The Effect of Additives on the Hydrothermal Synthesis and Thermochromic Performance of Monoclinic Vanadium Dioxide Powder

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Abstract: Monoclinic vanadium dioxide VO₂(M) is a well-known thermochromic material, with its critical transition temperature (68 °C) being the closest to room temperature (RT). Among the variety of grown methods, hydrothermal synthesis is a simple and cost-effective technique to grow thermochromic VO₂ in the form of powder. In the present work, VO₂ nanoparticles were prepared by hydrothermal synthesis in mild conditions, followed by a thermal annealing process at 700 °C under nitrogen flow for two hours. Vanadium pentoxide (V₂O₅) was used as the vanadium precursor, while two different reducing agents, namely oxalic and succinic acid, were employed for the reduction of V₂O₅ to VO₂. Additionally, urea as well as thiourea were used as additives, in order to investigate their effects on the thermochromic performance of VO₂. As a result, the VO₂(M) phase was obtained after annealing the crystalline powder, grown hydrothermally using oxalic acid and thiourea as a reducing agent and additive, respectively. This synthesis had a high yield of 90%, and led to a VO₂(M) powder of high purity and crystallinity. In particular, the VO₂(M) nanoparticles had an average crystallite size of approximately 45 nm, a critical transition temperature of approximately 68 °C and a hysteresis width of 11 °C.

Keywords: vanadium dioxide; thermochromic; hydrothermal synthesis; additives; reduction

1. Introduction

The global demand for reduced gas emissions and optimization of energy management in the building sector has attracted much research interest in recent decades. Thus, materials with specific properties can play an important role in reducing the energy consumption in buildings [1–3]. Thermochromism is a property of selected materials whose optical properties change by the external stimuli of temperature. In the case of vanadium dioxide, thermochromism is enabled through passive heat regulation, i.e., reflecting or transmitting the infrared spectrum, based solely on the ambient environment temperature. Thus, when applied on the exterior surfaces of buildings, such as on the glazing system, this constitutes a facile technology capable of regulating heat transmission, leading to enhanced energy efficiency and living comfort for human activities indoors [4]. Vanadium dioxide can be found in many polymorphs, such as VO₂(A), VO₂(B), VO₂(D) and VO₂(M) [5]. The latter exhibits an inherent and reversible first-order phase transition at a critical transition temperature of T_C = 68 °C for pristine VO₂(M). Specifically, below the T_C, it adopts a monoclinic (M) crystal structure, while being an insulator and infrared (IR) transparent; and above the T_C, it reversibly transforms to the rutile tetragonal structure VO₂(R), being a conductor with metallic behavior, and highly reflective in IR [6–8]. However, its
transparency in visible radiation remains the same, independently of temperature, thus it has been extensively investigated as a coating for “smart” windows [9,10].

Various deposition techniques such as sputtering [11–14], pulsed laser deposition (PLD) [15–17], chemical vapor deposition (CVD) [18–20] and sol-gel [21–23] have been employed to grow thermochromic VO₂ (M). However, these techniques demand expensive instrumentation and time-consuming processes, along with high temperatures (>250 °C) in order to grow the thermochromic monoclinic phase of VO₂. In contrast, hydrothermal synthesis is a technique which utilizes controllable and scalable parameters even for large-scale production lines, while minimizing the environmental impact through the advantages of a closed system synthesis. In addition, the hydrothermal method is expected to meet the demand of low-temperature synthesis for various high-energy crystalline products, by applying high pressure in well-known synthetic routes, minimizing temperature requirements of crystallization [24–26]. Moreover, another advantage of the hydrothermal synthesis of VO₂(M) in powder form is its facile deposition as film at low temperatures (<100 °C) onto flexible substrates such as polyethylene terephthalate (PET) [27].

