Thermolysis-Driven Growth of Vanadium Oxide Nanostructures Revealed by In Situ Transmission Electron Microscopy: Implications for Battery Applications

Dnyaneshwar S. Gavhane, Atul D. Sontakke, and Marijn A. van Huis*

ABSTRACT: Understanding the growth modes of 2D transition-metal oxides through direct observation is of vital importance to tailor these materials to desired structures. Here, we demonstrate thermolysis-driven growth of 2D V$_2$O$_5$ nanostructures via in situ transmission electron microscopy (TEM). Various growth stages in the formation of 2D V$_2$O$_5$ nanostructures through thermal decomposition of a single solid-state NH$_4$VO$_3$ precursor are unveiled during the in situ TEM heating. Growth of orthorhombic V$_2$O$_5$ 2D nanosheets and 1D nanobelts is observed in real time. The associated temperature ranges in thermolysis-driven growth of V$_2$O$_5$ nanostructures are optimized through in situ and ex situ heating. Also, the phase transformation of V$_2$O$_5$ to VO$_2$ was revealed in real time by in situ TEM heating. The in situ thermolysis results were reproduced using ex situ heating, which offers opportunities for upscaling the growth of vanadium oxide-based materials. Our findings offer effective, general, and simple pathways to produce versatile 2D V$_2$O$_5$ nanostructures for a range of battery applications.

KEYWORDS: in situ transmission electron microscopy, thermolysis, 2D materials, V$_2$O$_5$, VO$_2$, ex situ growth

INTRODUCTION

Vanadium pentoxide (V$_2$O$_5$), the semiconductor in the transition-metal oxides family with a two-dimensional (2D)-layered structure, has attracted significant attention from the scientific community. Featuring high theoretical capacity, low cost, abundant source, good safety, and easy preparation methods, V$_2$O$_5$ has attracted enormous interest in rechargeable batteries. Because of the typical lamellar crystal structure of orthorhombic V$_2$O$_5$, it has been extensively studied for application as a lithium-ion battery cathode material. Besides this, V$_2$O$_5$ has also attracted great attention as a potential candidate for catalysts and gas sensor applications.

Considering its exceptional and versatile role in various applications, a variety of synthesis methods to prepare V$_2$O$_5$ nanostructures has been developed including hydrothermal/solvothermal synthesis, sol–gel processing, template-based methods, electrochemical deposition, etc. Nanostructures of V$_2$O$_5$ consist of 1D nanorods, nanobelts, nanofibers, 2D nanosheets, 3D hollow porous, and hierarchical nanostructures. One-dimensional V$_2$O$_5$ nanostructures are prepared mostly with sol–gel and hydrothermal methods, which are relatively simple, using a V$_2$O$_5$ powder or V$_2$O$_5$ crystals as a precursor. Two-dimensional nanosheets are prepared with the liquid exfoliation of bulk V$_2$O$_5$ crystals and the hydrothermal method. All of these V$_2$O$_5$ nanostructures that are grown through different methods are continuously being used in rechargeable battery applications.

