Supplementary information.

Summary

1. Surface area measurements. The surface area of the dusts (TiO_2 50 m^2/g, CM-TiO_2 47 m^2/g, amorphous silica 50 m^2/g) has been measured by means of the BET methods based on N_2 adsorption at 77K (Micrometrics ASAP 2010).

2. UV-Vis Diffuse Reflectance. Diffuse Reflectance UV-Visible spectra (DR UV-Vis) were recorded by a Varian Cary 5 spectrometer using a Cary win-UV/scan software.

3. Irradiation equipment. Irradiation experiments were performed with a 500 W mercury/xenon lamp (Oriel instruments) equipped with a IR water filter. Simulated solar light was obtained by applying a 400nm cut-off filter. This filter let to pass about 5% of UV light in the UV A region.

4. X ray diffraction. XRD spectra were collected on a diffractometer (PW1830, Philips) using Co(Kα) radiation, in the (20 – 90) 2θ range, with step width 2θ = 0.05 and diffraction peaks have been indexed according to ICDD database (International Centre for Diffraction Data).

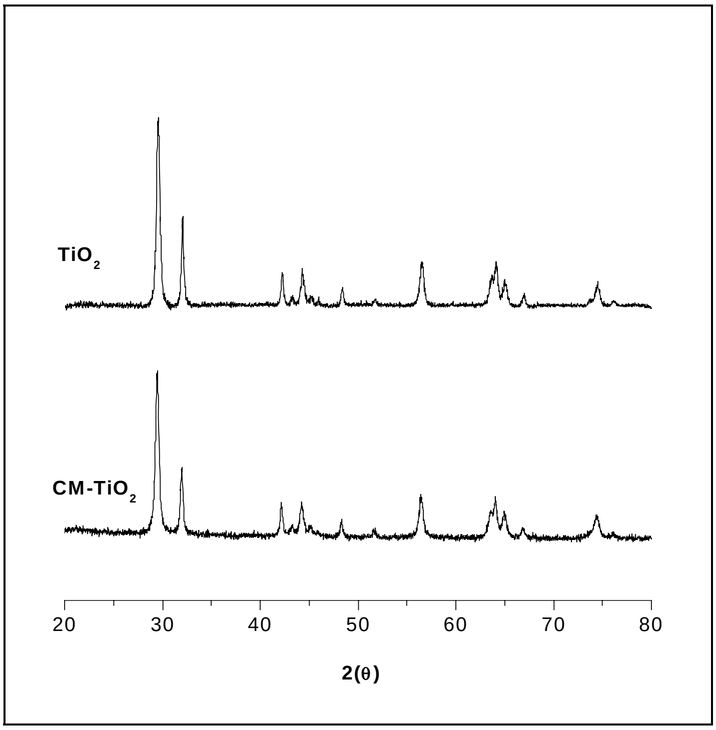
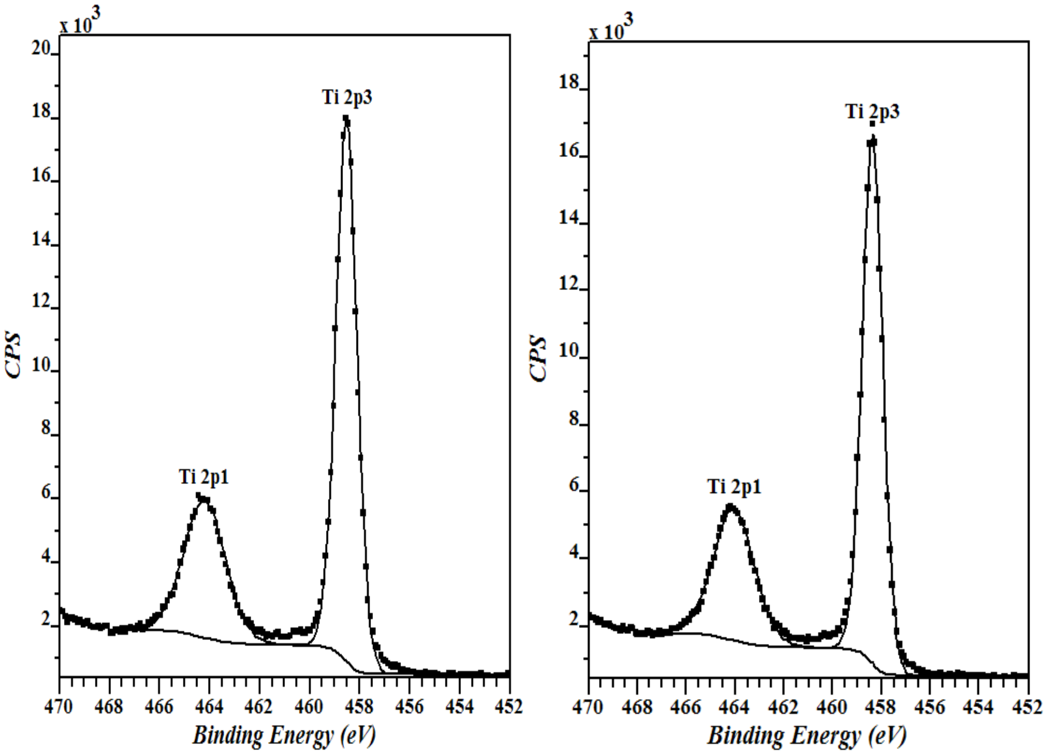


