



Cite this: *New J. Chem.*, 2017, **41**, 9216

# Particle size, morphology and phase transitions in hydrothermally produced VO<sub>2</sub>(D)<sup>†</sup>

Diana Teixeira,<sup>a</sup> Raul Quesada-Cabrera,<sup>a</sup> Michael J. Powell,<sup>a</sup> G. K. L. Goh,<sup>b</sup> G. Sankar,<sup>a</sup> I. P. Parkin<sup>a</sup> and R. G. Palgrave<sup>\*a</sup>

Different morphologies and sizes of VO<sub>2</sub>(D) particles were synthesised *via* hydrothermal synthesis using ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) or vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) 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 VO<sub>2</sub>(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 V<sub>2</sub>O<sub>5</sub> as a precursor and hydrazine as a reducing agent. The transition from VO<sub>2</sub>(D) to thermochromic VO<sub>2</sub>(R) in micron scale particles occurred at 350 °C under vacuum. However, the nanoparticles of VO<sub>2</sub>(D) had a significantly lower VO<sub>2</sub>(D) to thermochromic VO<sub>2</sub>(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 VO<sub>2</sub> material *via* another VO<sub>2</sub> phase. After the conversion of VO<sub>2</sub>(D) microparticles to thermochromic VO<sub>2</sub>(R), the metal to insulator transition temperature is 61 ± 1 °C for the heating cycle and 53 ± 1 °C for the cooling cycle. However, VO<sub>2</sub>(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 VO<sub>2</sub>. 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-VO<sub>2</sub>(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.

Received 16th June 2017,  
Accepted 21st July 2017

DOI: 10.1039/c7nj02165h

rsc.li/njc

## 1. Introduction

VO<sub>2</sub> has been investigated for a wide range of technological applications, including optical and electrical switching devices, multifunctional spintronics,<sup>1</sup> IR sensors and vision equipment, as coatings to prevent detection by reducing the IR transmittance of blackbody emitters,<sup>2</sup> to missile seeker sensors, and various other applications.<sup>3</sup> VO<sub>2</sub> nanorods have been used to prepare Li-ion batteries with a discharge capacity of 152 mA h g<sup>−1</sup>.<sup>4</sup> W-Doped VO<sub>2</sub>(B) nanobelts are used in supercapacitors.<sup>5</sup> VO<sub>2</sub> nano-flowers were synthesized by Kang *et al.* for energy-storage devices and supercapacitors.<sup>6</sup> TiO<sub>2</sub>/VO<sub>2</sub> nanofibers are reported to photocatalyze the degradation of pollutants from wastewater by Zhao *et al.*<sup>7</sup> VO<sub>2</sub>(B) nanosheets were fabricated as a cathode

electrode presenting a high initial discharge and stable cyclability compared to bulk VO<sub>2</sub>(B) as Want *et al.* reported in their work.<sup>8</sup>

VO<sub>2</sub> has also been widely studied for architectural applications due to its thermochromic properties: VO<sub>2</sub> displays a reversible phase transition from a low temperature, monoclinic insulating phase, VO<sub>2</sub>(M) to a high temperature, rutile, metallic phase, VO<sub>2</sub>(R) at 68 °C.<sup>9</sup> 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 VO<sub>2</sub> as a thermochromic material, able to change its optical properties with temperature. Specifically, VO<sub>2</sub> 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 VO<sub>2</sub>(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

<sup>a</sup> Department of Chemistry, Materials Chemistry Centre, University College London, 20 Gordon St., London WC1H 0AJ, UK. E-mail: r.palgrave@ucl.ac.uk

<sup>b</sup> Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A\*STAR), 2 Fusionopolis Way, Singapore 138634, Singapore

