Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Materials

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

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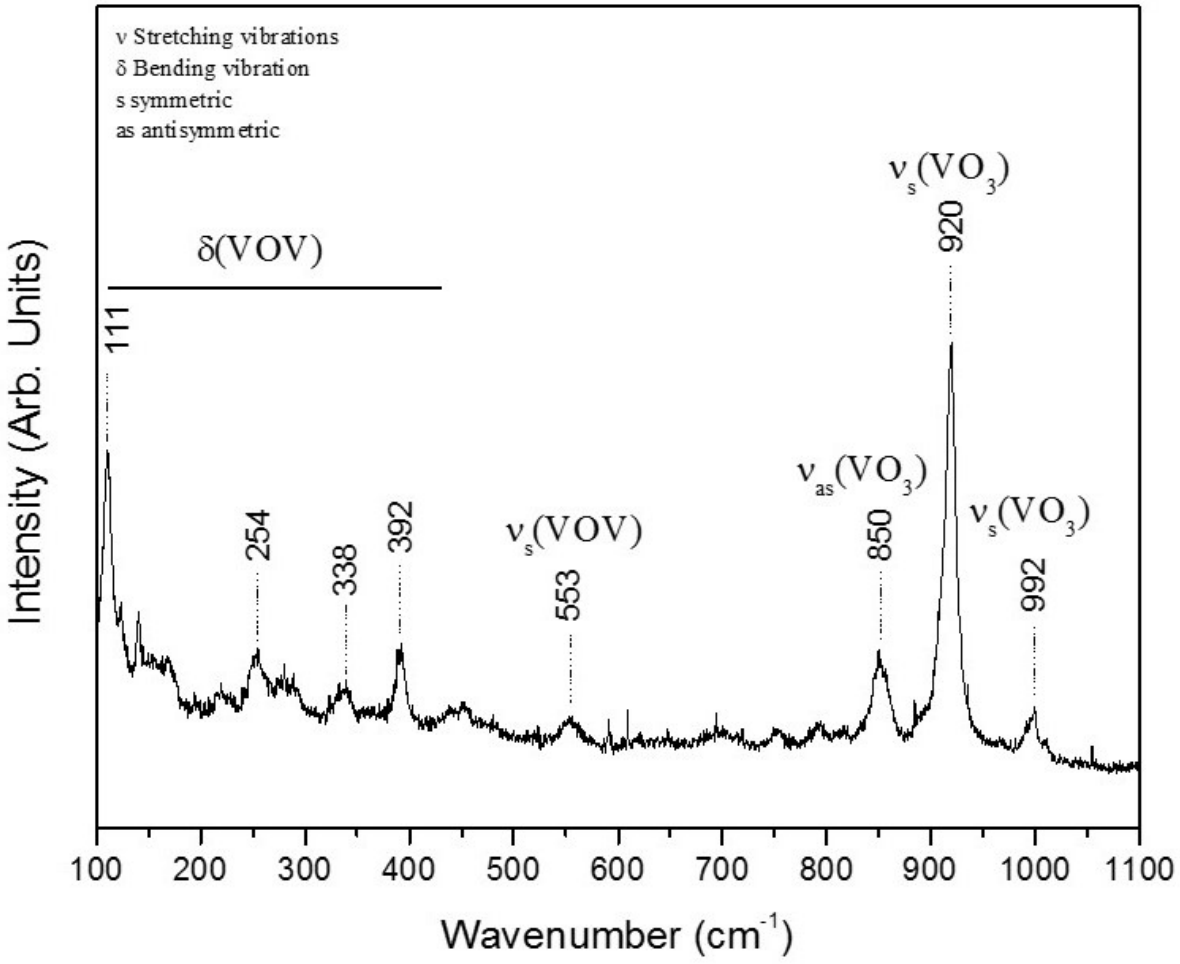

Figure S1. Raman Spectrum of α-$Cu_2V_2O_7$.

