Microwave assisted synthesis of VO$_2$ nanocrystals

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Abstract

This is a novel project since no previous work in stabilization of VO$_2$ nanocrystals in suspension has been performed. In this project, VO$_2$(M) nanocrystals are synthesized in a one-step microwave assisted technique. It is an efficient method since no post annealing processes are needed. Moreover, vanadyl acetylacetonate is the only precursor to form the adequate nanocrystals. The crystallinity, size and surface were characterized by X-ray diffraction (XRD), dynamic light scattering (DLS), infrared (IR), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR). The nanocrystals are stabilized by a combination of oleylamine and oleic acid as surfactants. This results in stable and monodisperse VO$_2$(M) elongated nanocrystals suspended in chloroform. This work is a first step towards a DSD experiment to optimize the synthesis parameters in order to prepare high quality and size appropriate VO$_2$(M) nanocrystals for smart windows.
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Chapter 1

Introduction

Nowadays, science is evolving towards the optimization of saving and transport of energy generated. Energy consumed in the building sector consists of residential and commercial end users and accounts for 20.1% of the total delivered energy consumed worldwide [1]. Therefore, there is a lot of new research every year coming up to try to mitigate it.

One approach is to improve the insulation of the windows because heating and cooling the houses represent the largest portion of the bill, 54%, and through windows a 25% of the total heat is lost [2]. Coating the windows with smart materials is one of many solutions available now, since they have properties that react to changes in their environment, such as temperature, light, pressure or electricity, in a reversible way.

1.1 Thermochromic materials

Thermochromic materials modify their optical properties due to a change in temperature. Over a range of temperatures, these materials exhibit the thermochromic effect which variates the colour of the material. Therefore, there is a phase change after a transition temperature ($T_c$) that can be reversible or irreversible depending on the thermodynamics of the system [3].

They have a potential application in window insulation since they have the ability to modify their reflection properties among others like absorbance, in the near infrared region (NIR) of the electromagnetic spectrum, due to temperature variations. The application of these materials into buildings has an effect in reducing the cooling loads in the summer and allowing pas-
sive heating during winter, since selective reflection of infrared radiation (IR) allows the material to change its transparency to the radiation depending on the temperature [4], [5].

![Figure 1.1: Principle of smart windows [6].](image)

### 1.2 Vanadium dioxide

Vanadium dioxide (VO$_2$) has been studied for its thermochromic properties since the $T_c$ for a pure single crystalline vanadium (IV) is approximately 341 K [3], [5], [7], [8]. This characteristic allows VO$_2$ to perform as a thermochromic material because the glass temperature is higher than its environment due to the specific heat of the glass increasing it to the needed $T_c$. At temperatures below the transition temperature the material is transparent for light in the visual and infrared region of the electromagnetic spectrum [3].

At $T > T_c$, the material reflects most of the NIR [6]. The fully reversible phase transition involves an abrupt change in NIR transmittance and reflectance simultaneously [9]. The NIR reflection makes VO$_2$ suitable for the application in isolating buildings since in winter the temperature in the interior is warmer and in summer cooler because the main source of heat is the NIR (Figure 1.1).

The $T_c$ can be adjusted by doping the compound with high valent metal ions ($W^{6+}$, $Nb^{5+}$) if there is a need to lower the $T_c$ to room temperature or it
can be increased by doping the compound with low valent ions (Al$^{3+}$,Cr$^{3+}$) [9].

A brief and simple summary is presented in the following lines in order to get a more clear understanding of the basics of the process. In the rutile phase ($T > T_c$) there are 2 vanadium and 4 oxygen atoms per cell unit while in the monoclinic phase ($T < T_c$) the vanadium atoms changed its positions and the unit cell is comprised of 4 vanadium and 8 oxygen atoms [7], [8], the structural change is illustrated in Figure 1.2.

There is a loss of symmetry from the rutile phase to the monoclinic. Performing a Raman analysis gives different active modes, 18 and 4 respectively, which indicate the structural change [7], [8]. The change of the symmetry group affects the splitting of the electronic levels $d_{II}$ making them collapse in the rutile phase (Figure 1.2). This structural shift happens once the $T_c$ is reached where VO$_2$ structural phase changes from monoclinic (M)
to a rutile (R) structure. This is a metal-insulator transition (MIT) because there is no longer a band gap and the electrons have a metal behaviour since the Fermi level remains the same as the population of electrons remains constant. Therefore, VO$_2$ becomes a metal due to a structural change and new interactions within the unit cell [3], [5], [7], [8].

Many other theoretical studies support different models to explain the MIT in VO$_2$. The Mott model of MIT explains why there is a band split of the d band since it includes the effect of electron interaction [10], [11]. Including this interaction adds another length scale (d) to the lattice spacing that is the Bohr radius (a$_B$) for a Coulomb interaction. If d $\gg$ a$_B$ the system is an insulator but when d $\ll$ a$_B$ the system becomes a metal [10], [11]. The change in the critical value of d happens when the system is perturbed, for example with an increase of temperature as in the system of the VO$_2$.