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c7nj02165h



$T_c$  in the optimum range for thermochromic windows.<sup>10–12</sup> 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 ( $\text{VO}_2$ ) has a well-known range of stable phases, such as  $\text{VO}_2(\text{M})$  and  $\text{VO}_2(\text{R})$ , as well as metastable phases, such as  $\text{VO}_2(\text{A})$ ,  $\text{VO}_2(\text{B})$  and  $\text{VO}_2(\text{C})$ .<sup>13,14</sup> Most of these phases consist of octahedrally coordinated  $\text{V}^{4+}$  ions with different linkages of octahedra leading to different crystal structures.<sup>15</sup>  $\text{VO}_2(\text{A})$  has a MST temperature of 162 °C. The solid has a good thermal stability and oxidation resistance in air below 408 °C.<sup>16</sup>  $\text{VO}_2(\text{B})$  has been commonly used as a convenient route to achieving the  $\text{VO}_2(\text{M})$  phase by annealing at 450 °C or above under an inert atmosphere.<sup>17</sup>

$\text{VO}_2(\text{D})$  is a newly discovered meta-stable phase<sup>17,18</sup> that has gained attention in the  $\text{VO}_2$  field as it allows the direct transition to  $\text{VO}_2(\text{M})$  at relatively low temperatures (250–400 °C).<sup>13,18</sup> Moreover, once the monoclinic phase is obtained from the  $\text{VO}_2(\text{D})$  phase, the MST temperature of the resulting  $\text{VO}_2(\text{M})$  material is lower (61 °C) than that widely reported in the literature (68 °C).<sup>13</sup>

$\text{VO}_2$  can be produced from a wide range of methods, including atmospheric pressure chemical vapour deposition (APCVD),<sup>10,19</sup> sputtering and spin coating<sup>20</sup> and, continuous hydrothermal flow synthesis<sup>21</sup> (CHFS) and hydrothermal synthesis<sup>22</sup> among others. Nevertheless, the challenge to find an easy, scalable and affordable process to produce  $\text{VO}_2(\text{M})$  at low temperatures remains. A new approach to obtain  $\text{VO}_2(\text{M})$  in one step *via* hydrothermal synthesis has been reported recently,<sup>11,22</sup> 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  $\text{VO}_2(\text{D})$  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  $\text{VO}_2(\text{D})$  to (M) phase transition could be achieved at annealing temperatures as low as 165 °C, significantly lower than previous reports on the  $\text{VO}_2(\text{D})$  to (M) phase transformation (*ca.* 400 °C). Moreover, the  $\text{VO}_2(\text{R})$  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  $\text{VO}_2$  are that they can give superior luminous transmittance and solar energy transmittance modulation compared to  $\text{VO}_2$  films, as is reported in the literature by S.-Y. Li *et al.*<sup>23</sup>

## 2. Experimental section

### 2.1 Synthesis of $\text{VO}_2(\text{D})$ 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 ( $\text{NH}_4\text{VO}_3$ ), 2.52 g of oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) 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  $\text{VO}_2$  powders synthesized by the reaction between  $\text{NH}_4\text{VO}_3$  and  $\text{C}_2\text{H}_2\text{O}_4$  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  $\text{V}^3$  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  $\text{VO}_2(\text{D})$  microparticles synthesised using 2–7 at% of  $\text{WCl}_4$  (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 $\text{VO}_2(\text{D})$ nanoparticles

To prepare  $\text{VO}_2(\text{D})$  nanoparticles, 0.45 g [0.0024 mol] of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), 0.75 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 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  $\text{VO}_2(\text{D})$  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  $\text{VO}_2$  powders synthesized by the reaction between  $\text{V}_2\text{O}_5$  and  $\text{H}_2\text{SO}_4$  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 $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) between 10 and 60,  $2\theta$ . Field Emission Scanning Electron



Microscopy (FESEM) analysis was performed using a JEOL JSM-6700F 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<sup>-1</sup>. 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 VO<sub>2</sub> powder characterization

VO<sub>2</sub> 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 VO<sub>2</sub>(D) phase with different morphologies. The conditions used in the VO<sub>2</sub>(D) microparticle synthesis are summarized in Table 1.

