Adjusting the pH of the initial reactant mixture with 1.0 M NaOH proved to be an easy and reproducible route to obtain microparticles of the VO₂(D) phase with different morphologies. The conditions used in the VO₂(D) microparticle synthesis are summarized in Table 1.

Fig. 1 shows the XRD pattern of the prepared VO₂(D) phase using NH₄VO₃ as a precursor with different pH values of the starting solution. All peaks shown in the as-prepared samples are indexed to the D phase of VO₂. Fig. 1 presents the VO₂(D) pattern reported in the literature for comparison purposes. All the VO₂(D) peaks of the prepared samples match with the literature pattern.¹⁷

VO₂(D) nanoparticles (20–40 nm) were obtained by hydrothermal synthesis using V₂O₅, hydrazine hydrate and sulfuric acid as starting reagents. In this case, changing the pH appears to affect the phase of vanadium oxide produced rather than the morphology. VO₂(D) is formed only at pH between 6.6 and 6.9, outside this range, other phases, VO₂(B) and VO₂(A), or mixed phases of VO₂ are obtained.

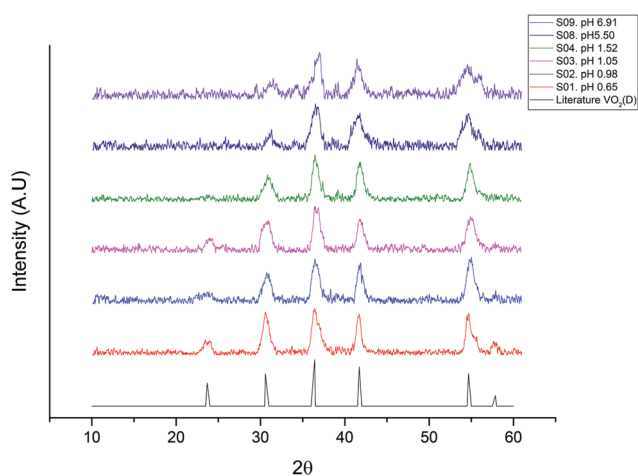


Fig. 1 XRD patterns of the VO₂(D) microparticles as synthesised from the ammonium metavanadate precursor under different pH conditions. A reference XRD pattern of VO₂(D) has been obtained from the literature.¹⁷

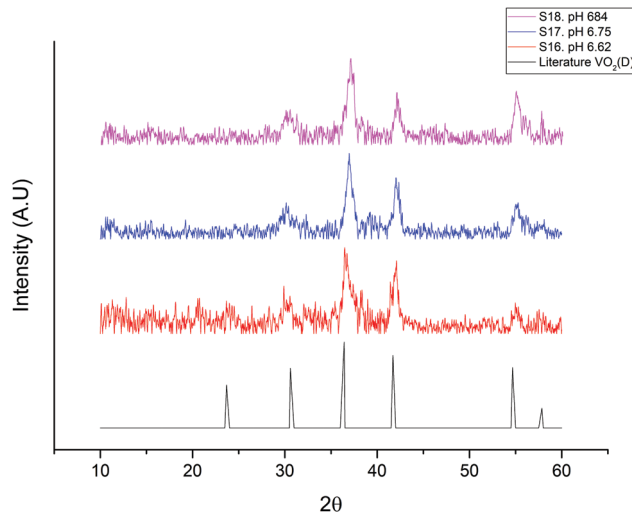


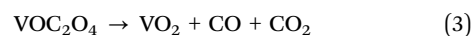
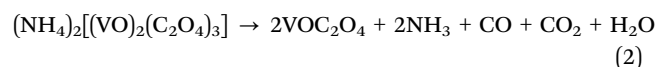
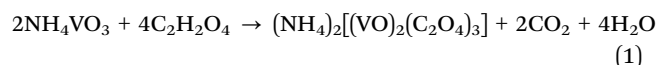
Fig. 2 XRD pattern of the prepared samples using vanadium pentoxide as a precursor and NaOH to adjust the pH of the solution. All peaks correspond to the VO₂(D) phase shown in the literature.¹⁷