Recently reported works [28–31] on the hydrothermal synthesis of thermochromic vanadium dioxide powder are focused on high-energy, high-crystallinity materials acquired through elevated temperatures in the hydrothermal synthetic step (≥260 °C). However, lower synthesis temperatures (180–230 °C) may result in intermediate or metastable products of ambiguous crystallinity, only to be converted to the thermochromic monoclinic phase by post-annealing at elevated temperatures (≥600 °C), while being in the solid state [32–36]. Lowering the energy requirements of thermochromic vanadium dioxide synthesis is challenging and requires a parametric optimization approach. Along these lines, many efforts have been reported lately, investigating different synthesis parameters such as the stoichiometry between the vanadium precursor and the reducing agents [5,37], the duration and the optimum temperature of the hydrothermal reaction [5,38–42], the presence of dopants in order to lower the transition temperature, or the introduction of promoters to regulate resulting materials [5,43–45] as well as the use of high-temperature synthetic routes in order to achieve single-step highly crystalline materials [46–48]. However, taking advantage of the complex solution chemistry of vanadium species, the high-energy demands of the VO₂ (M) synthesis could be met by introducing additives acting as promoters, to pursue activation of leached vanadium species towards a more easily and desirable precipitating form. To the best of our knowledge, there is a lack in the literature for such an approach [28,31,49,50].

In this paper, we report on a low-temperature hydrothermal synthesis using different reducing agents (oxalic acid and succinic acid) and different additives (urea and thiourea). It was found that VO₂ nanoparticles of high purity and crystallinity can be obtained by using oxalic acid as a reducing agent and thiourea as an additive, through a high-yield hydrothermal reaction, while assisted by subsequent annealing of the powders. Following this approach, the resulting VO₂ (M) particles showed notable thermochromic performance. Finally, a possible mechanism for the additive-assisted hydrothermal step of our synthetic procedure is proposed.

2. Materials and Methods

Solid vanadium (V) oxide, V₂O₅ (98+%), was used as a starting precursor reagent, being the source of vanadium. Solid oxalic acid dihydrate, C₂H₂O₄·2H₂O (≥99.0%), as well as succinic acid, C₄H₆O₄ (≥99.0%), were used as a reducing agent. Solid thiourea, SC(NH₂)₂ (≥99.0%), and urea, NC(NH₂)₂ (≥99.5%), were used as additives. All reagents mentioned were used without further purification and purchased from Sigma-Aldrich, Merk (St. Louis, MO, USA).

VO₂ in the form of powder was synthesized by a hydrothermal method, using a 125 mL stainless steel Parr Teflon-lined autoclave. In a typical procedure, 0.365 g (0.05 M) of solid V₂O₅ and 8 mmol (0.2 M) of the reducing agent (oxalic acid or succinic acid) were dissolved in 40 mL of deionized water. After 15 minutes of stirring, the original dark yellow
mixture turned into a dark green/blue solution. Subsequently, a specific amount of solid additive (molar ratio of urea or thiourea: V₂O₅ = 1:4) was introduced into the stirring mixture, and kept under vigorous stirring for 10 more minutes. Then, the precursor mixture was transferred to the Teflon-lined acid digestion vessel and placed into a vacuum furnace for treatment at 220 °C for 12 hours (ramp from room temperature). After the hydrothermal treatment, the autoclave was cooled naturally to room temperature. The ‘as obtained’ blue-black-colored solid products were isolated via centrifugation (20 min at 6000 rpm), and they were dried in a furnace at 80 °C for 4 hours, under dynamic-vacuum at a pressure of 0.1 MPa. Finally, to acquire the ‘final’ products, solid powders were annealed at 700 °C for 2 hours, with a heating rate of 5 °C/min, under constant nitrogen gas flow of 3 mL/min. The annealing temperature of 700 °C was selected based on the literature review [28–31] that is presented in the introduction part of this manuscript [37–41], when lower synthesis temperatures on the hydrothermal process are deployed a mixture of VO₂(B) and VO₂(A) are received as the ‘as obtained’ product, then an annealing at a greater temperature than 600 °C should suffice for the synthesis of VO₂(M). This is in accordance to the authors’ previous experience with this system since, early tests on synthetic procedures without additives suggested that annealing below 600 °C of the as obtained samples (synthetic routes without additives) would not result in the monoclinic phase.