1.3 Nanocrystals

In order to apply it to windows the material needs to have a certain luminous transmittance. It has been theoretically proved that nanocomposites with VO$_2$-type particles offer much higher luminous and solar enhanced transmittance over VO$_2$-based continuous films because the sizes of nanocrystals (NCs) are smaller than the NIR wavelengths, making them invisible to that particular radiation [4]. Therefore, this project is focusing its efforts to synthesize suitable nanoparticles to enhance the coating for windows. It needs to be taken into account that because of quantum-size confinement, absorption of light becomes discrete and size dependent [12].

Furthermore, particle size distribution also has to be taken in account since it has a direct effect on the particle aggregation. To have less aggregation, particles with a narrow range in size distribution are needed [12].

Smaller NCs have more surface volume ratio (S/V) and this influences the physicochemical properties making them more suitable for specific utilities such as catalyst [13] and thermoelectric [14]. That is because S/V increases when the scale is reduced since the volume decreases in a cubic function while the area in a quadratic behaviour. Due to S/V rate increase, chemical adsorption conditions have a greater impact than electrostatic in-
teractions [12]. These conditions are to be optimized because they seriously affect the performance of the process [15], [16]. Another property that can change is the conductivity of the metal oxide nanocrystals (MONCs), transitions between conductor, semi-conductor and isolating are possible when the particle size is decreased [8]. The confinement of the electrons in a more narrow potential space changes the energy bands that leads to a change in the band gap.

In addition, MONCs tend to minimize their energy in order to be more stable so structural stability directly relies on having low surface free energy. The size reduction can affect the parameters of the unit cell and its structure due to the change in the thermodynamic stability since the ratio of S/V increases [7]. That means that nanostructured materials have more surface to stabilise than bulk materials. However, what is interesting is that materials that are not stable in bulk can become stable when they are nanostructured since the surface can be passivated to mitigate the higher chemical activity due to the increase of surface [12].

The type of bond in a metal oxide can vary from partially covalent to partially ionic and vice versa. The metal-oxygen bond depends on the size of the particles in the following way: the size reduction enlarges the ionic component of the bond [17].

Nanostructured oxides present far more modifications in their surface properties than 2D infinite surfaces. Due to this fact, the consequent solids present unique adsorption or acid/base characteristics such as dissociation of carboxylates on the surface of the MONCs or the charge balanced by the protons and not the cations [12], [16], [18].

Moreover, there are some defects on the surface like under-coordinated atoms or oxygen vacancies that produce traps in the band gap allowing more transitions to be permitted [18]. These states increase the chemical activity of the system.
1.4 Coating

The aim in this project is to synthetize VO$_2$ NCs that can be added in the silica matrix to form polymer film so it can be coated on windows.

A typical method to prepare VO$_2$ films is the sol-gel process because of its low cost, facility to dope it with metals and its deposition [19]. The sol used is a solution of tetraethoxysilane (TEOS), ethanol, water and acetic acid which condensates during a heat treatment. This silica matrix is optimal due to its hardness and transparency to visible light and infrared [20].

Even though the most common precursor to obtain VO$_2$ nanocrystals is V$_2$O$_3$ [9], vanadyl acetylacetonate (VO(acac)$_2$) is used as an only precursor due to its clean decomposition at low temperatures and its economic price if you compare it to other alternative precursors. In addition, it requires no further steps in order to reduce the vanadium since the composite is in the right oxidation state to exhibit the thermochromic properties, V$^{4+}$. These facts make VO(acac)$_2$ ideal as a starting precursor.

All the synthesis regarding VO$_2$ have a post annealing process to yield the right oxidation state and phase for the thermochromic effect [5], [21][26], but not the synthesis stablished in this project. In a NCs suspension there is no stress/strain to be reduced, no bonding towards the matrix neither improve the quality of the surface; so there is no need for a post annealing process. Moreover, the crystalline phase is already achieved during the synthesis. These facts make VO(acac)$_2$ ideal as a starting precursor.

1.5 Microwave assisted synthesis

There are different paths to synthesize VO$_2$ NCs such as sol-gel [25], hydrothermal synthesis [27], polymer-assisted deposition [22], electrochemical [28], microwave assisted [6], [24], solution based methods [21] and gas-based deposition processes [29], [30].

In this project, microwave assisted synthesis ($\mu$WAS) is the used technique because of wide range of advantages and possibilities that offers. This technique is energy saving because it is an electromagnetic irradiation, from
the infrared to radiofrequencies, which produces volumetric heating [31]. In µWAS only solvents with dipolar moment can be used in order to internally heat the sample by direct coupling of the microwave energy with the reactants in the vial [31].

Figure 1.3: (a) Conventional heating; (b) microwave heating; (c) Inverted temperature gradients in microwave versus oil-bath heating. Temperature profiles (modelling) 1 min after heating microwave irradiation (left) compared with treatment in an oil-bath (right) [31].

