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Synthesis and Characterization of Micro/nano VO₂ (M) Through Vanadyl Ethylene Glycolate (VEG)

Decomposition

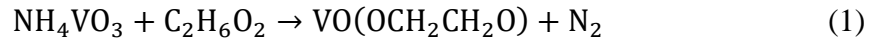
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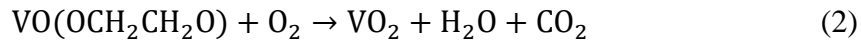
Vanadium dioxide (VO₂) undergoes a reversible metal-insulator transition (MIT) assisted with crystallographic structure change from monoclinic (M) to rutile (R) phase at ~68°C, accompanied by remarkable modifications in electronic and optical properties.¹⁻³ VO₂ has been attracting much attention owing 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.* V₂O₅, VO₂, V₃O₇, V₆O₁₃, V₂O₃). The existence of multiple oxidation states (3+, 4+, 5+) turns into a synthetic challenge of VO₂. Besides, VO₂ in a valence state of 4+ appears very sensitive to oxydo-reductions. Micro/nano-scale and highly crystallized VO₂ are more favorable, leading to excellent thermochromic performances, *e.g.* narrower hysteresis and larger amplitude in properties changes at the transition.^{4,5} 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 VO₂ crystallinity with moderate micro-nano particle size.

A variety of approaches were explored to prepare VO₂.⁶⁻¹⁰ Thermal pyrolysis gives rise to the prospect of mass production. Vanadyl ethylene glycolate (VEG, VO(OCH₂CH₂O)) is a widely used vanadium precursor for VO_x synthesis.¹¹⁻¹⁵ Ammonium metavanadate (NH₄VO₃) could be reduced by ethylene glycol (EG, C₂H₆O₂) with the consequent formation of VEG complex (V⁴⁺),²⁵ 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.^{11, 14, 17} 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 VO₂ 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 V₂O₅ formation. Thus, the decomposition temperature is largely limited in air (<300°C). Zou *et al*¹² reported VO₂ synthesis from VEG decomposition at 170-200°C, the decomposition time decreased accordingly from 2 h to 15 min. In our earlier work,¹⁷ VEG decomposition time could be

further shortened to 3 min when 300°C was applied, and around 33 wt% amorphous part exists in VO₂ compound.¹⁷ The existing amorphous parts would largely hurt its thermal stability, making VO₂ could hardly bear 300°C-heating in air and turning into V₂O₅ quickly.

High-temperature synthesis is of benefit for preparing highly crystallized inorganic compounds, but the easy formation of V₂O₅ impedes to apply high temperature under air atmosphere. To eliminate or weaken the effect of energy surplus, and further avoid V₂O₅ formation, Zhang *et al*¹³ tried a two-step process by dividing the pyrolysis process, but the results were not so satisfying, no relatively purer and better-crystallized VO₂ was synthesized. Post-annealing treatment at higher temperatures (*e.g.* 500°C) can increase crystallinity, the whole synthesis could be shorted as VEG→VO₂ (low crystallinity) $\xrightarrow{\text{Post-annealing}}$ VO₂ (high crystallinity).¹⁷ To simplify the synthesis process, researchers investigated inert atmospheres (argon, nitrogen) or sealed vacuum system. Unfortunately, V₂O₃ was usually stabilized to the detriment of VO₂.^{11-13, 17, 19} Thus, VO₂ 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 VO₂ is obtained by merging VEG decomposition and VO₂ (M) crystallization at high temperatures. Inspired by our previous work,¹⁷ V₂O₅ could be perfectly reduced to VO₂ *via* carbo-thermal strategy in the DVS, no over-reduction (leading to V₂O₃ formation) is found. It is believed some reductive gas (*e.g.* CO) generated in reduction process (V₂O₅→VO₂), is removed as soon as it forms thanks to the continued pumping system, thus the second-step reduction (VO₂→V₂O₃) is avoided. We assume the

DVS to be helpful for VO_2 synthesis through a direct VEG decomposition at high temperatures.