Fig. 2 shows the XRD of three as-prepared samples of VO₂(D) nanoparticles with different pH values compared to the VO₂(D) pattern reported in the literature.¹⁷

Raman spectroscopy was performed for the as-prepared samples with different pH values of the starting solution. The result obtained in all cases was the typical Raman spectroscopy bands for V₂O₅.²⁴ When VO₂ powder is exposed to air the surface of the sample tends to oxidize, thus when performing surface analysis as Raman, it is not unusual to obtain V₂O₅ in the results, which represent the 5+ oxidation state, the most stable one. In this case, Raman spectroscopy bands show typical bands of V₂O₅, indicating that some degree of oxidation has taken place in our samples.

SEM images of the VO₂ microparticles are shown in Fig. 3, as can be seen, increasing the pH of the starting solution without changing any other condition results in the growth of the particle size, and also a change in the morphology. At pH 0.65 a “flower shape” morphology made of small attached long particles is seen, while moving towards neutral pH, larger smooth spheres are obtained.

In the present work ammonium metavanadate reacts with oxalic acid to produce vanadium(IV) oxide, carbon monoxide and carbon dioxide as can be seen in eqn (1)–(3), this solution have an acid pH, thus, small particle size, good homogeneity and low agglomeration are expected (and obtained in the as prepared samples):



However, when adding sodium hydroxide in the process to adjust the pH of the solution, we are also producing sodium



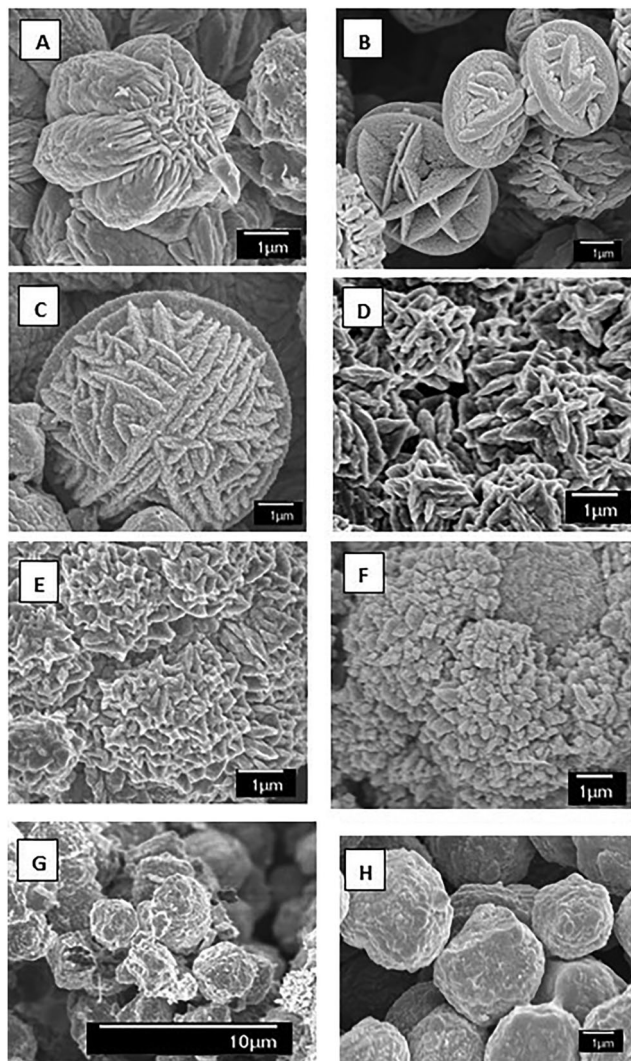
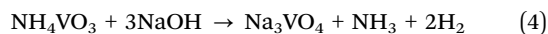


Fig. 3 SEM of the prepared samples using ammonium metavanadate as a precursor with different pH values: (A) 0.65 (B) 0.98 (C) 1.05 (D) 1.52 (E) 2.50 (F) 3.51 (G) 4.60 (H) 6.91.

orthovanadate, ammonia and water, as can be seen in eqn (4). This could affect the homogeneity of particles, due to greater agglomeration and growth of the particles. This explains the growth and the agglomeration of our particles due to the increase of the pH of the initial solution.