In a conventional heating process, the heat is transferred to the vial surface and then to the volume of mixture closer to the walls creating temperature gradients from the walls to the sample as it is shown in Figure 1.3 (c). On the other hand, µWAS increases the temperature of the vial all at once in other words that is bulk heating.

Moreover, the microwave (µW) that heats the sample enhances the synthesis speeding it up 10 to 1000 times [24], [31]. It has many other favourable points in comparison to the other techniques [6], [24], [31]:

i. Increased yields

ii. Higher reaction temperatures

iii. Allowing higher temperatures than the solvents boiling point

iv. No direct contact between the energy source and the reacting chemicals

v. Gradient of temperature from the bulk to the surface
vi. Uniformity of the particles, narrow size distribution

vii. Smaller size of the nanoparticles

The vials need to be transparent to µW so they can be penetrated through such as glass or quartz[31][33].

1.6 First step to DSD and characterization

In the process of obtaining nanocrystals, there are some key parameters to take in account in order to optimize the synthesis. A Definitive Screening Design (DSD) allows investigating which parameters are influencing the most the process since they will have quadratic effects on the responses instead of linear [34]. A DSD requires three levels: minimum, centre and maximum; for each factor so the detection and identification of a factor causing a strong nonlinear effect is possible [34]. Material properties or responses are denoted by Y and synthesis parameters or factor are called X [34]. The model proposed is the following one:

\[
Y = b_0 + b_1 x_1 + ... b_n x_n + \sum b_{ik} x_i x_k + \sum b_{ii} x_i^2
\]

In the process of obtaining the nanocrystals, we are going to focus in the following material properties:

- Y1 is the nanocrystal size
- Y2 is the percentage of crystalline phase of VO$_2$
- Y3 is the shape of the nanocrystal
- Y4 is the yield

The factors to adjust are:

- X1 is the microwave temperature
- X2 is the duration of the microwave assisted synthesis
- X3 is the concentration of precursor, VO(acac)$_2$. 
In these designs, the number of experiments are noted by the following rule: $2X + 1$. Therefore, seven experiments will be performed in future research.

In order to do the DSD method the responses must be measurable hence there is a need to have a stable suspension of the VO$_2$ NCs without aggregates. One of the pillars of this project is to find a way to stabilise them. An understanding of the surface chemistry will help to find the right ligands and solvents. Some studies related to the stabilization of MONCs show that there is an acid/base equilibrium to stabilize the charge when the synthesis is performed in polar solvents like in this project [16].

This project is focused in the characterization of the size and the phase of the nanocrystals. A clear NCs suspension is needed since the size is characterized with Dynamic Light Scatering (DLS). In the DLS measurement, it is used a sphere model to define the particle size that works better with regular sized particles while worse with needles or elongated particles. VO$_2$ NCs are believed to be elongated as previous work showed in TEM images [23], [35]. DLS measures the hydrodynamic diameter and it refers to the way the particle diffuses within a fluid. That is the reason why, additional size characterization with TEM is performed since the NCs are no longer dispersed in a solvent.
Chapter 2

Experimental methods

2.1 Nanocrystal synthesis

Several methods were tested with a variation in temperature, time, pH and concentration. Only the results of Method 9 (M9) are presented here as this method resulted to give the monoclinic phase needed in the NCs together with an acceptable starting NC size. The difference between M9 and the other methods is in the starting precursor and its solvent.

All reagents were of analytical grade and were used without further purification. In a typical procedure, 0.1367g VO(acac)\(_2\) (97.0% Sigma Aldrich) is dissolved in 5 mL of distilled water in order to have a starting concentration of 0.1 M. The solution was vigorously stirred in a microwave furnace (CEM Discover SP with autosampler) during 20 min at 60 °C. A following step of 60 min heating at 160 °C is needed to have the desired MONCs.

The product after the microwave synthesis was collected and precipitated with THF. A centrifugation step at 5000 rpm during 1 min with Eppendorf 5804 centrifuge followed with air-dry procedure is used. Addition of surfactants, oleylamine (OAm) (70% Sigma Aldrich) and oleic acid (OA) (80% Sigma Aldrich) to the dry NCs is needed to stabilize the NCs in an apolar solvent. The NCs are dispersed in 1 mL of chloroform. Mixing by hand or ultra sound may be needed because there could be some agglomerates until the suspension is clear. Once the clear suspension is achieved, the purification process starts. A nonsolvent, a substance incapable of dissolving a given component of a solution and miscible with the solvent, is
needed to reprecipitate the NCs. Acetone is used as a nonsolvent to purify the suspension since the addition of consecutive small amounts makes the NCs precipitate again. Then the suspension is centrifuged at 5000 rpm during 1 min and air-dried for a latter resuspension in 1 mL of CHCl₃. The sample is purified with this method five times to ensure its stability.

An alternative synthesis was performed, method 9 HCl (M9 HCl), which differs from M9 in the addition of 1 mL HCl 1 M without changing the initial concentration of VO(acac)₂ before the μWAS.