Thermolysis of ammonium metavanadate (AMV), an amorphous single solid-state precursor, produces crystalline V$_2$O$_5$ structures. Decomposing AMV precursor is a quite straightforward and feasible method to produce V$_2$O$_5$ nanostructures with no complex requirements or conditions. This unique and simple synthesis method has not been explored significantly compared to the conventional routes. An exploration of the underlying growth mechanisms of V$_2$O$_5$ nanostructures through the thermolysis of an amorphous single solid-state precursor provides an extraordinary opportunity to grow these nanostructures with great control. Real-time observations at the atomic scale of various physical and chemical processes of phase transitions, growth, and sublimation can be achieved by in situ transmission electron microscopy (TEM) with high spatial and temporal resolution. The in situ TEM technique has been extensively used to study the dynamic processes in various materials. In situ TEM growth of MoS$_2$ through thermolysis of a single solid-state precursor was observed in several experiments. In other experiments, 2D WS$_2$ vertical and horizontal layers were grown...
in TEM through thermal decomposition of a single solid-state precursor. Metal oxide nanomaterials were also observed to grow during in situ TEM experiments. In this work, with the combination of in situ TEM heating and thermolysis of ammonium metavanadate (NH$_4$VO$_3$) inside the TEM, we have observed the real-time growth of crystalline V$_2$O$_5$ nanostructures on the SiNx membrane of the heating chip. The heating of the precursor inside the TEM shows multiple growth stages to finally yield the shape of crystalline V$_2$O$_5$ nanostructures. The formation of mesoporous structures on an amorphous precursor due to the removal of NH$_3$ and H$_2$O to the crystallization at a small scale was observed in real time during the thermolysis. Two different types of final nanostructures are observed during this in situ TEM thermolysis process for the V$_2$O$_5$; 1D nanobelts and 2D nanosheets. The phase transformation of 2D V$_2$O$_5$ to 3D VO$_2$ nanostructures is also observed at elevated temperatures in the in situ TEM experiment. All these intermediate processes cannot be observed and controlled by means of conventional growth methods, while with in situ TEM, it is possible to observe these in real time and to gain control over the different growth stages of V$_2$O$_5$ nanostructures to obtain the desired materials. These in situ TEM results can be used to fine-tune the growth parameters during the thermolysis to design V$_2$O$_5$ nanomaterials, which are highly relevant for rechargeable battery applications.

### EXPERIMENTAL SECTION

**In Situ Transmission Electron Microscopy.** In situ TEM heating experiments were performed on a DENsolutions heating holder and Wildfire S3 heating chip with electron transparent ~30 nm thick SiNx windows. Before the in situ TEM heating, the samples were prepared by dissolving high purity NH$_4$VO$_3$ (AMV) (Sigma-Aldrich, 99.9%) in ethanol to form 5 vol% solutions. These solutions were sonicated for 15 min, drop cast onto the plasma cleaned heating chip, and dried in air. The heating chip was then introduced into an FEI Talos F200X TEM operated at 200 kV for imaging. In all the TEM heating experiments, samples were preheated to 100 °C for at least 10 min to remove organic residues. The temperature was then increased from 100 to 700 °C in steps of 20 °C. During in situ TEM heating, after each 100 °C, the temperature was held constant to observe and image growth changes in the mesoporous structure at 440 °C, evident from the appearance of dots in the FFT in the inset. During in situ TEM heating, after each 100 °C, the temperature was held constant to observe and image growth changes in the mesoporous structure at 440 °C, evident from the appearance of dots in the FFT in the inset. The corresponding FFT in the inset shows an increased number of dots. (i) The TEM image of one of the V$_2$O$_5$ nanobelts (NB) grown out of AMV precursor. (j) The high-resolution TEM image of the nanobelt showing atomic columns. (k) The HAADF-STEM image of the V$_2$O$_5$ structures from panel d. (l–m) STEM-EDS elemental maps for vanadium (V) and oxygen (O) in V$_2$O$_5$ structures. (n) Scheme presenting the overall process of thermal decomposition of AMV precursor to fully grown V$_2$O$_5$ structures with temperature.
\[ 2\text{NH}_4\text{VO}_3(s) \xrightarrow{\Delta} 2\text{NH}_3(g) \uparrow + \text{H}_2\text{O}(g) \uparrow + \text{V}_2\text{O}_5(s) \]

(400 – 500°C)  

The reaction is much more complicated than shown in the above equation where different intermediate products at intermediate temperatures can be obtained, but these are mostly very poorly crystalline or even amorphous. This suggests that thermal decomposition of the AMV precursor leads to the growth of the only pure crystalline structure, V_2O_5. This is one of the easiest and less complex methods to grow crystalline V_2O_5 structures, which can be used for various applications. Apart from one of the in situ TEM experiments where amorphous V_2O_5 was transferred to crystalline orthorhombic V_2O_5, not