Fig. 1 shows the XRD pattern of the prepared VO<sub>2</sub>(D) phase using NH<sub>4</sub>VO<sub>3</sub> 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 VO<sub>2</sub>. Fig. 1 presents the VO<sub>2</sub>(D) pattern reported in the literature for comparison purposes. All the VO<sub>2</sub>(D) peaks of the prepared samples match with the literature pattern.<sup>17</sup>

VO<sub>2</sub>(D) nanoparticles (20–40 nm) were obtained by hydrothermal synthesis using V<sub>2</sub>O<sub>5</sub>, 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. VO<sub>2</sub>(D) is formed only at pH between 6.6 and 6.9, outside this range, other phases, VO<sub>2</sub>(B) and VO<sub>2</sub>(A), or mixed phases of VO<sub>2</sub> are obtained.

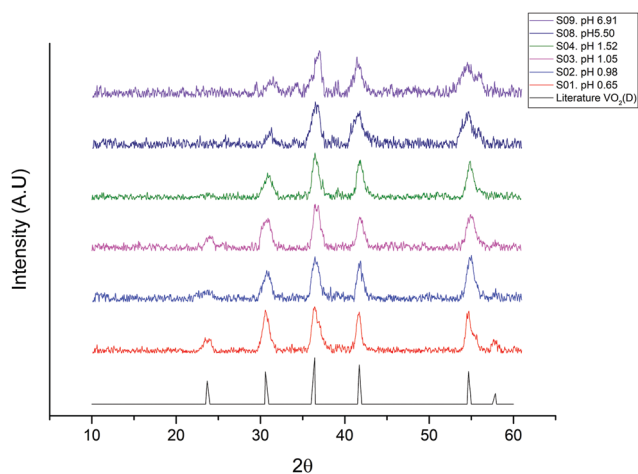


Fig. 1 XRD patterns of the VO<sub>2</sub>(D) microparticles as synthesised from the ammonium metavanadate precursor under different pH conditions. A reference XRD pattern of VO<sub>2</sub>(D) has been obtained from the literature.<sup>17</sup>

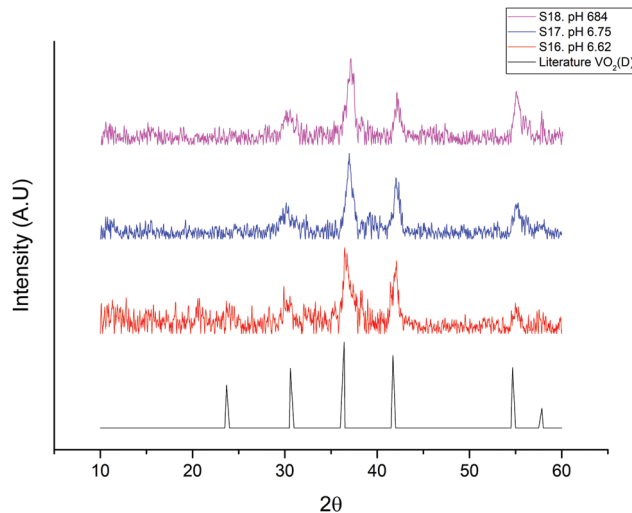


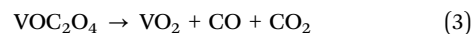
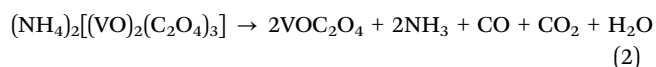
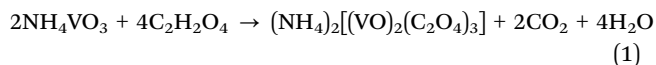
Fig. 2 XRD pattern of the prepared samples using vanadium pentoxide as a precursor and NaOH to adjust the pH of the solution. All peaks correspond to the VO<sub>2</sub>(D) phase shown in the literature.<sup>17</sup>

Fig. 2 shows the XRD of three as-prepared samples of VO<sub>2</sub>(D) nanoparticles with different pH values compared to the VO<sub>2</sub>(D) pattern reported in the literature.<sup>17</sup>

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 V<sub>2</sub>O<sub>5</sub>.<sup>24</sup> When VO<sub>2</sub> 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 V<sub>2</sub>O<sub>5</sub> in the results, which represent the 5+ oxidation state, the most stable one. In this case, Raman spectroscopy bands show typical bands of V<sub>2</sub>O<sub>5</sub>, indicating that some degree of oxidation has taken place in our samples.