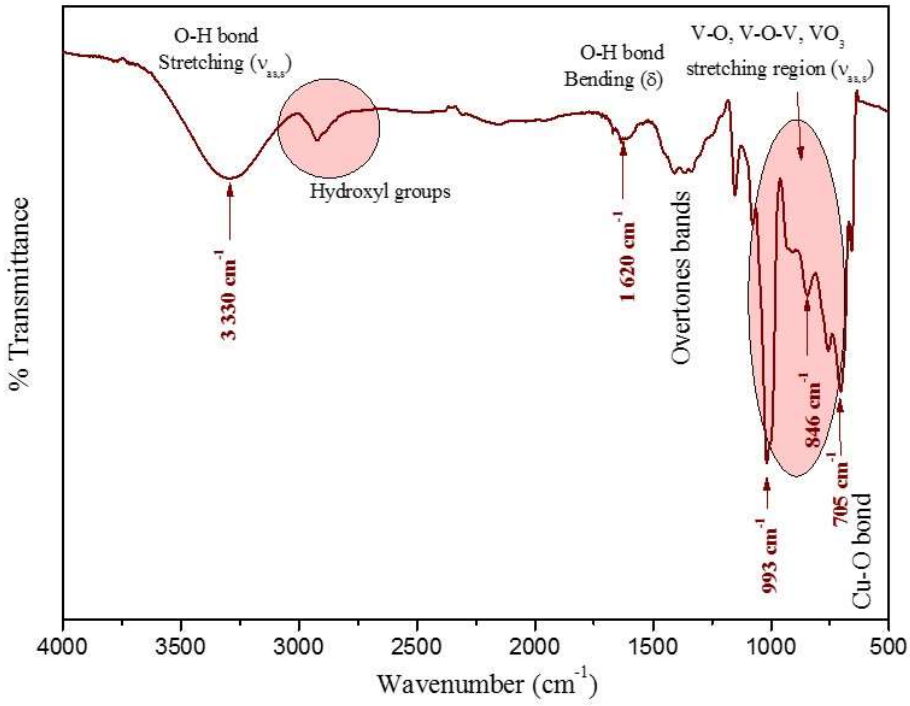

Figure S2. IR Spectrum of α-$Cu_2V_2O_7$.

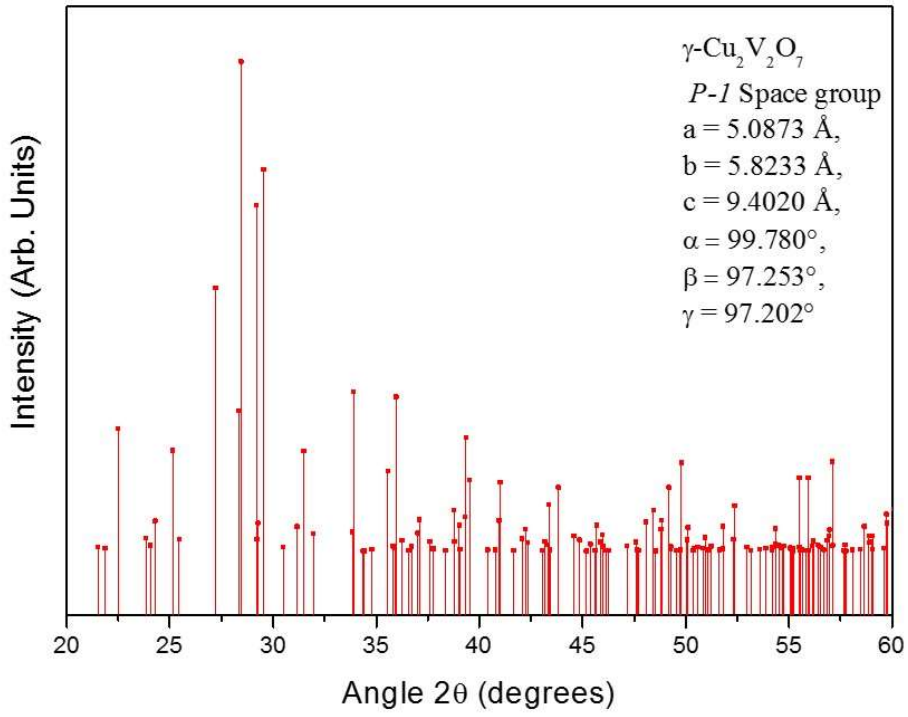

Figure S3. XRD reference pattern of γ-$Cu_2V_2O_7$ [1].

