

# Hydrothermal growth of $V_2O_5$ photoactive films at low temperatures

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## ABSTRACT

It is shown that the surface morphology and the photoactivity of hydrothermally grown  $V_2O_5$  films at 95 °C are greatly affected by the deposition time. Well-defined phase of  $V_2O_5$  films grown for a deposition period of 2 h were found to exhibit significant photocatalytic activity, degrading stearic acid by 57%. The films presented a relatively porous structure, appearing as a wall-like network. The correlation of deposition period with the structure, morphology and the photoinduced properties of the materials are discussed.

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## 1. Introduction

Photocatalysis offers a convenient technology to assist and accelerate chemical reactions under UV illumination. Therefore, the growth of novel, inexpensive photocatalytic materials has attracted significant interest, because it may provide solutions to industrialization and environmental pollution problems and applications [1–5] like deodorization, anti-bacteria,  $NO_x$  decomposition, air and wastewater treatment [6].

$V_2O_5$  (vanadium oxide), with a band gap energy of 2.80 eV [7], is a subject of intensive study because its unique physical and chemical properties allow a wide range of practical applications such as electrochromic devices, cathodic electrodes for lithium batteries, gas sensors and so on [8–12]. Among its interesting properties and possible applications, the photocatalytic action of  $V_2O_5$  makes it a promising candidate for the degradation of organic pollutants such as hydrocarbons (not only alkenes but also alkanes) [13]. This is a great advantage since degradation of propene using illuminated  $TiO_2$  gives carbon dioxide even at a low conversion level [14]. On the other hand, the photodegradation of alkenes over silica-supported vanadium oxide produces aldehydes and ketones mainly [15,16]. Recently, Fei et al. synthesized by solvo-thermal route hollow  $V_2O_5$  microspheres exhibiting excellent photoactivity for degradation of rhodamine B (RhB) under UV light [17]. Furthermore, uniform

$V_2O_5 \cdot xH_2O$  nanobelts and nanorolls with high aspect ratios were synthesized by hydrothermal route in the presence of sulfuric acid or acetic acid. As was observed, their morphology and composition had an evident impact on their photocatalytic activities [18]. Finally, multiple layered semiconductor systems have been prepared and used for photocatalytic reactions, like  $V_2O_5/SmVO_4$  [19] and  $V_2O_5/BiVO_4$  [20] for the degradation of acetone and methylene blue, respectively.

However, the commercial applications of  $V_2O_5$  powders can be hindered by the difficulty for their reuse and the achievement of efficient separation and recovery from wastewater after UV illumination. To avoid the use of powders, various ways have been developed for the deposition of  $V_2O_5$  coatings on various substrates. The coating's advantages are the increase of material's thermal, mechanical or chemical stability, wear protection, durability or lifetime [21]. Many chemical routes, such as chemical vapour deposition [22–25], sol–gel method [26], electrochemical deposition [27] and hydrothermal growth [28–30] have been employed to prepare vanadium oxides. Among these methods, hydrothermal synthesis is a ‘solution chemical processing’, which provides an easy, simple, cost-effective and environmental friendly route to prepare (amorphous or crystalline) metal oxide thin films at low temperature and short reaction time [31,32].

In the present work, we deposited well-defined phase of  $V_2O_5$  thin films from an inorganic precursor,  $V_2O_5$ , using hydrothermal growth at 95 °C for a range of deposition periods. The effect of growth time on the microstructural evolution, crystal phase, surface area and photocatalytic capability of vanadium oxide thin films was investigated.

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## 2. Experimental

The growth of vanadium oxide on microscope glass was performed by hydrothermal method using commercial  $V_2O_5$  powder, NaOH (sodium hydroxide) and MilliQ  $H_2O$  as precursors. In a typical procedure, the solution preparation involved the stirring of 50 ml, 0.2 M NaOH with 0.0016 M  $V_2O_5$  for approximately 30 min. In each case, the solution was placed in a Pyrex glass bottle with polypropylene autoclavable screw cap, with the substrate positioned on the bottom and heated at 95 °C for various time periods in the range 1–30 h in a regular laboratory oven. After deposition, the samples were thoroughly washed with MilliQ  $H_2O$  in order to eliminate residual salts, and dried in air at 95 °C. Deposition is achieved with the parallel formation and subsequent precipitation of  $V_2O_5$  crystals on the bottom of the bottle.