The morphology of the VO₂ powder was examined by scanning electron microscopy (SEM) using a JEOL JSM-6390LV (JEOL Ltd., Akishima, Tokyo, Japan) microscope, operating at 20 keV, while the structure identification was performed by the X-ray diffraction (XRD) technique, using a RIGAKU RINT 2000 system, with a Cu-Kα radiation source of λCuKa = 0.154 nm. The θ/2θ scan detection from 10° to 80°, with a step of 0.05 °/s, was used. Using the data provided by the XRD pattern, the average crystallite size was calculated, according to Scherrer’s formula [51]

\[
D_{hkl} = \frac{K \times \lambda}{B_{hkl} \times \cos(\theta_{hkl})}
\] (1)

where \(D_{hkl}\) is the crystallite size in the direction perpendicular to the lattice planes, \(hkl\) are the Miller indices of the planes being analyzed, \(K\) is a numerical factor referred to as the crystallite-shape factor, here considered equal to 0.9 as an approximation, \(λ\) is the wavelength of the X-rays, which is 0.154 nm in our case of a Cu K-alpha source, \(B_{hkl}\) is the width (full-width at half-maximum) of the X-ray diffraction peak in radians, and \(θ_{hkl}\) is the Bragg angle for the main characteristic peak of VO₂(M) at 27.8°, corresponding to (011) direction. Moreover, the interplanar distance of the crystal lattice was calculated using Bragg’s law [52]

\[
d_{hkl} = \frac{\lambda}{2 \times \sin(\theta_{hkl})}
\] (2)

where \(λ\) and \(θ_{hkl}\) were defined above. Finally, the ATR-FTIR spectra were recorded on a Thermo-Electron Nicolet 6700 FT-IR optical spectrometer with a DTGS KBr detector at a resolution of 2 cm⁻¹.

The phase transition was studied by differential scanning calorimetry technique (DSC) using a PL-DSC system (Polymer Laboratories), at a temperature range from 20 °C to 170 °C with a step of 10 °C/min, under nitrogen flow of 20 cc/min, while connected with a liquid nitrogen cooling system. Using the DSC measurements, the critical transition temperature during heating (\(T_h\)) and cooling (\(T_c\)) procedure were determined. Thus, the critical transition temperature (\(T_C\)) as well as the width of the hysteresis loop (\(ΔT_C\)) of the VO₂ powder were calculated using the equations below:

\[
T_C = \frac{T_h + T_c}{2}
\] (3)

\[
ΔT_C = T_h - T_c
\] (4)
3. Results and Discussion

From the synthetic route that was employed for the growth of VO$_2$, two products were isolated and studied, regardless of the synthetic parameters: the ‘as obtained’ dried powder, which was isolated after the hydrothermal process, and the ‘final’ powder, which was isolated after the annealing process at 700 °C under nitrogen gas flow.

In order to evaluate the applicability of the solution based hydrothermal synthesis in regard to different reducing agents and additives, the yield of each reaction was calculated using the following equation:

\[
\text{Yield (\%)} = \frac{\text{mass of V}_2\text{O}_5 \text{ precursor}}{\text{mass of “as obtained” material}} \quad (5)
\]

In Table 1, the calculated yields of the ‘as obtained’ dried materials for the solution based hydrothermal step are presented. Hydrothermal reactions using oxalic acid as reducing agent without the presence of additives showed higher yields of approximately one order of magnitude than those using succinic acid as a reducing agent. Interestingly, the presence of additives promote synthesis yields in both the oxalic and succinic acid routes, especially in the case of thiourea. More specifically, for the synthesis with oxalic acid without the presence of additives, the calculated yield was 75%; however, the addition of urea seems to have no effect on the yield, while the addition of thiourea improves the yield significantly, reaching 90%. For the synthesis with succinic acid, the yield was extremely low (3%) without the presence of additives, while upon adding urea or thiourea, a significant increase in the yield was observed, reaching 50 and 70%, respectively.