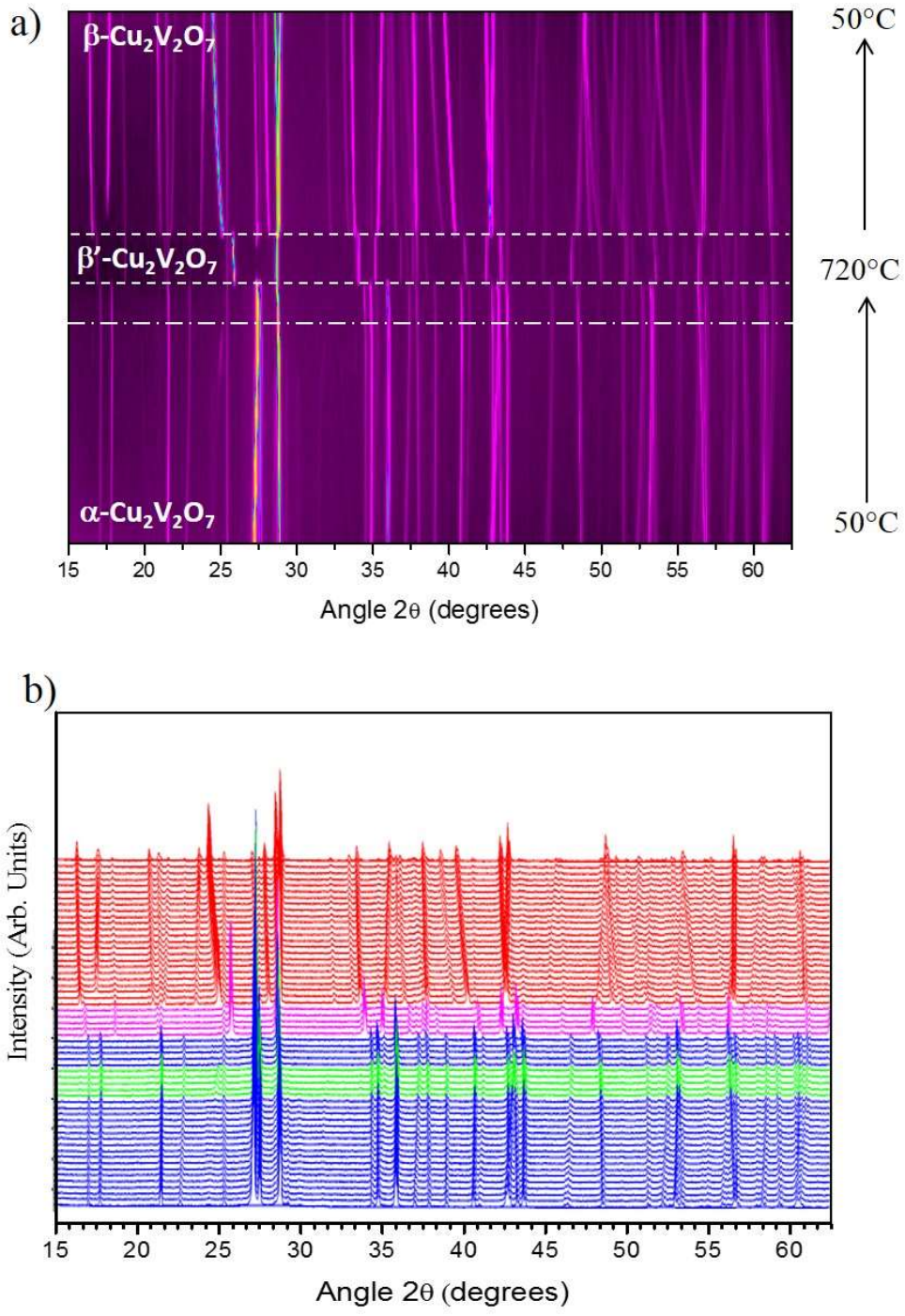

Figure S4. a) 2D map and b) 3D map of thermo-diffraction patterns for heating/cooling cycle between 50°C to 720°C.