The change in the morphology and size by simply changing the pH is interesting as the $\text{VO}_2(\text{D})$ phase can be used for different applications depending on the morphology and size.

The pH of the starting precursor solution had a dramatic effect on the morphology observed in the synthesized VO_2 particles Fig. 3. At a pH of 0.65, Fig. 3(A), a star/flower shape can be seen, similar to the desert rose formation of minerals. This morphology has been previously observed in other hydrothermally produced materials^{4,25} Increasing the pH of the starting solution to 0.98, Fig. 3(B), causes the flower shape to disappear and a series of circular fused plates can be seen,

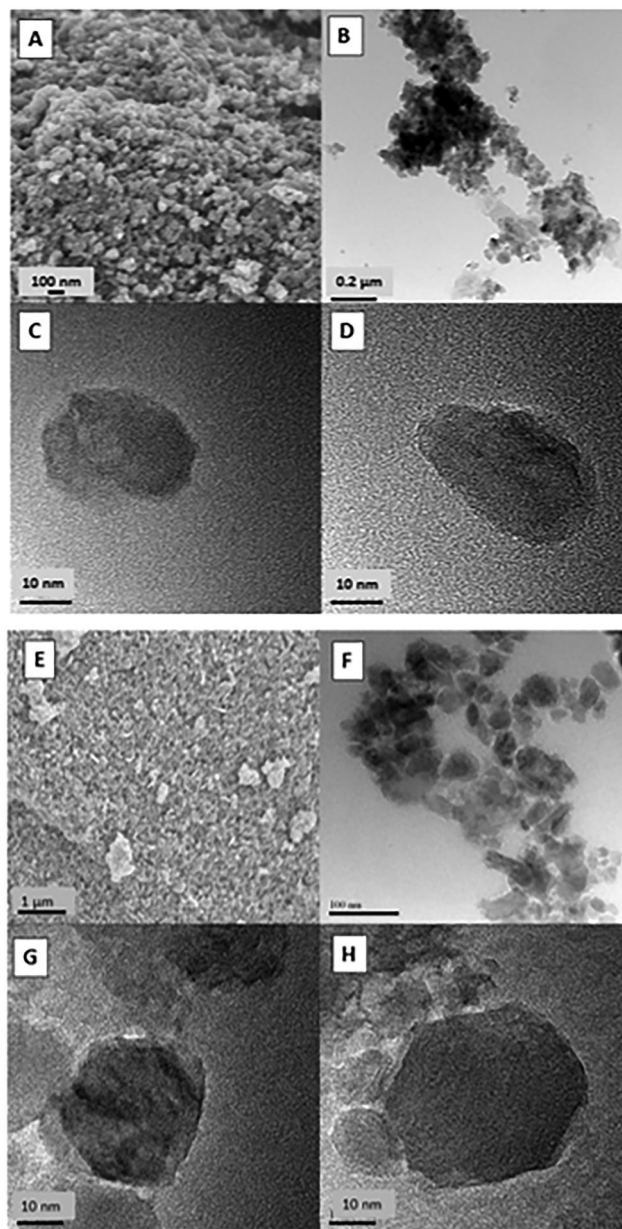


Fig. 4 (A) SEM image of sample 16 (B–D) TEM images of sample 16 (E) SEM image of sample 17 (F–H) TEM images of sample 17.

apparently formed by small long particles well attached to one another, almost forming a solid sphere. At a pH of 1.05, Fig. 3(C), the particles appear to be more spherical, with ridges present on the surface of the particles. Further increasing the pH to 1.52, Fig. 3(D), results in the formation of small cross-shape structures that are well defined can be seen to overlap to form larger structures. At a pH of 2.50, Fig. 3(E), the individual well-defined structures can still be seen; however it seems like their growth rate has been retarded. At pH values above 3.5, the particle shapes become more homogeneous, eventually adopting a sphere like shape. This can be seen in Fig. 3(F–H), where the higher pH of the starting precursor solution can be clearly seen to prevent the formation of smaller crystallite structures.



