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# Synthesis and Characterization of Micro/nano VO<sub>2</sub> (M) Through Vanadyl Ethylene Glycolate (VEG) Decomposition

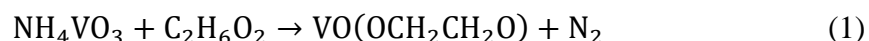
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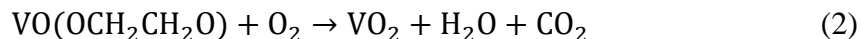
Vanadium dioxide (VO<sub>2</sub>) undergoes a reversible metal-insulator transition (MIT) assisted with crystallographic structure change from monoclinic (M) to rutile (R) phase at ~68°C, accompanied by remarkable modifications in electronic and optical properties.<sup>1-3</sup> VO<sub>2</sub> has been attracting much attention owing to its potential applications in high-tech fields, such as lithium-ions batteries, storage medium, and smart windows. However, vanadium oxides have been known for multi-oxidation states consisting of several homo- and mixed-valent oxides (*e.g.* V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, V<sub>3</sub>O<sub>7</sub>, V<sub>6</sub>O<sub>13</sub>, V<sub>2</sub>O<sub>3</sub>). The existence of multiple oxidation states (3+, 4+, 5+) turns into a synthetic challenge of VO<sub>2</sub>. Besides, VO<sub>2</sub> in a valence state of 4+ appears very sensitive to oxydo-reductions. Micro/nano-scale and highly crystallized VO<sub>2</sub> are more favorable, leading to excellent thermochromic performances, *e.g.* narrower hysteresis and larger amplitude in properties changes at the transition.<sup>4,5</sup> Unfortunately, the particle size usually increases with its crystallinity. Namely, a highly crystallized compound is always accompanied by a large particle size. Ball milling is proposed to

destroy highly crystallized compounds and reach a small size, but the additive largely deteriorates end-product purity and increases process complexity. Thus, it is required to develop new route allowing high VO<sub>2</sub> crystallinity with moderate micro-nano particle size.

A variety of approaches were explored to prepare VO<sub>2</sub>.<sup>6-10</sup> Thermal pyrolysis gives rise to the prospect of mass production. Vanadyl ethylene glycolate (VEG, VO(OCH<sub>2</sub>CH<sub>2</sub>O)) is a widely used vanadium precursor for VO<sub>x</sub> synthesis.<sup>11-15</sup> Ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) could be reduced by ethylene glycol (EG, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) with the consequent formation of VEG complex (V<sup>4+</sup>),<sup>25</sup> as illustrated in equation 1:



Elongated cuboid or rod-like shapes VEG forms and aggregates into spherical micro-particles to reduce total energy of the system.<sup>11, 14, 17</sup> The synthesis is typically performed using 0.1 M of metavanadate full dissolution (low precursor concentration) and VEG precipitation (high concentration). Beyond precipitate formation temperature, the synthesis temperature almost shows no effect on VEG morphology. The synthesis step from VEG to VO<sub>2</sub> is described in equation 2:



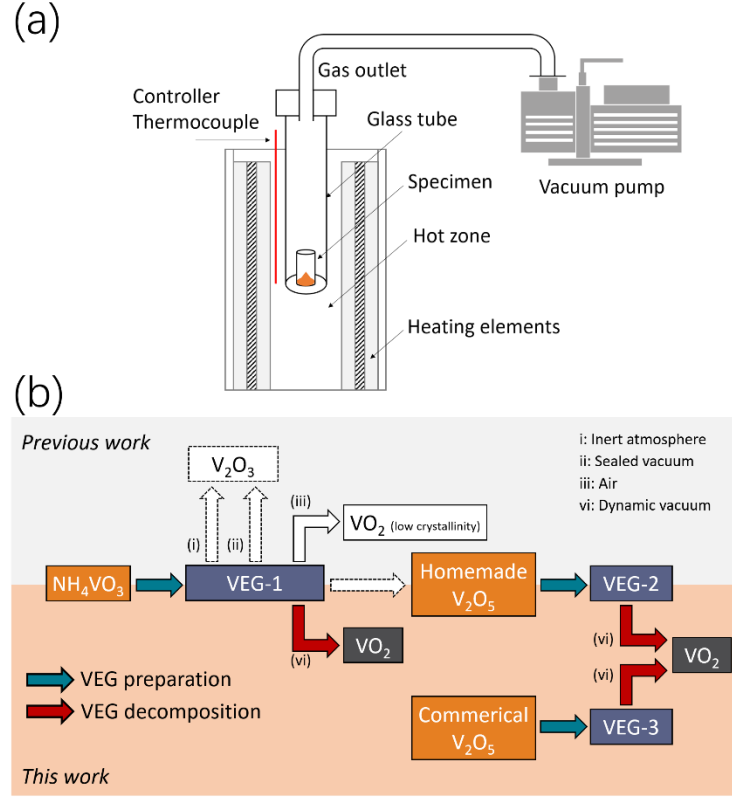
Due to instability of V (4+), an exothermic peak at ~280°C (from TG analysis) involving a weight increase of 0.74 wt% occurs as a result of V<sub>2</sub>O<sub>5</sub> formation. Thus, the decomposition temperature is largely limited in air (<300°C). Zou *et al*<sup>12</sup> reported VO<sub>2</sub> synthesis from VEG decomposition at 170-200°C, the decomposition time decreased accordingly from 2 h to 15 min. In our earlier work,<sup>17</sup> VEG decomposition time could be

further shortened to 3 min when 300°C was applied, and around 33 wt% amorphous part exists in VO<sub>2</sub> compound.<sup>17</sup> The existing amorphous parts would largely hurt its thermal stability, making VO<sub>2</sub> could hardly bear 300°C-heating in air and turning into V<sub>2</sub>O<sub>5</sub> quickly.

High-temperature synthesis is of benefit for preparing highly crystallized inorganic compounds, but the easy formation of V<sub>2</sub>O<sub>5</sub> impedes to apply high temperature under air atmosphere. To eliminate or weaken the effect of energy surplus, and further avoid V<sub>2</sub>O<sub>5</sub> formation, Zhang *et al*<sup>13</sup> tried a two-step process by dividing the pyrolysis process, but the results were not so satisfying, no relatively purer and better-crystallized VO<sub>2</sub> was synthesized. Post-annealing treatment at higher temperatures (*e.g.* 500°C) can increase crystallinity, the whole synthesis could be shorted as VEG→VO<sub>2</sub> (low crystallinity)  $\xrightarrow{\text{Post-annealing}}$  VO<sub>2</sub> (high crystallinity).<sup>17</sup> To simplify the synthesis process, researchers investigated inert atmospheres (argon, nitrogen) or sealed vacuum system. Unfortunately, V<sub>2</sub>O<sub>3</sub> was usually stabilized to the detriment of VO<sub>2</sub>.<sup>11-13, 17, 19</sup> Thus, VO<sub>2</sub> synthesis through a direct VEG decomposition at high temperatures is still a challenge.

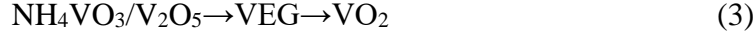
Herein, significant improvement in synthesis process comes from the design of dynamic vacuum system (DVS) (**Figure 1a**), which is created by keeping pumping during the whole annealing process. Highly crystallized VO<sub>2</sub> is obtained by merging VEG decomposition and VO<sub>2</sub> (M) crystallization at high temperatures. Inspired by our previous work,<sup>17</sup> V<sub>2</sub>O<sub>5</sub> could be perfectly reduced to VO<sub>2</sub> *via* carbo-thermal strategy in the DVS, no over-reduction (leading to V<sub>2</sub>O<sub>3</sub> formation) is found. It is believed some reductive gas (*e.g.* CO) generated in reduction process (V<sub>2</sub>O<sub>5</sub>→VO<sub>2</sub>), is removed as soon as it forms thanks to the continued pumping system, thus the second-step reduction (VO<sub>2</sub>→V<sub>2</sub>O<sub>3</sub>) is avoided. We assume the

DVS to be helpful for  $\text{VO}_2$  synthesis through a direct VEG decomposition at high temperatures.



