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# Synthesis of naked vanadium pentoxide nanoparticles

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Vanadium pentoxide is the most important vanadium compound by being the precursor to most vanadium alloys. It also plays an essential role in the production of sulfuric acid as well as in metal-ion batteries and supercapacitors. In this paper, pulsed laser ablation in liquids is used to synthesize “naked” vanadium pentoxide nanostructures. The resulting particles take up “nearly-spherical” and “flower-like” morphologies, composed of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\beta$ -V<sub>2</sub>O<sub>5</sub> crystalline phases. Even “naked”, the nanostructures are stable in time with a zeta potential of  $-51 \pm 7$  mV. In order to maximize the production of vanadium pentoxide nanostructure, the optimal repetition rate was determined to be @  $\sim 6600$  Hz when irradiating a pure vanadium target in DI-water. This corresponds to a cavitation bubble lifetime of around  $\sim 0.15$  ms. At that repetition rate, the production reached  $\sim 10$  ppm per minute of irradiation. Finally, from the characterization of the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\beta$ -V<sub>2</sub>O<sub>5</sub> nanostructures, the surface energy of each phase has been carefully determined at 0.308 and 1.483 J cm<sup>-2</sup>, respectively. Consequently, the  $\beta$ -phase was found to display a surface energy very close to platinum. The exciton Bohr radius has been determined at 3.5  $\pm$  0.7 nm and 2.0  $\pm$  0.6 nm for  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\beta$ -V<sub>2</sub>O<sub>5</sub> phases, respectively.

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## 1 Introduction

Vanadium (V) is a transition metal discovered in 1801 by the mineralogist Andrés Manuel del Río in Mexico.<sup>1</sup> It is the 6<sup>th</sup> most abundant transition metal on Earth, the 21<sup>st</sup> most abundant chemical element in the Earth's crust and the 2<sup>nd</sup> most abundant chemical element in seawater.<sup>2-5</sup> The world top 3 producers and reserve holders are China, South Africa and Russia.<sup>2,6</sup> Domestically, the United States has reserves estimated to 45 000 tons. Utah is the primary producer with its White Mesa mill located South East of the state on the Colorado Plateau; while Arkansas, Delaware, Ohio, Pennsylvania and Texas are secondary producers.<sup>6</sup> The importance of vanadium in chemistry is due to its wide range of oxidation states. Indeed, vanadium is often found in oxides with the following oxidation states +5 (V<sub>2</sub>O<sub>5</sub>), +4 (VO<sub>2</sub>), +3 (V<sub>2</sub>O<sub>3</sub>) and even +2 (VO). The most important oxide is vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>, also known as *vanadia*) which is used as a catalyst for the production of sulfuric acid.<sup>5</sup> Platinum used to be the catalyst for this chemical reaction; however, as platinum reacts with arsenic impurities possibly present in the sulphur feedstock, V<sub>2</sub>O<sub>5</sub> is now preferred. V<sub>2</sub>O<sub>5</sub> is also suitable in electrochemical

applications.<sup>7,8</sup> Indeed, V<sub>2</sub>O<sub>5</sub> has been extensively studied as electrode materials in lithium-ion batteries (LIBs),<sup>9-11</sup> in aluminum-ion batteries (AIBs),<sup>12</sup> zinc-ion batteries (ZIBs)<sup>13,14</sup> and in supercapacitors<sup>15,16</sup> due to its unique crystalline structure. It is also used as a nano-powder in latent finger print detection (LFPD).<sup>17</sup> Furthermore, the surface of V<sub>2</sub>O<sub>5</sub> undergoes an insulator-metal transition (IMT) around  $\sim 350$ – $550$  K (ref. 18 and 19) and this property has been successfully used to build nitrogen dioxide sensors.<sup>20</sup> Additionally, V<sub>2</sub>O<sub>5</sub> is also used in photo-detectors.<sup>21</sup>

Vanadium pentoxide has three polymorphs,  $\alpha$ -V<sub>2</sub>O<sub>5</sub> (orthorhombic),  $\beta$ -V<sub>2</sub>O<sub>5</sub> (monoclinic or tetragonal) and  $\delta$ -V<sub>2</sub>O<sub>5</sub> (orthorhombic).<sup>22</sup> The  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase is the most stable phase and the other two phases can be obtained under high pressure and high temperature.

V<sub>2</sub>O<sub>5</sub> nanostructures (NSs) has been produced by wet-chemistry<sup>23</sup> and pulsed laser deposition.<sup>24</sup> But only a small number of groups have investigated the synthesis of vanadium oxide NSs by Pulsed Laser Ablation in Liquids (PLAL).<sup>25,26</sup> PLAL synthesis has several advantages compared to wet-chemistry, the main one is that the surface of the synthesized nanoparticles is totally free of any contaminants *i.e.* left-over from chemical reactions or surfactants. This surface purity is really important for nanoparticles used as catalysts or bio-medical agents. In this work, we present a new synthesis protocol to produce “naked” (*i.e.* free of any contaminants) V<sub>2</sub>O<sub>5</sub> NSs. Those V<sub>2</sub>O<sub>5</sub> NSs are great candidates to be used in catalytic and biomedical applications. The synthesis and characterization are

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detailed in Sections 2 and 3, respectively. The results and discussion are mentioned in Sections 4 and 5, respectively. Finally, the conclusions are described in Section 6.