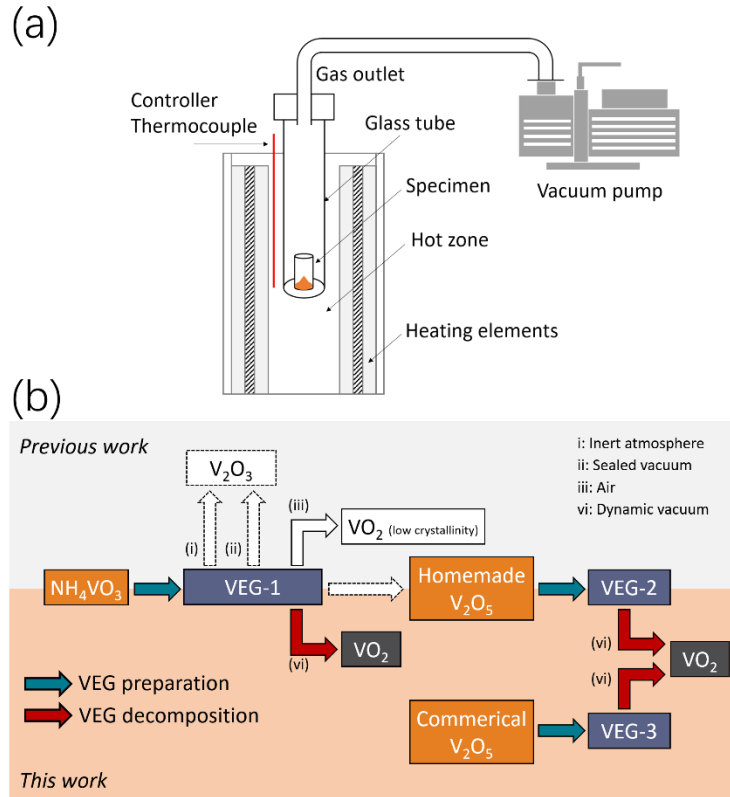
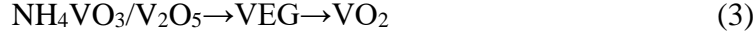


Figure 1. (a) Schematic of homemade dynamic vacuum system (DVS); (b) illustration of VO_2 synthesis based on "VEG preparation" and "VEG decomposition" in different atmospheres. *i*: inert atmosphere,^{12,13,17,19} *ii*: sealed vacuum,¹⁸ *iii*: air,^{12,13,17} *vi*: dynamic vacuum.^{this work}

This work shows how to prepare highly crystallized 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 NH_4VO_3 , homemade V_2O_5 , and commercial V_2O_5 , were used and reacted with EG over 2 h at 160°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°C) and a long annealing time (15 h) to guarantee a 100% crystallinity of end-product VO_2 ,¹⁷ 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 NH_4VO_3 and V_2O_5 , is reduced to $\text{V}(4+)$ in VEG. After VEG-1 precursor being annealed at 700 and 1000°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 VO_2 microstructures are presented in **Figure 2c-2d**. Interestingly, when the decomposition temperature is set to 700°C , VO_2 displays a similar morphology as VEG-1 precursor (same rod-like shape and size). When the temperature is 1000°C , the aggregated rod-like 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.

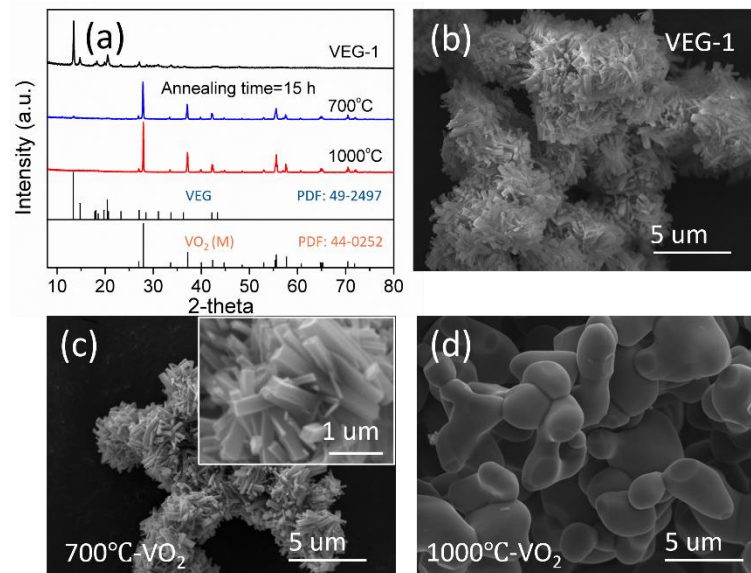


Figure 2. (a) XRD pattern of VEG-1 and VO₂, VO₂ is synthesized through VEG decomposition at 700°C and 1000°C for 15 h in dynamic vacuum system (DVS), respectively; and the corresponding SEM images of (b) VEG-1, (c) 700°C-VO₂ and (d) 1000°C-VO₂.

Overall, VEG precursor can be used for VO₂ synthesis through a direct annealing at high temperatures, being beneficial for its high crystallinity. More interestingly, the VO₂ morphology is templated by VEG morphology. Encouraged by this finding, the modified VEGs morphology was further explored following VEG→VO₂ route.