Particle sizes range from 1 μm at the most acidic pH to $\sim 4 \mu\text{m}$ when pH is close to neutral. It is interesting that the morphology in most of the cases has a round shape but always present a “Ball-shape” made of small long rods attached; the round shape can be attributed to the use of PVP as this has been reported as a crystal growth modifier.¹⁷ The presence of PVP in this experiments seems to be essential in the formation of the $\text{VO}_2(\text{D})$ phase as reported by Liu Liang *et al.*;¹⁷ if no PVP is added the product shows a pure $\text{VO}_2(\text{B})$ phase.

The nanoparticles of $\text{VO}_2(\text{D})$ were prepared using V_2O_5 as a precursor. In Fig. 4 SEM and TEM images of the as-prepared samples can be seen. The particle size is around 20–40 nm and presents mainly a round shape. The $\text{VO}_2(\text{D})$ nanoparticles do not show any growth after heat treatment to convert to $\text{VO}_2(\text{R})$, meaning that the final products remain as nanoparticles.

Hydrazine is well known to promote nanoparticle formation as it can coordinate to metal ions during hydrothermal synthesis.²⁶ Hence we believe that hydrazine plays a critical role in the production of $\text{VO}_2(\text{D})$ nanoparticles here.

3.2 Functional properties

The typical approach to obtain $\text{VO}_2(\text{R})$ for thermochromic applications is by annealing the $\text{VO}_2(\text{B})$ phase under vacuum at temperatures that range between 420 and 700 $^\circ\text{C}$.^{27,28} The actual transformation temperature depends on the morphology of the $\text{VO}_2(\text{B})$ particles; we noticed in this work that nanoparticles of $\text{VO}_2(\text{D})$ require less time/temperature to transform into $\text{VO}_2(\text{M})$ than $\text{VO}_2(\text{D})$ microparticles. Importantly, the $\text{VO}_2(\text{D})$ phase can be converted to thermochromic $\text{VO}_2(\text{R})$ by thermal treatment at temperatures as low as 250 $^\circ\text{C}$.²⁹ This is highly significant, as low temperature conversion allows preservation of the nanostructure of the parent phase, and as mentioned before, nanostructures show superior luminous transmittance and solar energy transmittance modulation, with this being a key point of the production of thermochromic VO_2 . The nano and microparticles produced in this work showed a significantly different phase transition behaviour. DSC was attempted to study the $\text{VO}_2(\text{D}) \rightarrow \text{VO}_2(\text{R})$ transition in our microparticles. However, the maximum temperature of our DSC was 300 $^\circ\text{C}$, and the desired transition did not occur in this temperature range. It was found that by annealing under vacuum the $\text{VO}_2(\text{D}) \rightarrow \text{VO}_2(\text{M})$ transition occurred in our microparticles at around 350 $^\circ\text{C}$. Once converted to thermochromic $\text{VO}_2(\text{R})$, cooling to room temperature will cause a further transition to $\text{VO}_2(\text{M})$. This $\text{VO}_2(\text{M})$ material was then subjected to DSC to study the $\text{VO}_2(\text{M}) \rightarrow \text{VO}_2(\text{R})$ transition, and the results are shown in Fig. 5. All studied samples present the same T_c to within 5 $^\circ\text{C}$ and for convenience only two samples are shown. As is shown in Fig. 5 there is a slight difference between the critical temperature for each sample, this may be due to morphology. In general the T_c is at $61 \pm 3 \text{ }^\circ\text{C}$ for the heating cycle and $55 \pm 2 \text{ }^\circ\text{C}$ for the cooling cycle, thus the thermal hysteresis width calculated from DSC is $6 \pm 1 \text{ }^\circ\text{C}$.