X-ray diffraction (XRD) measurements were performed using a Rigaku (RINT 2000) diffractometer with  $Cu K\alpha$  for  $2\theta = 10.00$ – $50.00^\circ$ , a range of step sizes and time step  $30 s^\circ$  with various glancing angles,  $0.5^\circ$ ,  $1^\circ$ ,  $1.5^\circ$  and  $2^\circ$ . Raman measurements were performed with a Nicolet Almega XR micro-Raman system operating at wavenumber range  $100$ – $1100\text{ cm}^{-1}$  using a 473 nm laser. UV–Vis transmittance measurements were carried out using a Perkin–Elmer Lambda 950 spectrometer over the wavelength range of  $250$ – $700\text{ nm}$ . Surface imaging was carried out on an atomic force microscopy (AFM) in tapping mode (Digital Instruments – Nanoscope IIIa). The tip used was Si. Scanning electron microscopy (SEM) was done on a Jeol JSM-6390LV electron microscope. For the SEM characterization, all samples were over-coated with a thin film of carbon, in order to make them more conductive. Finally, the photocatalytic activity of the samples was assessed utilizing a stearic acid test [33]. Samples were initially coated with stearic acid by spin coating a  $30\text{ }\mu\text{L}$ , 0.1 M stearic acid diluted in chloroform and subsequent dried in air at 80 °C for 10 min. The test concerns the investigation of the decomposition of stearic acid under UV illumination through the recording of the reduction of the IR absorbance peaks of its C–H stretching bands ( $2820$ – $2980\text{ cm}^{-1}$ ). The integrated area under these peaks was measured as a function of UV illumination time with a Fourier transform infrared spectrometer (FTIR) (IRPRESTIGE-21, Shimadzu), in transmission mode while UV illumination was provided by a black light blue lamp centred at 365 nm, having an intensity of  $2\text{ mW cm}^{-2}$ . Each characterization method was conducted on at least three samples prepared under the same conditions for consistency and reproducibility.

## 3. Results and discussion

Since, there is not much work reported regarding the synthesis of vanadium oxide thin films using hydrothermal growth, the initial growths were focused on the determination of the optimum conditions that can lead to the deposition of well-defined  $V_2O_5$ , as was also done for other oxides [31,32]. Initially, the effect of deposition time was examined. Samples grown for deposition periods shorter than 1 h showed no efficient coverage of the substrate, the observed behaviour known as induction or incubation time. For deposition periods of the order of 5 h or larger, the vanadium oxide films were significantly washed away during the cleaning procedure, a behaviour that can be attributed to the possible creation of surface cracks instead of a normal deposition of material. The adhesion of this cracked film is rather weak, allowing an easy removal of the material during any surface treatment. Hence, the deposition period had to be restricted in the range 1–5 h. Regarding the use of sodium hydroxide, this was based on similar reports in the literature [34], which indicate that in such a way, nanostructures of different sizes can be obtained by simply varying the deposition period. The sodium hydroxide concentrations were kept around 0.2 M since for higher concentrations no hydrothermal growth occurred, resulting in powdery films. All grown samples for a deposition period shorter than 5 h and 0.2 M NaOH concentration passed the Scotch tape test (removal of an X shaped piece of sticking tape [35]). Furthermore, these films presented similar properties (structural, optical, morphological and photocatalytic) after six months, indicating their stability for long periods after deposition.

XRD patterns of the as-deposited films showed no diffraction peaks, indicating that the films were amorphous. On the other hand, Raman spectroscopy indicated the growth of well-defined  $V_2O_5$  phase. Fig. 1, shows the Raman spectrum of the as-deposited film grown on microscope glass for 2 h. The high-frequency Raman peak at  $994\text{ cm}^{-1}$  corresponds to the terminal oxygen ( $V=O$ ) stretching mode [36]. V–O–V stretching and bending modes are assigned

