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1. Introduction

For many years, research on materials that can convert solar energy into electrical/chemical energy represents a tremendous scientific and societal challenge. The main objective is to produce energy devices with good conversion efficiency and with eco-responsible energy sustainability. Today, several devices exist to meet these challenges allowing a conversion of solar energy into electrical or chemical energy (H₂): photovoltaic cells, photocatalysts for water splitting, Photo-Electrochemical Cells (PEC), *etc....*^{1,2} In these devices, the use of efficient photo-active materials in terms of both absorption of light energy and conversion efficiency is essential. For this, a great deal of research has already been carried out on the use of semiconductor oxides such as ZnO or TiO₂.³ These oxides have

Photoelectrochemical properties of copper pyrovanadate ($Cu_2V_2O_7$) thin films synthesized by pulsed laser deposition[†]

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Polymorphic phases of copper pyrovanadate (α - and β -Cu₂V₂O₇) were synthesized by solid state reaction and the mechanisms governing the phase transitions have been highlighted by the ThermoGravimetric Analysis (TGA) and the Differential Scanning Calorimetry (DSC). The thermal evolution of the lattice parameters was determined by high temperature X-ray Diffraction revealing negative thermal expansion coefficients. The thermogravimetric analysis coupled with differential scanning calorimetry was also used to determine the optimal conditions to obtain a dense target in order to produce thin films by the Pulsed Laser Deposition (PLD) technique. Thin films elaborated under different oxygen pressures and temperatures exhibit a β -Cu₂V₂O₇ polycrystalline phase and their band gap indicates absorption in the visible range. These oxides can be used as photoanodes and their photoelectrochemical properties were studied for both bulk (α -Cu₂V₂O₇) and thin films (β -Cu₂V₂O₇), as a function of the wavelength and/or intensity of the luminous flux. The best photocurrent efficiency was obtained under 450 nm illumination. Moreover, in the case of thin films, we have observed a linear evolution of the current density with the luminous flux. Finally, the photostability of thin films was measured and shows a reduction in the photocurrent of 8% after 1 h of measurement. This photocorrosion phenomenon was also highlighted by the elemental mapping performed on thin films by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDS).

> a high chemical stability and are relatively inexpensive, which are advantageous for large-scale industrial production. Nevertheless, it has been shown in the literature that best materials must absorb the maximum visible light and their band gap must be between 1.8 and 2.4 eV.4,5 Consequently, to be effective in visible light, the oxides described above must be combined with another absorbing compound in order to allow efficient conversion in the visible range. For example, TiO_2 can be associated with an organic dye in order to design solar cells called dye-sensitized solar cells or associated with another semiconductor to create n/p hetero-junctions, as TiO₂/Cu₂O to design all-oxide solar cells.6 Of course, the absorption is not the only criterion, the efficiency of materials will also depend on their intrinsic properties to separate charges with a good balance between transfer and recombination rate. The diffusion length and the carrier's lifetime can also be conditions limiting the conversion efficiency.7

> Today, many ternary metal oxides are studied for applications as photoelectrodes because they have suitable bandgaps and bands edge positions for being used in water-splitting photoelectrochemical tandem cells under solar irradiation. Among these ternary metal oxides, there are main families such as spinels (CuFe₂O₄,⁸ CaFe₂O₄,⁹...), delafossite-type oxides (CuFeO₂,¹⁰ AgRhO₂,¹¹...), perovskites (LaFeO₃,¹² BiFeO₃,¹³...)

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and many others.¹⁴ Copper pyrovanadate (Cu₂V₂O₇) oxides is also promising candidates for the design of photo-electrodes which can be used in PEC cells. For example, Guo et al.15 obtained a current density of 12 μ A cm⁻² (at 1.23 V vs. NHE) on thick films of β -Cu₂V₂O₇ produced by the drop-casting technique in 0.1 M sodium borate buffer solution. However, these properties can be improved by controlling the microstructure of the oxide. Thus, Khan et al.¹⁶ highlighted a significant improvement in current density $(0.70 \text{ mA cm}^{-2})$ for thick films made up of micro-flakes arranged in channels; C. Gadiyar et al.¹⁷ indicated a current density of 0.23 mA cm⁻² (always at 1.23 V vs. NHE) in 0.1 M sodium borate buffer solution (pH =9.2) containing 0.1 M Na₂SO₃ as a hole scavenger. Their study shows an optimal crystallite size at 40 nm corresponding to the hole diffusion length, estimated between 20 and 40 nm.18 Copper pyrovanadates (α - or β -Cu₂V₂O₇ oxides) have also been studied for other applications, in particular for: (i) magnetoelastic and ferromagnetic coupling properties; (ii) ferroelectric properties induced by a magnetic order;¹⁹ (iii) photodegradation properties of azo-dye in water;^{20,21} (iv) solar water splitting;^{22,23} (v) catalytic SO₃ decomposition;²⁴ (vi) cathode materials in high voltage Li-batteries.25-27

