

Electronic Supplementary Information

Preparation and photoactivity of nanostructured anatase, rutile and brookite TiO₂ thin films

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XRD patterns of the powders were recorded at room temperature in a PW 1130 Philips X-ray diffractometer using the Cu K α radiation and a 2θ scan rate of 0.025°/s. UV-vis spectra of the powders were obtained using a Shimadzu UV-2401 PC instrument with BaSO₄ as the reference sample. The specific surface areas were determined in a Flow Sorb 2300 apparatus (Micromeritics) by using the single-point BET method.

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a LabSys Setaram thermobalance operating in the range 293–1273 K, with a heating rate of 10 K min⁻¹, under 100 mL min⁻¹ He flow.

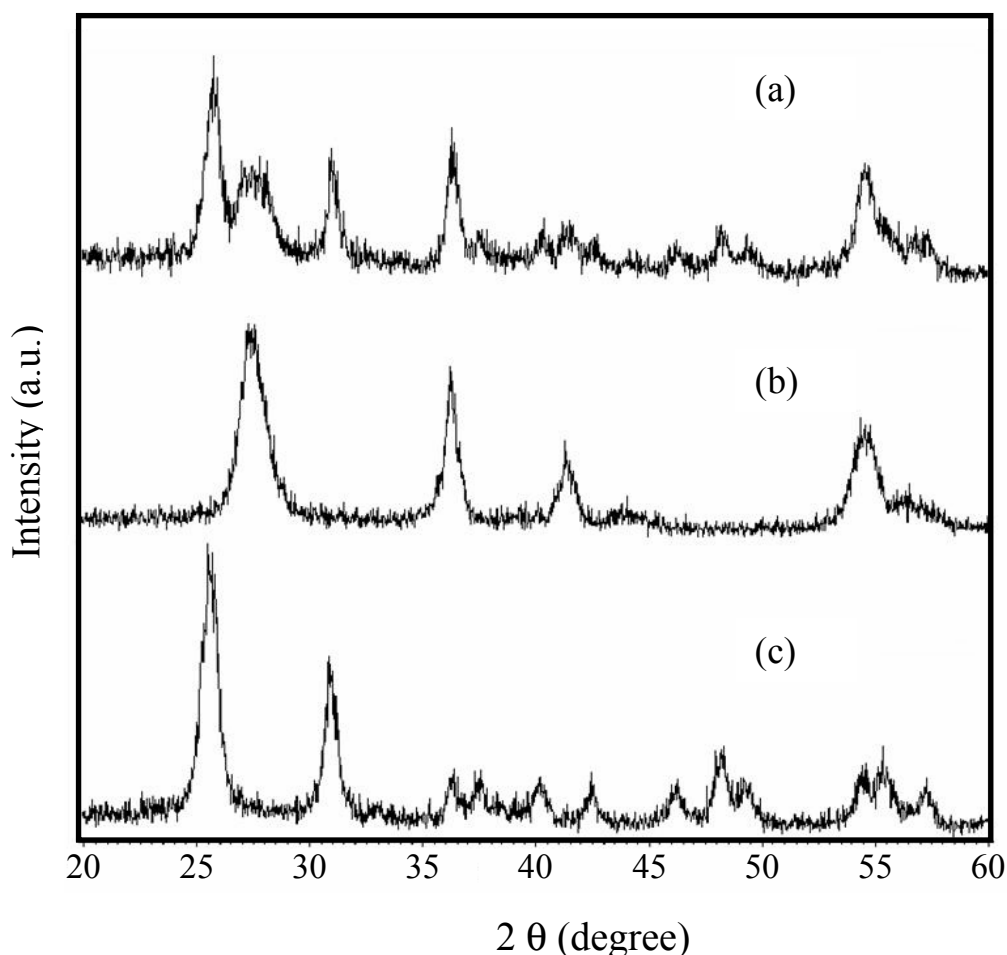


Figure S1: XRD patterns of TiO₂ powders consisting of: (a) mixture brookite – rutile; (b) pure rutile; (c) pure brookite.

Figure S1a shows the X-ray diffractogram of the mixture rutile-brookite. After separation the spectra showed peaks attributable to the pure single phases (27.7°, 36.4° and 54.5° for rutile; 25.7°

and 31° for brookite, see Figure S1b and Figure S1c). The Sherrer equation allowed to calculate the primary particle sizes that are reported in Table 1 along with the BET specific surface areas of the powders recovered from the dispersions used to prepare the films.

