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Milling effect on the photo-activated properties of TiO₂ nanoparticles: electronic and structural investigations

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Abstract:

Commercial PC105 titanium dioxide nanoparticles were studied under mechanical milling process. The effect of milling time and speed on the structural and electronic properties of TiO₂ powder was then investigated using X-ray powder diffraction (XRD), dynamic light scattering (DLS), transmission electronic microscopy (TEM), electron paramagnetic resonance (EPR) and UV–visible spectroscopy. The related photo-catalytic properties of the milled nanoparticles were probed following the degradation rate of methylene orange (MO) under UV-light irradiation and through EPR spincavenging approach. Comparison with pristine powder shows that milled nanoparticles are significantly less reactive upon illumination, despite decreased radius and hence, higher specific area. Such low yield of reactive species is attributed to the apparition of the amorphous TiO₂ and brookite phase upon milling, as well as increased charge carrier recombination as pointed out by the presence of sacrificial electron donor.

Introduction:

Nowadays, nanoparticles (NPs) find numerous and increasing uses in many fields of technology. This trend is foreseen to considerably expand in the near future, ranging from biology to medicine, energy storage, environment, pigment or cosmetic industries^{1–3}. This wide variety of applications is undoubtedly related to their peculiar characteristics that include particle shape, specific area, charge, chemistry, dispersion and/or agglomeration characteristics, aggregate size and shape distribution, solubility and porosity^{4–7}. Remarkably, the research towards the development of highly active heterogeneous photo-catalysts, naturally oriented towards transition metal oxides (TMOs, such as TiO₂, ZnO, SnO₂) that are semiconductors (SC) with a gap allowing good absorption of light in the UV and/or in the near-visible range. These SC-based NPs often exhibit improved photocatalytic properties due to enhanced surface/volume ratio.

When combined with the so-called methods of advanced oxidation processes (AOP)⁸, these materials are known to be efficient decontaminant: neutralizing bacteria and viruses^{9,10}, as well as degrading organic pollutants within air and water¹¹. Such high applicative potential involves various processes ranging from photolysis via H₂O₂¹², to Fenton or photo-Fenton effect¹³, where photo-mediated reactive oxygen species (ROS) are playing central role. Among TMOs, TiO₂ is considered as one of the most promising for wide environmental- and energy-applications, because of its suitable valence and conduction band positions, long-term stability, cost-effectiveness and strong oxidizing power¹⁴. It is a polymorphic material with three mains distinct phases¹⁵: anatase (tetragonal phase, I4₁/amd spacegroup, indirect band gap, $E_g = 3.2$ eV), rutile (stable tetragonal phase, P4₂/mnm space group, direct band gap, $E_g = 3.0$ eV) and brookite (stable orthorhombic phase, Pbca space group, direct band gap $E_g = 3.3$ eV)^{16,17}.

While with a higher surface adsorption capacity to hydroxyl groups, anatase was shown to present lower charge carrier recombination rate than rutile^{18,19}. Indeed, the lifetime of photo-generated electrons and holes in anatase is about an order of magnitude greater than one of the rutile. This greatly promotes their contribution to surface chemical reactions²⁰. Moreover, the average effective mass of photo-generated electrons and holes in anatase displays smaller value in comparison to rutile and brookite²¹. The transfer rate of photo-generated electrons and holes being inversely proportional to their effective masses¹⁷, the photo-excited charge carriers of anatase is thus transferred faster to the semiconductor surface²². These facts bear out the idea that TiO₂ in its anatase form shows better photo-catalytic performance than rutile and brookite^{12,23,24}. Regarding the present study, it was shown that ROS are photo-generated via TiO₂ NPs suspension under UV illumination^{25,26}. There are several methods to prepare TiO₂ NPs, such as sol-gel²⁷, micro emulsion²⁸, hydro- and solvothermal²⁹ precipitations or co-precipitations^{30,31}. Mechanical milling (MM) is also widely used, as it is a cheap, efficient and relatively simple technique to handle. During the process, powder particles are subjected to severe mechanical deformations and are repeatedly deformed, heat-treated (cooling and warming), welded and fractured, inducing their gradual refinement to nanometer scale^{22,32-34}. Consequently, unusual properties could appear via the emergence of structural defects that can be charged or not.