Copper pyrovanadate oxides have three polymorphic phases: (i) α -Cu₂V₂O₇ (blossite) has an orthorhombic structure with *Fdd2* space group and lattice parameters: a = 20.68 Å, b = 8.411Å and c = 6.448 Å;²⁸ (ii) β -Cu₂V₂O₇ (ziesite) crystallizes in a monoclinic structure with A2/a space group and lattice parameters: a = 10.094(15) Å, b = 8.020(13) Å, c = 7.711(10) Å and $\beta = 110.43(9)^{\circ}$;²⁹ (iii) γ -Cu₂V₂O₇ (observed at high temperature in the range of 710 °C to 780 °C) has a triclinic structure with $P\bar{1}$ space group and the following lattice parameters: a =5.0873(10) Å, b = 5.8233(11) Å, c = 9.4020(18) Å, $\alpha = 99.780(3)^{\circ}$, $\beta = 97.253(3)^\circ$, $\gamma = 97.202(3)^\circ$.³⁰ Under normal pressure and temperature conditions, α - or β -Cu₂V₂O₇ phase can be synthesized. For example, the reaction between V₂O₅ and CuO, at low temperature (T < 550 °C), lead to the stabilization of β -Cu₂V₂O₇. While for syntheses at higher temperature (T > 560 °C), α -Cu₂V₂O₇ phase will be privileged.³¹ However, fairly long calcination times are required,³² to achieve a pure phase. The β - $Cu_2V_2O_7 \rightarrow \alpha$ - $Cu_2V_2O_7$ phase transition takes place around 605 °C. However, the β-Cu₂V₂O₇ phase can also be obtained from α -Cu₂V₂O₇ phase by heating it up to 710 °C and then performing a rapid cooling. In this case, the phase transition process is as follows: α -Cu₂V₂O₇ \rightarrow γ -Cu₂V₂O₇ \rightarrow β -Cu₂V₂O₇.³¹

In the literature, several synthetic routes are described, for example solid-state reaction,³¹ wet chemical method,²¹ Sol–gel synthesis,³³ hydrothermal synthesis,³⁴ thermal decomposition method³⁵ and finally flux method in close crucible to obtain single crystals.³⁶ In thin film form, studies are scarce and to the best of our knowledge only films produced by electrospraying,²² simplified Successive Ionic Layer Adsorption and Reaction (s-SILAR) method³⁷ and drop casting method¹⁵ have been described.

In this present work, we studied the photoelectrochemical properties of $Cu_2V_2O_7$ thin films synthesized by Pulsed Laser Deposition (PLD). The first part of the work, devoted to the synthesis of pure powder and the preparation of the PLD target

will highlight the difficulties of obtaining a dense target. In the second part, and for the first time, we present the optimal conditions for the growth of thin films, in particular the influence of pressure and temperature. Finally, we will compare the photoelectrochemical properties of PLD-based thin films with bulk form.

2. Experimental section

Copper pyrovanadate powder was synthesized by solid-state reaction using copper oxide (CuO – 99.5% – strem chemicals) and ammonium vanadate (NH₄VO₃ – 99% – strem chemicals) precursors. These precursors were weighed in stoichiometric proportions and ground for 20 min to ensure a good homogeneity. Then, the mixture was calcined in an alumina crucible at 620 °C under air for 15 hours. The PLD target (1 in. diameter) was produced by pressing the Cu₂V₂O₇ powder (15 kbar) in a circular uniaxial press, then by sintering the pellet. The thermal cycle consists of a ramp up/down in temperature at 4 ° C min⁻¹ and a step of 60 min at 720 °C.

The thin films were synthesized by PLD technique using a Compex Pro 102 Laser (KrF excimer laser with a wavelength of 248 nm). The synthesis conditions are: $1.5 \text{ J} \text{ cm}^{-2}$ for the laser density energy, 4.5 cm for the target-substrate distance and 4 Hz for the pulse repetition rate. Before the deposition, a preablation of 15 min is carried out in order to clean the target's surface.

The substrate temperature during deposition and the oxygen pressure are variable parameters studied in this work.

The structural properties of both powders and thin films were performed by X-Ray Diffraction (XRD) and Raman Spectroscopy. For the bulk form, the XRD patterns were recorded in the 15-70° range with a step of 0.02° and a scan speed of 0.4° per min, using a Rigaku Ultima IV X-ray diffractometer equipped with Cu anticathode ($\lambda_{K\alpha} = 1.5418$ Å). Nickel foil filter and Soller slits are used to attenuate Cu K_{β} radiation and to limit the divergence of X-ray beam, respectively. While the thermodiffraction patterns were recorded on a D8 Bruker device. For the thin films, the XRD patterns were recorded using a Rigaku SmartLab diffractometer attached to a 9 kW rotating anode Xray generator ($\lambda_{K\alpha_1} = 1.54056$ Å) and monochromatized with a double Ge (220) monochromator. Raman spectra were recorded in back scattering geometry using a Horiba Labram HR800 spectrometer coupled with a microscope which focused the 784 nm laser beam to a 1 µm spot. The spectra were recorded in the 100–1100 cm^{-1} range.