Reported DSC in the literature of $\text{VO}_2(\text{R})$ obtained in one step *via* hydrothermal synthesis shows a T_c temperature at

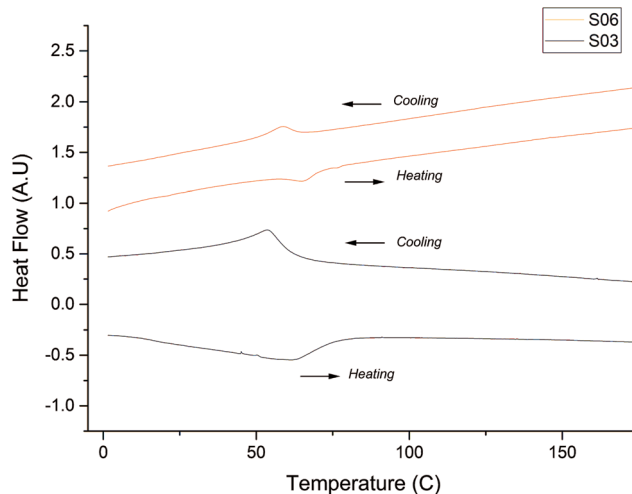


Fig. 5 DSC curves of $\text{VO}_2(\text{R})$ obtained *via* micro- $\text{VO}_2(\text{D})$ after heat treatment.

65 $^\circ\text{C}$ for the heating cycle and 53.5 $^\circ\text{C}$ for the cooling sample,³⁰ while samples of $\text{VO}_2(\text{R})$ obtained *via* $\text{VO}_2(\text{A})$ using the hydrothermal synthesis method have a T_c for the heating cycle of 69 $^\circ\text{C}$ and 61 $^\circ\text{C}$ for the cooling sample.³¹ Samples of $\text{VO}_2(\text{R})$ obtained *via* $\text{VO}_2(\text{D})$ have a T_c of 67.5 $^\circ\text{C}$ for the heating cycle and 59.7 $^\circ\text{C}$ for the cooling cycle,¹³ while our results, using the same method present a T_c for the heating cycle of $61 \pm 3 \text{ }^\circ\text{C}$ and $55 \pm 2 \text{ }^\circ\text{C}$ for the cooling cycle, this represents 4–6 $^\circ\text{C}$ lower than that reported previously. The difference can be explained due to particle size and strain effect on our samples; it has to be noted that the microparticles shown here are formed by the accumulation of nanoparticles.

In the literature Lopez *et al.* reported the fabrication of VO_2 nanoparticles using the ion implantation method, in their work it is demonstrated that the transition temperature it is decreased due particle size effects and moreover as a result of defects in VO_2 that causes nucleation spots for the phase transition.³²

Phase nucleation is reported to be due to vacancies, substitutions, *etc.*,³³ oxygen vacancies are usually reported in the literature as defects on nanostructure surfaces;³⁴ therefore while the size of the particles decreased, the surface ratio increased, consequently the nucleation defect density is higher in smaller particles causing the diminution of the transition temperature in the as-prepared nanoparticles, compared to the as-prepared microparticles.

In Table 3 DSC measurements of critical temperatures for the mentioned $\text{VO}_2(\text{R})$ reported in the literature and in the present work are shown.

Tungsten doped $\text{VO}_2(\text{D})$ microparticles samples were synthesized in order to study the change in the transition temperature once the rutile phase is obtained after heat treatment of the prepared sample. It is well known in the literature that the addition of tungsten to the vanadium thermochromic samples decreases the transition temperature. In our case samples were doped with 2, 3 and 4 at% of tungsten(IV) chloride.



Table 3 Comparison of DSC transition temperatures for heating and cooling cycles of VO₂(R) (to VO₂(M))

Process	T_c heating cycle (°C)	T_c cooling sample (°C)	Hysteresis (°C)
VO ₂ (R) one step hydrothermal synthesis ¹¹	65	53.5	12.5
VO ₂ (B) → VO ₂ (R) hydrothermal synthesis ³⁵	68.75	59.77	8.98
VO ₂ (D) → VO ₂ (R) hydrothermal synthesis ²⁹	67.5	57.9	9.6
VO ₂ (D) → VO ₂ (R) hydrothermal synthesis (present work)	61 ± 3	55 ± 2	8