**RESULTS AND DISCUSSION**

**Thermal Decomposition of Ammonium Metavanadate.** A single solid-state precursor, ammonium metavanadate (NH_4VO_3, abbreviated as AMV), was heated in the in situ TEM experiments to observe and investigate the growth of crystalline vanadium oxide structures, V_2O_5 and VO_2, using a dedicated in situ heating holder. The previous research reported on the thermal decomposition of AMV in different gaseous environments (vacuum, argon, nitrogen, and air) to produce V_2O_5, which can be shown with the following simple equation:

\[ 2\text{NH}_4\text{VO}_3(s) \xrightarrow{\Delta} 2\text{NH}_3(g) \uparrow + \text{H}_2\text{O}(g) \uparrow + \text{V}_2\text{O}_5(s) \]

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many attempts were made to observe the growth of vanadium oxide-based materials via in situ TEM. The V$_2$O$_5$ nanobelts$^{59}$ and nanosheets$^{38,60,61}$ prepared with this method of thermal decomposition of AMV precursor show to be an excellent candidate as a cathode for Li-ion battery applications in comparison to the conventionally grown nanobelts and nanosheets using amorphous or crystal V$_2$O$_5$ precursors.$^{17,19,56,62,63}$ Although precise control over the thickness and growth of the nanobelts or nanosheets is not a strong feature of this method, it provides a great opportunity to observe and investigate the growth of V$_2$O$_5$-based structures through in situ TEM experiments with no requirements of specialized instruments. Besides this, the synthesis route can be likely scaled up and fine-tuned with the help of the in situ TEM findings.

**In Situ TEM Growth of V$_2$O$_5$ Nanostructures.** An AMV precursor in ethanol solution was drop cast onto the ~30 nm thick SiN$_x$ membrane of a TEM heating chip and dried in air to prepare samples for in situ TEM experiments. With the help of a controlled heating setup, the prepared heating chip was introduced into the TEM column. The schematics in Figure S1 depict the whole scenario of preparing a heating chip for the in situ TEM experiments. To remove any residues present in the solvent on the heating chip, it was heated from room temperature to 100 °C for ~10 min (see Figure S2 and Supporting Note 1 in the Supporting Information for more details). The temperature was then increased to 700 °C in steps of 20 °C withholding the temperature at different stages for a few minutes to monitor and capture the frames of the changes in the precursor.

A brief story of the growth of crystalline V$_2$O$_5$ structures through thermal decomposition of a single, solid-state, and amorphous AMV precursor with in situ TEM heating is shown in Figure 1. The amorphous AMV precursor at room temperature (RT) in TEM gives an image as shown in Figure 1a. Figure 1e shows a close-up look at the amorphous AMV precursor along with the diffuse ring in the fast Fourier transform (FFT) shown in the inset, from which it is evident that the precursor is amorphous prior to any heat treatment. With the temperature reaching 300 °C in Figure 1b, the amorphous precursor starts to form a mesoporous structure by forming holes that are clearer in Figure 1f and the structure remains amorphous as is evident from the absence of any bright dots in the FFT in the inset in Figure 1f. The first appearance of the crystalline structures on the mesoporous amorphous structure was captured at a temperature of 440 °C. The high-magnification TEM image along with the presence of dots in the FFT in the inset in Figure 1g manifests the amorphous-to-crystalline transition at 440 °C. Figure 1d shows the emergence of well-defined shapes of nanobelts (NBs) of crystalline V$_2$O$_5$, which becomes clearer in Figure 1h and with the larger number of bright spots in FFT in the inset. The V$_2$O$_5$ NBs are seen to be grown along the $b$ axis as shown in Figure 1i. A close inspection at the edges of the V$_2$O$_5$ NB in Figure 1i suggests that it has a multilayer configuration, which is typical of the structure of an NB. Figure 1j shows the high-resolution TEM (HRTEM) image from the part of the V$_2$O$_5$ NB in Figure 1i. This shows the typical arrangements of atomic lattices in orthorhombic V$_2$O$_5$ structures.

A slightly zoomed-in HAADF-STEM image of the grown V$_2$O$_5$ structures at 500 °C, along with the STEM-EDS maps for vanadium and oxygen, is shown in Figure 1k–m, respectively. The schematic in Figure 1n represents the overall process of the growth of crystalline V$_2$O$_5$ structures from amorphous precursor with increasing temperatures. The mesoporous structure forms after heating the precursor to 300 °C after the removal of NH$_3$ and H$_2$O as mentioned in eq 1. This becomes clearer once the crystallization of V$_2$O$_5$ starts after heating to 440 °C as evidenced by the difference in contrast as seen in Figure 1c. Increasing the temperature further to 500 °C forms fully grown, nicely defined, and crystallized V$_2$O$_5$ structures.