| Reducing Agent | Additives | “As Obtained” Product Phases by XRD | Hydrothermal Synthesis Yield (%) (Dried Product Mass) |
|---------------|-----------|-----------------------------------|-----------------------------------------------------|
| Oxalic acid   | No        | VO$_2$ (B) and VO$_2$ (A)         | 75% (277 mg)                                         |
|               | Urea      | unidentified peaks                | 75% (270 mg)                                         |
|               | Thiourea  | unidentified peaks                | 90% (320 mg)                                         |
| Succinic acid | No        | VO$_2$ (B) and VO$_2$ (A)         | 3% (11 mg)                                           |
|               | Urea      | unidentified peaks                | 50% (191 mg)                                         |
|               | Thiourea  | unidentified peaks                | 70% (245 mg)                                         |

In regard to the lower yields of succinic acid, we assume that the acidity must be the main factor. Since the pKa of succinic acid is way above that of oxalic acid (4.2 and 5.6 in contrast to 1.25 and 4.14) and the pH of the precursors is ~1 and that of the final reaction is below 4, it would make sense that in short reaction times such as those we use, succinic alone would not provide enough OH- to act as an effective reducing agent to V$_2$O$_5$. However, upon addition of urea or thiourea in our system, the pH gradually increases (as explained from the proposed mechanism in this paper) activating both the organic acids (pKa) and the vanadium precursor (leaching of vanadium species). This effect, could potentially explain the yield increase when utilizing additives, especially in the case of thiourea. Another possible interpretation could be found in the organic acids behavior as ligands. As per literature [53,54], both oxalic and succinic acids can form vanadium complexes of hexacoordinate geometry. Oh, however oxalate is a stronger complexation agent resulting in greater vanadium complexes (increased leaching) though bridging of vanadium cations, while succinic acid could also act as a bidentate chelating agent, isolating vanadium cations and prolonging reaction times needed for a high-yield reduction in the vanadium precursor. The later would also suggest smaller nuclei growth in the case of succinic acid which could be related to the smaller features morphology we observe in our results in the case of crystalline products (with additives urea or thiourea—Figure 2e,f vs. Figure 2b,c for the case of oxalic acid).

The diffraction patterns of the synthesized materials can be seen in Figure 1. For the ‘as obtained’ products (Figure 1a), the hydrothermal procedures without the presence of
additives resulted in mixtures of metastable crystal phases of monoclinic VO$_2$ (B) and tetragonal VO$_2$ (A), as identified by the powder diffraction files #81-2392 and #42-0876, respectively. This is in agreement with the literature reports for low-temperature (≤230 °C) hydrothermal synthesis of VO$_2$ and can be attributed to the lower formation energy of the metastable phases [5,55,56]. Thus, these low-temperature synthetic routes require an additional annealing step in order to obtain the monoclinic VO$_2$ (M) thermochromic phase [40,57,58]. In this work, this is the case for the ‘as obtained’ materials for both the oxalic acid and the succinic acid reducing agents. However, in the case of the latter, a number of unidentified peaks, such as at 2θ = 12.6°, 19.9°, 22.5° and 48.15° can be noticed, suggesting that organic-metal compound residues may also be present in the sample. Moreover, for both reducing agents, it was observed that the presence of additives in the hydrothermal process led to less crystalline products, as this arises by the presence of broader peaks at 2θ = 12.9°, 44.9°, 57.4°, 61.45°, 69.25°, and 77.1° of the XRD patterns presented in Figure 1a.

Figure 1. X-ray diffraction patterns of the ‘as obtained’ (a) and ‘final’ (b) synthesized materials before and after an annealing process. Peak identification was achieved by the following powder diffraction files (PDF): #81-2392 for VO$_2$ (B), #80-0690 for VO$_2$ (A), #44-0252 for VO$_2$ (M), and #27-1318 for V$_6$O$_{13}$.