## 2 Materials and methods

A Q-switched Nd:YAG laser from Electro Scientific Industries operating @ 1064 nm was used to irradiate a vanadium target. Bulk vanadium flakes (99.5% from Johnson Matthey) were used as the target in this experiment. The dimensions of the flakes are  $\sim 2$  mm by  $\sim 2$  mm. The flakes were rinsed in DI water and then immersed in 5 ml of DI water, contained in a 50 ml rounded single neck glass flask. Consequently, the height of the liquid above the surface of the target was measured to be 8 mm. The pulse repetition rate of the laser was varied from 1 kHz to 10 kHz. Consequently, the pulse duration time varied slightly from 70 ns to 200 ns depending on the repetition rate. The laser shined a pulsed beam with an energy per pulse around 10 mJ per pulse @ 1000 Hz. The beam was deflected by a flat mirror oriented @  $45^\circ$  angle (with respect to the laser rail) in order to irradiate the target from the top and was then focused by using an 83 mm focal length lens. The beam's spot size on the target was measured by scanning electron microscopy (SEM) to be around  $\sim 45$   $\mu\text{m}$ . Therefore, the intensity of the laser is determined to be around  $\sim 8 \times 10^5$   $\text{W cm}^{-2}$ . At 1000 Hz, the fluence is calculated to be  $\sim 6 \times 10^2$   $\text{J cm}^{-2}$ . The target was finally irradiated for 5 min.

The colloidal solutions were characterized by UV-visible spectroscopy (Cary 60 from Agilent), Atomic Emission Spectroscopy (4210 MP-AES from Agilent), Raman Spectroscopy (EZRaman-N from Enwave Optronics, Inc.), X-ray diffraction (Bruker D8-Discover Diffractometer), X-ray Photoelectron Spectroscopy (K-Alpha XPS from Thermo Scientific), Dynamic Light Scattering (NanoBrook 90Plus Zeta from Brookhaven Instruments Corporation), Scanning Electron Microscopy (JEOL JSM – 7000F SEM, equipped with a field emission gun and operating at 30 kV) and Transmission Electron Microscope (JEOL-JEM-2100F TEM operating at 80 kV).

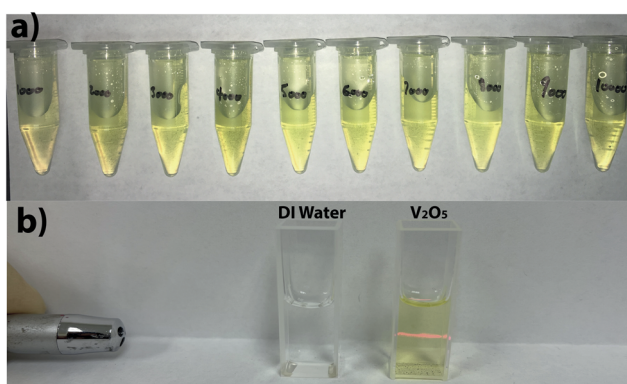


Fig. 1 (a) Photo of the colloidal solutions synthesized at different repetition rate from 1000 Hz to 10 000 Hz. (b) Tyndall effect observed on one of the  $\text{V}_2\text{O}_5$  colloidal solution.

To perform Raman, XRD and SEM analysis, a droplet of the colloidal solution was deposited onto a silicon wafer and dried in an environmentally controlled glove box. The TEM analysis was performed using a copper TEM grid. X-ray Photoelectron Spectroscopy (XPS) has been performed by using the following etching condition, 200 eV for 20 seconds. The XPS spectra was analyzed with the fitting software, called Avantage.

## 3 Results

From the direct observation of all the colloidal solutions, it is observed that they all exhibit a yellow color (Fig. 2a). The vanadium oxide stoichiometry of the NSs can be guessed directly from the color of the colloidal solution.<sup>9</sup> Indeed, vanadium exhibits four common oxidation states +5, +4, +3, and +2, each of which can be distinguished by its color, yellow for +5, blue for +4, green for +3 and violet for +2.<sup>9</sup> As the color of the colloidal solutions obtained by pulsed laser ablation is yellow, it