Thermal Analyses have been performed using a TGA/DSC3+ STARe System (Mettler Toledo). The sample was analyzed in the range 50 °C–750 °C with a rate of 10 °C min⁻¹ under a flow of air of 50 mL min⁻¹ in 70 μ L Al₂O₃ crucible.

Infrared (IR) analysis was conducted using a Shimadzu IR Prestige 21 instrument with the addition of single-reflection diamond module (ATR). IR spectra were recorded in the range 500–4000 cm⁻¹ with a 1 cm⁻¹ resolution. A Nova made scanning electron microscope (SEM) model NanoSEM-450 was employed for investigation of morphology and grain size and the elementary maps were recorded with a Hitachi SU3800 SEM coupled with Energy Dispersive X-ray Spectrometry (EDS). The optical properties were characterized using a Shimadzu UV-visible spectrophotometer UV-2600 in the range of 190–800 nm with a resolution of 1 nm. This spectrophotometer was equipped with an integration sphere ISR-2600+, a photomultiplier tube and a InGaAs detector. The UV-visible diffuse reflectance spectra can be used to determine the optical gap band (E_g) using the Tauc plot defined by the following equation:

$$\alpha h\nu = A(h\nu - E_{\rm g})^n \tag{1}$$

where α is the coefficient of absorption, $h\nu$ the photon energy, A is a constant and n = 1/2 or 2 for direct or indirect, respectively, allowed transition of the semiconductor.

The photoelectrochemical measurements were performed using a three-electrode cell (PEC 15 mL Redox.me®). The cell is calibrated for an illumination of 1 cm² from the backside of the ITO/glass substrate (Delta Technologies, USA). The Pt wire was used as counter electrode and Ag/AgCl in saturated KCl electrode was employed as the reference electrode. The working electrode consists of a Cu₂V₂O₇ deposited either by drop casting using the powder directly (a suspension of nanopowders is prepared in *N*,*N*-dimethylformamide/distilled water with the 1 : 1 ratio, then annealed at 250 °C during 1 h in order to obtain a layer whose thickness is ~50 µm) or by PLD technique.

The photoelectrochemical measurements were carried out using a PGSTAT204 potentiostat/galvanostat (Metrohm) expanded with Electrochemical Impedance Spectroscopy (EIS) module and coupled with optical bench consisting of highly focused LED source. The intensity of the light beam can be controlled as well as the excitation wavelength *via* the use of low spectral dispersion LEDs. The whole is controlled by NOVA 2.0 software. Finally, the electrolyte solution consists of 0.1 M sodium borate buffer solution also called NaBi Buffer (pH 9.2) with 0.1 M sodium sulfite as a hole scavenger. This electrolyte was used to preserve the chemical stability of $Cu_2V_2O_7$ (ref. 38) and to improve the intensity of the collected photocurrent.³⁹

3. Results and discussions

3.1 Bulk characterizations

The XRD pattern of Cu₂V₂O₇ synthesized by solid state reaction is presented in Fig. 1a. This first result highlights the presence of a pure phase of α -Cu₂V₂O₇ (*Fdd*2 space group). All the XRD lines can be indexed and the lattice parameters determined by least-squares refinement using MAUD software⁴⁰ are: a =20.688(3) Å, b = 8.410(7) Å and c = 6.449(1) Å. The Raman spectrum confirms the presence of a unique α -Cu₂V₂O₇ phase with the characteristic vibrational modes (Fig. S1 - ESI⁺). D. De waal *et al.*⁴¹ have studied these modes for α and β phases. α - $Cu_2V_2O_7$ has an orthorhombic structure with $C_{2\nu}^{19}$ symmetry in which the $V_2 O_7{}^{4-}$ group are nearly staggered. These anions group are located in parallel sheets bonded by Cu²⁺ cations.²⁸ The VO₃ stretching components are centered at 992, 920 (symmetric stretching) and 850 cm⁻¹ (antisymmetric stretching). The VOV symmetric bridge stretch has a very low intensity at 553 cm⁻¹ and at 790 cm⁻¹.⁴² Therefore, one can conclude that



Fig. 1 (a) XRD pattern of α -Cu₂V₂O₇ as prepared and α -Cu₂V₂O₇ reference; (b) SEM images of α -Cu₂V₂O₇ powders; (c) absorbance spectrum of α -Cu₂V₂O₇ (inset the calculated Tauc plot).

the VO₃ and/or OVO₃ bending components are centered at 392, 254 and 111 cm⁻¹.