**Figure 1.** (a) Schematic of homemade dynamic vacuum system (DVS); (b) illustration of  $\text{VO}_2$  synthesis based on "VEG preparation" and "VEG decomposition" in different atmospheres. *i: inert atmosphere,<sup>12,13,17,19</sup> ii: sealed vacuum,<sup>18</sup> iii: air,<sup>12,13,17</sup> vi: dynamic vacuum.*<sup>this work</sup>

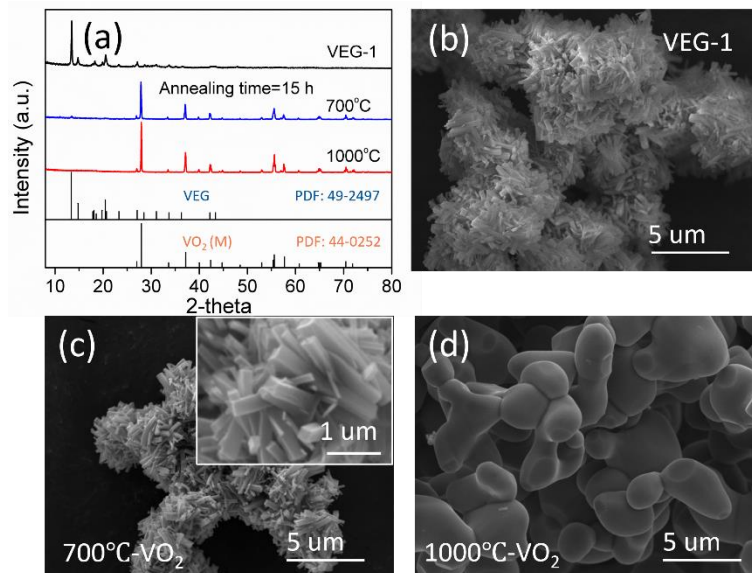
This work shows how to prepare highly crystallized  $\text{VO}_2$  with tuned morphologies (crystallite sizes and shapes). Differing from previous reports ( $\text{VEG} \rightarrow \text{VO}_2$ ), high annealing temperatures ( $>500^\circ\text{C}$ ) are *in-situ* applied to guarantee a full crystallinity, while no second step annealing process is needed. Two steps are included (**Figure 1b**): (i) VEG preparation; and (ii) VEG decomposition, as illustrated in equation 3:



In first step, three vanadium sources  $\text{NH}_4\text{VO}_3$ , homemade  $\text{V}_2\text{O}_5$ , and commercial  $\text{V}_2\text{O}_5$ , were used and reacted with EG over 2 h at  $160^\circ\text{C}$  for VEG preparation (named as VEG-1/2/3). In second step, all VEGs were annealed in the DVS with high temperatures ( $500$ ,  $700$ , and  $1000^\circ\text{C}$ ) and a long annealing time (15 h) to guarantee a 100% crystallinity of end-product  $\text{VO}_2$ ,<sup>17</sup> And vacuum pressure remains  $\sim 10^{-4}$  mbar during the whole annealing process.

Coordination agent EG plays a crucial role in valence-state reduction of vanadium. Here  $\text{V}(5+)$  in  $\text{NH}_4\text{VO}_3$  and  $\text{V}_2\text{O}_5$ , is reduced to  $\text{V}(4+)$  in VEG. After VEG-1 precursor being annealed at  $700$  and  $1000^\circ\text{C}$  for 15 h, XRD patterns (**Figure 2a**) of obtained powders match well with the standard JCPDS card (NO. 49-2497 and 44-0252), corresponding to vanadyl ethylene glycolate (VEG) and monoclinic  $\text{VO}_2(\text{M})$ , respectively. No peaks of other phases or impurities are observed, indicating  $\text{V}(4+)$  is well maintained in the DVS during high temperatures decomposition. Besides, the higher intensity of diffraction peaks implies the enhanced crystallinity with temperatures.

