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Electronic Supplementary Information

Thermo-selective $Tm_xTi_{1-x}O_{2-x/2}$ nanoparticles: from Tm-doped anatase TiO_2 to rutile/pyrochlore $Tm_2Ti_2O_7$ mixture. An experimental and theoretical study with a photocatalytic application

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I. Procedure for semi-quantitative assessments from XRD patterns

Mass fraction of anatase and rutile phase: The mass fraction of anatase phase (f_A) was calculated using the equation

$$f_A = \left(1 + 1.26\frac{I_R}{I_A}\right)^{-1} \quad \text{(S1)}$$

where I_R is the intensity of the reflection of the (110) plane for rutile phase, and I_A is the intensity of the reflection of the (101) plan for anatase phase.[1] For the assessment of the mass fraction of rutile phase, only the presence of the anatase and rutile phases was considered.

Average crystallite size: The average crystallite size (t) was calculated using the Scherrer equation; that is

$$t = \frac{0.9\lambda}{\beta\cos\theta} \quad \text{(S2)}$$

where θ is the diffraction angle, β is the full-width-at-half-maximum (FWHM) in radians, and λ is the wavelength of X-ray radiation, that is Cu Kα (0.154 nm).[2] The values of θ and β used are those corresponding to the major peaks of each phase, that is, planes (101) and (110) for anatase and rutile phases, respectively.

Unit cell volume: The volume of the unit cell (V) was calculated and used for obtaining the value of the specific surface area. The values of V were obtained from the values of the lattice constant as $V = ac^2$ ($a = b \neq c$, for anatase and rutile phase).[3] The values of a and c were estimated from the two peaks with the highest intensity of the patterns, that is reflection of the planes (101) and (200) for anatase phase, and planes (110) and (211) for rutile phase, and using the equation typical for tetragonal systems[4]

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{S3}$$

where h, k, l are the Miller indexes of the planes used, and d is the interplanar distance.

Specific surface area: the specific surface area (s_a) was calculated from XRD patterns using the equation[3]

$$s_a = \frac{6}{t\rho} \tag{S4}$$

where ρ is the density obtained by means of XRD as[3]

$$\rho = \frac{nM}{NV} \tag{S5}$$

where N is Avogadro's number, M is the molecular weight, n = 2 for rutile phase and n = 4 for anatase phase, and V is the unit cell volume calculated as described above. In turn, the molecular weight was calculated considering the empirical formula obtained from the ICP-AES and XPS results.

Finally, to obtain the best values of the calculated properties, an adequate baseline correction of the patterns was applied.

Figure S1. Evolution of mass fraction of anatase phase (f_A) according to annealing temperature.

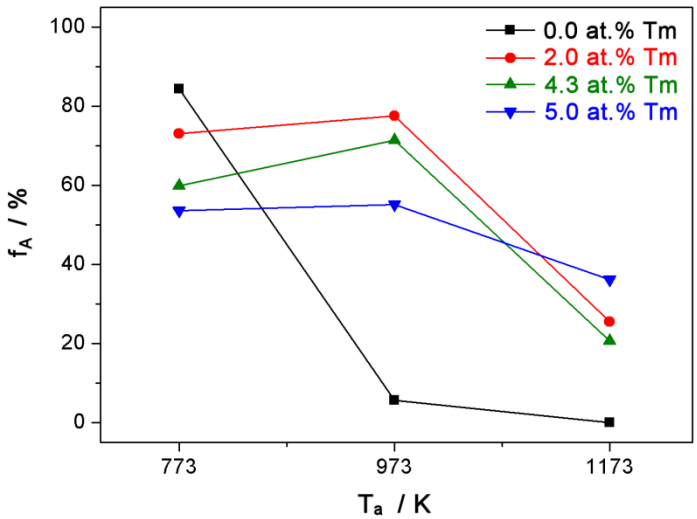


Figure S2. Evolution of mass fraction of anatase phase (f_A) according to atomic percentage of Tm.