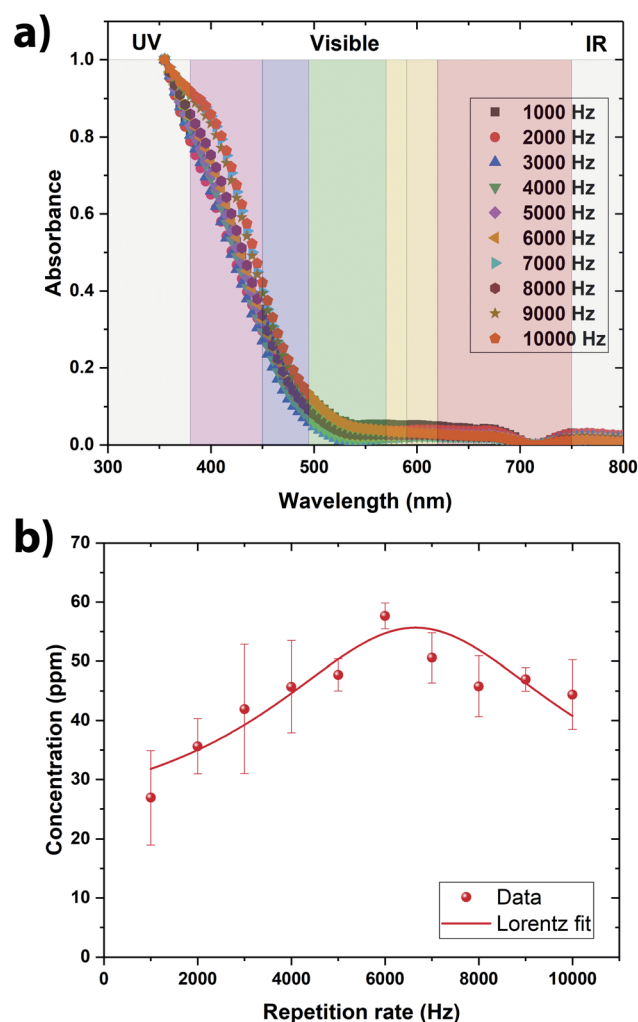


Fig. 2 (a) UV-visible spectra of all the samples. (b) Concentration of vanadium versus the laser repetition rate. The vanadium concentration was measured by Atomic Emission Spectroscopy (4210 MP-AES from Agilent). The maximum is reached at  $\sim 6600$  Hz. The irradiation time was set to 5 min for all samples.



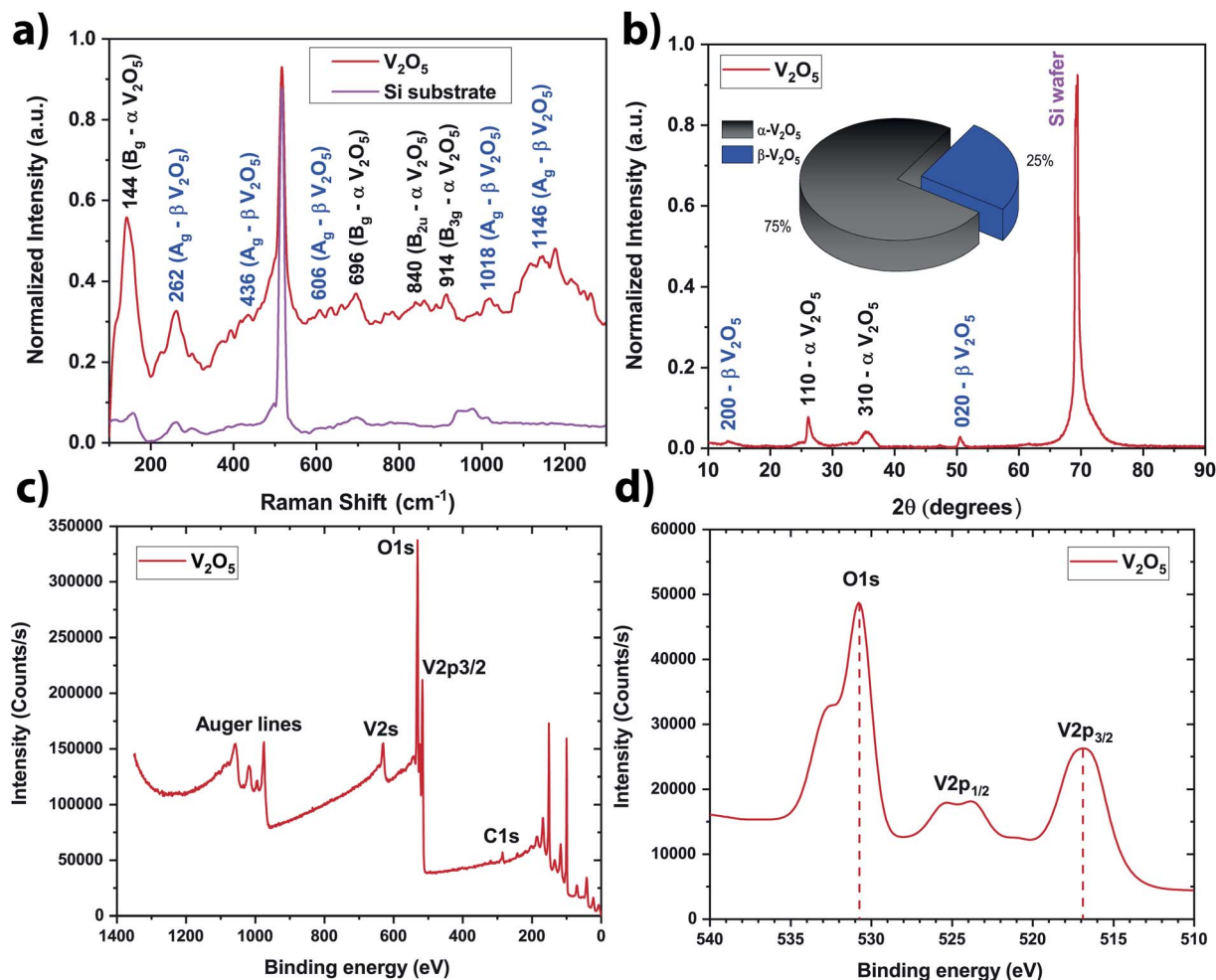


Fig. 3 (a) Raman spectra of the NSs synthesized @ 6600 Hz and the silicon substrate. The identified modes of vibration indicates the formation of  $V_2O_5$  structure. The laser of the Raman spectrometer was 532 nm and its power was 0.5 mW. (b) XRD spectrum of the NSs synthesized @ 6600 Hz. Inset: crystallinity repartition between  $\alpha$ - $V_2O_5$  and  $\beta$ - $V_2O_5$  (c) wide and (d) narrow XPS spectra of the NSs synthesized @ 6600 Hz.