The in situ TEM observations suggest that there are different types in the final morphology of the V$_2$O$_5$ structures, which can be subdivided into 1D NBs and 2D nanosheets (NSs). Figure 1 shows the dominant growth of few-layered 1D NBs of V$_2$O$_5$, whereas Figure 2 shows the growth of V$_2$O$_5$ structures progressed along 2D, which are designated as NSs. Figure 2 shows the gradual growth of crystalline V$_2$O$_5$ structures in a completely independent experiment, at the same temperatures shown in Figure 1 but with a major difference in the final morphology. The blurred TEM image in Figure 2a at RT along with the corresponding FFT in the inset of Figure 2e confirms the amorphous nature of the AMV precursor. Figure 2b,i confirms the formation of the porous structure of the precursor at 300 °C after the removal of NH$_3$ and H$_2$O molecules as mentioned in an earlier section. Crystallization of V$_2$O$_5$ starts to appear at 440 °C, which is evident from the clear appearance of lattice fringes in Figure 2g and the increased number of bright spots in the FFT in the inset of Figure 2g, which gives the contrast difference in Figure 2c. Figure 2d shows fully grown crystalline V$_2$O$_5$ structures at 500 °C, which is different from the structures (NBs) seen in Figure 1d. One of the nicely crystalline structures is shown in Figure 2h, which gives an impression of a few-layered 2D nanosheet. Figure 2j shows an image of typical NBs observed at a different location on the heating chip at the temperature of 500 °C. The colors overlayed in Figure 2j on the V$_2$O$_5$ structures (red and dark cyan, respectively), along with the schematic models, suggest the one-directional growth of NBs, whereas the golden yellow color overlayed on the V$_2$O$_5$ structure, and the schematic model in Figure 2k, proposes the 2D growth of NSs. Figure 2l depicts the HAADF-STEM image and EDS maps for vanadium and oxygen for the same area as shown in Figure 2d, which also helps to confirm the observed structures of V$_2$O$_5$. A typical atomic column image for orthorhombic V$_2$O$_5$ along with the FFT is shown in Figure 2m. A filtered TEM image of the atomic columns in V$_2$O$_5$ is matched with the simulated image and atomic model for orthorhombic V$_2$O$_5$ in Figure 2n. This suggests that the observed image is visualized along the $c$ axis. Figure 2o shows the sketch of an orthorhombic unit cell of V$_2$O$_5$. The highly resolved atomic column images of V$_2$O$_5$ are viewed through the $c$ axis direction of the unit cell. Most of the NBs and NSs are oriented in the [001] zone axis, which is the basal plane, with a few of them oriented in other directions as well. However, we specifically choose to monitor those that are oriented in the [001] zone axis to obtain better images and hence obtain a better understanding of the crystal structure.

It was found that the electron beam did not have a significant influence on the observations, which became clear from reference measurements (see Supporting Note 2 and Supporting Figure S3): after keeping one of the precursor areas on the heating chip under the exposure of the electron beam at room temperature for more than 10 min, it did not lead to any significant changes in it, as evidenced by the absence of any visible lattice fringes in the TEM images in Figure S3a, b. A similar process of the thermal decomposition of AMV precursor as observed in the in situ heating with continuous exposure of precursor to the electron beam is observed when the precursor
was kept away from the electron beam by blanking it during the entire period of heating (see Figure S3c–f and Supporting Note 2).