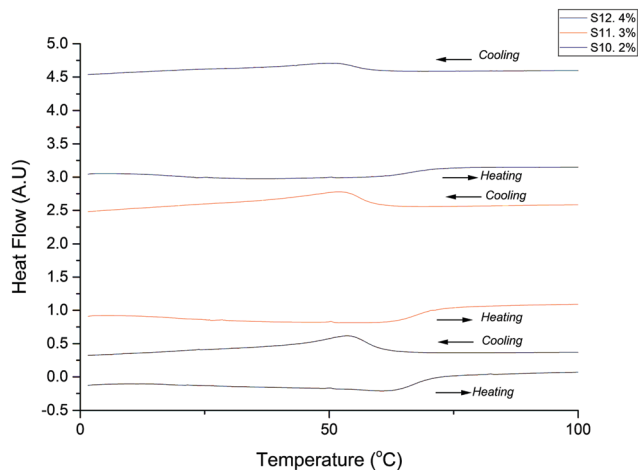
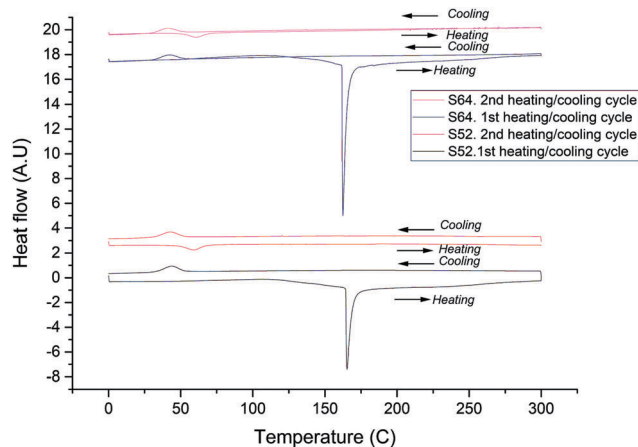
**Fig. 6** DSC curves of tungsten doped VO₂(R) obtained via tungsten doped micro-VO₂(D) after heat treatment.

Fig. 6 shows the DSC of three tungsten doped (2, 3 and 4 at%) VO₂(M) samples, obtained via VO₂(D). In all three samples the T_c for the heating cycle is at 62 ± 1 °C and the T_c for the cooling cycle in all cases is at 52 ± 1 °C. It is surprising that there is no significant change in the transition temperature as expected. It appears as if pre-doping of VO₂(D) particles with W is not an effective method to lower the T_c in subsequently produced VO₂(M); our results in fact suggest that W is not incorporated into the VO₂(D) lattice using the hydrothermal approach used here, see the ESI,[†] for full details of W doping experiments.

As discussed above, VO₂(D) microparticle samples required annealing at 350 °C to obtain VO₂(R). However for VO₂(D) nanoparticles, a much lower annealing temperature is required. DSC illustrating the phase transitions occurring upon annealing under N₂ of VO₂(D) nanoparticles is shown in Fig. 7. In the first heating cycle of the as made materials, the first significant feature in the DSC curve occurs at 163 ± 2 °C, where a strong endothermic peak is seen. This is assigned to the VO₂(D) → VO₂(R) transition. No further transitions are seen upon heating up to 300 °C. In the first cooling cycle, no feature is seen at around 163 °C, showing that the phase transition observed in the heating cycle is irreversible. Upon further cooling, an exothermic peak is observed at 42 ± 1 °C; this is assigned to the VO₂(R) → VO₂(M) transition. In the second heating cycle, the system displays typical thermo-chromic behaviour. An endotherm peak is now observed at 59 ± 1 °C (VO₂(M)–VO₂(R)). No further signals are seen up to 300 °C. In the second cooling cycle, an exothermic peak is again observed at 42 ± 1 °C (VO₂(R)–VO₂(M)). It is noteworthy that in these samples the VO₂(D) → VO₂(R) transition temperature of

**Fig. 7** DSC curves of VO₂(R) obtained via nano-VO₂(D) samples showing the transition from the D to R phase and then, the reversible thermo-chromic behaviour of VO₂(R).