is evident that  $V_2O_5$  has been produced (Fig. 1a). By shining a pointer laser beam through each sample, the Tyndall effect was observed as illustrated in Fig. 1b. Indeed, the Tyndall effect is the scattering of light as a laser beam passes through a colloidal solution. The presence of particles scatter and reflect the laser light, making the laser beam visible.<sup>27,28</sup> The high oxidation state of vanadium make the NSs absorbing mainly in the violet region, consequently displaying the complementary color in the yellow region (Fig. 2a). From the UV-visible spectroscopy analysis, it seems that the colloidal solutions synthesized at 6000 Hz and 7000 Hz were the ones that absorb the most in the UV-visible region meaning consequently that they contain the largest amount of NSs (Fig. 2a).

In order to be quantitative, the vanadium concentration contained in each colloidal solution was determined by Atomic Emission Spectroscopy (AES). The data were plotted in Fig. 2b. By fitting the data, the optimal repetition rate producing the highest vanadium concentration was determined to be around  $6652 \text{ Hz} \pm 290 \text{ Hz}$ . By taking the reciprocal value of this repetition rate, the cavitation bubble lifetime can be estimated

around  $0.15 \text{ ms} \pm 0.01 \text{ ms}$ . This value is similar to the one obtained when irradiating metallic target in deionized water.<sup>29–32</sup> Hitting the target at the repetition rate higher than 6652 Hz is not going to produce more nanoparticle in solution because the laser beam is going to hit the cavitation bubble shielding the target from the beam. Therefore, in a static configuration (the laser beam hits always the same spot on the target), the optimal repetition rate was set to 6600 Hz (the smallest repetition rate increment on the ESI laser is 100 Hz). At this repetition rate, the vanadium concentration in the colloidal solution reaches  $\sim 55 \text{ ppm}$  within 5 min of irradiation (Fig. 2b). As  $V_2O_5$  has several polymorphs, Raman spectroscopy and XRD analysis were performed to determine the exact crystalline structure of  $V_2O_5$  contained in the colloidal solution. The crystalline structure adopted by the NSs produced @ 6600 Hz was the  $\alpha$ - and  $\beta$ - $V_2O_5$  phases as shown by the Raman and XRD spectra (Fig. 3a and b).<sup>7,35</sup> As shown in the inset of Fig. 3b, the quantities of  $\alpha$ - and  $\beta$ -phases of  $V_2O_5$  have been evaluated to 75% and 25%, respectively, by calculating the surface area underneath each peak. The  $\beta$ -phase is the first high pressure



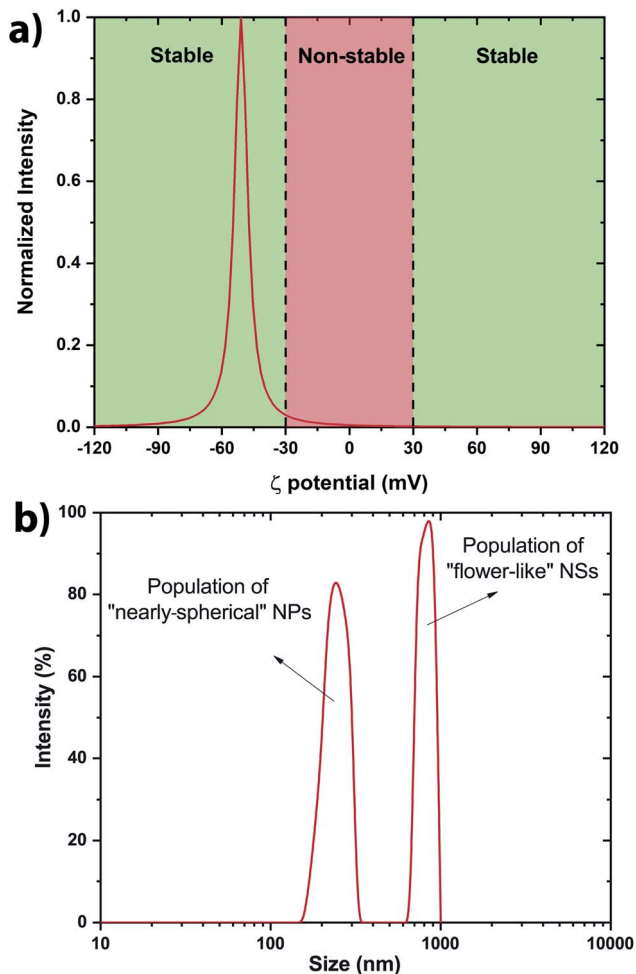


Fig. 4 (a) Zeta potential of  $V_2O_5$  colloidal solution synthesized by PLAL @ 6600 Hz. It has been determined at  $-51 \pm 7$  mV. (b) Size distribution measured by dynamic light scattering of  $V_2O_5$  colloidal solution synthesized by PLAL @ 6600 Hz. Two populations have been identified.