SEM images of the VO<sub>2</sub> 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





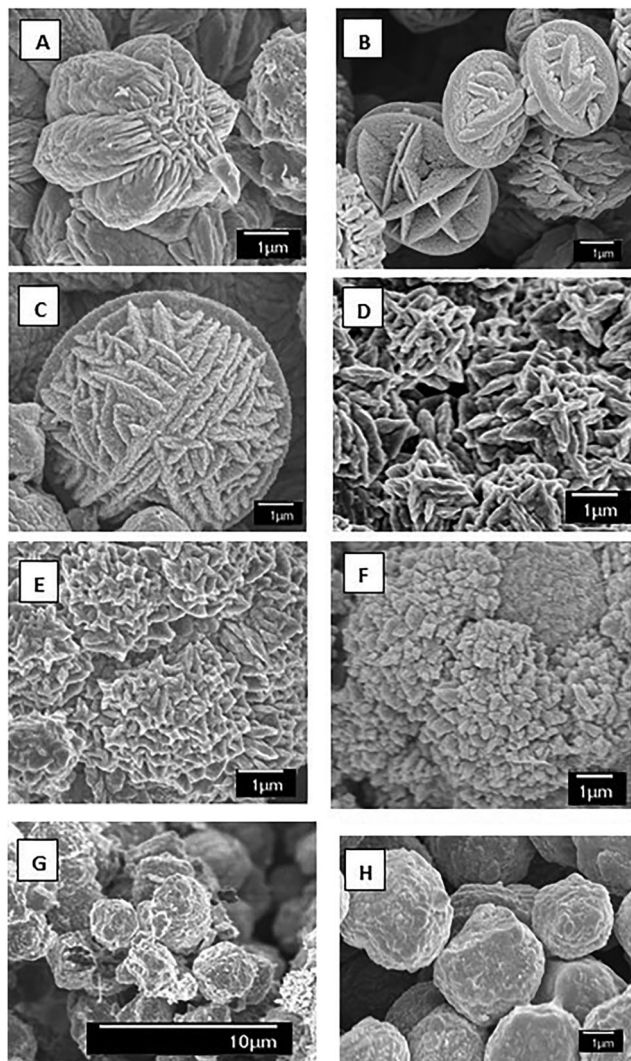
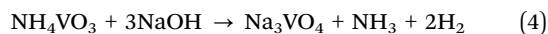


Fig. 3 SEM of the prepared samples using ammonium metavanadate as a precursor with different pH values: (A) 0.65 (B) 0.98 (C) 1.05 (D) 1.52 (E) 2.50 (F) 3.51 (G) 4.60 (H) 6.91.

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  $\text{VO}_2$  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<sup>4,25</sup> 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,