Figure 1: XRD diffraction patterns of pristine and carbon modified TiO_2.

5. XPS analysis. XPS measurements have been performed with an AXIS ULTRA Spectrometer (KRATOS Analytical, UK). Instrument calibration was performed using a clean pure Au/Cu sample and pure Ag sample (99.99%). Measured values for electron binding energies (BE) were 84+/-0.02 eV, and 932+/-0.04eV.

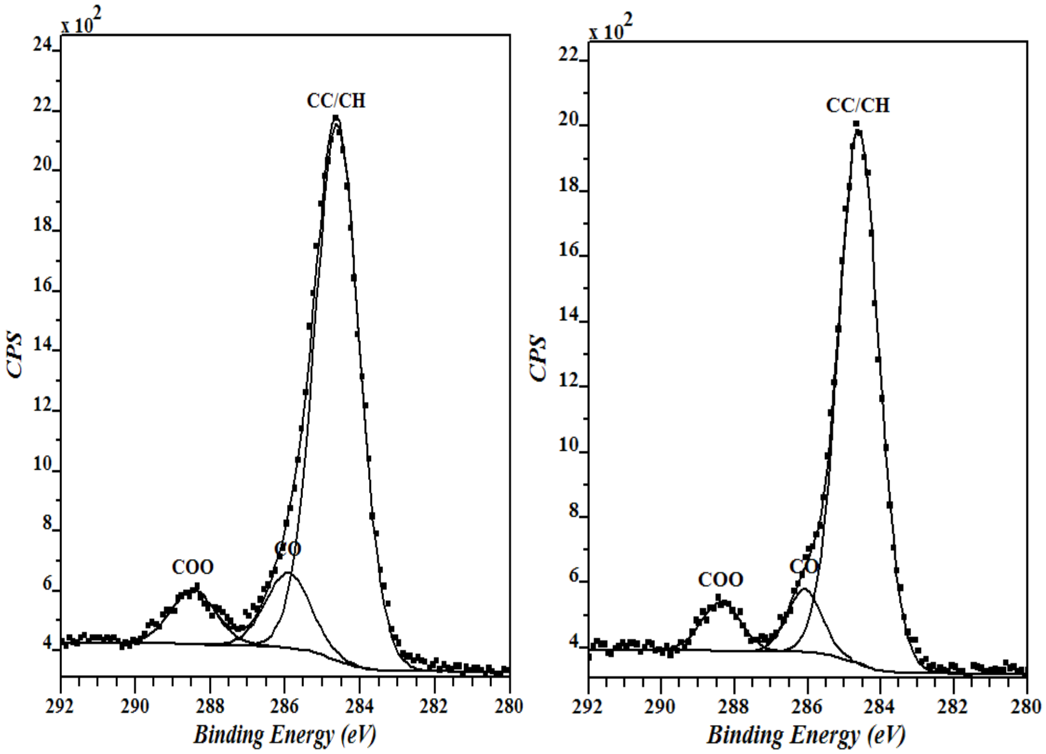
The samples were irradiated with monochromatic AlKα X-rays (hν=1486.6eV) using X-ray spot size of 400x700μm^2 and a take off angle (TOA) of 90° with respect to the sample surface. The analyzed area was 700x400μm. The base pressure of the instrument was better than 8x10^{-10} Torr and the operating pressure better than 3x10^{-9} Torr. Surface charging was compensate by means of a filament (I=1.9A, 3.6V) inserted in a magnetic lens system and all spectra were corrected by setting the C1s hydrocarbon component to 284.60eV.