163 °C is significantly lower than that previously reported (250 °C),⁵ which we attribute to the small size of the particles. The thermo-chromic material thus produced also shows a lower MST temperature than expected from bulk vanadium dioxide. This has also been seen previously with nanoscale VO₂.²⁵

4. Conclusion

VO₂(D) microparticles were synthesised using NH₄VO₃ and oxalic acid as a precursor and a reducing agent, respectively via a hydrothermal synthesis reaction. We demonstrate in this work that it is possible to obtain pure VO₂(D) with different morphologies by simply changing the pH of the starting solution using NaOH at 1 M concentration. A phase transformation from D to M is possible at 350 °C under vacuum obtaining a pure monoclinic phase with MST reported at 61 °C for the heating cycle and at 55 °C for the cooling cycle.

W doping of VO₂(D) microparticles was attempted, yet the MST temperature for each nominally doped sample was unchanged from undoped VO₂, indicating that W doping of VO₂(D) followed by conversion into VO₂(R) does not appear to be successful.

VO₂(D) nanoparticles were synthesized using vanadium pentoxide and sulfuric acid as a precursor and a reducing agent respectively. The size of the obtained particles oscillates between 20 and 40 nm. To obtain VO₂(M) in this case the heat treatment of the sample is required at 165 °C for a few minutes under a nitrogen atmosphere. After the samples are heat



treated a fully thermochromic sample is obtained with a MST for the heating cycle at 59 °C and 42 °C for the cooling cycle. This is the lowest VO₂(D) → VO₂(R) transition temperature reported in the literature, and shows the importance of particle size on phase transition temperatures. In addition the reported MST temperature in this work for VO₂(M) nanoparticles obtained from VO₂(D) is lower than that reported for bulk VO₂. We attribute this to the particle size and strain in nanoparticles of VO₂(R) produced from VO₂(D).