VEG-1 shows a spheroidal aggregate structure composed of rod-like crystallites (**Figure 2b**). And the as-prepared  $\text{VO}_2$  microstructures are presented in **Figure 2c-2d**. Interestingly, when the decomposition temperature is set to  $700^\circ\text{C}$ ,  $\text{VO}_2$  displays a similar morphology as VEG-1 precursor (same rod-like shape and size). When the temperature is  $1000^\circ\text{C}$ , the aggregated rod-like  $\text{VO}_2$  evolves into microsphere shapes ( $d \approx 3\text{-}5 \mu\text{m}$ ) with smooth surfaces (**Figure 2d**), revealing a clear and strong sintering effect due to the extensive energy from high annealing temperature.



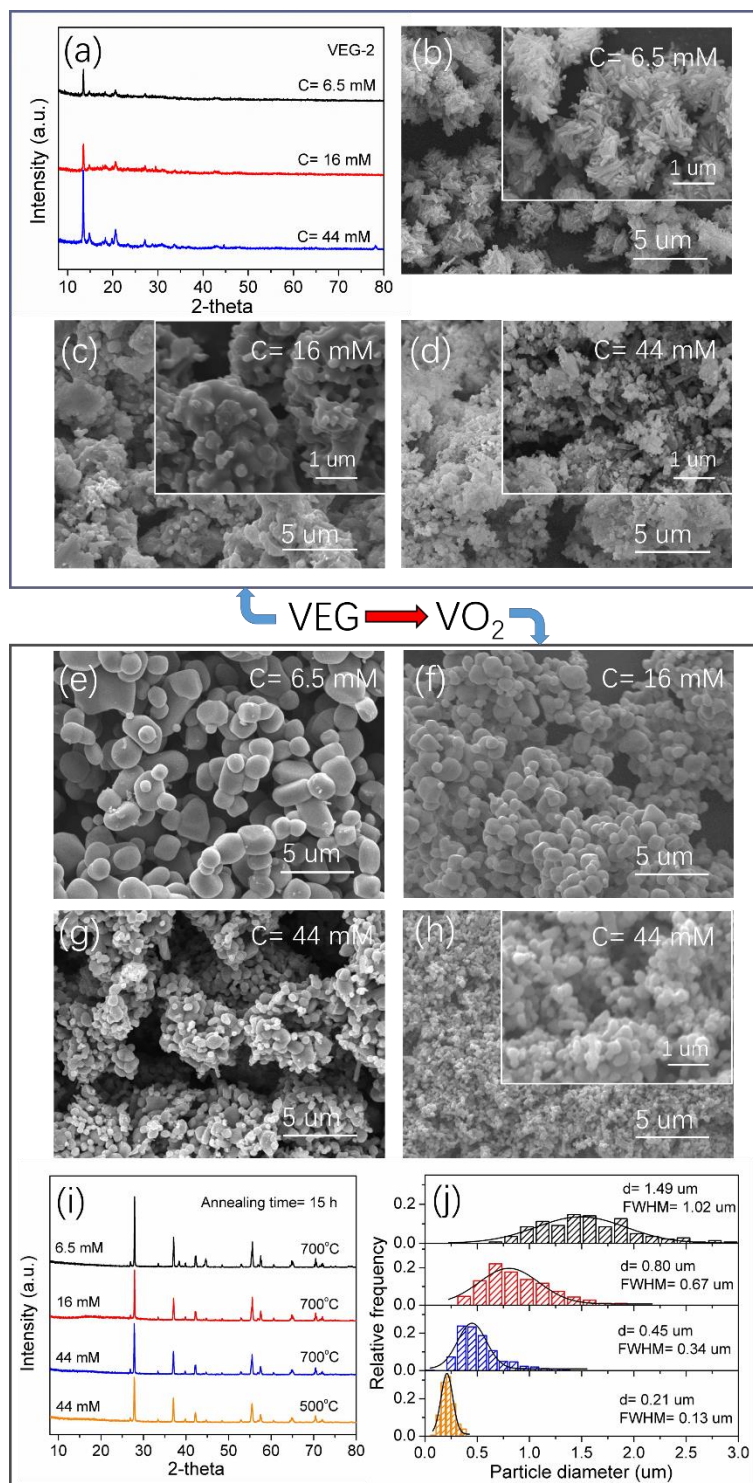
**Figure 2.** (a) XRD pattern of VEG-1 and VO<sub>2</sub>, VO<sub>2</sub> is synthesized through VEG decomposition at 700°C and 1000°C for 15 h in dynamic vacuum system (DVS), respectively; and the corresponding SEM images of (b) VEG-1, (c) 700°C-VO<sub>2</sub> and (d) 1000°C-VO<sub>2</sub>.