Although numerous articles report on the correlation between photo-catalytic activity and the physical properties^{35,36} (particle size³⁷, crystal structure^{38,39}, surface area⁴⁰), recent investigations challenged such conclusions^{41,42}. Among the available experimental approaches, MM at high energy is an established method to modify physical properties⁴³, aiming to improve the material properties. Nevertheless, the consequences of milling on TiO₂ NPs are still debated. Rezae *et al*⁴⁴ showed that MM for 6 h causes a complete conversion of the anatase phase to the brookite and rutile phases. Other recent studies indicate that milling of TiO₂ NPs results in an amorphous material^{45,46}, which is photo-catalytically inactive⁴⁷. Moreover, Bégin *et al*⁴⁵ observed the degradation of the photo-catalytic properties of TiO₂ NPs after MM and attributed it to new channels of radiative recombination produced upon milling. Indeed, partial amorphization of NP surfaces induces an increase of surface defect density and offers electron/hole (e^-/h^+) recombination pathways. The e^-/h^+ recombination rate in presence of amorphous phase occurs more quickly when compared to any pure crystalline phase³⁶. Such conclusions were also achieved in very recent work by Aggelopoulos *et al*⁴⁸, comparing ZnO and TiO₂ NPs. Nevertheless, Saitow and Wakamiya⁴⁶ showed an impressive 130-fold enhancement of the photo-catalytic properties of NPs TiO₂ prepared by planetary ball milling, pointing to the controversy of scientific debate. Such enhancement was attributed by the authors to the disordered, amorphous state together with the srilankite phase of TiO₂ NPs produced upon milling.

The present work deals with the effects of MM conditions (time and speed) on anatase TiO₂ NPs through the resulting structural modifications and electronic properties as well as the photo-catalytic activity towards MO degradation. The structural and morphological properties of the studied NPs were investigated by classical X-ray diffraction (XRD), transmission electron microscopy (TEM) and dynamic light scattering (DLS). The electronic properties were analysed by means of UV-visible spectroscopy of the solid state. Additionally, electronic paramagnetic resonance (EPR) spectroscopy was performed to probe the photo-mediated reactive species by using spin-scavenging approach via 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) reduction⁴⁹. All the obtained results are compared with the properties of pristine TiO₂ nanoparticles.

Materials and Methods:

- MM

Anatase TiO₂ (PC105) NPs were purchased from Crystal Global. Average NP size is of *ca.* 25 nm, surface area estimated at *ca.* 90 m² g⁻¹ and the weight purity is of *ca.* 95%. Samples of PC105 (1.7 g) with a ratio of 97:3 from ball masses vs. NP powders was charged under an Ar atmosphere in high-energy planetary ball mill (FRISCH premium line). Milled NPs were successfully obtained with two speed conditions ($\Omega = 200$ and 400 rpm) and four different milling times ($t = 1, 3, 5$ and 7 h) for each speed.

- XRD

TiO₂ NPs XRD spectra were carried out with a panalytical Phillips X'Pert Pro diffractometer, equipped with a CuKα1 anticathode ($\lambda = 0.15406$ nm). The XRD patterns were recorded between 20 and 90° with a monitoring step of 0.03°.

- DLS

A Zetasizer Nano ZS (Malvern, $\lambda = 633$ nm) and a disposable folded capillary cell were used to measure the hydrodynamic diameter of the aggregated TiO₂ NPs in aqueous suspension. All the hydrodynamic diameter distributions correspond to number distributions.

- TEM

The morphology and crystalline structure of TiO₂ NPs were studied with a Tecnai G2 20 Twin TEM. An aqueous suspension of TiO₂ (0.1 g l⁻¹) was sonicated for 15min to reduce the granulation. Five microlitres of this suspension was deposited onto a grid covered by a thin carbon film.