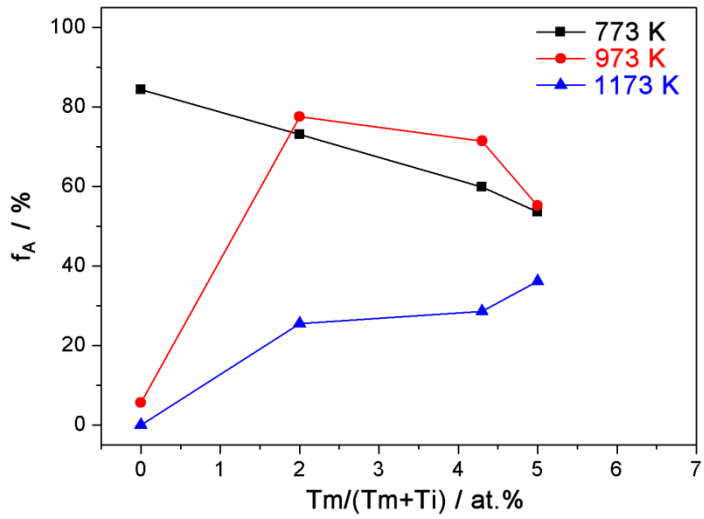


Figure S3. Evolution of specific surface area (s_a) according to annealing temperature.

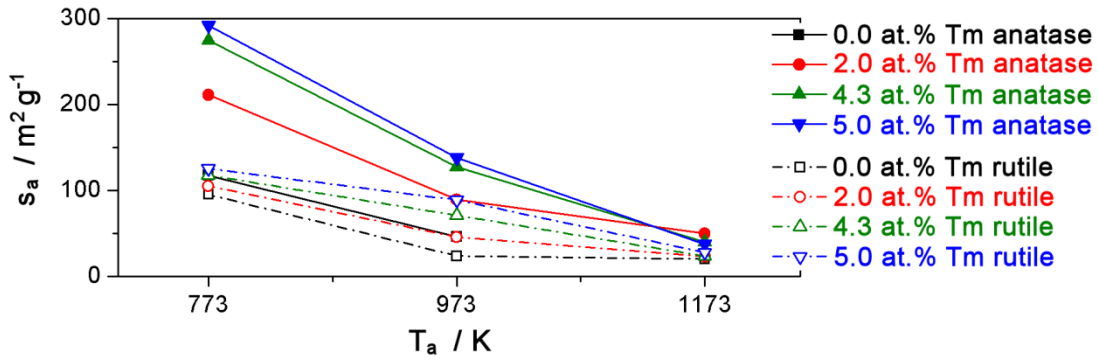
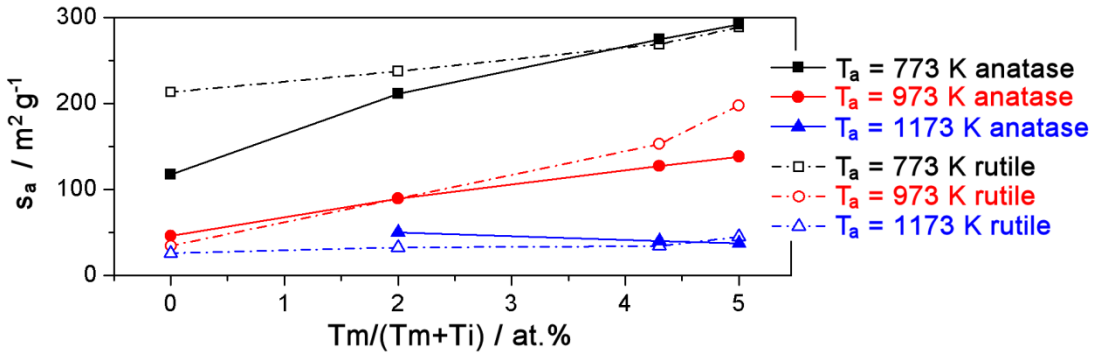


Figure S4. Evolution of specific surface area (s_a) according to atomic percentage of Tm.