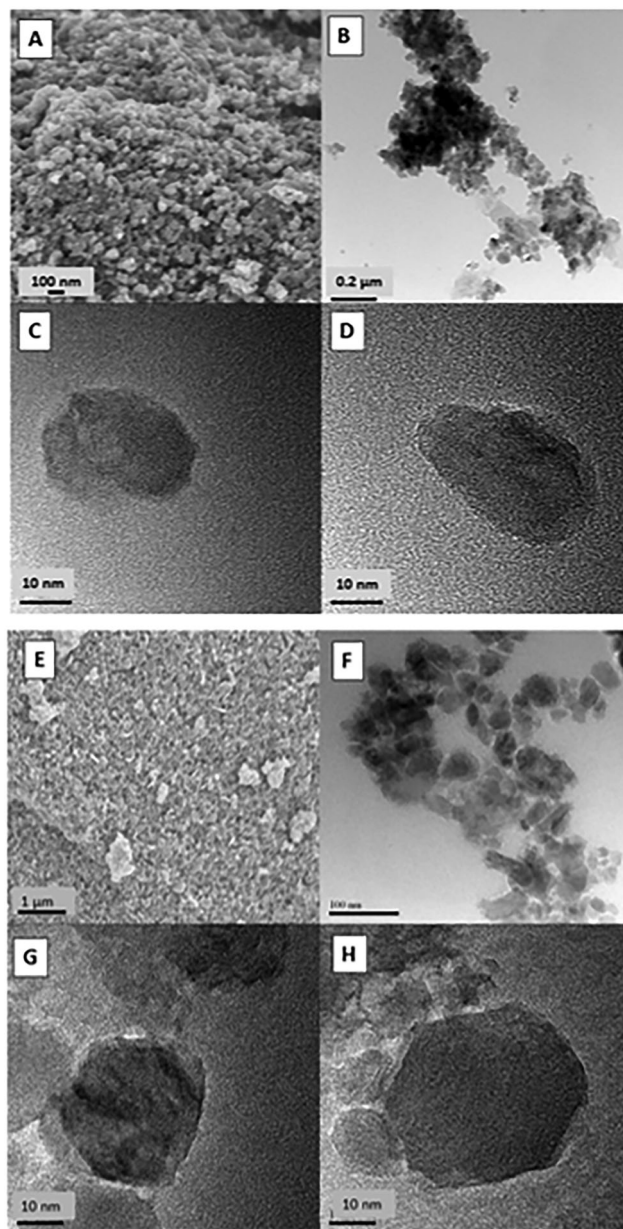


Fig. 4 (A) SEM image of sample 16 (B–D) TEM images of sample 16 (E) SEM image of sample 17 (F–H) TEM images of sample 17.

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  $\mu\text{m}$  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.<sup>17</sup> 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.*<sup>17</sup> 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  $\text{V}_2\text{O}_5$  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.<sup>26</sup> 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  $^\circ\text{C}$ .<sup>27,28</sup> 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  $^\circ\text{C}$ .<sup>29</sup> 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  $\text{VO}_2$ . 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

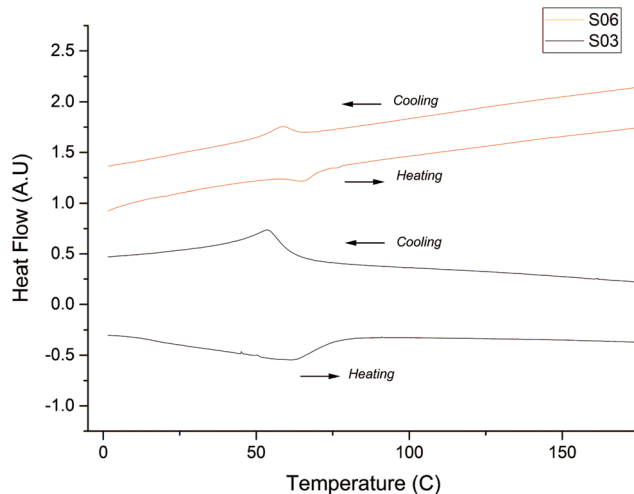


Fig. 5 DSC curves of  $\text{VO}_2(\text{R})$  obtained *via* micro- $\text{VO}_2(\text{D})$  after heat treatment.

65  $^\circ\text{C}$  for the heating cycle and 53.5  $^\circ\text{C}$  for the cooling sample,<sup>30</sup> 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.<sup>31</sup> 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,<sup>13</sup> 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  $\text{VO}_2$  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  $\text{VO}_2$  that causes nucleation spots for the phase transition.<sup>32</sup>

Phase nucleation is reported to be due to vacancies, substitutions, *etc.*,<sup>33</sup> oxygen vacancies are usually reported in the literature as defects on nanostructure surfaces;<sup>34</sup> 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 VO<sub>2</sub>(R) (to VO<sub>2</sub>(M))