- Optical characterization

Band gaps were determined via optical measurements. UV–visible spectra of TiO₂ powders were recorded at room temperature in reflection mode in the range of 200–800 nm with a JASCOV-750 spectrometer, equipped with an integrating sphere model #ILN-725.

- Photo-catalytic activity

- *MO degradation*: Aqueous suspensions (250 ml) of TiO₂ NPs (200 mg l⁻¹) and 45 μM of MO (purchased from Aldrich) were prepared. Prior to any illumination step, the suspensions were stirred in the dark for 30 min. The suspensions were subsequently irradiated with a UV lamp (Vilber Lourmat VL-215-BL, $\lambda_{\max} = 365$ nm, P = 60 W) located at 15 cm from the sample to avoid heating of the suspension and pigment bleaching. The suspensions were stirred during the whole experiment and the temperature was kept at 298 ± 2K. Two and a half millilitres of the working solution was repeatedly withdrawn from the working suspension, centrifuged and the supernatant was analysed by UV–visible spectroscopy performed in transmission mode with a JASCO V-750 spectrometer. The present experimental data show the decay of the absorbance recorded at the wavelength of $\lambda = 480$ nm (see supplementary figure S1b) and normalized to the value obtained prior to the first illumination. The adsorption of the MO onto the NPs surfaces was found to be negligible (<5% of the dye concentration after 3 h in contact with the TiO₂ suspension), the threshold being reached after 30 min (data not shown).

- *EPR spin-scavenging*: Experimental protocol was derived from the existing methodology described elsewhere^{50,51}. Continuous-wave (cw) EPR spectra were recorded at room temperature using an X-band ECS 106 (Bruker- Biospin GmbH, Germany) spectrometer equipped with a regular TE102 resonator. This setup was used to record the conventional field-swept spectra from the aqueous suspensions containing TiO₂ suspensions (0.1 g l⁻¹) and 200 μM of TEMPOL (purchased from Aldrich) in ultrapure water (18.2 M_Ω cm⁻¹). TEMPOL is a paramagnetic probe (i.e., active) known to react with small-sized radicals leading to diamagnetic and hence, EPR silent byproducts⁵⁰. Therefore, its decay is testimony of the photo-mediated generation of reactive species. The EPR spectrum of 200 μM prior illumination is presented in supplementary figure S1a. Ethylenediamine tetraacetic acid (EDTA, purchased from Aldrich) was also used in this work as electron sacrificial donor. Prior to measurements, the solutions (1 ml) were sonicated (15 min in a sonicator bath). Afterwards, the solutions were immediately transferred into thin-wall glass capillaries (Hirschmannrin caps, 50 μl), which were sealed at both ends. Illumination of the sealed capillaries was performed outside the cavity with a UV light source Vilber Lourmat T-4.L ($\lambda_{\max} = 365$ nm and $E(1\text{ cm}) \approx 1.5$ mW cm⁻² measured with a power meter 1936-C Newport). The EPR spectra were recorded after each irradiation step. The main experimental parameters were: microwave power of 2 mW, time constant of 40 ms, conversion time of 80 ms and sweeping of 100G leading to ca. 80 s of accumulation per scan. All experiments were performed at room temperature (295 ± 2K).

- EPR measurements at low temperature

Sixty milligrams of TiO₂ powder were introduced in a 4 mm outer diameter quartz tube and degassed for ca. 10 min at room temperature. The cw-EPR spectra were recorded at 25K with a micro X-EMX spectrometer (BrukerBiospin GmbH, Germany) equipped with a high sensitivity resonator (4119HS-W1, BrukerBiospin GmbH, Germany) and liquid He cryostat (ESR900, Oxford Instrument).