Overall, VEG precursor can be used for VO<sub>2</sub> synthesis through a direct annealing at high temperatures, being beneficial for its high crystallinity. More interestingly, the VO<sub>2</sub> morphology is templated by VEG morphology. Encouraged by this finding, the modified VEGs morphology was further explored following VEG→VO<sub>2</sub> route.

Homemade- and commercial-type V<sub>2</sub>O<sub>5</sub> were used as new vanadium sources for VEG preparation. The homemade V<sub>2</sub>O<sub>5</sub> with a rod-like structure originated from VEG-1 template, prepared *via* VEG→V<sub>2</sub>O<sub>5</sub> after 90 min decomposition in air,<sup>17</sup> was firstly tried. By varying V<sub>2</sub>O<sub>5</sub> concentration from 6.5, to 16 and 44 mM, the obtained VEG-2s (C= 6.5, 16, 44 mM) reveal different morphologies in **Figure 3a-3d** and **Figure S1**. VEG-2 (C= 6.5 mM) exhibits similar but smaller spheroidal aggregates (d=~2.0 μm) when comparing with VEG-1 (d=~5.0 μm). As V<sub>2</sub>O<sub>5</sub> concentration increases to 16 mM, the VEG rods turn into small spherical

particles. Such phenomenon is more obvious when  $V_2O_5$  concentration reaches 44 mM, the rod-like VEG-2 is further damaged and becomes an aggregate of small nanoparticles, showing a loose morphology (**Figure 3d**). In polyol method, the particle size is formed through a homogeneous nucleation separated from growth step. A higher vanadium concentration probably leads to more crystallized nuclei and rapid growth of particles, thus produces smaller particles.<sup>20</sup>





**Figure 3.** (a) XRD pattern of VEG-2, synthesized with different concentrations of homemade  $\text{V}_2\text{O}_5$  ( $C = 6.5, 16$  and  $44$  mM) in EG; (b-d) the corresponding VEG morphologies. SEM images of  $\text{VO}_2$ ,

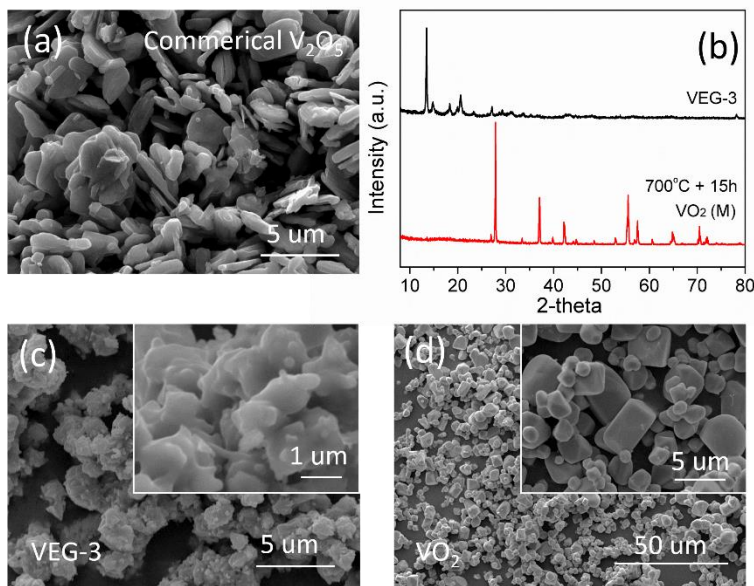
*synthesized from VEG-2s decomposition: (e)  $C = 6.5 \text{ mM}$ ,  $700^\circ\text{C}$ ; (f)  $C = 16 \text{ mM}$ ,  $700^\circ\text{C}$ ; (g)  $C = 44 \text{ mM}$ ,  $700^\circ\text{C}$ ; (h)  $C = 44 \text{ mM}$ ,  $500^\circ\text{C}$ ; the corresponding (i) XRD and (j) particle size.*