The characteristic vibrational modes were also highlighted by IR spectroscopy using ATR configuration (Fig. S2 – ESI†). The bands located at 3330 and 1620 cm⁻¹ are assigned to the traditional vibrations of OH stretching and bending vibration of adsorbed water molecules, respectively. The band centered to 993 cm⁻¹ can be attributed to V–O stretching vibration and the band located around 700 cm⁻¹ can be assigned to Cu–O bond. Moreover, the bands located between 750 $\rm cm^{-1}$ and 900 $\rm cm^{-1}$ can be assigned to the VO₃ symmetric and asymmetric stretching vibrations.

The morphology of as prepared α -Cu₂V₂O₇ is presented on SEM image (Fig. 1b). The powder has a granular morphology with a mostly spherical shape with heterogeneous size. The energy dispersive spectroscopy (EDS) confirms the correct stoichiometric ratio (% at. Cu/% at. V = 1) without heterogeneity.

The optical band gap energy was determined from the UVvisible absorption spectrum using Tauc method (Fig. 1c), knowing that α -Cu₂V₂O₇ has an indirect band gap (n = 1/2).⁴³ The determined value of the optical band gap is 2.35 eV (*i.e.* 528 nm). This value is particularly interesting because it is very close to the maximum intensity of the solar spectrum.

In order to prepare the PLD target, it is essential to study the $Cu_2V_2O_7$ oxide stability by performing a thermal analysis by ThermoGravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements. For DSC, two heating/cooling thermal cycles are carried out between 50 °C to 750 °C with 10 °C min⁻¹ and 20 °C min⁻¹ rate, respectively. The results obtained are presented in Fig. 2a.

During the first cycle, an endothermic peak (I) is observed on heating, attributed to $\alpha \rightarrow \gamma$ phase transition (677 °C).⁴⁴ Then, on cooling, three exothermic peaks appear. The first peak (III) corresponds to $\gamma \rightarrow \beta$ phase transition (~595–600 °C). The two other peaks (IV and V) correspond to crystallization at low temperature of β-Cu₂V₂O₇ phase. Indeed, B. V. Slobodin et al.44,45 indicates that above 720 °C, a small amount of CuVO3 is formed which forms an eutectic with the α and β phases having a low crystallization temperature.44 For the second cycle, a difference is observed. Indeed, the appearance of a new endothermic peak (II) is observed, which is related to the formation of β -Cu₂V₂O₇ phase during the cooling step of the first cycle. This peak is attributed to $\beta \rightarrow \alpha$ transition (557 °C). The second cooling step took place in the same way as that of the first cycle (the difference between peaks IV and V is only due to the different cooling rates thus confirming that it is an enthalpy of crystallization). The analysis of the weight loss with temperature presented in Fig. 2b, highlights the reduction of copper observed during the cooling step of the first cycle. The weight loss after 715 °C thus highlights a copper reduction (oxygen release) and the start of peritectic transformation around 770 °C. Indeed, above 725 °C, Cu₂V₂O₇ undergoes a congruent fusion followed by an incongruous transformation towards 770 °C (peritectic decomposition).45

In order to understand this low crystallization temperature (IV and V peaks) due to the presence of the eutectic, additional measurements were undertaken but this time with a temperature limited to 720 °C. At this temperature, $Cu_2V_2O_7$ phase is not reduced and therefore should not form eutectics. The TGA/DSC analysis cycles limited to 720 °C are shown in Fig. 3. As already observed by B. V. Slobodin *et al.*,⁴⁴ the first heating step leads to the transformation $\alpha \rightarrow \gamma$ at 705 °C (the XRD reference pattern is shown in Fig. S3 – ESI†). Then, the first cooling is accompanied by a release of heat due to the transformation $\gamma \rightarrow \alpha \rightarrow \beta$. The second cycle shows an endothermic peak due to the transition from $\beta \rightarrow \alpha$ at 604 °C (this peak is due to β -Cu₂V₂O₇

which is formed during the first cooling), then comes the $\alpha \to \gamma$ phase transformation, as during the first heating. The following cycles are similar and the crystallization peaks at low temperature are no longer observed, thus confirming the presence of an eutectic with the phase formed above 725 °C. This decomposition at a temperature higher than 725 °C is problematic because it limits the sintering temperature of the PLD target and therefore its densification.

To confirm this behavior, *in situ* high temperature X-ray diffraction was performed over the temperature range 50 °C to 725 °C (heating/cooling in the same cycle). Fig. 4a shows a partial 2D map (XRD patterns *vs.* temperature) of α -Cu₂V₂O₇ powder (the complete 2D map is presented in Fig. S4 ESI[†]).

