Supporting information

Detailed experimental method

Phase identification of the powders used in this study was made by means of X-ray diffraction analyses performed in a Siemens D-5000 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) operated at 50 kV and 30 mA, with Cu Kα radiation and Ni-filter, the 2θ range selected was 20-80°. The scanning step was 0.05°, the time/step 1.5 s and the rotation speed used was 15 rpm.

The band gap of the different titanium oxide powders was determined measuring the absorbance in ultraviolet-visible (UV-vis) range of the powders using spectrophotometer (UV-Vis-NIR Lambda 950, Perkin Elmer, USA). The measurements are carried out in the diffuse reflectance (DR) mode, in wavelength between 200-1000 nm. The band gap was calculated using the equation according to Van Leeuwen et al. [1] where the absorption coefficient (α) is related with the photon energy (hv).

1,1-diphenyl-2-picryl-hydrazy radical (DPPH·) was used to study the scavenging activity of the proposed samples. DPPH· is a semi-stable radical which, according with Kedare et al. [2] shows a strong absorption band at 517 nm due to its odd electron and solution appears a deep violet colour. The absorption vanishes as the electron pairs off. The resulting decolourization is stoichiometric with respect to the number of electrons taken up. The DPPH· concentration can be measured by UV-Vis absorbance aided by a calibration curve.

The calibration curve was prepared with different concentrations of DPPH· (Sigma #D9132), 0, 0.01, 0.02, 0.04, 0.1, 0.2, 0.3, 0.4mM, in 2-propanol (Sigma). And DPPH· 0.1 mM was selected to carry out the experiments. 50 mg of the different titanium oxide samples were incubated 500 μl of 0.1mM DPPH· solution in 2-propanol in the dark at 21°C with agitation during 30 min. The suspension was centrifuged at 20,000 rcf, at 21°C. An extra-centrifugation of the supernatant was made in the same conditions. All the experiments have been carried out in dark conditions. Then the absorbance of the supernatant solutions was measured in a Power Wave XS (BIOTEC). 200 μl of supernatants were used in each case.

Subsequently, the percentage of DPPH· eliminated was calculated from the ratio between concentration corresponding to the maximum of absorbance (initial solution of DPPH·, 0.1 mM) and concentrations corresponding to the absorbance of supernatants solutions. The materials studied possessed different specific surface areas, which increase the kinetic of the reaction. In order to know the role of Ti^{4+} and/or Ti^{3+} on the neutralization of DPPH·, the influence of specific surface area of the powders was eliminated by plotting the percentage of DPPH· eliminated calculated per m^2 of specific surface area. Specific surface area was determined for all materials (Table 1) by the Brunauer–Emmett–Teller B.E.T. method in a Monosorb Analyzer MS-13 (QuantaChrome Instruments, Boynton Beach, FL, USA). Then, scavenging activity of different powders is compared according % of DPPH· eliminated per mg of powder incubated and per m^2 of specific surface area in each case. It is related with the oxidation state of Ti in each phase and the corresponding band gap.

[1] Robert A. Van Leeuwen, Chen-Jen Hung, Daniel R. Kammler and Jay A. Switzer. Optical and Electronic Transport Properties of Electrodeposited Thallium (II) Oxide Films. J. Phys. Chem. 1995, 99:15247-15252

[2] Kedare S.B. and Singh R.P. Genesis and development of DPPH method of antioxidant assay. J. Food Sci. Technol. 201, 48(4):412-422.