phase of  $V_2O_5$  obtained from  $\alpha$ - $V_2O_5$  by the application of isotropic pressure between 4 to 10 GPa at temperatures between room temperature and 1023 K.<sup>36</sup> Based on the synthesis conditions encountered in PLAL, the  $\alpha$ -phase seems to be produced during the early stages of bubble expansion while the  $\beta$ -phase seems to be produced at the end during the cavitation bubble collapse.<sup>37</sup> By using the Scherrer equation,<sup>38</sup> the crystallite size in both phases has been determined around  $\sim 13$  nm and  $\sim 6$  nm for the  $\alpha$ - and  $\beta$ - $V_2O_5$  phases. Furthermore, the XPS spectra are shown on Fig. 3c and d. The C 1s, O 1s, and V 2p core levels were measured. The peak located at  $\sim 517$  eV corresponds to the  $V^{5+}$  oxidation state meaning that  $V_2O_5$  is found at the surface of the NSs.<sup>39–41</sup>

The stability of the NSs present within the colloidal solution has been determined by measuring the  $\zeta$  potential.<sup>42,43</sup> It has been measured at  $-51 \pm 7$  mV indicating a stable colloidal solution (Fig. 4a). Indeed, solutions with  $\zeta$  potential smaller than  $-30$  mV or larger than  $+30$  mV are considered as stable. The negative sign of the  $\zeta$  potential means that the net charge of

the scattering NS is negative. This prevents the structure from further reacting within its own environment. A rough estimation of the size distribution has been performed by Dynamic Light Scattering (DLS) revealing two main populations within the colloidal solutions (Fig. 4b). Scanning electron microscopy (SEM) was also performed to determine accurately the morphology of the  $V_2O_5$  NSs.

From Fig. 5, it is clear that two main populations were produced. One population is made of “nearly-spherical” NPs with sizes below 100 nm. The other population is made of “flower-like” type of NSs with an overall size of almost a micron. The flower like structure seems to be linked to the natural tendency of  $V_2O_5$  to grow as a monolayer.<sup>44</sup> Furthermore, a closer look at the NSs by Transmission Electron Microscopy (TEM) revealed that the “nearly-spherical” NPs were adopting an  $\alpha$ -phase  $V_2O_5$  while the “flower-like” type NSs were adopting the  $\beta$ -phase  $V_2O_5$  (Fig. 6). Finally, the energy bandgap of both types of NSs was determined by using the Tauc plot (Fig. 7). The Tauc plot is achieved by plotting  $(\alpha h\nu)^{1/r}$  versus the energy of light using  $1/2$  as numerical value for the parameter  $r$ . The value of  $r$  denotes the nature of the transition:  $r = 1/2$  for a direct transition while  $r = 2$  for an indirect transition. By extrapolating the linear regime of the Tauc plot to the abscissa yields to the energy bandgap.<sup>45,46</sup> From Fig. 7, two energies bandgap were determined at 2.50 eV and 3.65 eV, both corresponding to a direct transition. At the bulk scale, the energies bandgap of  $\alpha$ - and  $\beta$ - $V_2O_5$  have been determined at 2.30 and 3.45 eV, respectively.<sup>47,48</sup> Therefore, it is normal to measure a slightly larger value for each energy bandgap due size effects affecting material properties at the nanoscale.<sup>49,50</sup>

## 4 Discussion

The first paper reporting the synthesis of vanadium pentoxide nanoparticles by PLAL was published by Celestino-Santos *et al.*<sup>33</sup> in 2011. The particles were distributed into two populations, one around  $\sim 10$  nm and another one around  $\sim 60$  nm. The nanoparticles are a mixture of amorphous and  $\beta$ - $V_2O_5$  phases. The second paper from the same group was published in 2012 by Bezerra *et al.*<sup>34</sup> who also reported the synthesis of  $\beta$ - $V_2O_5$  NPs. The size of nanoparticles ranges from a couple of nm to more than 100 nm.

In this paper,  $\alpha$ - and  $\beta$ - $V_2O_5$  NSs were obtained by irradiating, at high repetition rate *i.e.* in the kHz regime, a target made of vanadium flakes immersed into de-ionized (DI) water. A new morphology was synthesized beside the “nearly spherical” NPs, and it looks like a “flower-like” NSs. All the groups used either distilled or de-ionized water as solvent. All the groups used a nanosecond laser meaning that the pulse duration is in the nanosecond regime. A table summarizing the synthesis conditions of all the groups is shown in Table 1.

To be complete, there is a paper published in 2019 by Val'vano *et al.*<sup>51</sup> who reported the synthesis of  $V_{16}O_{33}$  by PLAL. The average nanoparticle size was around  $\sim 45$  nm. Most of the synthesized nanoparticles were amorphous. The target was rotating at 2 rpm so the irradiation spot was circularly displaced on the target surface. Therefore, the key parameters to produce