The XRD patterns of the ‘final’ products are presented in Figure 1b, after the annealing process at 700 °C. Materials synthesized with oxalic acid as the reducing agent, without the presence of additives, showed strong diffraction peaks, which can be indexed to monoclinic VO$_2$ (M) with notable impurities attributed to V$_6$O$_{13}$ (powder diffraction file #27-1318). In contrast, materials obtained with succinic acid as the reducing agent, without the presence of additives were mostly amorphous. However, for both reducing agents, the introduction of additives (urea or thiourea) led to the appearance of strong diffraction peaks corresponding to the monoclinic VO$_2$ (M), according to the powder diffraction file #44-0252. Therefore, the formation of high purity and crystalline VO$_2$ (M) phase can be achieved by adding urea or thiourea in the hydrothermal-based two-step synthesis, independent of the reducing agent that is used.
In order to calculate the crystallite size as well as the interplanar distance of the VO$_2$ (M) powder, its characteristic peak at $2\theta = 27.8^\circ$ corresponding to the (011) direction of VO$_2$ (M) was used in Equations (1) and (2), respectively. The calculated crystallite size and interplanar distance as well as the different phases of vanadium oxides that were present after the annealing process are presented in Table 2. The crystallite size of the ‘final’ products that were synthesized with oxalic acid as the reducing agent, without additives, was 46.7 nm. The addition of thiourea or urea improve the purity of VO$_2$ (M) particles, while marginally changing the crystallite size to 44.3 and 47.7 nm, respectively. On the other hand, in the ‘final’ products synthesized with succinic acid as the reducing agent, the VO$_2$ (M) phase was grown only in the presence of urea or thiourea additive, having a crystallite size equal to 36.5 and 47.5 nm, respectively.

Table 2. Calculated crystallite size and interplanar distance of the ‘final’ materials.

| Reducing Agent | Additives | ‘Final’ Materials Phases | (hkl) | $2\theta$ ** (deg) | Crystallite Size $D_{hkl}$ (nm) | Interplanar Distance $d_{hkl}$ (nm) |
|----------------|-----------|--------------------------|-------|-------------------|-------------------------------|-----------------------------------|
| Oxalic acid    | No        | VO$_2$ (M) (with V$_6$O$_{13}$ impurities) | (011) | 27.76             | 46.7                          | 0.32                              |
|                | Urea      | VO$_2$ (M)               | (011) | 27.77             | 47.7                          | 0.32                              |
|                | Thiourea  | VO$_2$ (M)               | (011) | 27.77             | 44.3                          | 0.32                              |
|                | No        | amorphous                | (011) | -*                | -*                            | -*                                |
|                | Urea      | VO$_2$ (M)               | (011) | 27.74             | 36.5                          | 0.32                              |
|                | Thiourea  | VO$_2$ (M)               | (011) | 27.77             | 47.5                          | 0.32                              |

* No VO$_2$ (M) peaks. ** Diffraction angle of the main characteristic peak of the (011) plane of VO$_2$ (M) as obtained after Gauss fitting.

The morphology of the ‘final’ products was investigated by SEM, the images of which are presented in Figure 2. It can be observed that the ‘final’ products consist of particles with various morphologies and a size of several microns. Powders produced without the presence of additives (Figure 2a,d) consist of larger and bulkier particles, especially in the case of the succinic acid (Figure 2d), compared to the rest. The addition of urea and thiourea led to the formation of particles with different morphologies, for both reducing agents. The formation of these finer morphologies can be attributed either to differences in the pH, or the fact that urea and thiourea acted as complexation agents for newly formed vanadium species, which would delay the sintering of particles towards larger morphologies at high annealing temperatures [53]. Among them, the materials that were synthesized with oxalic acid as reducing agent and urea or thiourea as additive, led to particles with more homogeneous morphology.

More specifically, the SEM images reveal that particles grown using oxalic acid have the form of microrods and spheres in the absence of additives (Figure 2a), while in the presence of additives, urea (Figure 2b) as well as thiourea (Figure 2c), micro-flowers consisting of sub-micron spheres and flakes were formed, respectively. In the case of succinic acid as a reducing agent, a rod-like morphology was preferred in the presence of urea additive (Figure 2e), while upon thiourea additive (Figure 2f) particles of mixed morphology were obtained.