Initially, the presence of a pure α phase is observed. When the temperature increases, some diffraction peaks shift towards the large angles (as shown in Fig. S5 – ESI[†]), highlighting the presence of a negative Coefficient of Thermal Expansion (CTE).⁴⁶ This shift is not identical according to the crystallographic planes. This reflects an anisotropic evolution of the unit cell as a function of temperature.⁴⁷

Around 710 °C, a phase transition is observed (dashed lines in Fig. 4a). This transition corresponds to the transformation of the α phase towards a phase which can be attributed to the Cu_{1.98}V_{1.96}O_{6.92} phase with C_{2/c} space group, previously described by S. A. Petrova *et al.*⁴⁸ and called β' -Cu₂V₂O₇ (Fig. S7 – ESI[†]). The presence of this phase also explains the mass loss observed in the TGA (oxygen release and Cu²⁺ reduction) measurements and we can note that a slight part seems to have melted in the sample holder, as observed at the end of the DSC thermal cycle. During cooling, a phase transition is also observed from the β' -Cu₂V₂O₇ phase to the β -Cu₂V₂O₇ phase at 600 °C. This phase is then preserved when returning to room temperature. From a structural point of view, the $\beta' \rightarrow \beta$ phase transition causes a decrease in the V-O-V angle and a slight expansion of the VO4 tetrahedra.48 Here, a discrepancy with the TGA/DSC thermal analysis has to be noted. In the literature, $\alpha \rightarrow \gamma$ transition is observed around 700 °C (as described in the DSC analysis part). However, in this present case, the XRD patterns indicate unambiguously that the obtained phase is β' - $Cu_2V_2O_7$ phase ($Cu_{1.98}V_{1.96}O_{6.92}$). Consequently, the $\alpha \rightarrow \gamma$ phase transition previously claimed is in fact a $\alpha \rightarrow \beta'$ transition. Thus, all of the ATG data can be re-interpreted in the same way but this time by replacing the γ phase by the β' phase (structural evolution of Cu₂V₂O₇ oxide is presented in Fig. S8 -ESI†).

Concerning β -Cu₂V₂O₇, X-ray thermodiffractograms show a negative expansion behavior (as depicted in Fig. S9 and S10 – ESI†) which correlates with the literature.⁴⁹ In addition, the dotted circles in Fig. 4a reveal the formation of a small amount of β -Cu₂V₂O₇ from 500 °C then disappears around 600 °C (corresponding to the $\beta \rightarrow \alpha$ transition as observed on the DSC curve in Fig. 3). In summary, a good correlation between DSC and HT-XRD experiments is highlighted shading some light on the complex thermo-structural behavior of copper vanadate.

Those results also make possible to define the optimal conditions for developing the PLD target. For sintering, the temperature is limited to 720 °C (start of melting of a small part



Fig. 2 (a) DSC curves with two heating/cooling cycle with 10 °C min⁻¹ (cycle 1) and 20 °C min⁻¹ (cycle 2) performed on α -Cu₂V₂O₇; (b) TGA measurements performed on four cycles showing the weight loss.

of Cu₂V₂O₇ oxide) which allows solidification/densification of the target which is necessary for the PLD technique. The α -Cu₂V₂O₇ powder was then shaped into a pellet *via* uniaxial press (15 kbar), then sintered at 720 °C for 1 hour. To avoid the diffusion of the elements into the alumina plate, a platinum sheet was used during the sintering step. The pellet obtained is dark brown and the XRD pattern indicates as expected the presence of β -Cu₂V₂O₇ phase (Fig. 4b). It is important to note that after use, this target remains stable in air for a few weeks and then starts to disintegrate gradually. This phenomenon can be explained by the negative thermal expansion coefficient which induces strong mechanical stresses when the target is subjected to temperature variations caused by the laser impact.

3.2 Thin film characterizations

The PLD target was used to develop thin films grown on ITO/ glass substrates. Among all different parameters intervening in PLD synthesis, we chose to study two important parameters (dynamic oxygen pressure and substrate temperature) in this work. The laser pulse number is fixed at 6000 pulses, the targetsubstrate distance is fixed at 45 mm and the frequency/fluence of the laser are 4 Hz and 2 J cm⁻². Films thickness, determined by spectroscopic ellipsometry, is 150 nm, *i.e.* a growth of 0.25 Å per pulse. Fig. 5a shows the evolution of XRD patterns as a function of substrate temperature under a fixed pressure of 10^{-3} mbar.

The presence of a β phase with a (200) preferential orientation is highlighted for the temperatures of 230 and 300 °C. Note



Fig. 3 (a) DSC and TGA measurements realized with two heating/cooling cycles; (b) fragment of the curves highlighting the observed transitions.

that a parasitic phase of CuV₂O₆ (legend with the Δ symbol) is also present at this pressure. At 150 °C and 400 °C, no reflection is highlighted except the reflections of Indium Tin Oxide (ITO). A temperature above 150 °C is necessary for the β -Cu₂V₂O₇ crystallization. In addition, at high temperature also leads to the production of an amorphous thin film.