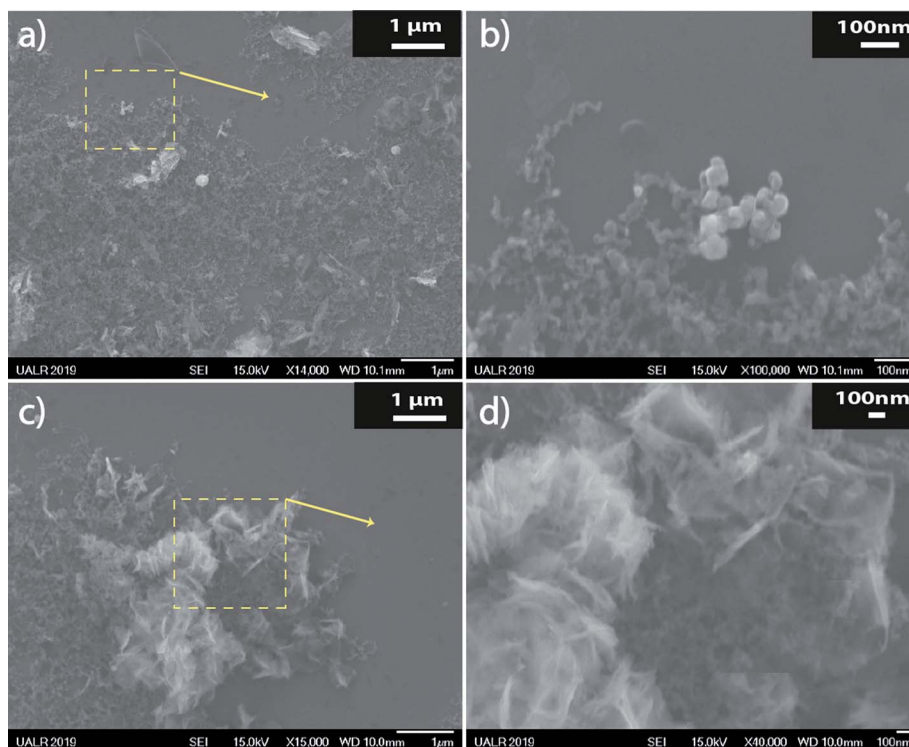


Fig. 5 (a)–(d) SEM images of the NSs synthesized @ 6600 Hz (JEOL JSM – 7000F SEM). Various populations of  $V_2O_5$  NSs are observed but two main populations can be distinguish such as nearly-spherical NPs (a and b) and such as some flower-type of nanostructure (c and d). Images (b) and (d) have been taken within the red square indicated in images (a) and (c), respectively.

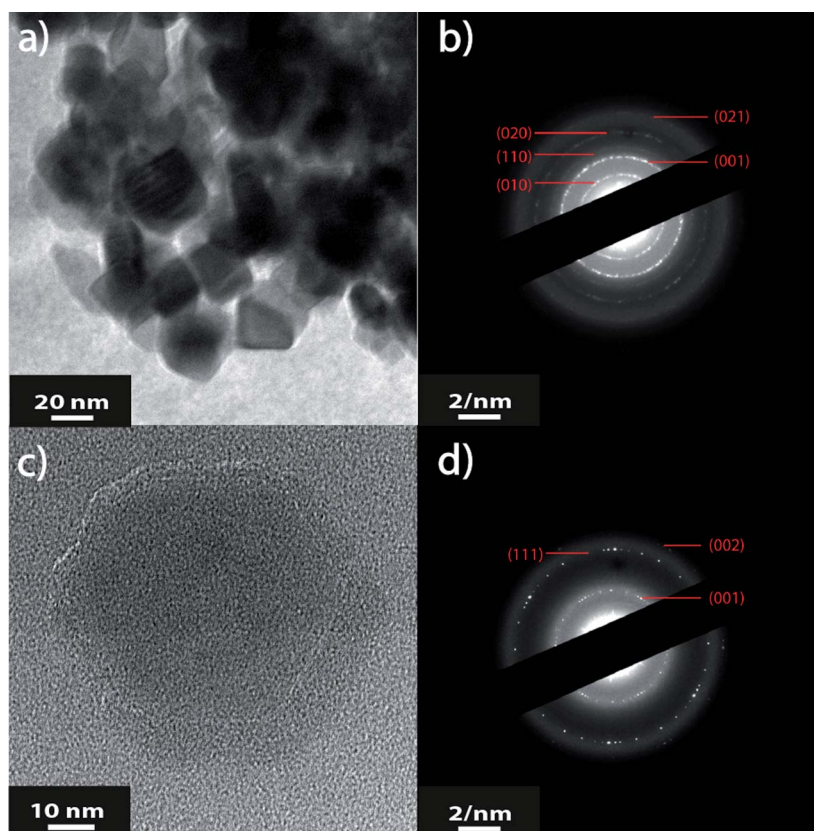


Fig. 6 (a) TEM image of the nearly spherical  $V_2O_5$  NPs. (b) Diffraction pattern corresponding to (a) and revealing the alpha-phase of  $V_2O_5$ . (c) TEM image of the “flower-like” type of  $V_2O_5$  NSs. (d) Diffraction pattern corresponding to (c) and revealing the  $\beta$ -phase of  $V_2O_5$ .