Several in situ TEM experiments were carried out in which both these structures of V$_2$O$_5$ (NBs and NSs) are observed on the same heating chip and at the same locations in mixed forms. This can be the result of multiple factors, out of which the thickness of the AMV precursor before heating could be one. In our previous work on WS$_2$ growth through thermolysis, we observed the selective growth of vertical and horizontal WS$_2$ flakes depending on the thickness of the precursor. In the present study, however, controlling the thickness of AMV precursor was not a straightforward task, and besides that, both structures are observed to grow in a mixture without a clear clue on how to gain control over the one type of structure. This keeps an interesting question open for a further scientific explanation to obtain the desired type of growth of V$_2$O$_5$ through this clean method. Because of the random mixture of these morphologies, it is difficult to specify the distribution of them within the sample, but for all of the experiments, the appearance of growth of NBs and NSs is similar.

Real-time observations of the growth of nanostructured materials provide interesting and vital information with the help of which understanding of and control over the growth process can be gained much more efficiently. The time-series frames captured at different growth stages for V$_2$O$_5$ NSs are presented in Figure 3a. The movie (Supporting Movie1) was recorded at the midway temperature of 460 °C after the crystalline V$_2$O$_5$ grows out of an amorphous precursor. Movie frames recorded after 0, 6, 11, and 19 s are displayed in Figure 3a and show the gradual in-plane growth of the NS in two directions. The zeroth second in the first frame in Figure 3a is indexed to show the beginning of the growth of NS, and the following times refer to the different growth stages. It can be seen from the frames in Figure 3a that the NS grows with sharp edges and corners with good crystallinity. Figure 3b shows a filtered image from the last frame of the movie, which displays atomic columns in the orthorhombic V$_2$O$_5$ NS that is oriented horizontally parallel to the SiN$_x$ membrane of the heating chip. In all of the in situ experiments, it has been observed that almost all of the V$_2$O$_5$ structures are lying flat on the SiN$_x$ membrane with a c axis parallel to the viewing direction. This is evident from all of the figures (Figures 1, 2, and 3) discussed in earlier sections. The FFT in the inset of Figure 3b displays the single-crystalline nature of the grown orthorhombic V$_2$O$_5$ NS. The multicolored contour maps in Figure 3c showing the time evolution give an idea about the average growth of the V$_2$O$_5$ structures. This show that, during the growth, the area of the NS initially increases fast, while it grows relatively slowly further on as shown in the plot in Figure 3d. The growth rate plot in Figure 3e shows that it increases sharply for a few seconds and then drops down gradually until the twentieth second when the NS does not show any further growth. This in turn explains the limited area growth of NBs and NSs displayed in Figures 1 and 2.

Movies of NB growth are not included as these were found to grow too fast after changing the temperature to the growth temperature. We attempted to capture the real-time growth process of NBs but these either grew fast with the growth temperature, or did not transform into a clear shape when continuously imaged with the electron beam. This could be the effect of the electron beam on the growth, an effect that was not observed during the growth of NSs. In situ movies of NB growth are therefore not included in order not to report results that may be the result of the electron beam effects.

**Phase Transition of 2D V$_2$O$_5$ to 3D VO$_2$ Nanostructures.** Obtaining two different materials of the same elements from one precursor can be an efficient way of synthesis. Phase transitions in materials provide the capability to produce two differently characterized materials that can be used in multiple applications individually. As discussed in earlier sections, the
amorphous AMV precursor transforms into various crystalline V$_2$O$_5$ nanostructures. It has been observed previously that the V$_2$O$_5$ can be transformed into multiple phases of VO$_2$.\textsuperscript{64–67}

Figure 4a shows the amorphous AMV precursor at room temperature, which then transformed into the thin-crystalline V$_2$O$_5$ NBs and NSs at 500 °C as shown in Figure 4b. When increasing temperature further, the V$_2$O$_5$ nanostructures show good thermal stability until the temperature reaches 700 °C. At that temperature, the thin nanostructures of V$_2$O$_5$ collapse into sharp-edged three-dimensional nanoparticles, which is evident from their shape as displayed in Figure 4c. These nanoparticles show various shapes and sizes along with different thicknesses, but their three-dimensional and strongly faceted nature is a common factor, unlike thin V$_2$O$_5$ nanostructures. The crystallinity difference of the V$_2$O$_5$ nanostructures from the obtained nanoparticles is shown in Figure 4d with the help of filtered HR-TEM images, simulated images, schematics of atomic models, and FFTs. The EDS elemental maps in Figure 4d,i for vanadium and oxygen from a group of nanoparticles, and of the larger individual sharp-edged nanoparticle, show a 1:2 stoichiometry between V and O, which confirms the VO$_2$ composition. The process of the phase transition from V$_2$O$_5$ to VO$_2$ was so rapid that capturing it through TEM was impossible, which is why there are no videos capturing this. Increasing the temperature to 700 °C made the V$_2$O$_5$ structures transform no time into particles of VO$_2$.