Further structural analysis of the ‘final’ products was conducted by FTIR spectroscopy. In order to examine the ageing effects on the stability of materials, measurements were conducted one month after materials’ production, during which they were kept at standard storage conditions (room temperature with average humidity of 50%RH and medium light conditions, inside transparent plastic vials).
Figure 2. Scanning electron microscopy images of the ‘final’ synthesized materials using oxalic acid—without additives (a), oxalic acid—urea (b), oxalic acid—thiourea (c), succinic acid—without additives (d), succinic acid—urea (e), and succinic acid—thiourea (f).

Figure 3 shows the FTIR spectra of the one-month-aged ‘final’ products, with characteristic peaks of vanadium oxides denoted [59]. Specifically, the band at 1000 cm\(^{-1}\), is attributed on many vanadium oxide compounds to be the stretching of short vanadyl bonds, V=O, involving the presence of vanadium ions in the IV oxidation state. In the case of particles prepared in the presence of additives, the vanadyl stretching band shifts to lower wave numbers (989 cm\(^{-1}\)), except for the product of oxalic acid with urea additive synthesis (1008 cm\(^{-1}\)). Bands at approximately 740 and 480 cm\(^{-1}\) can be attributed to the asymmetric (\(v_{as}\)) and symmetric (\(v_s\)) stretching modes of V–O–V bonds, respectively. It should be noticed that these reported wave numbers are shifted towards lower wavenumbers than previously reported in literature [59]. In the peculiar case of the succinic acid without the presence of additives, sharp bands at 1685, 1410, 1305 and 1202 cm\(^{-1}\) were observed, corresponding to organic bonds stretching and bending modes. Such modes are the \(\nu(C-O)\) stretching at 1681 cm\(^{-1}\), the bending vibration mode of C-H at approximately 1390 cm\(^{-1}\) or the coupled OH bending (\(\delta(OH-O)\)) at 1410 cm\(^{-1}\); the coupled \(\nu(C-O)\) stretches at 1306 cm\(^{-1}\) and the \(\omega(CH2)\) wagging modes at 1197 cm\(^{-1}\). All these modes are related to the residues of bulk succinic acid, a result which is in accordance to the amorphous XRD patterns of products synthesized with succinic acid without additives [60–62].
Moreover, materials that were grown using succinic acid as the reducing agent displayed the characteristic bands of water vapors, with sharp bands from 1600 to 1700 cm$^{-1}$, attributed to the deformation vibrations of the O–H modes and broader bands from 2500 to 3500 cm$^{-1}$, attributed to the stretching O–H modes [60,62]. Both areas are highlighted on Figure 3 by dotted lines. The presence of water vapor bands on these samples indicates that the particles are more prone to humidity absorption. Vanadium dioxide is known [63,64] to be oxygen sensitive in a humid environment and after extended exposure, vanadium atoms may become partially or totally oxidized from V$^{4+}$ to V$^{5+}$. In our case, a slight change from the characteristic blue-black color of vanadium dioxide to a darker green color was observed on materials grown using succinic acid after one month of ageing, indicating a partial oxidation of vanadium atoms, which is in agreement with water stretching bands detected by the FTIR measurements. In contrast, no water vapor peaks or color alteration was noticed for particles grown using oxalic acid, during the same ageing time that were stored under the same conditions, implying a greater stability for these materials.

Finally, from the FTIR spectra, no peaks suggesting the presence of urea or thiourea are evident, as they would display wide triplet peaks at the range of 1500–2000 cm$^{-1}$, corresponding to modes of C-H, N-H, C=O and C=S bonds. Thus, FTIR results confirm expectations of high-temperature degradation of any non-binding organic residues of thiourea or urea (boiling point < 200 °C).