### 2.2 Characterization

For size measurement Dynamic Light Scattering (DLS) a Malvern Nano ZS was used in backscattering mode (173 °). To discern the compounds within the suspension, Infrared spectres were collected with a Perkin Elmer FT-IR spectrometer spectrum 1000. Transmission Electron Microscopy (TEM) images were taken on a JEOL JEM-2200FS TEM with Cs corrector and with a voltage of 200kV. To comprehend the composition of the sample and the crystallinity, X-Ray Diffraction (XRD) characterization with a Thermo Scientific ARL Xtra X-ray diffractometer was utilized with the CuK line as primary source. To evaluate the presence of ligands on the surface of the NCs, Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance III spectrometer operating at a ¹H frequency of 500 MHz and equipped with a BBI-Z probe. For each NMR measurement a 750 µL ampule of dry deuterated chloroform was used. Chemical shifts (δ) were reported in ppm, referenced to tetramethylsilane (TMS) using the residual solvent signal (CDCl₃, ¹H at 7.27 ppm) as reference.
Chapter 3

Results and discussion

3.1 Crystal phase

The XRD diffractogram in Figure 3.1 confirmed the monoclinic crystal structure of VO$_2$ in sample M9.

![XRD diffractogram](image_url)

Figure 3.1: XRD diffractogram after µWAS of the M9 and M9 HCl synthesis where the inverse triangle shows the monoclinic peaks.
The monoclinic phase is present in M9 due to the correlation of the \(\text{VO}_2\)(M) reflections from the database. Moreover, the peaks are broad due to the existence of NCs and that can give a first idea of the crystallite size. The Scherrer equation allows and approximation of the crystallite size (L) since it is inversely proportional to the peak width (B):

\[
L = \frac{K \lambda}{B(2\Theta) \cos(\Theta)}
\]

Typically, better approximations result from diffraction peaks between 30 and 50 2-theta degrees because in \(<30\) 2-theta degrees asymmetry compromises profile analysis and in larger angles 2-theta the peak intensity is weaker.

A first theoretical approximation is used to calculate the crystallite size with the parameter value of Scherrer constant of \(K = 0.9\), Cu(K\(\alpha\)) radiation with a wavelength of 1.5406 Å and the diffraction angle for each peak. The resulting crystallite size (L) is \(17 \pm 9\) nm, the high standard deviation lead to believe that the NCs size is polydisperse. This theoretical approximation gives a first input of the crystallite size which is compared further in this project with characterization techniques such as DLS and TEM.

The sample M9 HCl has insufficient product to give significant reflections in the diffractogram so its phase it is uncertain despite having some evidence of monoclinic phase. The XRD diffractogram proved that there was crystalline material so it is possible that some NCs were formed. However, no conclusions can be stated because of the lack of information about M9 HCl synthesis regarding the composition of it.

### 3.2 Precipitation

There was precipitation of the NCs after the \(\mu\)WAS due to agglomeration but it was a slow process. Therefore, a precipitating agent was needed to accelerate the process and minimize the yield loss after centrifugation.

Particles can precipitate due to its net charge or its polarity so a previous understanding of the system can lead the path to precipitate them. Aprotic and miscible solvents with water were tried to precipitate the NCs together
with bases since it was known from previous experiments that they could precipitate the crystals.

Bases such as NaOH, OAm and pyridine, were proven to precipitate the crystals because of the charge neutralization on the NCs surface. This path was discarded because the addition of base could interfere with an acid/base reaction on the NCs surface making the system more complex to study. However, a first insight can be acquired from the missteps of this path. The pH of the solution is acid after synthesis, pH = 5.14, protonating the bases themselves realising OH\(^-\) to the medium. This fact is believed to prove that the NCs surface is positive since a distinct explanation could be that Na\(^+\) neutralizes the charge but then the other bases used would not be able to precipitate the suspension.

![Figure 3.2: Representation of the chemical equilibrium in water of OAm (a) and pyridine (b).](image)

On the other hand, nonsolvents as dioxane, tetrahydrofuran (THF) and acetonitrile precipitate the NCs. Acetonitrile and dioxane could only precipitate them because big aggregates are assembled after a certain period posterior to the µWAS. Moreover, stabilization was unsuccessful since all the samples resulted in turbid solutions. While THF could precipitate the NCs right after synthesis regardless the synthesis parameters.

In that case, precipitation is due to polarity since THF is less polar than water Figure 3.3 and the NCs are not suspended anymore.

For further studies THF should be the nonsolvent used to precipitate the VO(acac)\(_2\) NCs in M9 since until now it is the most suitable precipitating
3.3 Surfactants and stabilization

Since it was possible to precipitate the particles from the M9 synthesis, the next step towards a clear suspension are surfactants.