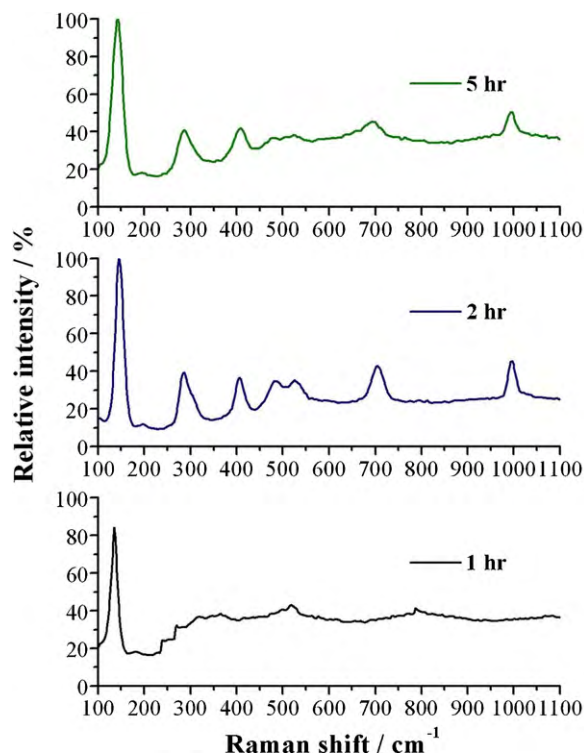


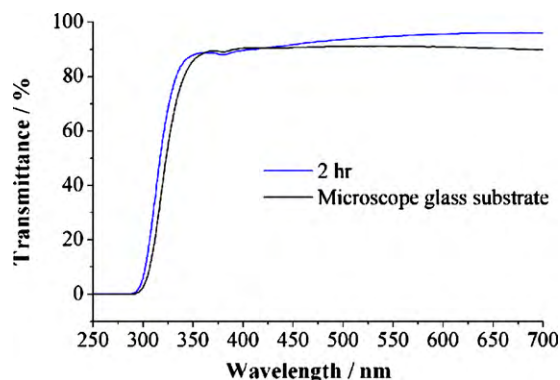
Fig. 1. Raman spectra of vanadium oxide films grown for a deposition time of 1 h, 2 h and 5 h, at 95 °C.

to the frequencies (Fig. 1)  $286\text{ cm}^{-1}$ ,  $408\text{ cm}^{-1}$ ,  $523\text{ cm}^{-1}$ , and  $694\text{ cm}^{-1}$  [37,38]. Furthermore, the prominent band at  $142\text{ cm}^{-1}$  is attributed to the skeleton bent vibration [39]. At low deposition periods (1 h), only the strong band at  $143\text{ cm}^{-1}$  was present (Fig. 1). This may be attributed to the partial vanadium oxide coverage of the substrate surface under the particular deposition conditions. On the other hand, at 5 h deposition periods, the  $V_2O_5$  Raman peaks were quite weak (Fig. 1), the observation related to the partial removal of vanadium oxide during cleaning.

Therefore, although, XRD results gave no indication for the presence of vanadium oxide in the as-deposited films, Raman analysis indicated the presence of well-defined phase of  $V_2O_5$ . Raman is a probe of the influence of even localized short-range order to the vibrational modes of bond configurations, while XRD is known to probe the long-range order crystallinity of materials [32]. Therefore, the observed behaviour suggests that the films are mainly amorphous retaining however a short range, within a few neighboring atoms, crystalline ordering.

Transmission spectra of the vanadium oxide samples prepared for deposition period, 2 h and the reference microscope glass substrate are shown in Fig. 2. The transmission in the visible region is higher for the oxide samples reaching 90%, which reveals that these oxide films may have reduced reflectance due to optical trapping [40,41]. In addition, a shift of the spectrum towards shorter wavelengths is observed and may be attributed to the amorphous behaviour (structural disorder) of the samples. The other deposition periods have similar spectra to the reference microscope glass substrate due to the low coverage of the surface substrate for the reasons mentioned above.

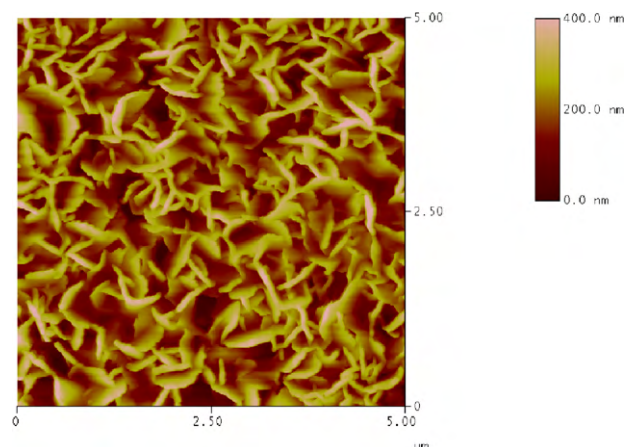
Fig. 3(a) shows the surface morphology of vanadium oxide samples for a deposition period of 2 h, obtained using SEM characterization. As shown, wall-like structures are formed, resulting in a relatively porous configuration with dense, uniform texturing. For shorter deposition periods (Fig. 3(b)), the wall-like configuration is less dense, the connection between walls being rather loose. The



**Fig. 2.** Transmission spectra of a vanadium oxide film prepared for a deposition period of 2 h and the reference microscope glass substrate.

formation of the wall network in this hydrothermal process may be due to an initial nucleation, growth and then branching process as can be concluded by comparing Fig. 3(a) and (b).