The thermochromic behavior of the synthesized ‘final’ products was studied by differential scanning calorimetry (DSC) and the resulting transition curves are presented in Figure 4. From the DSC curves and by applying Equations (3) and (4), the critical transition temperature ($T_C$) as well as the width of hysteresis loop between the heating and cooling procedures ($\Delta T_C$), respectively, were calculated. The values of $T_C$ and $\Delta T_C$ (Table 3) indicate that the materials grown using two different reducing agents, oxalic acid or succinic acid, exhibit similar thermochromic behavior. However, the materials synthesized with succinic acid, without the presence of additives, display no thermochromic transition. Additionally,
the presence of additives in the case of materials synthesized with oxalic acid seems to have no effect on the transition temperature; however, a small increase in the hysteresis width values can be noticed. In the case of materials synthesized with succinic acid, the presence of additives leads to crystalline materials with thermochromic properties similar to those of materials grown using oxalic acid. A small increase in the hysteresis width values is also noticed in this case, but with no relevant decrease in the $T_C$ in the case of thiourea additive, as would be expected according to literature if a substitutional anionic doping with sulfur was taking place (even at 0.3 at% sulfur) [65].

**Figure 4.** Thermochromic transition curves obtained by differential scanning calorimetry of hydrothermally synthesized VO$_2$ in the form of powder using (a) oxalic acid and (b) the succinic acid, as reducing agents, with and without the presence of additives.

**Table 3.** Calculated thermochromic properties from the DSC curves of synthesized ‘final’ products.

| Reducing Agent | Additives | $T_C$ ($^\circ$C) | $\Delta T_C$ ($^\circ$C) |
|----------------|-----------|-------------------|--------------------------|
| Oxalic acid    | No        | 67.8              | 10.1                     |
|                | Urea      | 67.6              | 10.4                     |
|                | Thiourea  | 67.9              | 11.4                     |
|                | No        | -                 | -                        |
|                | Urea      | 67.9              | 11.3                     |
|                | Thiourea  | 67.7              | 12.7                     |

* No evidence of thermochromic behavior.

The minimal impact of the additives urea and thiourea on the thermochromic properties of ‘final’ materials that were produced in this work, is indicative of the role of these molecules in the synthetic routes. Additives urea and thiourea seem not to alter the chemical composition and thermochromism of the desired ‘final’ materials, as in the case of additives used for doping, but rather to act as promoters towards higher yield and the selective production of highly crystalline VO$_2$ (M). Additionally, they seem to act as promoters of lower dimension particles and of higher uniformity in regard to the morphology of the products (Figure 2).

The resulting particles of higher uniformity in morphology upon using thiourea additive are in accordance to previous works where sulfuric acid (H$_2$SO$_4$) was used as an additive for the formation and morphology control of VO$_2$ (R) in the hydrothermal process [66]. Other works used sulfuric acid as a pH regulator [67] or as an additive to increase the vanadium leaching to the reaction solution during the reagents mixture preparation [68]. The later could be relevant to the observation of our system of yield
increase in the presence of thiourea in the hydrothermal reaction. However, in order to understand the effect of thiourea and urea additives in our system, along with a possible mechanism involved, a brief study of their degradation at high temperatures and pressures, such as in the hydrothermal system, must be examined.

So far, few studies with urea as an additive in hydrothermal synthesis of vanadium oxides have been reported [43,44,47]. In these works, the presence of urea is being suggested to be linked with the formation of the ‘final’ desired materials, while achieving greater crystallinity and morphology control towards thermochromic VO$_2$ (M). In the literature, urea is referred to be used as a homogeneous precipitation agent for various transition metal oxides [47,69]. Its decomposition produces ammonia and carbon dioxide for temperatures over 60 °C, accompanied by a slow, gradual and uniform rise in pH throughout the whole solution, which can result in the nucleation and growth of uniformly nano-sized particles. In the case of the hydrothermal synthesis of thermochromic VO$_2$, Li W. et al. [47] suggested that through the dissolution of urea in aqueous media Equation (6), the pentavanadyl cations (VO$_{2}^+$), the dominant vanadium cation in acidic aqueous solutions, can gradually be precipitated as VO$_2$ by a slow pH shift from the original acidic to a more alkaline Equation (7) as VO$_2^+$ for the hydrothermal reducing reaction system.