Surfactants as 2-[(2-Methoxyethoxy)ethoxy]acetic acid (MEEAA) and trimethylamine (TEA) were rapidly abandoned since the suspensions were turbid in the addition after the purifications steps. However, a combination of OAm and oleic acid OA stabilizes the suspension in chloroform. The addition of only one of these surfactants leads to a turbid suspension. From this tries it seems that longer alkyl chain surfactants are essential for the stabilization of the NCs due to steric stabilization.

A 4% in volume of surfactants is necessary to stabilise the particles in a chloroform suspension, 20 µL OAm and 20 µL OA in 1 mL of chloroform gave clear suspensions when the concentration of NCs was approximately 0.1 M. However, higher concentrations of surfactants are undesirable since the resulting solutions were turbid, not stable.

The M9 HCl synthesis was unsuccessful to be stabilized despite trying all the ligands from the previous stabilization. Therefore, suspensions were turbid and discarded. Further characterization was not performed due to the need of a clear suspension.

The $^1$HNMR spectrum of VO(acac)$_2$ NCs suspension in CDCl$_3$ is illustrated in Figure 3.4. It has resonances in the region between 0-2.2 ppm but the measurement was performed in 0-8 ppm, but just the solvent, CDCl$_3$, 

<table>
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<tr>
<th>Solvent</th>
<th>Dipole moment [D]</th>
<th>Dielectric constant</th>
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<tr>
<td>Water</td>
<td>1.85</td>
<td>80.1</td>
</tr>
<tr>
<td>THF</td>
<td>1.63</td>
<td>7.5</td>
</tr>
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</table>
has a sharp peak in 7.27 ppm. The integrals of the resonances in 2.19 and 1.27 ppm show a 1:6 relationship, thus the peak at δ2.19 that integrates for one proton corresponds to the CH while the peak at δ1.27 that integrates for 6 protons is assigned to the two equivalent methyl groups.

The bands in the 1HNMR spectra are broad when the surfactants are attached to the surface of the NCs. OAm and OA seem not to be attached to the NCs surface neither in the suspension since there were no other peaks in the 2-7 ppm region, when it is compared to a reference where the same surfactants are attached to the surface [16]. It could also be possible that the NCs are too big that the relaxation period of the spin is longer than the characterization technique itself. In order to study more in depth the surface, there is a need to have smaller NCs or use other surface characterizing techniques such as 2D NMR. The first option is to achieve since smaller particles will give better performance for the latter coating on windows.

Finally, OAm is still needed despite of being removed from the suspension with acetone afterwards; in order to have a stable suspension of NCs. This leads to believe that only a base needs to be added with the OA. Therefore, a stabilization process with TEA and OA was performed in the same concentrations but the suspension of NCs was turbid so in fact OAm could be attached to the surface since it cannot be substituted for a shorter chain alkyl base. That is a reason why, it is assumed that OAm is needed since its long alkyl chain could stabilize the NCs in chloroform due to steric effects.
Further research and $^1$HNMR studies for the understanding of the VO$_2$ surface have to be accomplished to gain knowledge about how the surfactant binds to the surface and its mechanism.

### 3.4 NCs surface

To support the statement that the NCs surface is positive, a zeta potential (ZP) measurement can be performed since it reflects the potential difference between the electric double layer (EDL) of electrophoretically mobile particles and the layer of the solvent around them at the slipping plane (Figure 3.5). During electrophoresis, there is a drift of the charged particles with the EDL towards the reversed charged electrode when an electric field is applied.

![Figure 3.5: Scheme of the zeta potential principle where a negative charged particle is suspended in a liquid and notional boundary are shown.](image)

Figure 3.5 is an example of a negative charged particle which has a positive strong adhered layer, Stern layer, and after it, the diffusion ion layer where the ions are mobile. These ions act as counter-ions of the ions in the particles surface which can dissociate from the particles surface leaving a net electric charge. In addition, the slipping plane is the interface between the mobile particles and the fluid and it has an electrokinetic potential, ZP.

However, in this system the NCs are suspended in chloroform ($\epsilon = 4.8$)
so parameters like the pH are irrelevant to the zeta potential measurement. Nevertheless, ions may also participate in acid/base reactions within the slipping plane because of the surfactants used, OAm and OA, which can affect the ZP. Another parameter to consider is the dilution of the sample since ions may desorb from the surface shifting the ZP.

A ZP measurement was performed to analyse the surface charge and stability of the NCs in a Zeta dip cell at 20ºC. The value obtained was 0 as it is stated in Figure 3.6.

![Figure 3.6: Zeta potential distribution of a M9 sample.](image)

ZP values of ± 30 mV are considered to be stable but ZP only takes in account the repulsive forces and it does not take in consideration the van der Waals attractive forces. With that being stated, it is possible to have stable suspensions with low ZP values as in this system since the suspension of NCs is stable due to its clearness. Therefore, it can be established that van der Waals attractive forces predominate in this system.

The neutral ZP in the surface support that NCs are not charge stabilized. It is believed that the alkyl chains are oriented towards the dispersant because of its affinity for it due to polarity. HNMR measurements are needed in order to prove what is stabilizing the system to confirm the assumptions.