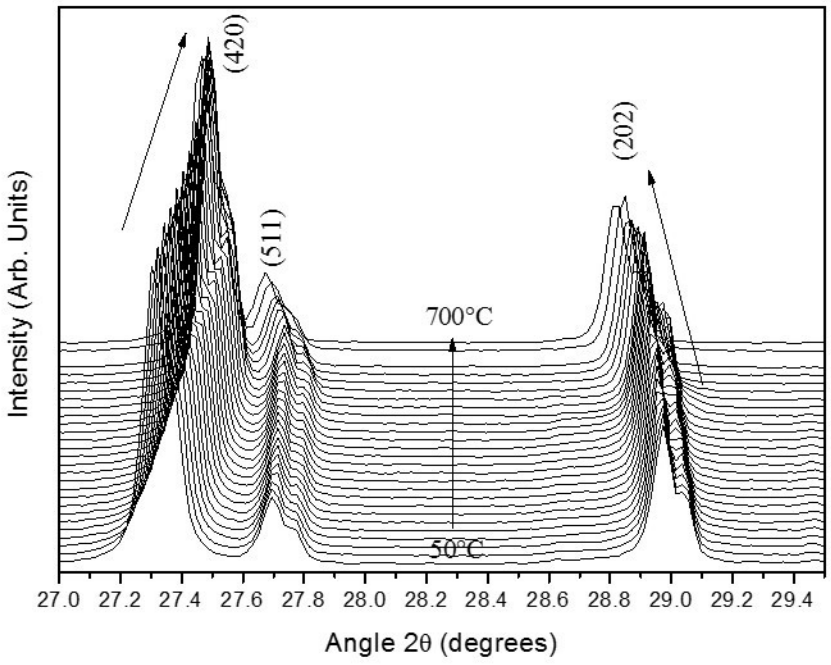

Figure S5. Fragment of HT-XRD patterns performed on α-$Cu_2V_2O_7$.

The lattice parameters of α-$Cu_2V_2O_7$ were refined and the orthorhombic structure is preserved between 50°C and 700°C. The evolution of the lattice parameters and of the unit volume are presented in Figure S6 (Supplementary Materials).

These evolutions displayed opposite effects between the lattice parameters: i) the a parameter remains almost constant from RT to 500°C. Beyond that, it increases drastically up to 700°C; ii) the b parameter decreases up to 600°C, then remains almost constant beyond this temperature and iii) the c lattice parameter increases linearly between RT and 550°C, then more rapidly beyond. Over the whole range, changes in lattice parameters do not follow linear changes. Concerning, the unit cell volume, this decreases in a nonlinear way between RT at 500°C, then re-increases between 500°C and 700°C. The demarcation of the two behaviors concerning the evolution of the unit cell volume is indicated in the Figure 4 by the centerlines. Similar behavior has already been observed by N. Zhang et *al.* [2]. The coefficients of thermal expansion (linear or volumic) can be calculated from our refined lattice parameter values according to the following equation [3]:

$$CTE_V = \frac{1}{V_0}\frac{\Delta V}{\Delta T} \text{ or } CET_L = \frac{1}{l_0}\frac{\Delta l}{\Delta T} \qquad (1.1)$$

Where V_0/l_0 are cell volume / cell parameter at Room Temperature (RT), $\Delta V / \Delta l$ is the variation of cell volume / cell parameters and ΔT the variation of temperature. The linear thermal expansion coefficients are: i) 3.35×10^{-7} and 6.67×10^{-6} K^{-1} from RT to 500°C and 500°C to 700°C, respectively (for a lattice parameter); ii) -2.05×10^{-5} and 3.71×10^{-6} K^{-1} from RT to 500°C and 500°C to 700°C, respectively (for b lattice parameter) and iii) 5.81×10^{-6} and 2.09×10^{-5} K^{-1} from RT to 550°C and 600°C to 700°C, respectively (for c lattice parameter). Concerning the volumic thermal expansion coefficients, they have to be divided into four distinct parts whose values of coefficients are: -1.89×10^{-5}, -1.50×10^{-5}, 6.43×10^{-6} and 3.30×10^{-5} K^{-1} from RT to 300°C, 300°C to 500°C, 500°C to 600°C and 600°C to 700°C, respectively. The values obtained are consistent with the literature describing the non-linearity behavior of CET as being mainly linked to the Jahn-Teller effect of the Cu^{2+} cation [2].