II. Procedure for estimating the band gap energy values from UV-Vis Spectroscopy using the Kubelka-Munk formulism and Tauc plot

The UV-Vis spectra were obtained in reflectance diffuse mode. The Kubelka Munk function for diffuse reflectance (R) is

$$f(R) = \frac{(1-R)^2}{2R}. \tag{S6}$$

The plot of $[f(R)h\nu]^n$ versus $h\nu$ for a semiconductor shows a linear region for n = ½ if the band gap is determined by direct transition, or for n = 2 if the transition is indirect.[5,6] So, as for TiO_2, the band gap is determined by a direct transition, the plot of $[f(R)h\nu]^{1/2}$ versus $h\nu$ shows a linear region which satisfies the following equation

$$[f(R)\cdot h\nu]^{1/2} = K(h\nu - E_g) \tag{S7}$$

where $h\nu$ is the photon energy, E_g is the band gap energy, and K a characteristic constant for the semiconductor.

Figure S5. Energy level diagram for Tm^{3+}.[7]

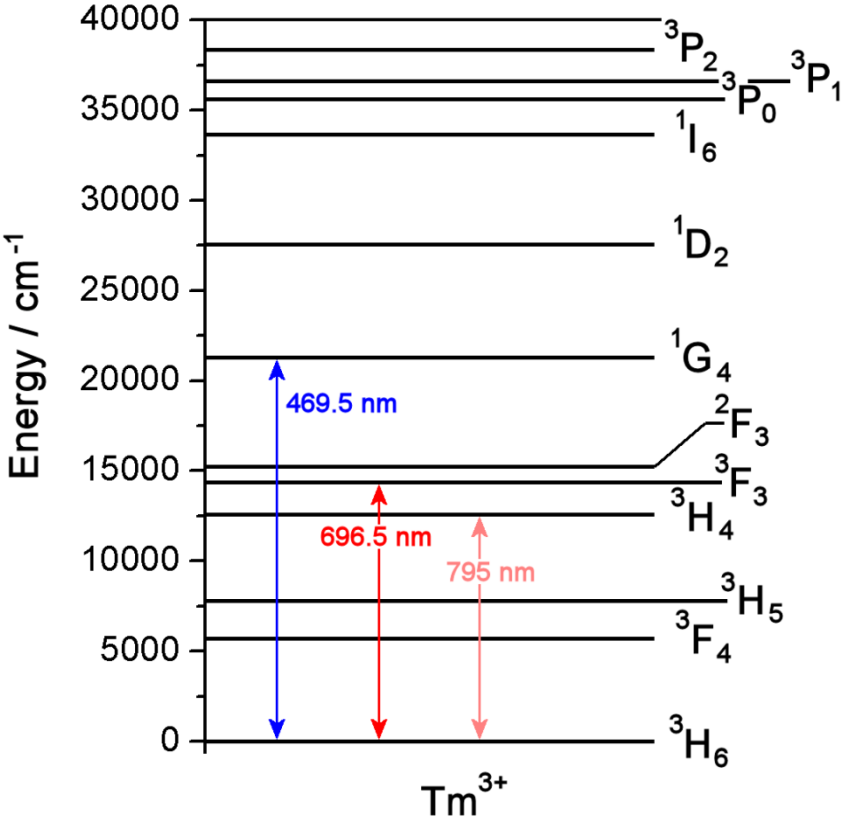


Figure S6. Raman spectra obtained using the red laser (emitting at 785 nm) as illumination source.