Thus, after setting the optimal temperature at 230 °C, we studied the influence of the dynamic oxygen pressure in the chamber. Fig. 5b shows the XRD patterns for different pressures. For thin film synthesized at 10^{-5} mbar, the pure β phase can be obtained but with the disappearance of the preferential orientation. At 10^{-3} mbar, a β phase is obtained but with the presence of a parasitic phase of CuV₂O₆ (Δ). For higher pressure (10^{-1} mbar), the (200) reflection of β -Cu₂V₂O₇ goes out completely, indicating either the presence of an amorphous film or no film at all. The surface of the film synthesized at 10^{-1}

mbar was thus analyzed by EDS at different points showing a homogeneous V/Cu ratio close to 1, in favor of the first hypothesis.

It should be noted that a freshly prepared target is necessary for the development of thin films and beyond \sim 20 deposition cycles, the target crumbles, probably due to the negative expansion coefficient of the compound, under the effect of the thermal stresses induced by the laser impact.

As observed on Fig. S11 (ESI[†]), the lower oxygen pressure is, the lowest band gap is. This results in an increasingly dark appearance visible to the naked eye of the deposited film. Thus, the band gap evolves from 2.2 to 2.4 eV for 10^{-5} and 10^{-3} mbar, respectively. The photo-electrochemical measurements presented in next paragraph will be performed on the film elaborated at 10^{-5} mbar and at 230 °C. Indeed, these optimal



Fig. 4 (a) Fragment of 2D map of thermo-diffraction patterns for heating/cooling cycle between 50 °C to 725 °C (δ indicates a reflection of the sample holder) and (b) XRD pattern of β -Cu₂V₂O₇ as prepared and β -Cu₂V₂O₇ reference (inset photograph of the PLD target). δ and * indicate the sample holder reflection and α -Cu₂V₂O₇ phase, respectively.

parameters lead to a pure $\beta\text{-}Cu_2V_2O_7$ phase (without CuV_2O_6 impurity).

3.3 Photoelectrochemical properties

The photoelectrochemical performances of photoanodes were studied in a three-electrode cell (Ag/ACl as the reference electrode and Pt as the counter electrode) and in 0.1 M NaBi buffer solution. The chronoamperometry results achieved on α -Cu₂V₂O₇ thick film are shown in Fig. 6a (in particular by plotting the variation of the current density between illumination and dark). A significant change in current density is observed when the backside of the working electrode is illuminated. In

addition, one can note the variation of the photocurrent density (Δj) shows better efficiency towards low wavelengths. The variation being maximum at 450 nm with a photocurrent density of 0.45 μ A cm⁻² with an applied potential of 0.4 V *vs.* Ag/AgCl and $\phi_0 = 23$ mW cm⁻² (while this drops to 0.11 μ A cm⁻² for 505 nm with the same luminous power). The evolution of the photocurrent with the intensity of luminous flux is presented in Fig. 6b showing a progressive evolution of the Δj according to the intensity received (Fig. 6c). The $\Delta j vs. \phi_0$ shows a two-step trend (dotted lines). Indeed, it follows a linear evolution ($\Delta j = 1.92 \times 10^{-3}\phi_0$) at first then evolves towards a power law ($\Delta j = 0.16 \times \phi_0^{0.533}$). This crossover from 1 to $\frac{1}{2}$ for the power of the



Fig. 5 XRD patterns of copper vanadate thin film deposited on ITO/glass substrate vs. substrate temperature (a) and dynamic oxygen pressure (b) – (inset photograph of $Cu_2V_2O_7$ thin film synthesized at 10^{-3} mbar of O_2 pressure and 230 °C).

luminous flux can be explained by the change of the dominant photocarrier decay mechanism from a trap-dominated recombination to an e-h recombination.⁵⁰ Indeed, T. S. $Moss^{51,52}$ indicates that the generation rate of photoelectrons by incident light (G_{pe}) follows the expression (2):

$$G_{\rm pe} = B_{\rm c} n_{\rm pe} (n_{\rm pe} + M) \propto \phi_0 \tag{2}$$

where B_c is the recombination coefficient, n_{pe} is the density of photoelectrons and *M* is the number of impurity levels per cm³. At low intensities ($n_{pe} \ll M$), the (2) expression becomes:

$$n_{\rm pe} = \frac{G_{\rm pe}}{B_{\rm c}M} \propto i_{\rm ph} \tag{3}$$

where $i_{\rm ph}$ is the intensity of photocurrent. As the luminous flux increases, the value of $n_{\rm pe}$ becomes greater than that of *M*. The expression (2) takes the following form:

$$n_{\rm pe} = \sqrt{G_{\rm pe}/B_{\rm c}} \propto \phi_0^{1/2} \tag{4}$$

Note that for higher intensities of the light beam, saturation can be achieved. This model therefore explains the

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Fig. 6 (a) Chronoamperometry (j-t) in dark and under illumination for different wavelengths with a constant light intensity of 23 mW cm⁻²; (b) difference in current density (Δj) under illumination or dark depending on the light intensity (450 nm) and with an applied potential of 0.4 V vs. Ag/ AgCl; (c) Δj vs. ϕ_0 plot and models in dotted lines; (d) Mott–Schottky plots for α -Cu₂V₂O₇ film deposited on ITO/glass performed at 1 kHz (a borate buffer solution (pH = 9.2) was used as the electrolyte).

experimental observations and the behavior of the electrode under different light power values.