For each sample, a survey spectrum (0-1150eV), from which the surface chemical compositions (at%) were determined, was recorded at pass energy of 160eV. In addition a set of high-resolution spectra (PE=20eV) was also recorded on each sample. The data were processed using the Vision2 software (Kratos, UK) and CasaXPS v2.3.15 (Casa Software, UK). Sample compositions were obtained from the survey spectra after linear background subtraction and using the RSF (Relative Sensitivity Factors) included in the software derived from Scofield cross-sections. This method is estimate to give an accuracy of 10% in the measurement of elemental compositions. Curve fitting of core level peaks was carried out using the same initial parameters and inter-peak constrains to reduce scattering. The core level envelopes were fitted with Gaussian-Lorentian function (G/L=30) and variable full width half maximum.



(a) (b)

Figure 2. Ti 2p core level spectra of (a) pristine TiO_2, (b) after carbon modification



(a) (b)

Figure 3: C1s core level spectra of: (a) pristine TiO_2, (b) after carbon modification

The Ti2p core level spectrum of the pristine sample (Figure 2a) shows a doublet at about 458.4eV with a spin orbit spitting of 5.67eV, compatible with the Ti^{4+} oxidation state.[3] The shape of the peak also excludes the presence other oxidation states. The carbon modification did not result in change of the Ti oxidation state (Figure 2b).

The C1s core level spectra of the pristine sample (Figure 3a) present three components that can be assigned to hydrocarbon (284.6eV), ether group (286.2eV) and to carboxylate (about 288.6eV). The relative amounts of these components are 80.5/11.3/8.2. After the carbon treatment, a slight change in the three components content is observed (83/10.5/6.5). We have not observed any component at 282eV correspondent to Ti-C type of bonds.[4,5]

The O1s core level spectra (data not shown) presents one major component at about 529.5eV (attributable to the Ti-O bulk bonds) and a minor broaden component at about 531eV that can be due to the different C-O species present at the surface and also to the Ti-O bonds at the surface. No major changes are observed in the O1s peak after treatment.

6. EPR spectroscopy of the powders. EPR spectra were run on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 KHz field modulation.

All spectra were recorded in vacuum condition at 77K and 10 mW of microwave power. Irradiation of pristine and carbon modified samples were performed at RT in air for 5 minutes and subsequently evacuated to record spectra.

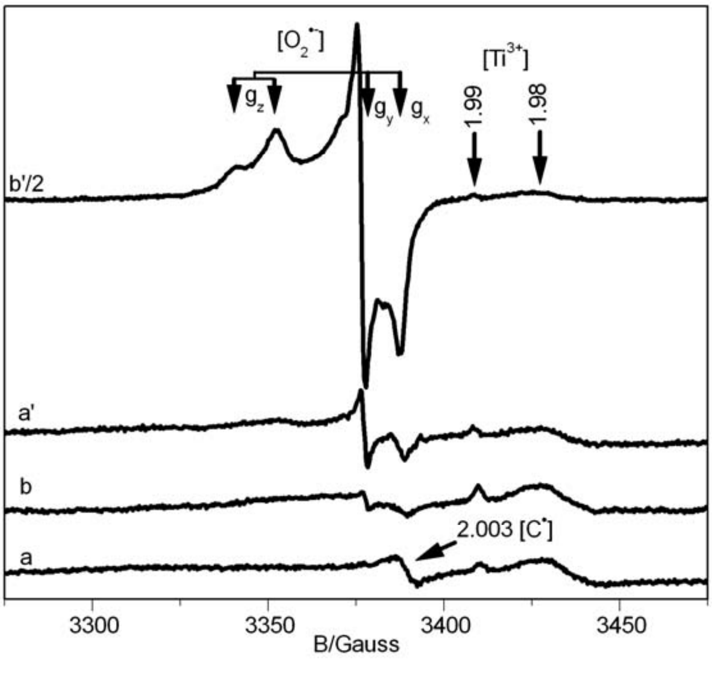


Figure 4: EPR spectra of a) pristine TiO_2 and b) CM-TiO_2 in dark. a') pristine TiO_2 and b') CM-TiO_2 after irradiation (λ 190-800 nm) in air.