Homemade- and commercial-type V₂O₅ were used as new vanadium sources for VEG preparation. The homemade V₂O₅ with a rod-like structure originated from VEG-1 template, prepared *via* VEG→V₂O₅ after 90 min decomposition in air,¹⁷ was firstly tried. By varying V₂O₅ 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 V₂O₅ 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.²⁰

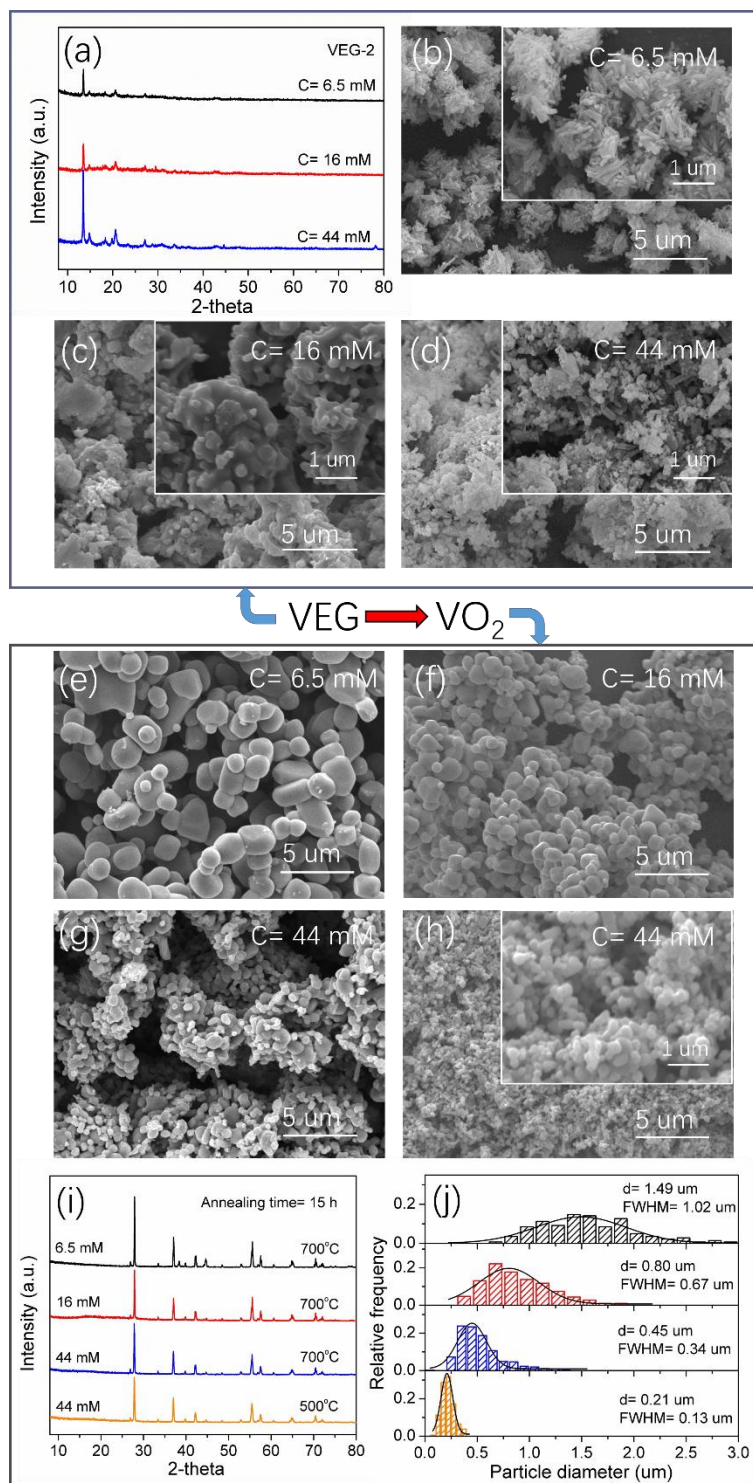


Figure 3. (a) XRD pattern of VEG-2, synthesized with different concentrations of homemade V_2O_5 ($C = 6.5, 16$ and 44 mM) in EG; (b-d) the corresponding VEG morphologies. SEM images of VO_2 ,

synthesized from VEG-2s decomposition: (e) C= 6.5 mM, 700°C; (f) C= 16 mM, 700°C; (g) C=44 mM, 700°C; (h) C= 44 mM, 500°C; the corresponding (i) XRD and (j) particle size.

Following VEG→VO₂, the three VEG-2 samples were annealed for 15 h in DVS at 700°C, respectively. The corresponding morphologies are shown in **Figure 3e-3g**. XRD patterns (**Figure 3i**) indicate that all samples are pure VO₂ (M) without any V₂O₃ or V₂O₅ observation, meaning VEG-2 can also decompose into VO₂ successfully at high temperatures. It proves a broad applicability and great adaptability of this dynamic vacuum system. All VO₂ samples exhibit similar spherical shapes, and their particle size decreases from 1.49 to 0.80 and 0.45 μm as V₂O₅ 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 μm. 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°C, which is still high enough to guarantee a full crystallinity.¹⁷ As illustrated in **Figure 3h**, VO₂ particle size decreases to 0.21 μm with a narrower size distribution (FWHM= 0.13 μm). More detailed SEM images are presented in **Figure S2**. It is believed, as demonstrated by current studies, that smaller but highly crystallized VO₂ particles can be obtained by simply tuning annealing temperatures or time.