Therefore, the neutral ZP in the surface supports that the surfactants are attached to the surface. In this system, a ZP measurement can check the attachment of the surfactants to the surface while NMR was unable to perform such measurement due to the size of the NCs.
3.5 Oxidation state and coordination

Vanadium exists in a range of oxidation states, from -3 to +5 but the most common ones are from +2 to +5. Electron-transfer processes can happen as charge-transfer transitions from the metal ion to the ligand or vice versa, because it is a coordination complex. Absorption of light by vanadium produces a characteristic intense colour depending of its oxidation state since the transitions occur in the visible region of the electromagnetic spectrum. Changing a metal's oxidation state affects its coordination environment altering the energy of the charge-transfer transitions. This alteration is responsible for the colour change of the complex. In this project, VO(acac)₂ exhibits a pale green colour in its initial powder condition.

![Figure 3.7: On the left picture, samples in a 4mL vial after synthesis of the M9 (black) and M9 HCl synthesis (blue). On the right picture, plastic cuvettes with [VO(OH₂)₅]²⁺ (blue) and VO(acac)₂ (dark green) before synthesis.](image)

As it is visible in Figure 3.7 (left), the concentration of NCs is higher in the M9 synthesis (black) than in the M9 HCl synthesis (blue). This fact can be explained by the key role of acetylacetonate in the assist to form the NCs since it is directly related with the yield of the synthesis. Acetylacetonate is significant in the synthesis since it helps nucleation and growth of the NCs because when it is coordinated with the vanadium oxide it gives a larger amount of NCs. A study of the chemical reactions that involve acetylacetonate in the system is performed for a better understanding of the processes. These reactions and equilibriums are schematized in Figure 3.8.
Figure 3.8: Scheme of the chemical reactions and equilibriums in the synthesis. (a) Dissolving the VO(acac)$_2$ powder in water. (b) Dissolving the VO(acac)$_2$ powder in water in acidic conditions. (c) Equilibrium of the acetylacetone in water. (d) Equilibrium between species present during the M9 synthesis.
The pH was measured after stirring and complete dissolution of the powder giving a value of 5.14 when the concentration of VO(acac)\(_2\) was 0.1 M. When the precursor A is dissolved in water, the solution becomes acid because the complex coordinates with OH\(^-\) decreasing its concentration versus H\(_3\)O\(^+\) as in Figure 3.8(a). The coordination geometry shifts from a square pyramid to octahedral since the V\(^{4+}\) is unsaturated in its initial powder state, compound A \([36][38]\). The compound B can also be coordinated with water instead of a hydroxyl, so both compete for the axial vacant in the compound A. A similar explanation would be that V\(^{4+}\) anionic species exist near neutral pH \([39]\). This solution resulted in a dark green colour as it is shown in Figure 3.7 (right).

On the other hand, addition of 1 mL HCl 1 M resulted in a light blue solution characteristic of [VO(OH\(_2\))\(_5\)]\(^{2+}\) showed in Figure 3.7(right) that is the precursor in M9 HCl synthesis. The addition of protons release acetylacetonate since there is a tautomeric equilibrium as it shows Figure 3.8(c) forming acetylacetone. If the pH is lowered enough, all the initial compound A proceeds to form the compound C as in Figure 3.8 (b). However, if the pH increases to \(\approx 4\), protons start to be lost and hydrolysed species can be formed like [VO(OH\(_2\))\(_4\)(OH)]\(^+\).

To prove the change in colour respect to the M9 precursor solution, an absorbance measurement with UV-1800 UV spectrophotometer from Shimadzu was conducted. The UV-Vis spectra was practically equivalent in the region of the visible so the shift in the absorbed wavelength could not be perceived.

As previously stated, there is an equilibrium with the acetylacetonate, water and hydroxyls for the coordination with the metal oxide in the form of more species. These species coexhist in the suspension together with other species that are coordinated with hydroxyls, but depending on the concentration of protons of the solution the equilibrium shifts.

It was observed that the supernatant, during the precipitation step with THF, had a different colour, green-yellow. However, the supernatant colour was transparent when acetone was used in further purification steps. Depending on the ligand, the band structure of V=O shifts to lower energies in the antibonding \(e_\Pi^*\) energy level. This decrease of energy affects the
colour seen by visual inspection to more yellow suspensions because lower wavelength can be absorbed showing the complementary colour reflected.

![Figure 3.9: Change in band I absorption energy as a function of the strength of the axial interaction: (a) strong interaction; (b) weak interaction and (c) no interaction](image)

A weak interaction would be THF, dioxane or water while no interaction would be chloroform as in Figure 3.9. From IR studies of VO(acac)$_2$, the band that corresponds to the stretching of the V=O is situated in 995 cm$^{-1}$ [41]. The IR measurement in this system supports the shift towards lower energies since there is $\nu$(V=O) in 980 cm$^{-1}$, when a ligand is coordinated. The coordination ligand is unclear because water and THF have similar behaviour due to its nature.