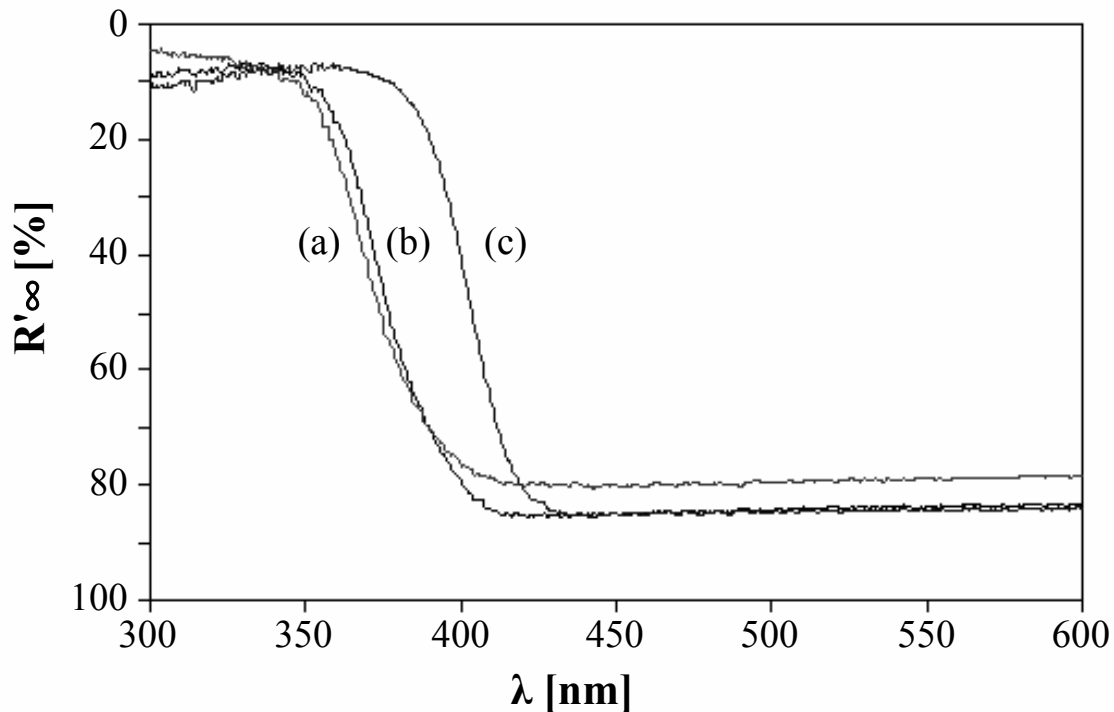


Figure S2: Diffuse reflectance spectra of: (a) anatase; (b) brookite; (c) rutile.

Figure S2 shows the diffuse reflectance spectra of the three powders. Assuming the materials to be indirect semiconductors, plots of the modified Kubelka-Munk function versus the energy of exciting light¹ allow to determine the band gap values of the three obtained phases, that are reported in Table 1. The band gap of brookite resulted the highest, close to that of anatase, while that of rutile the lowest. All the obtained values are in good agreement with those reported in literature.^{2,3}

Sample	Φ (nm)	SSA ($\text{m}^2\cdot\text{g}^{-1}$)	E_g (eV)
Anatase	15	200	3.17
Brookite	6	75	3.29
Rutile	4	11	2.95

Table 1: Primary particle size (Φ), specific surface area (SSA) and band gap (E_g) of the TiO_2 powders.

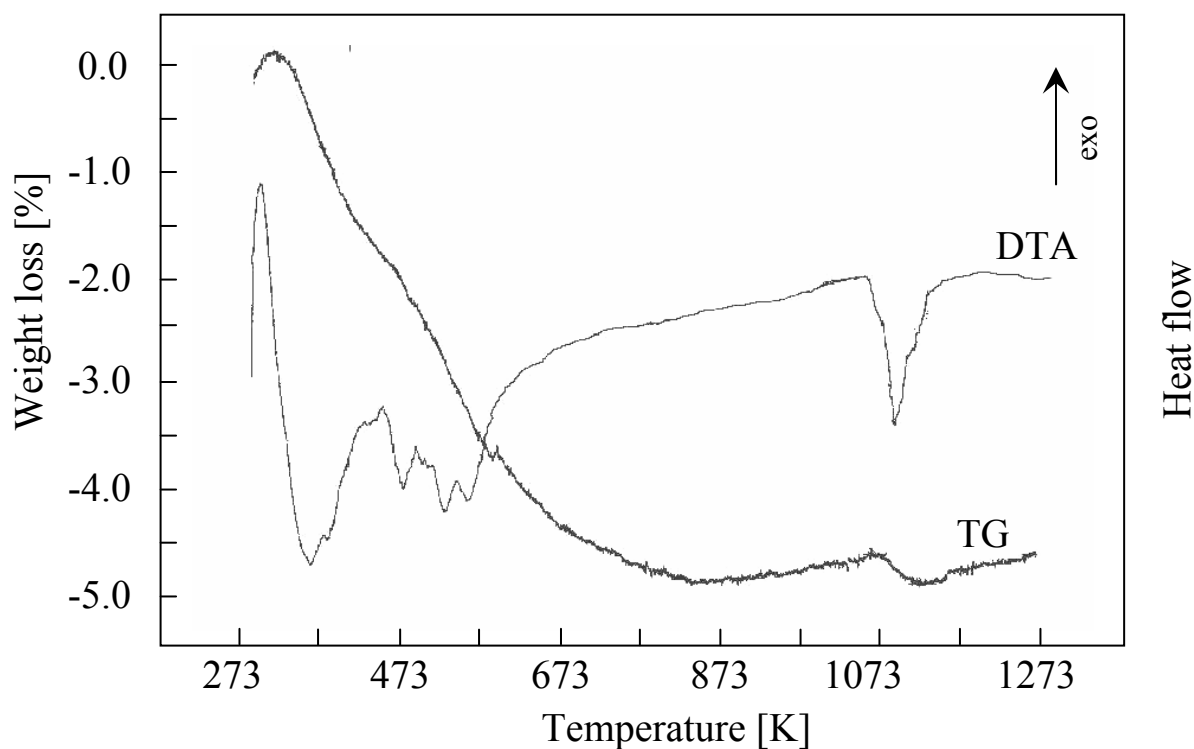


Figure S3: DTA and TG curves of the brookite powder obtained by drying the dispersion (2) under vacuum at 328 K.

Figure S3 shows differential thermal analysis and thermogravimetric analysis curves of the brookite phase. The endothermic peak at about 1104 K is due to the formation of rutile.⁴

References

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