A detailed analysis of the atomically resolved images in Figure 4d of the three-dimensional nanoparticles gives interplanar distances of 0.45 nm, which represents the (010) plane for monoclinic, and (100) and (010) planes for rutile, phases of VO$_2$.\textsuperscript{65} The insulator-to-metal transition between the two phases of VO$_2$ occurs near room temperature in which the monoclinic phase is the low-temperature phase, while rutile is the high-temperature phase.\textsuperscript{68,70} Thus, it suggests that the nanoparticles obtained after the phase transition from V$_2$O$_5$ at 700 °C show a rutile phase of VO$_2$, as it stays in this phase without showing any changes after heating to 740 °C. During the experiments, the monoclinic phase may have been formed as an intermediate phase as well while this was not recorded in the images as the temperature is quite high, or the rutile phase was formed directly not via the formation of the monoclinic phase. Increasing the temperature to 740 °C does not change the crystal structure, and this also suggests that the observed phase is rutile, which is stable at higher temperatures. As both these phases, monoclinic and rutile, have different properties (insulating and metallic), they have different applications based on their properties. In our experiments, we found that the rutile phase of VO$_2$ is stable at 740 °C, and therefore, it is possible to form this as a stable nanoscale phase under controlled experimental conditions. The VO$_2$ particles that converted from the NBs and NSs of V$_2$O$_5$ were found oriented in random directions as they can be seen in 3D shapes in contrast to the 2D NBs and NSs that were all found in (nearly) the same orientation. The temperature profile plot in Figure S2 shows the increased temperature from 700 to 760 °C with the same phase of VO$_2$. In a separate experiment, the AMV precursor was heated inside the microscope and the electron diffraction patterns (DPs) of the phase transition were recorded and are presented in Figure 4e–g. Figure 4e shows the blurred DP without any sharp rings at room temperature corresponding to the amorphous AMV precursor. At 500 °C, the phase transition occurred from amorphous AMV precursor to crystalline V$_2$O$_5$, which is evident from the bright rings in the DP in Figure 4f. Further increasing the temperature to 700 °C leads to the structural transition from orthorhombic V$_2$O$_5$ to rutile VO$_2$, and the corresponding bright rings in the DP are evident of this.
transition. The details on the DPs with indexing of the bright rings to the corresponding planes in the $V_2O_5$ and $VO_2$ structures are shown in Supporting Figure S4.

**Ex Situ Growth of $V_2O_5$ and $VO_2$ Nanostructures.** An *in situ* TEM experiment provides important information on optimization and control of the growth of materials along with insights into the evolution of the growth. To scale up the synthesis or fabrication of the materials, it is necessary to grow materials in regular laboratory conditions. Hence, to support the *in situ* findings in thermolysis-driven growth of vanadium oxide nanostructures, *ex situ* experiments were carried out in the vacuum oven as depicted in the schematic in Figure 5a. The heating chips drop cast with AMV precursor were kept in the central part of the vacuum oven after setting it for the temperature controls. Here, in the *ex situ* experiments, the same heating chips are used to keep the same substrate interaction with the precursor and to observe the grown structures directly in the microscope without carrying any distinct sample preparation method. This gave a feasible opportunity to observe the as-grown structures without any possible disturbance from the electron beam. The temperature profiles during the growth for both $V_2O_5$ and $VO_2$ are shown in Figure 5b. In both cases, the heating and cooling rates were kept the same at 200 °C/h, and the temperature platforms of 400 and 480 °C for the growth of $V_2O_5$ and $VO_2$ were kept for time periods of 10 and 12 min, respectively. The growth temperatures for both $V_2O_5$ and $VO_2$ were optimized by carrying out several pilot experiments. One of the examples of the *ex situ* grown thin nanosheets of $V_2O_5$ is shown in Figure 5c, and the high-resolution image with the colored simulated image in the indicated box, along with the FFT pattern, is shown in Figure 5d.