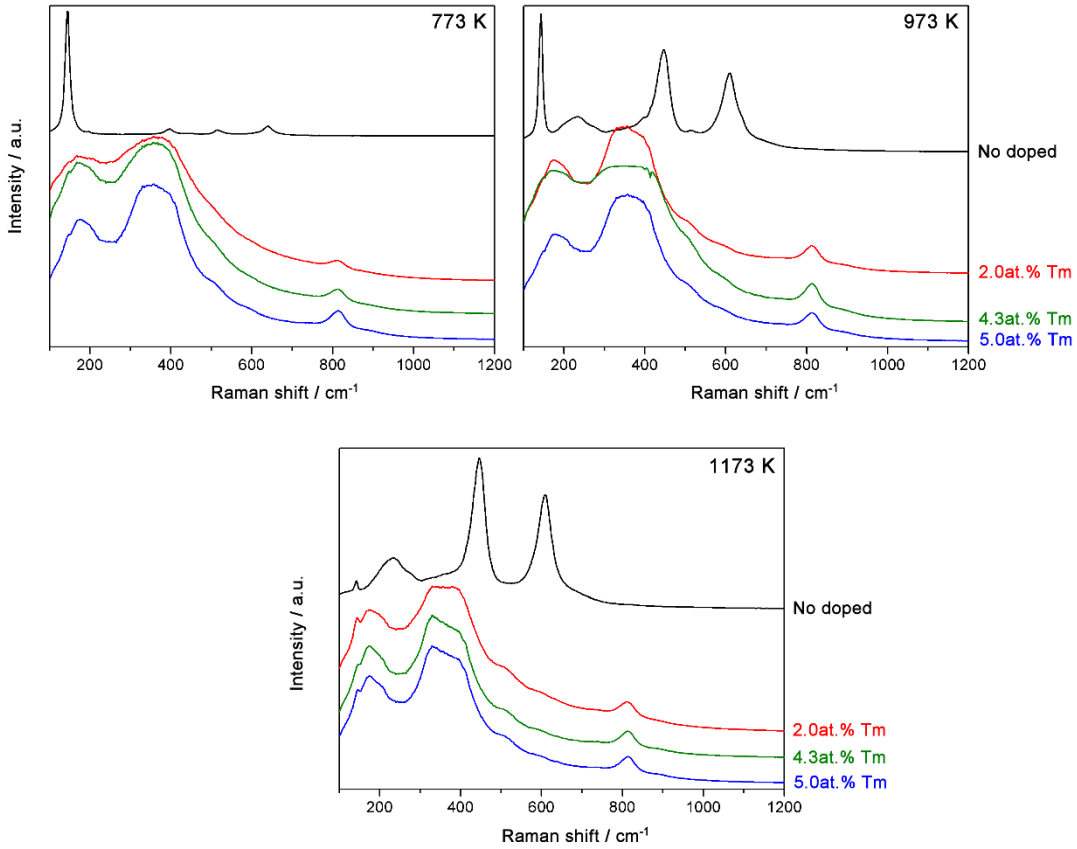


Figure S7. DOS and PDOS for anatase TiO_2 and $Tm_2Ti_{62}O_{127}$.