In fact, homemade V₂O₅ 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 V₂O₅.^{18, 25} Especially for Nb doping, the transition

temperature could be lowered to room temperature ($\sim 25^\circ\text{C}$).²⁵ It is reasonable to deduce that the doped VO_2 can be synthesized *via* VEG-2 decomposition (**Figure S3**). Thus VO_2 transition temperature could be tuned purposely using this method.

In parallel, commercial V_2O_5 with a flaky structure (**Figure 4a**) was also explored for comparison. VEG-3 and 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 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 μm (**Figure 4d**). The obtained VO_2 particle sizes are quite large with poor uniformity.

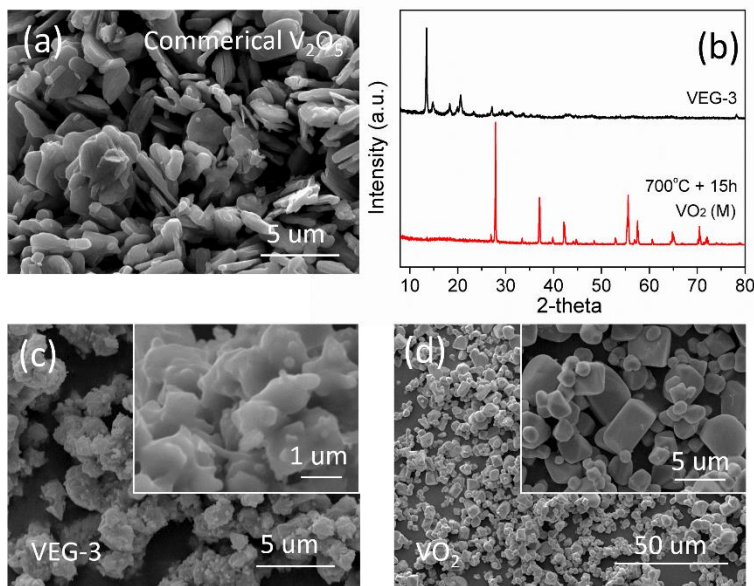


Figure 4. (a) SEM images of commercial V_2O_5 ; (b) XRD pattern of VEG-3 and VO_2 (M); the corresponding SEM images of (c) VEG-3 and (d) VO_2 .

In all, VEG shape plays a crucial role in VO_2 microstructure during decomposition. The ideal VO_2 synthesis through precursor decomposition usually includes three stages: (i) precursor

decomposition, (ii) burst nucleation, and (iii) size focusing.²¹ 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 VO₂ 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 VO₂ (M) at high temperatures (>500°C). We solve the unstable challenge of vanadium valence in VO₂ (4+) synthesis, *i.e.* V₂O₃ (3+) formation at inert atmospheres or V₂O₅ (5+) formation in air at high temperatures. The decomposition and crystallization steps merge into one without post-annealing treatment. Using homemade V₂O₅, well-defined and highly crystallized VO₂ 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 VO₂ powder as well as doping.

ASSOCIATED CONTENT

Supporting Information

Details SEM images of VEG-2 and VO₂, prepared following VEG-2→VO₂. XRD patterns of pure and Nb-doped VO₂, synthesized following VEG-2→VO₂.

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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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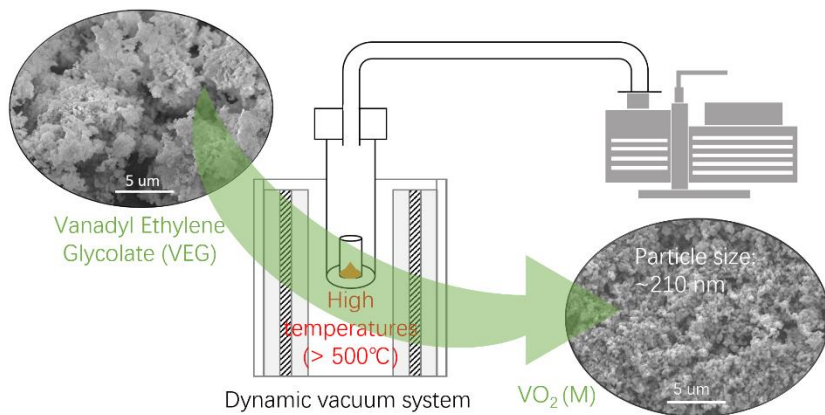
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Graphical abstract: Highly crystallized micro/nano VO₂ synthesis through a direct VEG decomposition