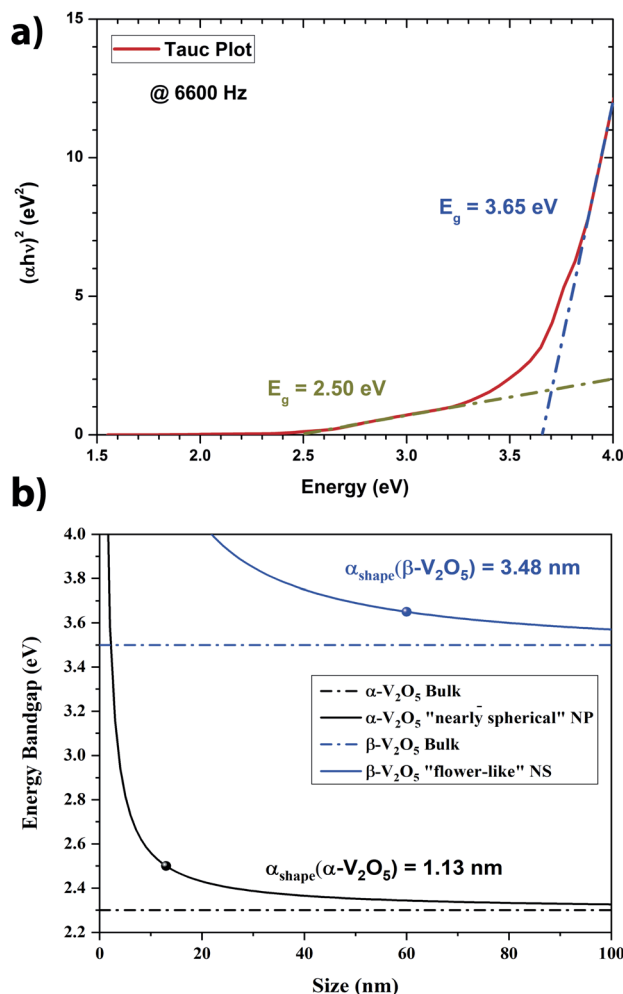


Fig. 7 (a) Tauc plot of the  $V_2O_5$  NSs synthesized @ 6600 Hz by PLAL. Two energy bandgaps have been identified at 2.50 eV and 3.65 eV. (b) Size effect on the energy bandgap of  $V_2O_5$  calculated by nano-thermodynamics.

Table 1 List of all vanadium pentoxide NPs and NSs synthesized by PLAL

Parameters	Ref. 33	Ref. 34	This work
Type of laser	Nd:YAG	Nd:YAG	Nd:YAG
Wavelength	1064 nm	1064 nm	1064 nm
Repetition rate	0.3 kHz	1 kHz	1–10 kHz
Pulse duration	150 ns	200 ns	75–200 ns
Fluence	$\sim 80 \text{ J cm}^{-2}$	$\sim 80 \text{ J cm}^{-2}$	76–764 $\text{J cm}^{-2}$
Irradiation time	10 min	265 min	5 min
Solvent	Distilled water	Distilled water	DI water
Populations	2	1	2
Size	$\sim 10 \text{ nm}$ & $\sim 60 \text{ nm}$	$\sim 6 \text{ nm}$	$\sim 13 \text{ nm}$ & $x \sim 200 \text{ nm}$ , $y \sim 300 \text{ nm}$ and $z \sim 60 \text{ nm}$
Crystalline structure	$\beta\text{-}V_2O_5$	$\beta\text{-}V_2O_5$	$\alpha\text{-}V_2O_5$ ; $\beta\text{-}V_2O_5$
Morphology	Spherical NPs	Spherical NPs	Nearly-spherical NPs; "flower-like NSs"
Potential application	Biomedical sensor	Biomedical sensor	Catalyst

those "flower-like"  $V_2O_5$  NSs seems to be the larger fluence used in this paper and the higher repetition rate.

Theoretically, the size effect on the energy bandgap of  $V_2O_5$  can be predicted by using nano-thermodynamics.<sup>49</sup> According to the theory, the energy bandgap of the nanostructure can be expressed as:

$$\frac{E_g(D)}{E_{g,\infty}} = 1 + \frac{\alpha_{\text{shape}}}{D} \quad (1)$$

where  $E_g(D)$  is the energy bandgap of a  $V_2O_5$  nanostructure having a size  $D$ .  $E_{g,\infty}$  is the energy bandgap of  $V_2O_5$  at the bulk scale.  $\alpha_{\text{shape}}$  is the parameter quantifying the size and shape effects on the considered material property. Furthermore, eqn (1) can be rewritten as:

$$\Delta E_g = \frac{\alpha_{\text{shape}}}{D} E_{g,\infty} \quad (2)$$

In Fig. 7a, the energy difference,  $\Delta E_g$ , between the  $V_2O_5$  nanostructure and the bulk has been determined to be 0.2 eV. Therefore, by using the Scherrer equation on the XRD spectra (Fig. 7b) the crystallite size has been determined around 13 nm for the  $\alpha\text{-}V_2O_5$  nanostructure. By assuming the crystallite size is the same as the size of the nanostructure, the  $\alpha_{\text{shape}}$  parameter for an  $\alpha\text{-}V_2O_5$  sphere has been determined at 1.13 nm. By assuming a rectangular morphology for the  $\beta\text{-}V_2O_5$  flake having the following dimensions,  $x \sim 200 \text{ nm}$ ,  $y \sim 300 \text{ nm}$  and  $z \sim 60 \text{ nm}$ , is estimated to be around 3.48 nm. It is possible to predict the surface energy of  $\alpha\text{-}V_2O_5$  and  $\beta\text{-}V_2O_5$  by using the definition of  $\alpha_{\text{shape}}$ . Indeed,  $\alpha_{\text{shape}}$  is defined as:

$$\frac{\alpha_{\text{shape}}}{D} = \frac{(\gamma_s - \gamma_l) A}{\Delta H_{m,\infty} V} \quad (3)$$

where  $\gamma_s$  and  $\gamma_l$  are the solid and liquid surface energy of  $V_2O_5$ .  $\Delta H_{m,\infty}$  is the bulk melting enthalpy of  $V_2O_5$ .  $A/V$  is the surface to volume ratio of the  $V_2O_5$  nanostructure.