Following  $\text{VEG} \rightarrow \text{VO}_2$ , the three VEG-2 samples were annealed for 15 h in DVS at  $700^\circ\text{C}$ , respectively. The corresponding morphologies are shown in **Figure 3e-3g**. XRD patterns (**Figure 3i**) indicate that all samples are pure  $\text{VO}_2$  (M) without any  $\text{V}_2\text{O}_3$  or  $\text{V}_2\text{O}_5$  observation, meaning VEG-2 can also decompose into  $\text{VO}_2$  successfully at high temperatures. It proves a broad applicability and great adaptability of this dynamic vacuum system. All  $\text{VO}_2$  samples exhibit similar spherical shapes, and their particle size decreases from 1.49 to 0.80 and  $0.45 \text{ }\mu\text{m}$  as  $\text{V}_2\text{O}_5$  concentration increases from 6.5 to 16 and 44 mM (**Figure 3j**). Such decrease is accompanied by a decrease of full width at half maximum (FWHM) of size distribution from 1.02 to 0.67 and  $0.63 \text{ }\mu\text{m}$ . In another word, the sintering effect is weakened as VEG microstructure collapses. Although the high synthesis temperature is beneficial to a high crystallinity, it leads to large particle size. To decrease crystallite size, the decomposition temperature is lowered to  $500^\circ\text{C}$ , which is still high enough to guarantee a full crystallinity.<sup>17</sup> As illustrated in **Figure 3h**,  $\text{VO}_2$  particle size decreases to  $0.21 \text{ }\mu\text{m}$  with a narrower size distribution (FWHM =  $0.13 \text{ }\mu\text{m}$ ). More detailed SEM images are presented in **Figure S2**. It is believed, as demonstrated by current studies, that smaller but highly crystallized  $\text{VO}_2$  particles can be obtained by simply tuning annealing temperatures or time.

In fact, homemade  $\text{V}_2\text{O}_5$  is quite attractive not only because of tuning of VEG morphology but also due to its easy elemental doping at the starting of polyol process. It has already been proved that some elements, such as Nb, Ti, Al, could be introduced into VEG-2 and delivered into homemade  $\text{V}_2\text{O}_5$ .<sup>18, 25</sup> Especially for Nb doping, the transition

temperature could be lowered to room temperature ( $\sim 25^{\circ}\text{C}$ ).<sup>25</sup> It is reasonable to deduce that the doped  $\text{VO}_2$  can be synthesized *via* VEG-2 decomposition (**Figure S3**). Thus  $\text{VO}_2$  transition temperature could be tuned purposely using this method.

In parallel, commercial  $\text{V}_2\text{O}_5$  with a flaky structure (**Figure 4a**) was also explored for comparison. VEG-3 and  $\text{VO}_2$  were successively prepared (**Figure 4b**). VEG-3 displays a new morphology, an aggregate with a flaky structure (**Figure 4c**). And the as-prepared  $\text{VO}_2$  (VEG-3 $\rightarrow\text{VO}_2$ ) shows a mixture of different polyhedral structures and spherical shapes with a size of around 2-4.5  $\mu\text{m}$  (**Figure 4d**). The obtained  $\text{VO}_2$  particle sizes are quite large with poor uniformity.



**Figure 4.** (a) SEM images of commercial  $\text{V}_2\text{O}_5$ ; (b) XRD pattern of VEG-3 and  $\text{VO}_2$  (M); the corresponding SEM images of (c) VEG-3 and (d)  $\text{VO}_2$ .