The typical arrangements of atomic columns in the orthorhombic $V_2O_5$ are visible in the experimental high-resolution image and in the simulated image under the same conditions as that of the *in situ* experiment. The same sample transforms to the $VO_2$ after being heated to 480 °C, and the nanostructures of $VO_2$ are shown in Figure 5e along with the high-resolution image from one of the nanostructures in Figure 5f, with a colored simulated image in the indicated box, and the FFT pattern in the inset. HAADF-STEM images show the thinness of the $V_2O_5$ NSs in Figure 5g along with the elemental maps for V and O in red and green colors, respectively. The thin nanosheets of $V_2O_5$ transformed into the thick nanoparticles of $VO_2$, which is evident from the HAADF-STEM image in Figure 5h, where the shape of the particles is seen to be different from that of the thin nanosheets. The EDS elemental maps for V and O are represented in red and green, respectively, and the quantification of the EDS information shows a stoichiometry of 1:2 in $VO_2$. Thus, overall, the *ex situ* experiments performed in the vacuum oven produced similar structures of $V_2O_5$ and $VO_2$ nanostructures at slightly different temperatures compared to those in the *in situ* TEM experiments. The pressure difference between the TEM column and vacuum oven can be a major factor causing the transformation or other thermodynamic processes to take place at quite different temperatures. Also, in the current case, the pressure difference in the TEM column and vacuum oven plays a role, and hence, the phase transformation of $V_2O_5$ to $VO_2$ occurred at 480 °C in the *ex situ* experiment. Another aspect is the local nature of the heating inside the *in situ* TEM heating setup vs the broad *ex situ* heating inside the vacuum oven, which might also have played a role resulting in
differences in the observed temperatures for phase transformations.

**CONCLUSIONS**

In summary, we observed thermolysis-driven growth of V$_2$O$_5$ nanostructures on SiN$_x$ membrane using a single solid-state precursor in combination with *in situ* TEM heating. Intermediate stages during the thermolysis of AMV precursor are observed in real time, which would be unreachable when using conventional methods. The growth temperatures required in the thermolysis of the AMV precursor to produce fully grown V$_2$O$_5$ nanostructures are optimized. The phase transformations from V$_2$O$_5$ to VO$_2$ are also observed in the *in situ* TEM experiments at elevated temperatures. Furthermore, the *ex situ* thermolysis of AMV precursor in a vacuum oven produced pure crystalline V$_2$O$_3$ and VO$_2$ nanostructures on the bare SiN$_x$ membrane of the heating chip, which validates the thermolysis-driven growth as observed by means of *in situ* TEM. Controlling the thickness of the precursor and hence the thickness of grown 2D V$_2$O$_5$ nanostructures, along with the optimization of the parameters to control the morphology of V$_2$O$_5$ nanostructures, are still open challenges of this method. Our study offers a relatively simple method to produce pure crystalline V$_2$O$_3$, 1D nanobelts and 2D nanosheets along with VO$_2$ nanostructures in a single-synthesis method that can be scaled up to produce desired materials for rechargeable batteries and catalytic applications.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.3c00397.

Additional figures show a schematic illustrating the drop-casting of ATT onto the heating chip and examination using the electron beam after the introduction of it in the TEM column for conducting the *in situ* TEM experiment, *in situ* heating temperature profiles of experiments describing the observed growth of different structures at particular temperature ranges, TEM images of the AMV precursor kept under the electron beam for more than 10 min at room temperature before and after the exposure, electron diffraction patterns (DP) during the *in situ* TEM heating experiment for the amorphous precursor, and orthorhombic V$_2$O$_5$ and rutile phase VO$_2$ structures (PDF).

Growth of the V$_2$O$_5$ layer at 450 °C (slowed down to 1/2 times of real time) (Supporting Movie 1) (AVI)

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**Notes**

The authors declare no competing financial interest.

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