The photocurrent transient response and especially the instantaneous pike and the subsequent decay towards the steady state current is due to the build-up of carriers in the surfaces states.⁵³ Likewise, the current overshoot observed when the light is switched off is due to the recombination of the remaining carriers in the surface states. So, the charge transfer and the recombination rate constants can be obtained by modeling the transient photocurrent response.^{53,54} Indeed, the time constant of the decay or the overshoot is given by the expression (5):⁵⁵

$$\frac{j(t) - j(\infty)}{j(0) - j(\infty)} = e^{-\frac{t}{\tau}} \text{ with } \tau = \frac{1}{k_{\text{rec}} + k_{\text{tr}}}$$
(5)

Moreover, the ratio of the steady state photocurrent to the instantaneous photocurrent observed when the illumination is switched on is given by the expression (6):⁵⁵

$$\frac{j(\infty)}{j(0)} = \frac{k_{\rm tr}}{k_{\rm rec} + k_{\rm tr}} \tag{6}$$

These two expressions make possible to calculate the values of $k_{\rm tr}$ and $k_{\rm rec}$. Considering 450 nm illumination ($\phi_0 = 23$ mW cm⁻²), the values of $k_{\rm tr}$ and $k_{\rm rec}$ are 6.19 × 10⁻² s⁻¹ and 5.58 × 10⁻² s⁻¹, respectively. The close values show that only half of the holes arriving at the surface are transferred to the solution under steady state conditions.

In addition, the capacitance *versus* potential (*C*-*V*) measurement is used to determine the conduction type, the flat band ($E_{\rm fb}$) and carrier density (*N*), which can be determined from the Mott–Schottky (MS) plot ($1/C^2 - V$). Fig. 6d shows the MS plot of the β -Cu₂V₂O₇ film performed at 1 kHz. The positive slope observed on the depletion zone indicates a n-type semiconductor behaviour. The $E_{\rm fb}$ is estimated at -0.08 V (*vs.* Ag/AgCl) which correspond to 0.66 V (*vs.* RHE). This value is consistent with the values described in the literature.¹⁵ The flat band potential reflects the position of the Fermi level.⁵⁶ For n-

type semi-conductors, the Fermi level lies close to the Conduction Band (CB). Therefore, knowing the band gap value, we can estimate the position of both valence and conduction bands (inset Fig. 6d). Moreover, in the depletion region, the MS plot follows the equation:⁵⁷

$$\frac{1}{C^2} = \frac{2}{Ne\varepsilon\varepsilon_0 S^2} \left[\left(E - E_{\rm fb} \right) - \frac{k_{\rm B}T}{e} \right] \tag{7}$$

where *C* is the interfacial capacitance ε the dielectric constant of β -Cu₂V₂O₇, ε_0 is the permittivity of free space (8.854 × 10⁻¹² F m⁻¹), *N* the carrier concentration (donor or acceptor), *E* is the applied potential, *T* is the temperature (298 K), $k_{\rm B}$ the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹), *S* the surface area of the electrode and e the electron charge (1.602 × 10⁻¹⁹ C). Considering dielectric constant at 1 kHz ($\varepsilon = 100$ –150),⁵⁸ the electron concentration is assumed to be ~8.26 × 1019 cm⁻³.

Regarding thin films, chronoamperometry measurements were also carried out on β -Cu₂V₂O₇ films produced by PLD. The photocurrent response to different wavelengths and for several increasing luminous flux intensity is shown in Fig. S12 (ESI⁺). We can also see that the best response is obtained under 450 nm illumination. Indeed, that drops by 66% and 86% for an excitation of 505 nm and 590 nm, respectively (for the same light intensity). Fig. 7a shows the variation of the current density between illumination and black (Δj) as a function of the intensity of the luminous flux (ϕ_0) for an applied potential of 0.4 V vs. Ag/AgCl. We can see a progressive and linear evolution of $\Delta j \nu s. \phi_0$ (Fig. 7b) as well as an improved current density response compared to the bulk of the α -Cu₂V₂O₇ phase. The photocurrent scales linearly with the illumination power ($\Delta i =$ $3.9 \times 10^{-3} \phi_0$ indicating an ideal trap-free state. β -Cu₂V₂O₇ can therefore be used as a photodetector. In addition, the instantaneous photocurrent spike is less intense (compared to the previous experiment performed on α -Cu₂V₂O₇) indicating a low recombination constant (compared to $k_{\rm tr}$) in the case of β - $Cu_2V_2O_7$ thin films. $k_{tr} = 9.58 \times 10^{-2} \text{ s}^{-1}$ et $k_{rec} = 2.39 \times 10^{-2}$ s⁻¹. Considering these values, the charge transfer dominates over the recombination if $k_{\rm tr}/k_{\rm rec} > 1$ for the thin films.