Colour change in the vanadium (IV) compounds and solutions give a first insight of the possible molecules present so it is important to analyse it while conducting the experiment.

### 3.6 Size parameters

There are many parameters in the synthesis that can be adjusted in order to enhance the size of the NCs. First, the preparation of the sample must be optimized so a reliable measurement can be obtained during the DLS analysis. DLS samples were measured with a set of common parameters in order to have the same conditions for each one as shows Figure 3.10.

In order to have a reliable DLS measurement, an optimal sample con-
Centration is crucial. On one hand, high concentrated samples could lead to smaller sizes since the scattered light from one particle interacts with other particles before reaching the detector, losing intensity. However, it is probable that agglomerations are formed if the particles are unstable, except the right surfactants are used. Precipitation jeopardizes the experiment since it confirms the presence of bigger particles due to a wrong sample preparation. On the other hand, there might not be enough scattered light to measure the sample if it is too diluted. Dilution factors of 1, 1/2, 1/4, 1/10 and 1/50 were tried to study the optimal concentration of the sample.
The dilution factor has a direct influence on the Z-Average diameter of the particles since the more diluted is the sample the smaller are the particles. In Figure 3.11, it is illustrated the linear relation between these two parameters. Moreover, the dilution factor affects the count rate of the particles in an unknown relation because the data does not follow a clear pattern. The most reliable measurement is the one with the count rate closest to 500 since it is believed that samples with 500-600 kcps should give a reliable analysis [42]. Therefore, a 1/10 dilution factor is needed which corresponds to a $\approx 280 \mu g/mL$ concentration. It is an approximate value since the yield of the synthesis may variate after precipitation either purifications with acetone.

Once the optimal concentration of the sample is achieved, the study of other parameters can start. In this project, the duration of the synthesis in the microwave is studied due to being one of the most relevant parameters that influence the size in a typical NC synthesis.

The starting time of the synthesis is 60 min established from previous knowledge in the group because 50 nm NCs were seen with TEM as a first approach. Periods around the initial time were tried to study its impact on the NCs size. The results obtained are shown in Figure 3.12:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Z-Average [nm]</th>
<th>Mean PDI</th>
<th>Mean count rate [kcps]</th>
<th>Measurement duration [s]</th>
<th>Mean S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9 10 min</td>
<td>189 ± 2</td>
<td>0.181</td>
<td>370</td>
<td>60</td>
<td>0.875</td>
</tr>
<tr>
<td>M9 30 min</td>
<td>252 ± 2</td>
<td>0.109</td>
<td>167</td>
<td>70</td>
<td>0.929</td>
</tr>
<tr>
<td>M9 45 min</td>
<td>218 ± 0.4</td>
<td>0.092</td>
<td>208</td>
<td>60</td>
<td>0.875</td>
</tr>
<tr>
<td>M9 60 min</td>
<td>137 ± 0.5</td>
<td>0.192</td>
<td>488</td>
<td>60</td>
<td>0.854</td>
</tr>
<tr>
<td>M9 75 min</td>
<td>119 ± 1</td>
<td>0.100</td>
<td>283</td>
<td>60</td>
<td>0.901</td>
</tr>
<tr>
<td>M9 90 min</td>
<td>147 ± 1</td>
<td>0.128</td>
<td>166</td>
<td>80</td>
<td>0.916</td>
</tr>
</tbody>
</table>

Figure 3.12: Values of Z-average, PDI, count rate and S/N obtained during the variation of time in the synthesis M9.

The mean polydispersity index (PDI) represents the intensity of light scattered by various fractions of the particles differing in their sizes. From previous studies [42], a $\text{PDI} \leq 0.1$ is treated as a monodisperse value while a $0.1 \leq \text{PDI} \leq 0.4$ values are considered to be polydisperse. The PDI reflects moderately polydispersity in all the samples besides in M9 10 min and M9 60 min that indicated higher polydispersity.
In addition, another parameter that is important to a DLS measurement is the signal to noise ratio (S/N) since the noise varies inversely proportional to the square root of photon counted. There is a minimal photon count to achieve a good S/N ratio. In general, all the samples have a good S/N with similar values.

The measurement time is related to the mean count rate as it increases when the mean count rate is under 200 kcps because it needs more time to obtain the data.

The Z-Average size has the minimum value in M9 75 min with a good PDI and S/N but the mean count rate should be higher so the measurement can be trusted. The DLS measurement of this sample is reflected in Figure 3.13 where the size distribution has its maximum diameter in 119 nm. This second size approximation with DLS will be compared with TEM like the first theoretical approximation with XRD.

![Figure 3.13: Size distribution by intensity of sample M9 75 min in a DLS measurement.](image)

Shorter reaction times were tried but the samples were unstable because big agglomerates and bigger particles precipitated giving a turbid suspension so a DLS characterization could not be performed.