\[
\begin{align*}
\text{CO(NH$_2$)$_2$} + 3\text{H}_2\text{O} & \rightarrow 2\text{NH}_4^+ + \text{CO}_2(g) + 2\text{OH}^- \\
\text{VO}^{2+} + 2\text{OH}^- & \rightarrow \text{VO(OH)$_2$}(s) \rightarrow \text{VO}_2(s) + \text{H}_2\text{O}
\end{align*}
\]  

Equation (6) and (7)

In regard to the thiourea additive, according to the literature, when thermally heated in an oven, thiourea will be either decomposed to ammonia and carbodiimide (at approximately 180 °C), or else will be decomposed to ammonia, isothiocyanic acid, H$_2$S and carbodiimide (above 220 °C) [70,71]. However, these are the products on the dry thermal decomposition of thiourea. In solution, in an aqueous medium and in the absence of acids and bases, when heated to 90–130 °C, thiourea dissolves to ammonium and thiocyanate ions, as shown in Equation (8) [72], whereas for concentrated acidic aqueous solutions of pH < 2, the thiocyanate ion begins to hydrolyze to ammonium ion Equation (9).

\[
\begin{align*}
\text{CS(NH$_2$)$_2$} & \leftrightarrow \text{NH}_4^+\text{NCS}^- \\
\text{CNS}^-(aq) + 3\text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^-\text{(aq)} + \text{H}_2\text{S(aq)} + \text{NH}_3\text{(aq)}
\end{align*}
\]  

Equation (8) and (9)

As we discussed above, decomposition of urea in heated solutions results in a gradual and uniform pH increase, in the presence of OH$^-$ ions, promoting the pentavanadyl cation (VO$_{2}^+$) precipitation as VO(OH)$_2$. In a similar way, it is proposed that heated thiourea in aqueous media will be decomposed to NH$_4^+$ and NCS$^-$ ions. As a result, it is expected that one of the two following procedures will take place. In the first case, thiocyanate ions could be hydrolyzed to ammonium ions (according to Equation (9)), due to the low pH (~1) of the precursor solution, accelerating the gradual increase in pH. In the other case, thiocyanate ions could promote the pentavanadyl cation (VO$_{2}^+$) precipitation, acting in a similar manner as the aforementioned hydroxyl ions produced from urea decomposition, resulting in the formation of a “VO(SCN)$_2$”, or a different solid complex, similar to the equivalent VO(OH)$_2$ of the Li W. et al. [47] study. Both of these suggested mechanisms would probably result in an increase in vanadium leaching in solution and intermediate product precipitation, thus enriching the chemistry of the system, leading to the results of crystal phase purity, higher yields and morphological homogeneity reported in this work. More studies with by-product identification during the synthetic process are to be performed in future works in order to enrich the above observations, and advance the discussion on the synthesis mechanism.
4. Conclusions

Thermochromic monoclinic VO₂ (M) in the form of powder was grown by hydrothermal synthesis, followed by thermal annealing treatment. It was found that the use of different reducing agents (oxalic and succinic acid) and the addition of two different additives (urea and thiourea) are crucial to achieve the monoclinic thermochromic VO₂ (M) phase with high yields as well as high crystallinity and purity. More specifically, the VO₂ (M) grown by using oxalic acid and thiourea as a reducing agent and additive, respectively, showed a high yield of 90% in the hydrothermal reaction step, while it was highly pure and crystalline. Moreover, the hydrothermally synthesized VO₂ (M) nanoparticles had an average grain size of approximately 45 nm, with a critical transition temperature of approximately 68 ºC and a hysteresis width equal to 11 ºC. To the best of our knowledge, no similar studies with additive thiourea have been reported, while synthetic mechanism discussions are often left out of original synthesis papers in the case of VO₂.

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