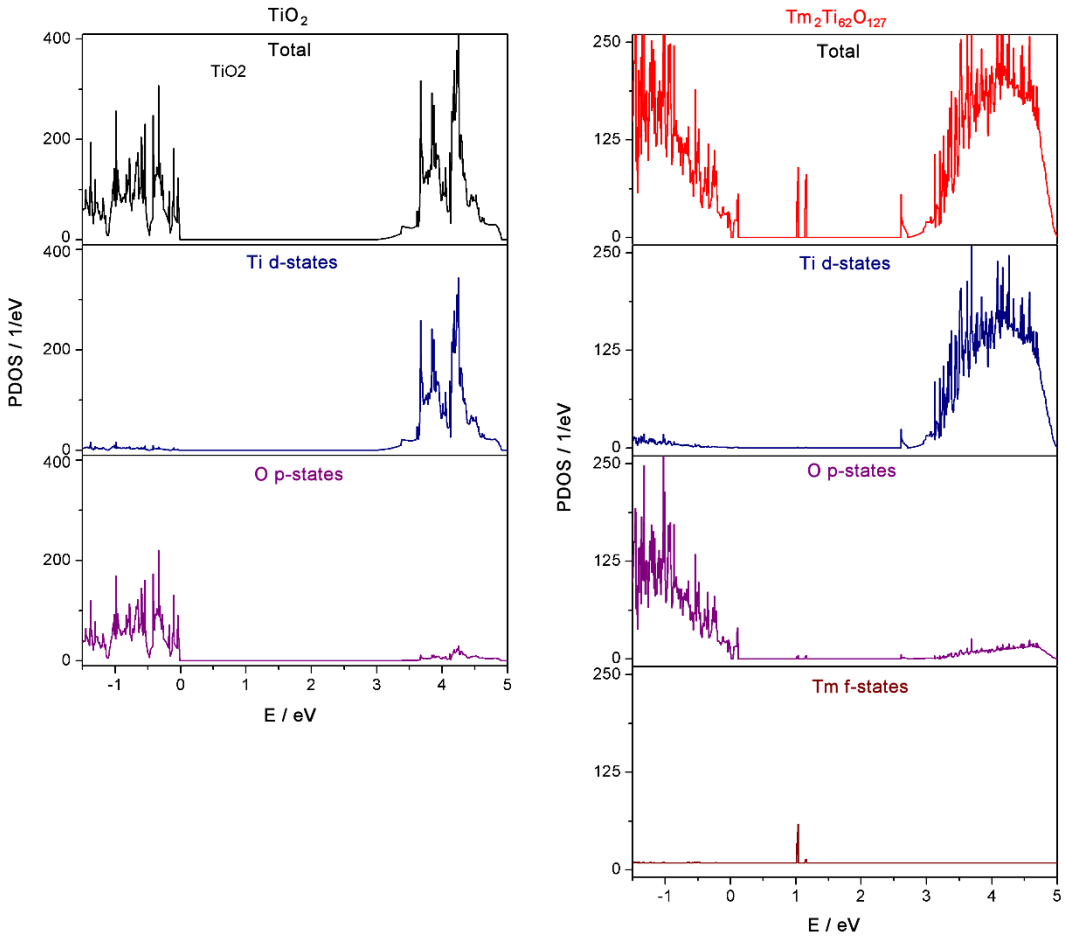
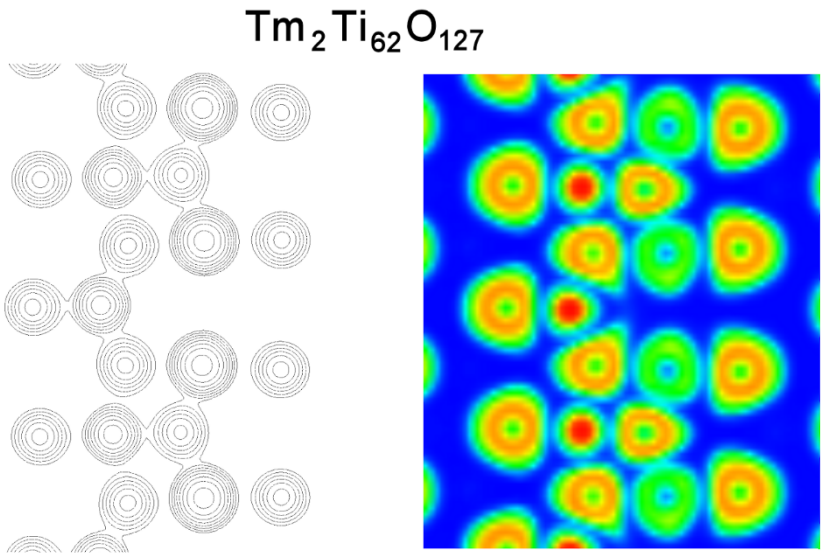


Figure S8. Charge density and ELF contour plot for $Tm_2Ti_{62}O_{127}$.



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