Results and discussion

- Structural properties:

XRD patterns of TiO₂ NPs are shown in figure 1a and b for the two values of milling speed ($\Omega = 200$ and 400 rpm, respectively), different milling times (1–7 h) and the reference sample ($t = 0$ h). Several diffraction peaks are observed for $\Omega = 200$ rpm (figure 1a) at the following angular positions: $2\vartheta = 25, 37.8, 48.5, 53.95, 55, 62.6, 68.9, 70.1, 75$ and 82° . These peaks were identified according to the JCPDS card (21-1272) as the (101), (112), (200), (105), (211), (204), (116), (220), (215) and (303) Bragg's planes of the anatase TiO₂ structure. The relative ratios between peaks, for a given sample, are almost constant. Furthermore, new peaks were detected for the two longer milling times ($t = 5$ and 7 h), where the small bump detected around $2\vartheta = 30.8^\circ$ can be testimony of brookite phase⁴¹. Clearly, the more the NPs were milled, the more the data appeared noisy and present a significant baseline at small angles, indicating the rising of an amorphous state. In contrast, for the high energy milling at $\Omega = 400$ rpm (figure 1b), the peak intensities decrease rapidly. After 1 h milling, the similar amorphous fingerprint is rising together with a peak close to $2\vartheta = 30.8^\circ$, pointing to brookite phase.

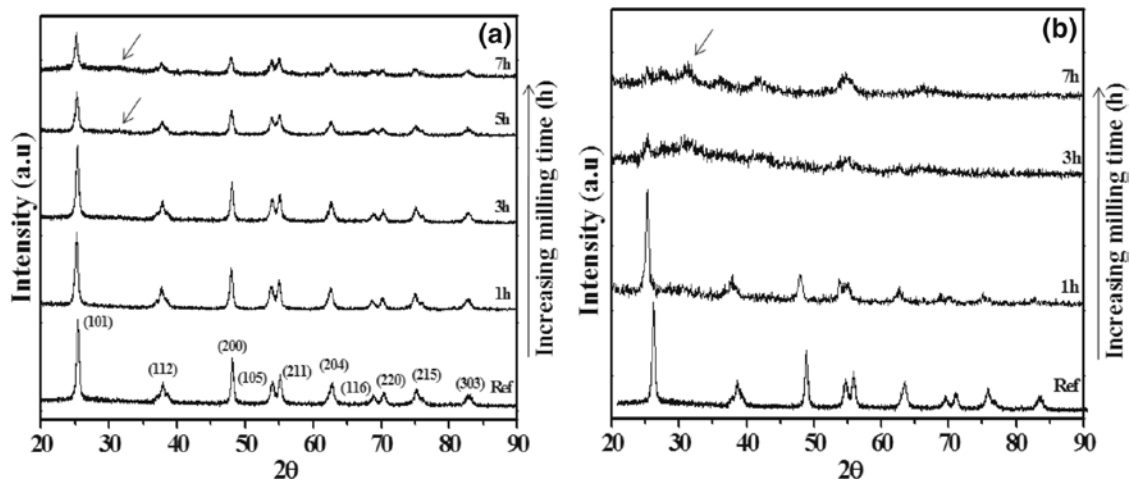


Figure 1. XRD patterns of NPs TiO₂ before milling and at various milling times for the milling speed (a) 200 and (b) 400 rpm.

- NPs characterization

Average of the grain sizes D of NPs TiO₂ were estimated with Scherrer formula, equation (1)^{52,53}.

$$D = K\lambda/\beta \cos \theta \quad (1)$$

where $K = 0.94$, ϑ is the angle of diffraction, λ the X-ray wavelength, β the full-width at half-height of a peak corresponding to a given orientation.

The grain sizes were also assessed from TEM observation and are summarized in table 1. The curves resulting from TEM data analysis and representing the grain size distribution (fitted with Gaussian functions) for all the samples milled at $\Omega = 200$ and 400 rpm are given in supplementary figure S2. Accordingly, the grain size varies between 5 and 45 nm. Whatever the XRD or TEM data, grain size

significantly decreases from *ca.* 20 to 12 nm after 3 h of milling at the lowest speed. At the highest speed, a similar trend is observed with a decrease from *ca.* 20 to 10 nm. The average size of the grain deduced from TEM observations is in good agreement with the one calculated from XRD using Scherrer formula (table 1).