In dark condition both samples showed two distinct signal at $g \approx 1.99$ and $g \approx 1.98$ due to Ti^{3+} in different chemical surround[1]. Pristine TiO_2 exhibited a small signal correspondent to a residual amount of $O_2^{\bullet -}$ species probably formed during ambient illumination while carbon modified samples showed a further signal at g = 2.003 ascribed to carbon centered radical ($C^\bullet$) but not superoxide radical was detected. Initial presence of $O_2^{\bullet -}$ species after ambient illumination exposure in the case of the only pristine sample clearly show a difference in reactivity respect to carbon modified system. This difference become much more evident after 5 minutes of UV-Vis (λ190-800 nm) irradiation in air. In this condition a clear signal of $O_2^{\bullet -}$ radical (g_x=2.003, g_y=2.009 and g_z= 2.024-2.030) adsorbed on different surface sites, as indicated by the g_z multiplicity[2], was observed in the pristine sample while on CM-TiO_2 only a weak signal was detected even though the two materials showed the same UV light absorption capability (Fig. 1).

7. Free radicals generation.

Generation of hydroxyl radicals. 28 mg of the powders were suspended in a buffer (phosphate buffer 0.2 M, pH 7.4) in the presence of a spin trap molecule 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 0.034 M) and than irradiated for 1h with simulated solar light. The EPR spectra (Miniscope 100 EPR spectrometer, Magnettech) were recorded on suspension. Splitting constants of the signal recorded: $a^N = a^H = 15.3$ G.

Generation of carbon centered radicals. 28 mg of the powders were suspended in 0.5 ml of a 1 M buffered solution of sodium formate and 0.085 M DMPO (0.25 M phosphate buffer, pH 7.4) After irradiation for 1h with simulated solar light (λ> 400 nm), the EPR spectra (Miniscope 100 EPR spectrometer, Magnettech) were recorded on the suspension. Splitting constants of the signal recorded: $a^N = 15.6$ G $a^H = 18.7$ G.

Generation of linoleic-derived free radicals. 21 mg of the powders were suspended in 0.8 ml of a 0.067 M solution of linoleic acid in cyclohexane containing the spin trap phenyl-buthyl-nitrone (PBN, 0.095 M). After exposure to simulated solar light for 1 h the EPR spectra were recorded on the suspension.

The experiment was repeated after removing the dissolved oxygen by cycles of freezing and thawing in vacuo. In this case the broadening of the signal due to oxygen was not observed and the hyperfine structure of the signal appeared (splitting constant a^N =13.4 G , a^H =1.7 G).