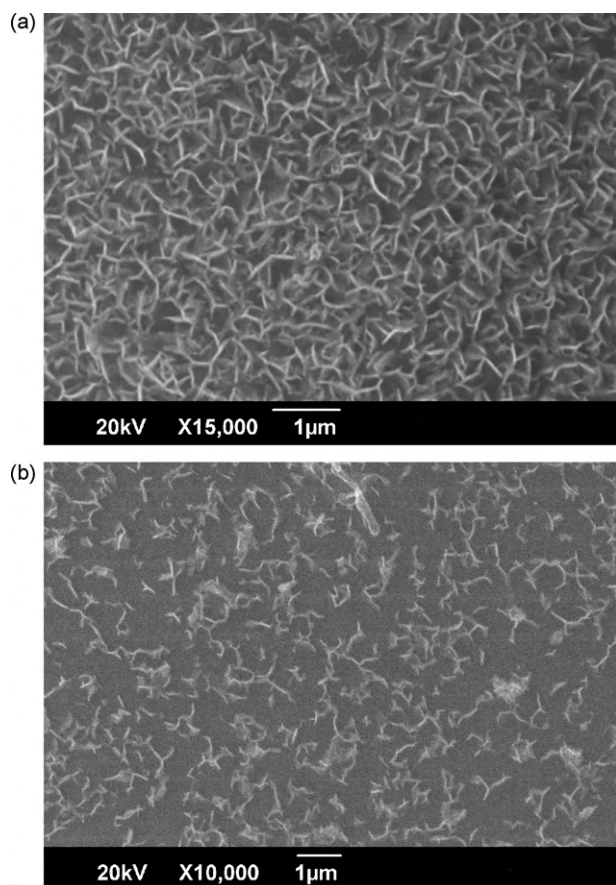
An AFM image of a vanadium oxide film deposited on microscope glass for a deposition period of 2 h is shown in Fig. 4. The network texturing morphological characteristics shown in this AFM image are well correlated with the morphology of the film recorded with SEM (see Fig. 3). Moreover, the dependence of the roughness ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) and the surface area ratio on the deposition time for the as-deposited vanadium oxide samples, determined using the AFM images, are shown in Fig. 5. It is indicated that both roughness and surface area ratio (defined as the fraction of the true, i.e. ironed surface divided by the scan dimensions) are maximized for a deposition time of 2 h being 116.7 nm



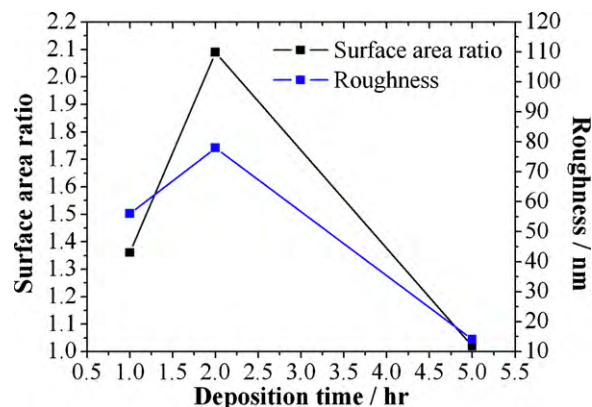
**Fig. 4.** AFM image of a vanadium oxide film grown for 2 h at 95 °C.

and 2.1, respectively. The observed decrease of both parameters for longer deposition periods is related to the partial removal of vanadium oxide during cleaning.

A measure of photocatalytic activity that is commonly used for thin films is the degradation of stearic acid [33]. The photocatalytic decomposition of stearic acid is of practical interest since the latter constitutes a model compound for the type of solid organic film that is deposited on indoor or enclosed glass surfaces (a window or a light cover in a road tunnel). The decomposition of stearic acid is readily monitored by FTIR spectroscopy, through the disappearance of the peak at  $2957.5\ \text{cm}^{-1}$ , related to the asymmetric in-plane C–H stretching mode of the  $\text{CH}_3$  group, and the peaks at  $2922.8\ \text{cm}^{-1}$  and  $2853.4\ \text{cm}^{-1}$ , which are due to the asymmetric and symmetric C–H stretching modes of the  $\text{CH}_2$  group, respectively [33]. In this work, the variation of the integrated area under these peaks was measured as a function of UV irradiation time (Fig. 6). Fig. 7 indicates that vanadium oxide samples grown for a deposition time of 2 h exhibit the most efficient photocatalytic activity, degrading stearic acid by 57% after 900 min of UV exposure. This behaviour may be attributed to the larger surface area ratio of the sample, as was found during AFM analysis (see Fig. 5). Since photocatalytic processes are chemical reactions on the surface, the increase of surface area should improve the efficiency of the process because it poses extended exposure to the pollutants [33]. Also, the increased roughness for the 2 h samples (see Fig. 5) is an important result since it can enhance the adsorption of water molecules, resulting also in an increased photocatalytic response [42]. Regarding the less efficient photocatalytic activity observed for longer deposition