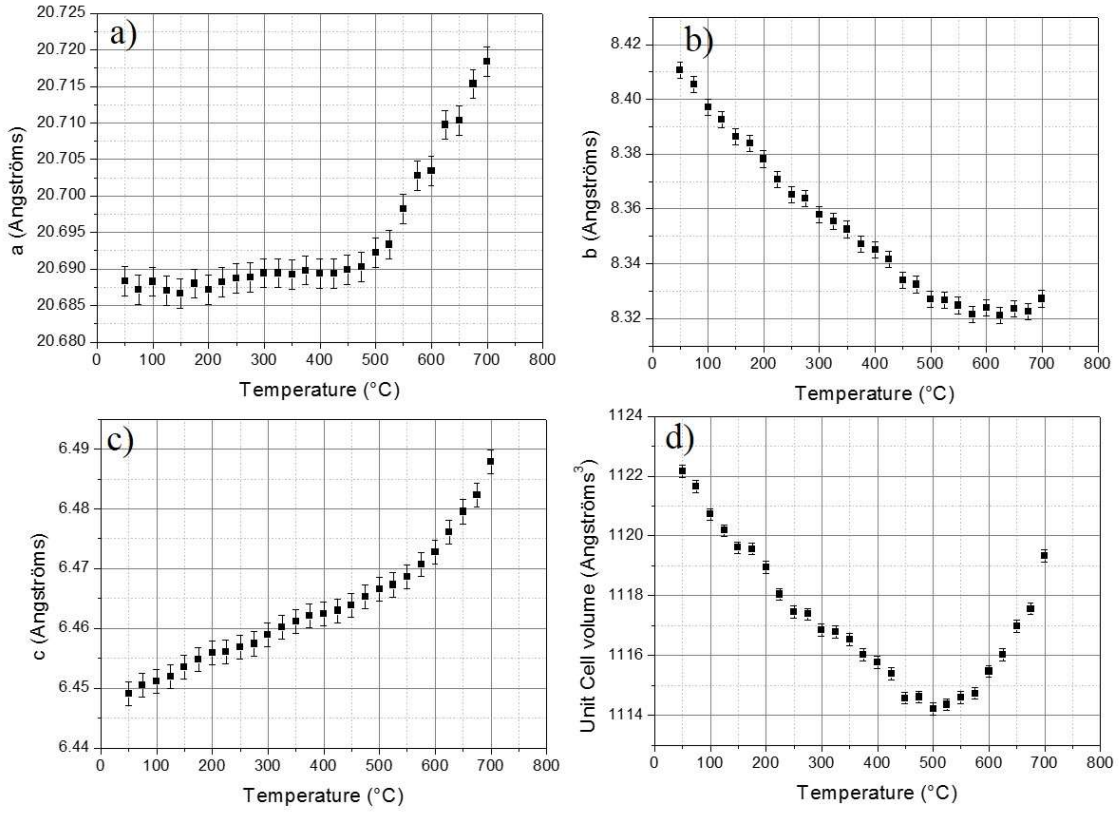

Figure S6. Lattice parameters and unit cell volume variations of α-$Cu_2V_2O_7$.

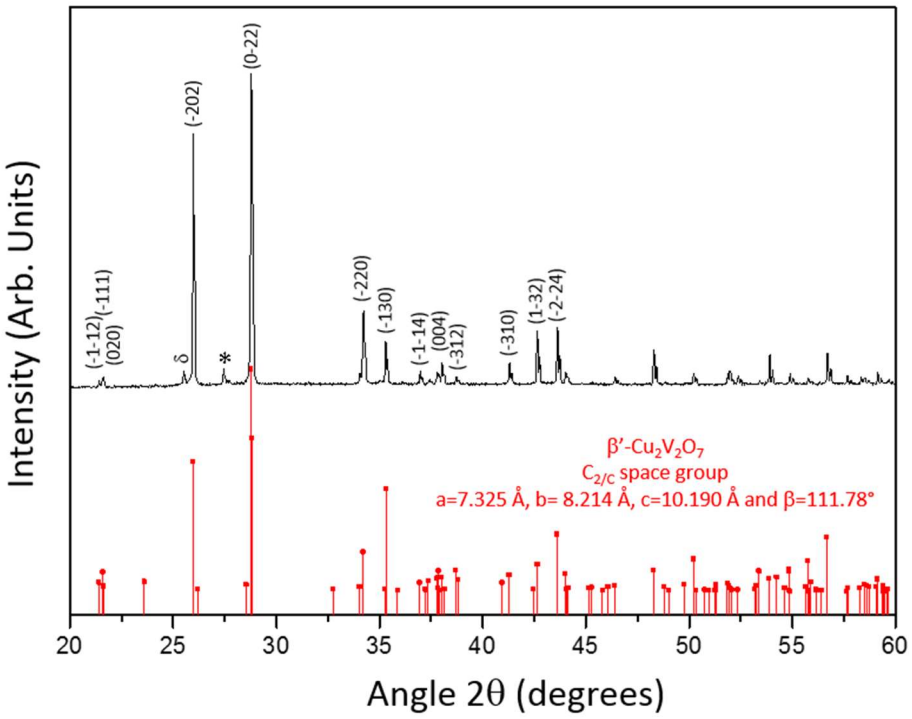

Figure S7. XRD patterns of β'-$Cu_2V_2O_7$ (experimental data obtained in this work and reference [4]). δ and * indicate the sample holder reflexion and α-$Cu_2V_2O_7$ phase, respectively.