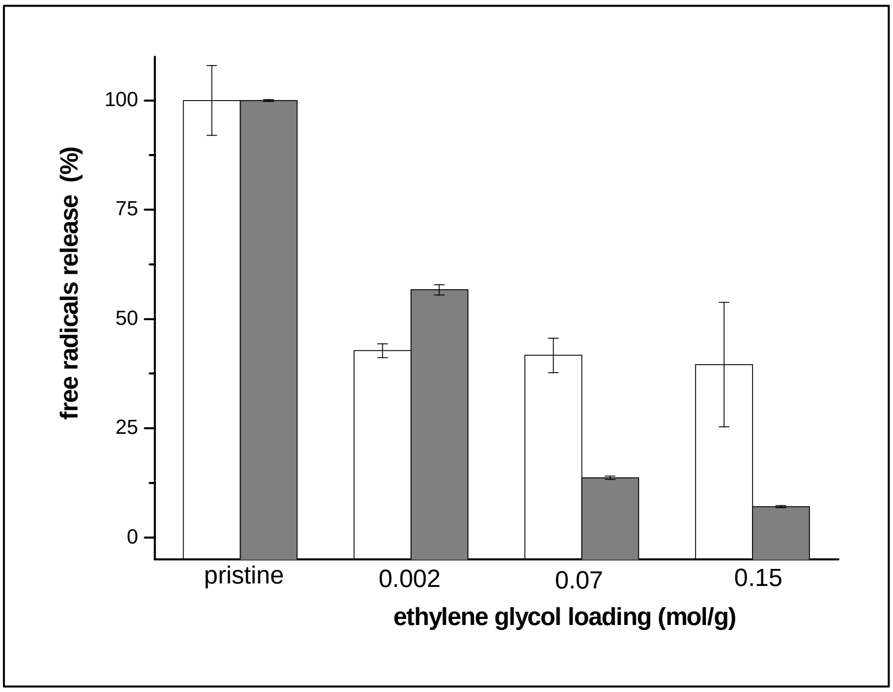


Figure 5. Generation of $HO^{\cdot}$ radicals (white bars) and $COO^{\cdot -}$ radicals (grey bars) by TiO_2 samples modified with different loading of ethylene glycol (concentration of solutions of ethylene glycol used 0.4, 1.5 and 3M). The data are expressed as intensity of the ESR signals obtained with the modified samples by respect to the signal obtained with the pristine TiO_2.

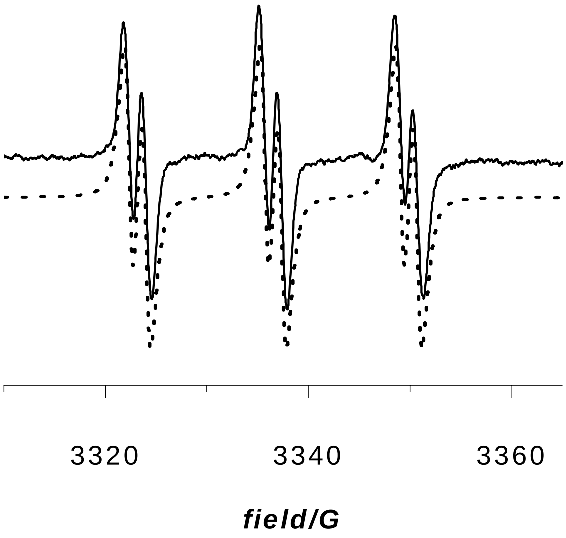


Figure 6: EPR spectra registered on the suspension of pristine TiO_2 in a solution of 0.067 M of linoleic acid and 0.095 M PBN in cyclohexane after eliminating the dissolved oxygen in the suspension. Solid line: experimental, dotted line: simulation.

8. TBA assay .

The assay, currently used as an index of lipoperoxidation, is based on the reactivity of MDA, a colorless end-product of degradation, with tiobarbituric acid (TBA) to produce a pink adduct that absorbs at 535 nm.

2 mg of the TiO_2 powders were suspended in 2 ml of a buffered (sodium phosphate buffer 10 mM, pH 7.4) emulsion of linoleic acid (1 mM) containing the 2.5 % w/w of ethanol. The mixture was stirred under the ambient light at 37 ºC for 72 h. The lipid peroxidation was stopped by adding 0.1 ml of an ethanolic solution of butyl hydroxyl toluene (BHT, 0.2 % w/w) to the suspension. The dust was removed by centrifugation and filtration (cellulose acetate filters, pore ø 0.20 mm). 2 ml of a solution of TBA (0.034 M) containing HCl (0.25 M) and trichloroacetic acid (TCA, 0.92 M) were added to 1 ml of the solution and the resulting mixture was heated at the temperature of 100 ºC for 15 min to favour the formation of the pink complex. After cooling in an ice bath, 3 ml of 1-propanol were added to extract the coloured complex. The absorbance at 535 nm was measured on the organic phase by means of a UV/Vis spectrophotometer (Uvikon, Kontron Instruments, Inc., Everett, MA). A pyrogenic ultrapure amorphous silica (AerosilOX 50, Evonik, Germany) was used as negative control.

References

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