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

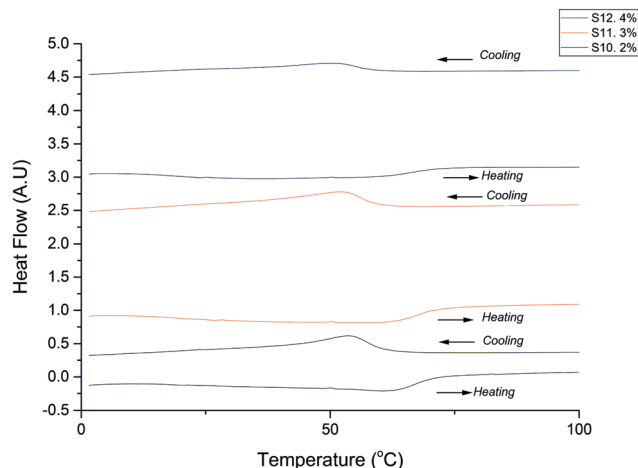
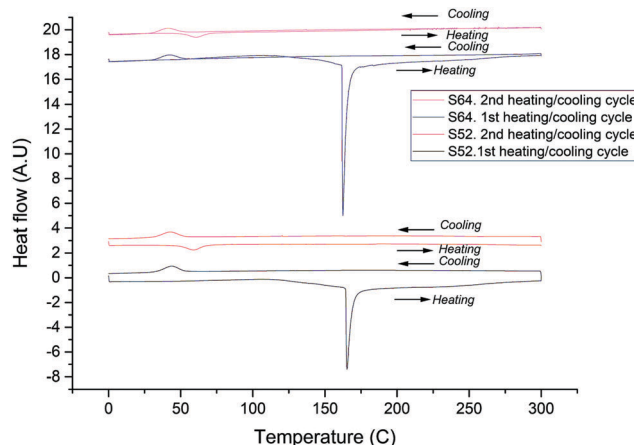
**Fig. 6** DSC curves of tungsten doped VO<sub>2</sub>(R) obtained via tungsten doped micro-VO<sub>2</sub>(D) after heat treatment.**Fig. 7** DSC curves of VO<sub>2</sub>(R) obtained via nano-VO<sub>2</sub>(D) samples showing the transition from the D to R phase and then, the reversible thermo-chromic behaviour of VO<sub>2</sub>(R).

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

As discussed above, VO<sub>2</sub>(D) microparticle samples required annealing at 350 °C to obtain VO<sub>2</sub>(R). However for VO<sub>2</sub>(D) nanoparticles, a much lower annealing temperature is required. DSC illustrating the phase transitions occurring upon annealing under N<sub>2</sub> of VO<sub>2</sub>(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  $163 \pm 2$  °C, where a strong endothermic peak is seen. This is assigned to the VO<sub>2</sub>(D) → VO<sub>2</sub>(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  $42 \pm 1$  °C; this is assigned to the VO<sub>2</sub>(R) → VO<sub>2</sub>(M) transition. In the second heating cycle, the system displays typical thermo-chromic behaviour. An endotherm peak is now observed at  $59 \pm 1$  °C (VO<sub>2</sub>(M)–VO<sub>2</sub>(R)). No further signals are seen up to 300 °C. In the second cooling cycle, an exothermic peak is again observed at  $42 \pm 1$  °C (VO<sub>2</sub>(R)–VO<sub>2</sub>(M)). It is noteworthy that in these samples the VO<sub>2</sub>(D) → VO<sub>2</sub>(R) transition temperature of

163 °C is significantly lower than that previously reported (250 °C),<sup>5</sup> 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 VO<sub>2</sub>.<sup>25</sup>

## 4. Conclusion

VO<sub>2</sub>(D) microparticles were synthesised using NH<sub>4</sub>VO<sub>3</sub> 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 VO<sub>2</sub>(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 VO<sub>2</sub>(D) microparticles was attempted, yet the MST temperature for each nominally doped sample was unchanged from undoped VO<sub>2</sub>, indicating that W doping of VO<sub>2</sub>(D) followed by conversion into VO<sub>2</sub>(R) does not appear to be successful.

VO<sub>2</sub>(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 VO<sub>2</sub>(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 VO<sub>2</sub>(D) → VO<sub>2</sub>(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 VO<sub>2</sub>(M) nanoparticles obtained from VO<sub>2</sub>(D) is lower than that reported for bulk VO<sub>2</sub>. We attribute this to the particle size and strain in nanoparticles of VO<sub>2</sub>(R) produced from VO<sub>2</sub>(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 VO<sub>2</sub> 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. Hagerman, 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.