From Table 2, and  $\gamma_l$  are well known experimentally; the surface to volume ratio of the  $\alpha\text{-}V_2O_5$  nanostructures is very similar to the one of a sphere ( $\sim 6/D$ ). Therefore, by using  $\alpha_{\text{shape}} = 1.13 \text{ nm}$ ,  $\gamma_s$  is predicted to be around  $0.308 \text{ J m}^{-2}$ . This value is well within the range of theoretical values, 0.171 and  $0.893 \text{ J m}^{-2}$ , announced by Kristoffersen *et al.* for  $\alpha\text{-}V_2O_5$  (ref. 56) as well as the range of theoretical values 0.047 and  $0.550 \text{ J m}^{-2}$  reported by Goclon *et al.*<sup>57</sup> By using  $\alpha_{\text{shape}} = 3.48 \text{ nm}$  for the  $\beta\text{-}V_2O_5$  flake, the  $\gamma_s$  is predicted to be around  $1.483 \text{ J m}^{-2}$ . It

Table 2 Some material properties of  $V_2O_5$  used to quantify the magnitude of the size effect and the quantum confinement

Material property	$\alpha\text{-}V_2O_5$	$\beta\text{-}V_2O_5$
$T_{m,\infty}$ (K) (ref. 52)	963	
$\Delta H_{m,\infty}$ ( $\text{J m}^{-3}$ ) (ref. 52 and 53)	$1.21 \times 10^9$	
$\gamma_l$ ( $\text{J m}^{-2}$ ) (ref. 54 and 55)	0.080	
$\gamma_s$ ( $\text{J m}^{-2}$ )	0.308	1.483
$E_{g,\infty}$ (eV) (ref. 47 and 48)	2.30	3.45
$a_b$ (nm)	$3.5 \pm 0.7$	$2.0 \pm 0.6$
$\alpha_{\text{shape}}$ (nm)	1.13	3.48



makes sense to get a larger surface energy value for the  $\beta$ -V<sub>2</sub>O<sub>5</sub> phase than for the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase, as the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is the most thermodynamically stable. Higher surface energies generally correspond to higher surface chemical reactivities; consequently,  $\beta$ -V<sub>2</sub>O<sub>5</sub> flake is more catalytically active than  $\alpha$ -V<sub>2</sub>O<sub>5</sub>.<sup>58</sup> Furthermore, the surface energy of  $\beta$ -V<sub>2</sub>O<sub>5</sub> flake is very close to the one of Platinum (Pt). Indeed, the surface energy of Pt ranges between 1.464 and 1.935 J m<sup>-2</sup> depending on its crystalline orientation.<sup>58</sup>

By using the following equation, the atomic Bohr radius of V<sub>2</sub>O<sub>5</sub> can also be predicted:<sup>50</sup>

$$\log(a_{B,ex}) = a + b \times \log(E_g) \quad (4)$$

where  $a_{B,ex}$  is the exciton Bohr radius expressed in nanometers,  $E_g$  is the bulk energy bandgap at 300 K expressed in electronvolts,  $a = 1.04434 \pm 0.04976$  and  $b = -1.37696 \pm 0.10488$ . Consequently, the exciton Bohr radius of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\beta$ -V<sub>2</sub>O<sub>5</sub> are determined at  $3.5 \pm 0.7$  nm and at  $2.0 \pm 0.6$  nm, respectively. Our values are in agreement with the one reported by Beke  $\sim 4.5$  nm.<sup>59</sup>

Consequently, in order to obtain quantum nanostructures of V<sub>2</sub>O<sub>5</sub> with the PLAL protocol, it is necessary to increase the irradiation time. This can be done by adding a second step irradiation to the current protocol; indeed, the first step is to produce the nanostructures in solution by irradiating the target, while the second step would just irradiate the colloidal solution without the target being present.

## 5 Conclusion

Vanadium pentoxide nanostructures have been successfully synthesized by PLAL. It is the first time that “naked” V<sub>2</sub>O<sub>5</sub> NSs were successfully synthesized by PLAL. The colloidal solution was very stable with time with a zeta potential of  $-51 \pm 7$  mV. The lifetime of the cavitation bubble ( $\sim 0.15$  ms) and the optimal repetition rate ( $\sim 6600$  Hz) have been determined when the target was kept static with respect to the laser beam. Two main population of NSs have been produced such as “nearly-spherical” NPs and “flower-like” type of NSs. The “nearly-spherical” NPs adopted an  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase while the “flower-like” NSs adopted a  $\beta$ -V<sub>2</sub>O<sub>5</sub> phase. Furthermore, the surface energies of  $\alpha$ - and  $\beta$ -phases have been estimated to 0.308 and 1.483 J m<sup>-2</sup>, respectively. Additionally, the bandgap energy is determined to be 2.5 and 3.48 eV for the “nearly spherical” NPs and “flower-like” type of NSs, respectively. Finally, a two-steps irradiation protocol is under development to synthesize V<sub>2</sub>O<sub>5</sub> quantum structures. Future work will focus on promoting the flower-like nanostructures, as they have similar surface energy to Pt, which makes it a candidate to replace Pt in most chemical reactions. More work is underway to promote the growth of naked “flower-like” nanostructures with a  $\beta$ -V<sub>2</sub>O<sub>5</sub> phase in order to design cheaper catalysts and make the synthesis protocol shape-selective.

## Conflicts of interest

There are no conflicts to declare.

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