**Fig. 3.** SEM images for vanadium oxide films grown for (a) 2 h and (b) 1 h, at 95 °C.



**Fig. 5.** Roughness ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) and surface area ratio dependence on deposition time for vanadium oxide films grown on microscope glass.



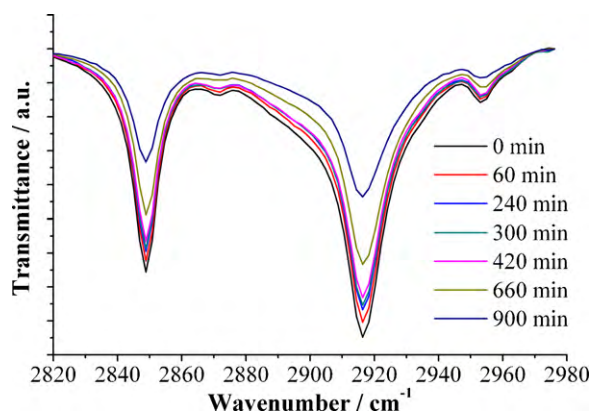


Fig. 6. FT-IR transmittance versus wavenumber spectra for the sample grown at 95 °C for 2 h coated with stearic acid as a function of UV irradiation time, using 2 mW cm<sup>-2</sup> UV light, at ambient conditions.

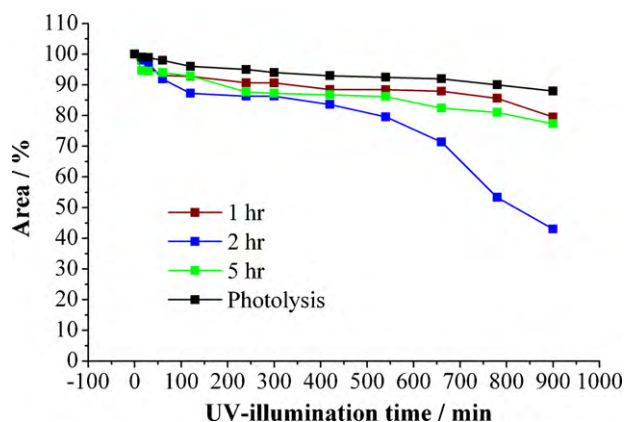


Fig. 7. Decomposition of stearic acid as a function of the UV illumination time of vanadium oxide films grown on microscope glass for deposition periods of 1 h, 2 h and 5 h. In addition, the photolysis curve (no oxide present) is included.

periods, this is simply related to the partial removal of vanadium oxide during cleaning, which also resulted in a significant decrease of the surface area ratio and the roughness.

It is shown for the 2 h sample that the degradation of stearic acid is carried out after 660 min falling rapidly to 47%. To explain this behaviour, the photolysis curve (no oxide present) is included showing that the UV light degrades stearic acid only by 12% after 900 min exposure (Fig. 7). Hence, it is presented that the stearic acid is stable after prolonged UV exposure and the degradation of stearic acid on the vanadium oxide film is only due to the catalyst.

The efficiency of the photocatalytic activity of the vanadium oxide films grown for this investigation is similar to that of TiO<sub>2</sub> thin films grown by hydrothermal method on microscope glass, which were found to degrade stearic acid by 65% after 560 min UV irradiation [43]. This indicates that vanadium oxide can be a promising and alternate material to TiO<sub>2</sub> for photocatalytic applications.

#### 4. Conclusions

In conclusion, we have demonstrated that it is possible to grow photoactive vanadium oxide films exhibiting a relatively porous structure forming a wall network. Depending on the growth time,

the deposition of well-defined and adhesive V<sub>2</sub>O<sub>5</sub> thin film is possible. The corresponding photocatalytic properties strongly correlate with the surface area ratio and the roughness. We propose that our method may find application as a cheap and environmentally friendly technique for photocatalytic thin film deposition at temperatures as low as 95 °C. Finally, we have shown that vanadium oxide may be a promising candidate with comparable activity to TiO<sub>2</sub> for photocatalytic applications.

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