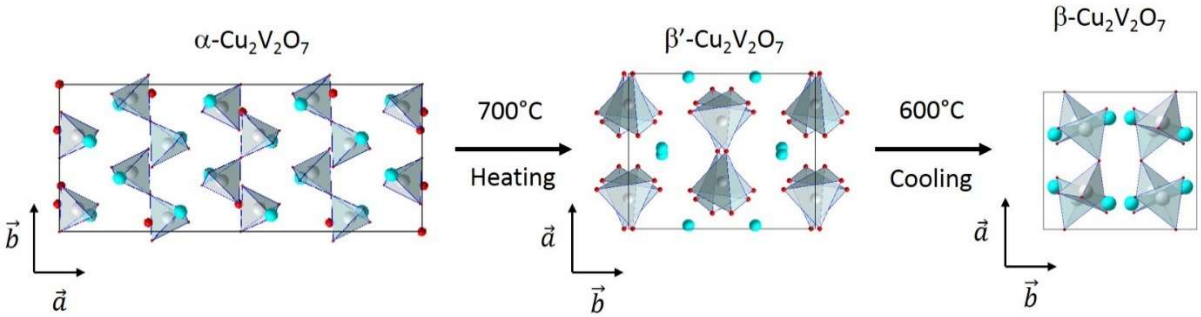

Figure S8. Structural transition observed in the first thermal cycle.

The evolution of the diffraction peaks *vs.* temperature (Figure S9 - Supplementary Materials) also indicates the presence of a negative thermal expansion coefficient. To investigate this behavior, we have plotted the evolution of lattice parameters and the unit cell volume in Figure S10 (Supplementary Materials). Refinement of the lattice parameters, shows a decrease in the a, c and β parameters and an increase in the b parameter. Note that the

evolution of the b lattice parameter is quasi-linear over the entire temperature range. The evolution of the linear thermal expansion coefficients as a function of the temperature are: i) -2.67x10^{-5} and -4.05x10^{-5} K^{-1} from RT to 450°C and 450°C to 550°C, respectively (for a lattice parameter); ii) 1.57x10^{-5} from RT to 575°C (for b lattice parameter) and iii) -9.51x10^{-6} and -5.21x10^{-6} K^{-1} from RT to 400°C and 400°C to 575°C, respectively (for c lattice parameter).

Concerning the volumic thermal expansion coefficient, it is not linear and can be divided into two distinct parts whose values of coefficients are: -1.11x10^{-5} and -2.63x10^{-5} K^{-1} from RT to 450°C, 450°C to 550°C, respectively. These values indicate that β-$Cu_2V_2O_7$ phase exhibits a negative expansion between 50°C and 575°C. In addition, these values are also correlated in the literature [5].