In all, VEG shape plays a crucial role in  $\text{VO}_2$  microstructure during decomposition. The ideal  $\text{VO}_2$  synthesis through precursor decomposition usually includes three stages: (i) precursor

decomposition, (ii) burst nucleation, and (iii) size focusing.<sup>21</sup> When vanadium precursor is heated to a critical temperature, the precursor decomposes instantaneously and creates an excess of monomers to form a highly supersaturated reaction system. Followed with a burst-nucleation stage, a large number of nuclei grow simultaneously, and quickly consume the monomers, restraining further growth of particles (size focusing). In our work, a series of distance between precursor monomers occurs in different VEG. VEG-1/3 display a dense and compact aggregate structure, meaning those generated monomers are localized together in a limited space, a fast nuclei growth takes place because of the sufficient monomers, and further leads to larger VO<sub>2</sub> particles. However, VEG-2 shows a relative less dense aggregate morphology, especially for VEG-2 (C= 44 mM). The precursor monomers are separated with a larger distance in the loose structure, resulting in a prolonged monomer step consumption to the detriment of the size growth, thus resulting in the formation of smaller particles.

In summary, a homemade dynamic vacuum system is proposed and applied for synthesis of highly crystallized VO<sub>2</sub> (M) at high temperatures (>500°C). We solve the unstable challenge of vanadium valence in VO<sub>2</sub> (4+) synthesis, *i.e.* V<sub>2</sub>O<sub>3</sub> (3+) formation at inert atmospheres or V<sub>2</sub>O<sub>5</sub> (5+) formation in air at high temperatures. The decomposition and crystallization steps merge into one without post-annealing treatment. Using homemade V<sub>2</sub>O<sub>5</sub>, well-defined and highly crystallized VO<sub>2</sub> NPs (d= ~210 nm) with a narrow distribution are synthesized at high temperatures (500°C). In addition, thanks to the DVS, the high reproducibility guarantees a large-scale preparation of VO<sub>2</sub> powder as well as doping.

ASSOCIATED CONTENT

**Supporting Information**

Details SEM images of VEG-2 and VO<sub>2</sub>, prepared following VEG-2→VO<sub>2</sub>. XRD patterns of pure and Nb-doped VO<sub>2</sub>, synthesized following VEG-2→VO<sub>2</sub>.

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### Notes

The authors declare no competing financial interest

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### Author Contributions

Shian Guan: Conceptualization, Characterization, Writing. Nicolas Penin: Vacuum system design, Characterization. Oudomsack Viraphong: Vacuum system design. Manuel Gaudon: Supervision. Aline Rougier: Supervision. All authors contributed to the discussions and revisions of the manuscript.

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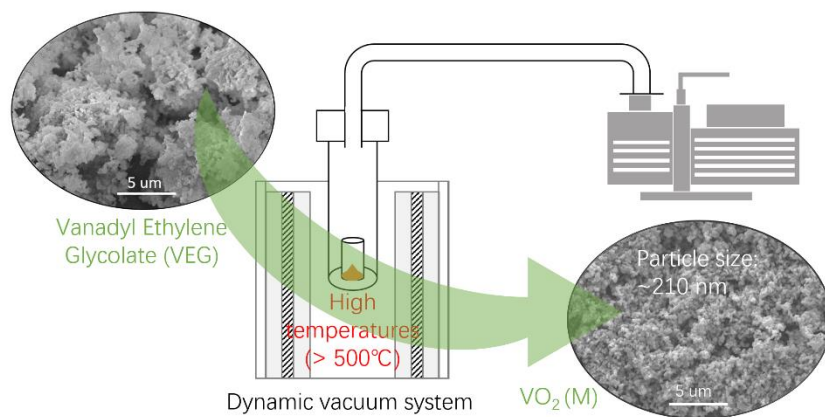
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## Table of Contents



Graphical abstract: Highly crystallized micro/nano VO<sub>2</sub> synthesis through a direct VEG decomposition