References

- 1 R. Molaei, R. Bayati, S. Nori, D. Kumar, J. T. Prater and J. Narayan, *Appl. Phys. Lett.*, 2013, **103**, 2–6.
- 2 C. Moffatt and A. Wigstein, *Sol-gel synthesis of VO₂ thin films and the effects of W and Re doping*, 2005.
- 3 H. Jerominek, F. Picard, N. R. Swart, M. Renaud, M. Lévesque, M. Lehoux, S. Castonguay, M. Pelletier, G. Bilodeau, D. Audet, T. D. Pope and P. Lambert, *Proc. SPIE*, 1996, **2746**, 60–71.
- 4 C. V Subba, E. H. Walker, S. A. W. Sr, Q. L. Williams and R. R. Kalluru, *Curr. Appl. Phys.*, 2009, **9**, 1195–1198.
- 5 Y. Zhang and Y. Huang, *Mater. Lett.*, 2016, **182**, 285–288.
- 6 X. Juan, J. Ming, X. Wen, F. Rui and Y. Xin, *Ceram. Int.*, 2016, **42**, 7883–7887.
- 7 K. Zhao, L. Teng, Y. Tang and X. Chen, *Ceram. Int.*, 2014, **40**, 15335–15340.
- 8 Q. Wang, J. Pan, M. Li, Y. Luo, H. Wu, L. Zhong and G. Li, *J. Mater. Sci. Technol.*, 2015, **31**, 630–633.
- 9 Z. Chen, Y. Gao, L. Kang, C. Cao, S. Chen and H. Luo, *J. Mater. Chem. A*, 2014, **2**, 2718.
- 10 M. J. Powell, R. Quesada-cabrera, A. Taylor, D. Teixeira, I. Papakonstantinou, R. G. Palgrave, G. Sankar and I. P. Parkin, *Chem. Mater.*, 2016, **28**, 1369–1376.
- 11 J. Zhu, Y. Zhou, B. Wang, J. Zheng, S. Ji, H. Yao, H. Luo and P. Jin, *Appl. Mater. Interfaces*, 2015, **7**, 27796–27803.
- 12 Y. Gao, S. Wang, H. Luo, L. Dai, C. Cao, Y. Liu, Z. Chen and M. Kanehira, *Energy Environ. Sci.*, 2012, 6104–6110.
- 13 Z. Song, L. Zhang, F. Xia and N. A. S. Webster, *Inorg. Chem. Front.*, 2016, **3**, 1035–1042.
- 14 D. Hagrman, J. Zubieta, C. J. Warren, L. M. Meyer, M. M. J. Treacy and R. C. Haushalter, *J. Solid State Chem.*, 1998, **182**, 178–182.
- 15 J. H. Park, J. M. Coy, T. S. Kasirga, C. Huang, Z. Fei, S. Hunter and D. H. Cobden, *Nature*, 2013, **500**, 431–434.
- 16 Y. Zhang, X. Tan, C. Huang, C. Meng, Y. Zhang, X. Tan, C. Huang and C. Meng, *Mater. Res. Innovations*, 2016, **10**, 295–302.
- 17 L. Liu, F. Cao, T. Yao, Y. Xu, M. Zhou, B. Qu, B. Pan, C. Wu, S. Wei and Y. Xie, *New J. Chem.*, 2012, **36**, 619.
- 18 L. Zhong, M. Li, H. Wang, Y. Luo, J. Pan and G. Li, *CrystEngComm*, 2015, **17**, 5614–5619.
- 19 D. Louloudakis, D. Vernardou, E. Spanakis, S. Dokianakis, M. Panagopoulou, G. Raptis, E. Aperathitis, G. Kiriakidis, N. Katsarakis and E. Koudoumas, *Phys. Status Solidi C*, 2015, **860**, 856–860.
- 20 Y. Shimizu, K. Nagase, N. Miura and N. Yamazoe, *Jpn. J. Appl. Phys.*, 1990, **29**, 1708–1711.
- 21 M. J. Powell, P. Marchand, C. J. Denis, J. C. Bear, J. A. Darr and I. P. Parkin, *Nanoscale*, 2015, **7**, 18686–18693.
- 22 J. H. Son, J. Wei, D. Cobden, G. Cao and Y. Xia, *Chem. Mater.*, 2010, **22**, 3043–3050.
- 23 S. Y. Li, G. A. Niklasson and C. G. Granqvist, *J. Appl. Phys.*, 2010, **108**, 1–8.
- 24 C. Sanchez, J. Livage and G. Lucazeau, *J. Raman Spectrosc.*, 1982, **12**, 3–7.
- 25 B. Lei, W. Qin, G. Kang, C. Peng and J. Wu, *J. Am. Ceram. Soc.*, 2015, **1633**, 1626–1633.
- 26 H. Zhu, D. Yang, G. Yu and H. Zhang, *Nanotechnology*, 2006, **17**, 2386–2389.
- 27 C. Wang, X. Wang, P. Gong and T. Yao, *Chemosphere*, 2016, **149**, 358–365.
- 28 S. A. Corr, M. Grossman, Y. Shi, K. R. Heier, D. Stucky and R. Seshadri, *J. Mater. Chem.*, 2009, **2**, 4362–4367.
- 29 G. Z. Song, L. Zhang, F. Xia, N. A. S. Webster, J. Song, B. Liu, H. Luo and Y. Gao, *Inorg. Chem.*, 2016, **3**, 1035–1042.
- 30 W. Li, S. Ji, Y. Li, A. Huang, H. Luo and P. Jin, *RSC Adv.*, 2014, **4**, 13026.
- 31 S. Rao, A. Artemenko, C. Labrugere and M. Miclau, *J. Solid State Chem.*, 2014, **213**, 79–86.
- 32 R. Lopez, T. E. Haynes and L. A. Boatner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 1–5.
- 33 L. Hongwei, L. Junpeng, Z. Minrui, T. S. Hai, S. C. Haur, Z. Xinhai and K. Lin, *Opt. Express*, 2014, **22**, 30748–30755.
- 34 J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant and S. S. P. Parkin, *Science*, 2013, **339**, 1402–1406.
- 35 M. Li, F. Kong, Y. Zhang and G. Li, *CrystEngComm*, 2011, **13**, 2204.