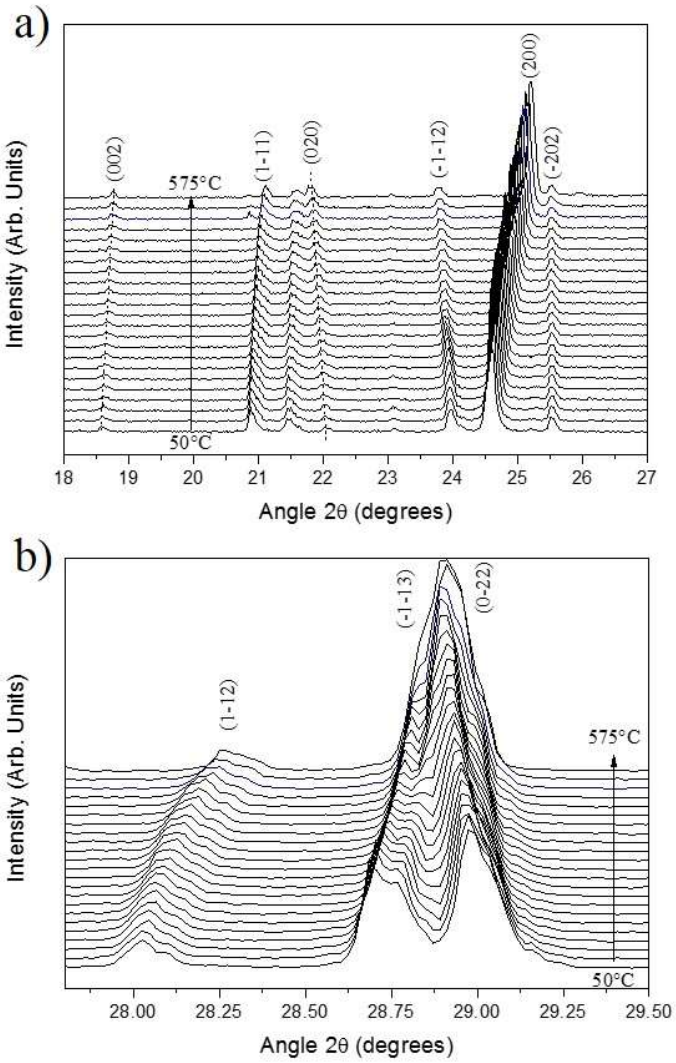

Figure S9. Fragments of HT-XRD patterns performed on β-$Cu_2V_2O_7$.

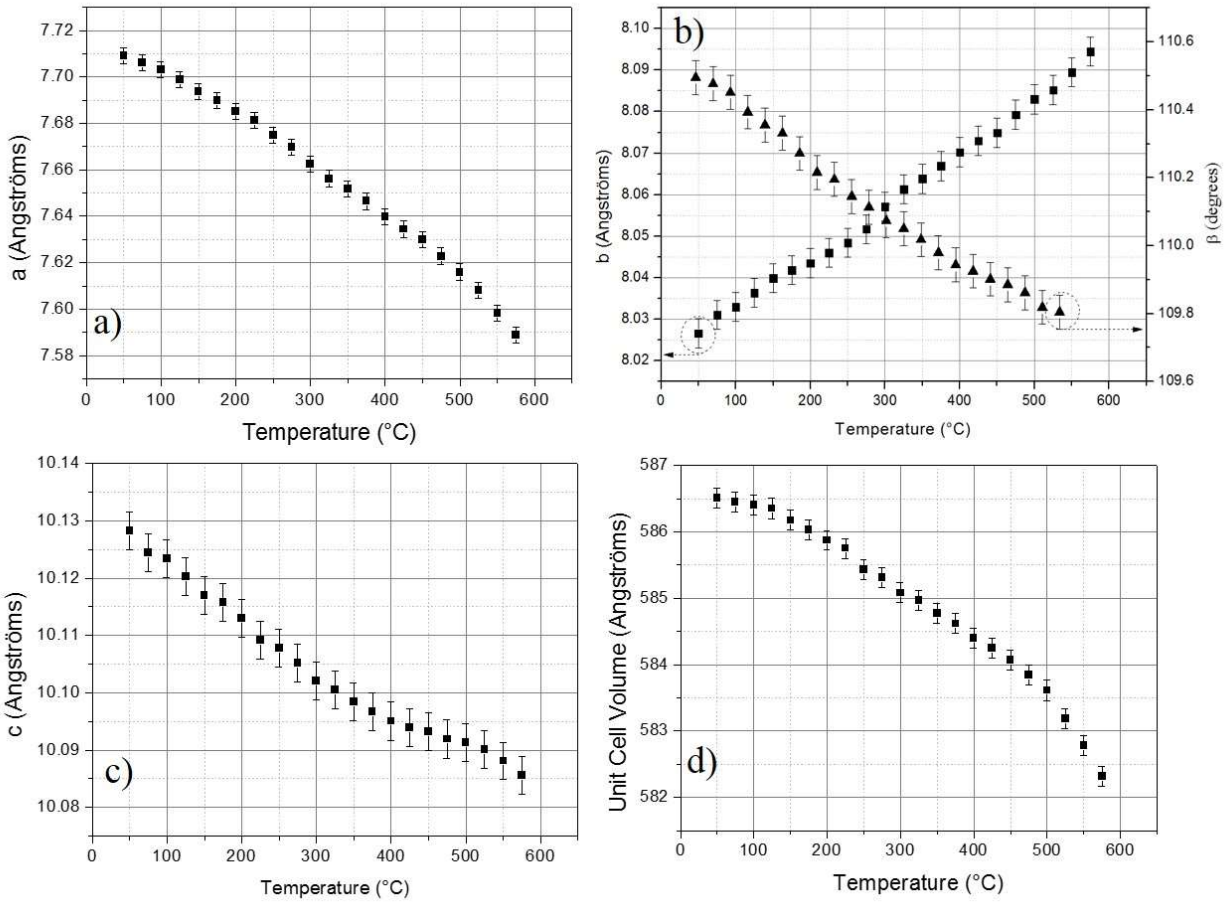

Figure S10. Lattice parameters and unit cell volume variations of β-$Cu_2V_2O_7$.