Synthesis with a shorter reaction time were also studied by the addition of 125 µL of HCl 1 M for more acidic conditions but the PDI showed high polydispersity and the size did not follow any pattern. NCs are believed to be bigger than the regular M9 synthesis but conclusions cannot be made since the results are inconclusive. This is another reason to believe that acetylacetonate acts like a nucleation agent in the synthesis since in acidic
conditions acetylacetonate is protonated and released from the initial precursor. However, by the addition of acid NCs were stabilized and measured from 20 min down to 5 min. It can be stated that more acidic conditions enhance the latter stabilization process in faster times but should not be performed size there is no control over the NCs size.

To decrease the NCs from the ones obtained with M9, synthesis with capping ligands were tried in order to decrease the NCs size. Citric acid monohydrate was added as a capping agent in a molar ratio of 1:10 to the VO(acac)₂ 0.1 M aqueous solution. The solution becomes clear dark green and the pH value is lowered to 1.56. From this solution two µM vials were prepared but in the second one NaOH 1 M was used to increase the pH. None of the solutions gave nanoparticles as a product so further research in capping the VO(acac)₂ is needed.

The understanding of the size is crucial to this study since it can lead to an understanding on how to improve the yield, to optimize the processes and to improve product performance.
3.7 TEM characterization

TEM measurements were performed to characterize the NCs size and its crystallinity. From previous data in this project, acetylacetonate is important to nucleation and growth of the NCs. It is also believed to be responsible for the elongated shape since it forces a preferential growth as it restricts the growth from the perpendicular axis.

![TEM images of the NCs obtained from a M9 sample.](image)

The TEM images in Figure 3.14 corroborate the starting theory of the elongation of the particles due to the presence of acetylacetonate. On the right image, it is clear that the sample is crystalline because of the presence of crystalline planes. To study in depth its growth, a calculation of the interplanar distance and its growing plane is done. The cell parameters of the possible monoclinic phases are listed in Figure 3.15.

The following formula is used to calculate the Miller indices (h,k,l) of the growing plane where a, b and c are the cell parameters; the angle between a and c; \(d_{hkl}\) is the distance between planes. The interplanar distance that was calculated from the TEM images is \(5.6 \pm 0.3 \text{ Å}\).

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{2hkcos(\beta)}{ac \sin^2(\beta)} + \frac{l^2}{c^2}
\]

With this \(d_{hkl}\), only the C2/m space group is possible because of the negative value of \(cos(\beta)\) in both monoclinic phases. Therefore, the only possible growing plane of the NCs is (010).
Electron diffraction patterns can show reflections corresponding to a resolution beyond X-rays. Therefore, selected-area electron diffraction (SAED) and convergent-beam electron diffraction (CBED) could be used to determine the space group and compare it with the one assumed for the calculations.

The NCs size was characterized also with TEM to compare it with the sizes obtained with XRD and DLS. A size distribution plot of the NCs is displayed in Figure 3.16. The NCs exhibit a wide range of sizes as the broad peak indicates. Therefore, control of the size needs to be achieved in further studies.

The mean size obtained from DLS is bigger than TEM because bigger particles disguise the result in DLS it is an intensity-based technique. In addition, DLS measures the hydrodynamic radius from the particles whereas
TEM grants the projected surface area based on the transmitted electrons through the sample. Moreover, DLS calculates the particle size in a solution so other ions and substances can be adsorbed on the surface making them bigger. The surfactants also have a role in enlarging the value from the DLS measurement since they are attached on the NCs surface whereas in the TEM images they are not considered. However, DLS provides more reliable data on size distribution since the amount of NCs counted is larger.
Chapter 4

Conclusions

The main conclusion of this paper is that VO$_2$(M) nanocrystals can be formed by a microwave assisted synthesis as a first step towards a DSD experiment to optimize the synthesis parameters.

Post annealing processes are not needed in order to get the right oxidation state and crystal phase because of the method and precursor used. Acetylacetonate is essential to obtain NCs and it assists its nucleation and growing. Furthermore, it affects its shape since it elongates the NCs in the preferential crystal plane (010). It controls the width of the NCs effectively while the length remain unrestrained. TEM is the most accurate technique used to measure the NCs size since length and width can be analysed whereas in DLS gave the size based in the hydrodynamic radius of the NCs. Further studies in surfactants and its concentration are needed to control also the length of the NCs so the global size can be reduced.

OAm and OA were able to stabilize the VO$_2$(M) NCs in chloroform. Moreover, a ZP measurement was able to determine than the NCs are not charge-stabilized. However, the presence of surfactants in the crystals surface needs to be further studied since the $^1$HNMR measurement were unable to confirm it

The colours of the vanadium helped to elucidate the composition in the solution. Furthermore, they can be used to have a first insight of the presence of the NCs in the right oxidation state.


[27] F. J. Quites and H. O. Pastore, Hydrothermal synthesis of nanocrystalline \( \text{VO}_2 \) from poly(diallyldimethylammonium) chloride and \( \text{V}_2\text{O}_5 \), 2010.