Milling time (h)	0	1	3	5	7
Grain size (nm) DRX (200 rpm)	23	18	13	13	13
Grain size (nm) $\pm \sigma$ via TEM (200 rpm)	19.9 \pm 6.9	14.9 \pm 5.1	11.9 \pm 3.9	12.8 \pm 5.2	13.4 \pm 4.4
Grain size (nm) DRX (400 rpm)	23	19	—	—	—
Grain size (nm) $\pm \sigma$ via TEM (400 rpm)	19.9 \pm 6.4	15.4 \pm 6.2	10.5 \pm 3.6	—	9.8 \pm 2.9

Table 1. Grain sizes as a function of milling time for the speeds $\Omega = 200$ and 400 rpm.

Figure 2 shows the TEM micrographs of TiO₂ NPs for various conditions of milling times ($t =$ reference, 1, 3, 5 and 7 h) and speeds ($\Omega = 200$ and 400 rpm). During MM, the NPs are subjected to severe mechanical deformations, leading to a progressive evolution of their shape and mean grain size. However, it seems that experiments at higher grinding times would have produced more uniform size distribution and homogeneous spherical shapes. This trend is expected when the high energy ball milling process reach a steady state, where a balance happens between cold welding and fracturing operations⁵⁴. It is to be noticed that these effects are sharper at higher speed (see figure 2).

It is also known that one of the possible consequences of the MM process is the appearance of amorphous and/or unstable phases⁵⁵. It was therefore, interesting to appreciate and observe these phases. For this purpose, TEM images were interpreted by means of a fast Fourier transform (FFT) for milling speed condition, $\Omega = 200$ rpm. Figure 3 shows the FFT of an amorphous grain (single spot) and well-defined crystalline grains (spots distributed with respect to the crystal symmetry). Two lattice spacings of 0.35 and 0.9 nm are measured, which are assigned to the (101) of anatase and (100) plane of the brookite phase⁵⁶, respectively, revealed after 3 h milling⁵⁷.