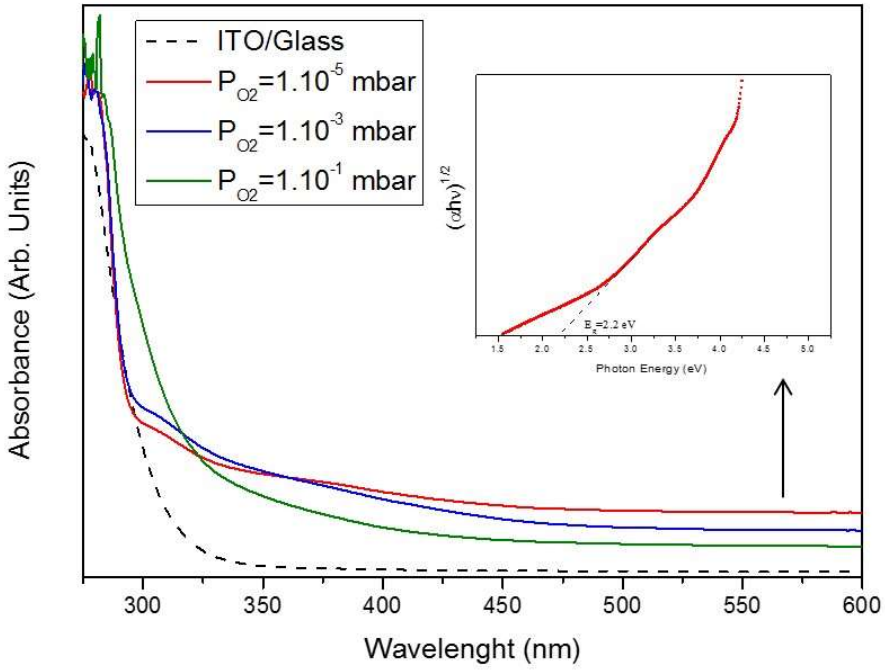

Figure S11. Absorbance spectra of β-$Cu_2V_2O_7$ thin films vs. dynamic O_2 pressure.

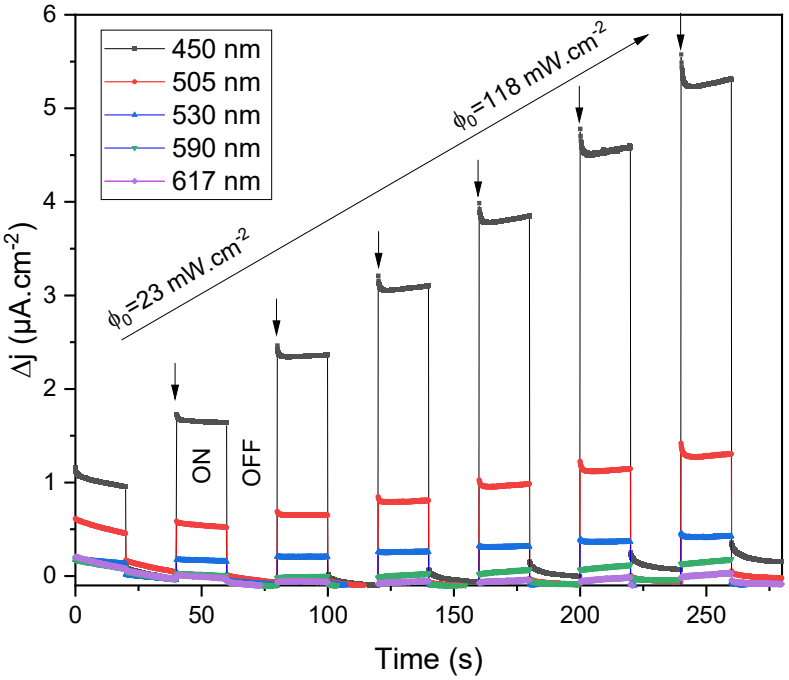

Figure S12. Variation of the current density (Δj) under illumination or dark depending on the intensity of the luminous flux (ϕ_0) and with an applied potential of 0.4 V *vs.* Ag/AgCl electrode.

References

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