Finally, Cu₂V₂O₇ is also known to exhibit photocorrosion phenomenon.⁸ The stability of the films was thus studied by chronoamperometry in 0.1 M NaBi buffer solution (pH = 9.2)and with a constant applied potential of 0.4 V vs. Ag/AgCl (Fig. 7c). For the β -Cu₂V₂O₇ thin films, one can see that the anode current density is relatively stable, then undergoes a slight decrease with time. This drops to 8% over 1 hour under 450 nm illumination ($\phi_0 = 95 \text{ mW cm}^{-2}$). This decrease is mainly due to a gradual dissolution of the photoanode in the electrolyte. Indeed, this deterioration can be induced by the formation of O2 bubbles at the interface and/or a reaction with the electrolyte because the zone of stability (pH) of the oxide is very small.⁵⁹ This phenomenon has also been observed in the case of Cu₂V₂O₇ films, e.g. I. Khan et al.¹⁶ indicate a decrease of 2% and 14% in 1000 s for $Cu_2V_2O_7$ produced at 500 °C and 250 ° C, respectively. In order to check this point, we performed an image of the surface of the Cu₂V₂O₇ thin film and maps for the V, In and Cu elements between a zone not subjected or subjected to the electrolyte. In Fig. 8, we can clearly observe the



Fig. 7 (a) Variation of current density (Δj) under illumination or dark depending on the light intensity (450 nm) and with an applied potential of 0.4 V vs. Ag/AgCl; (b) Δj vs. ϕ_0 plot and linear fit in dotted lines; (c) stability test on β -Cu₂V₂O₇ thin film at 0.4 V vs. Ag/AgCl under frontside illumination of 450 nm (61 mW cm⁻²) and in 0.1 M NaBi buffer solution (pH = 9.2).

demarcation zone between a part subjected to the electrolyte showing circular corrosion phenomena and a part corresponding to the initial thin layer having a smooth appearance whose surface is constituted of granular conglomerates. The absence of copper and vanadium in these cracks confirms the corrosion of the film during prolonged use. The effect of the



Fig. 8 (a) SEM image of $Cu_2V_2O_7$ thin film after the photocorrosion test (the interface delimits the submerged surface at the top of the image); (b)–(d) colorized elementary maps for vanadium, indium and copper elements, respectively.

electrolyte on the stability of the film is demonstrated and will require work on the formulation of the electrolyte in order to improve this stability. Nevertheless, the results obtained on the films of β -Cu₂V₂O₇ produced by PLD shows that it can be used for applications as a particularly active photoanode or as photodetector in the blue spectral region. Nevertheless, the photostability needs to be improved in the futures studies. We can consider two paths: (i) improved the chemical stability with respect to the electrolyte or (ii) the encapsulation in order to protect the photoanode. For this last point, this method has already been used successfully to protect hybrid halide perovskite by a double-layer graphite sheet/nickel (GS/Ni).⁶⁰

4. Conclusion

In this work, two polymorphic forms of copper pyrovanadate (α and β -Cu₂V₂O₇) were synthesized by solid-state reaction. The study of HT-XRD and TGA/DSC, allowed to determine the mechanisms governing phase transitions within copper vanadate. The evolution of the lattice parameters as a function of temperature has shown a non-linear evolution of the thermal expansion coefficient within the two phases (α -/ β -Cu₂V₂O₇). In addition, TGA/DSC analysis also determined the congruent melting temperature of Cu₂V₂O₇, thus obtaining dense ceramics that can be used as a target for the Pulsed Laser Deposition (PLD) technique. The photoelectrochemical properties have been studied both on thick films produced by the drop casting method and on thin films synthesized by PLD on glass/ITO substrates. In the case of thick Cu₂V₂O₇ films, the results showed the generation of a larger photocurrent in the blue spectral region. In addition, the evolution of the variation of the current density between illumination and dark shows a double tendency with a linear growth then evolution in power law. From the transient photocurrent response, the recombination and transfer constants were calculated, showing that $k_{\rm tr}$ is very close to $k_{\rm rec}$. In the case of thin films, the generated photocurrent presents a better efficiency for 450 nm illumination. In addition, the evolution of the variation in current density between illumination and dark shows a linear trend indicating the presence of a significant concentration of traps. However, the transient photocurrent response showed a lower instantaneous spike indicating a higher $k_{\rm tr}/k_{\rm rec}$ ratio. Finally, a phenomenon of photocorrosion within thin films representing 8% for one hour was demonstrated in this work.

Conflicts of interest

There are no conflicts to declare.

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