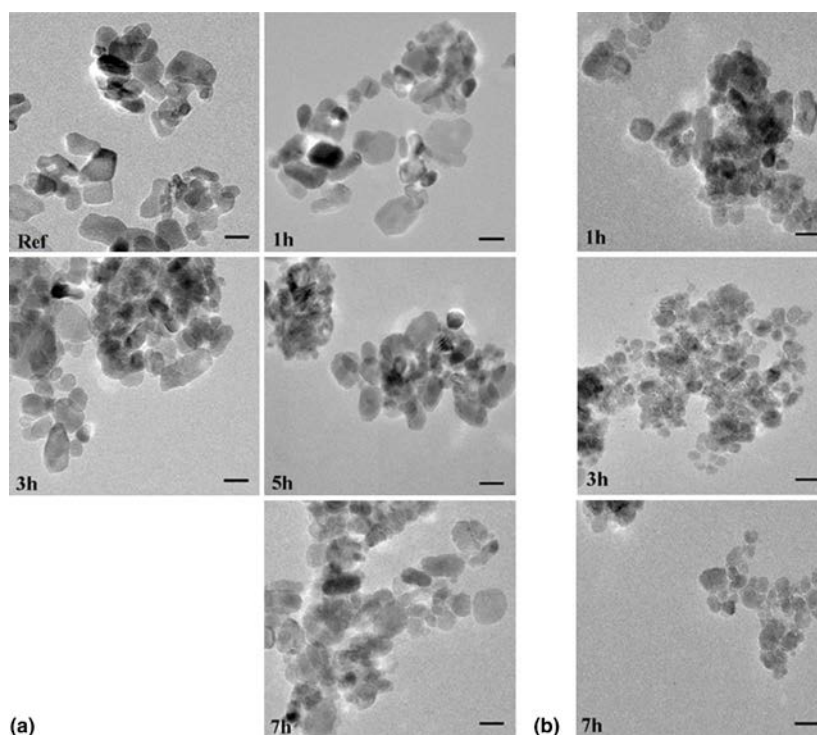


Figure 2. TEM images showing the morphology of TiO₂ NPs before and after milling $t = 0$ (reference), 1, 3, 5 and 7 h with speed $\Omega =$ (a) 200 and (b) 400 rpm. Scale bar corresponds to 20 nm.

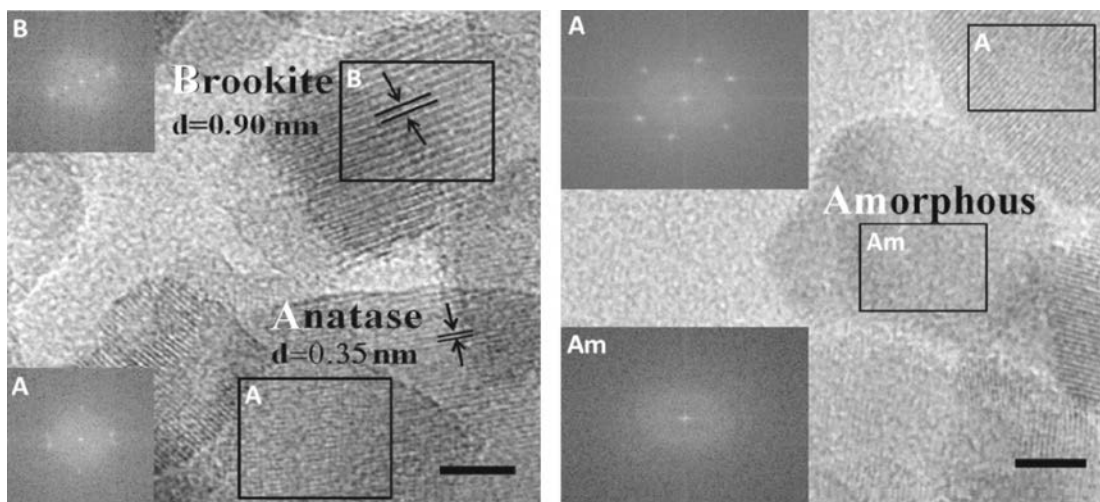


Figure 3. High-resolution TEM images of NPs TiO_2 (after 3 h of milling at $\Omega = 200$ rpm) showing the crystalline anatase (A), brookite (B) and amorphous (Am) phases. The insets correspond to the local FFT and the scale bars correspond to 5 nm.

- DLS analysis

It is known that the transition metal oxides aggregate considerably in aqueous solution^{58,59}. As the yield of reactive species is influenced by the available surface and the surface states, the knowledge of the characteristics of the aggregation state is required. For this purpose, both milled and reference samples were characterized by DLS to estimate the hydrodynamic diameter of aggregated NPs. All data were fitted with a Gaussian function and for clarity purpose, only the resulting fits are represented in figure 4.

The materials before milling ($t = 0$) in suspension have an average diameter of *ca.* 1 μm (figure 4). Notably, this size remains constant (*ca.* 550 nm) for all milled TiO_2 NPs at $\Omega = 200$ rpm. Surprisingly, the hydrodynamic diameter of sample milled at $\Omega = 400$ rpm dropped down to *ca.* 200 nm after 1 h milling time, but reproducibly returns to *ca.* 1 μm ; i.e., similar to 3 and 7h milling times as well as reference sample (figure 4b). Moreover, although the particle sizes obtained for both milling speeds and equivalent milling times are similar (see table 1), the subsequent hydrodynamic diameter do not present the same similarities. This suggests a considerable influence of the milling condition on the nature of the NPs surface states that drive the aggregation phenomenon.

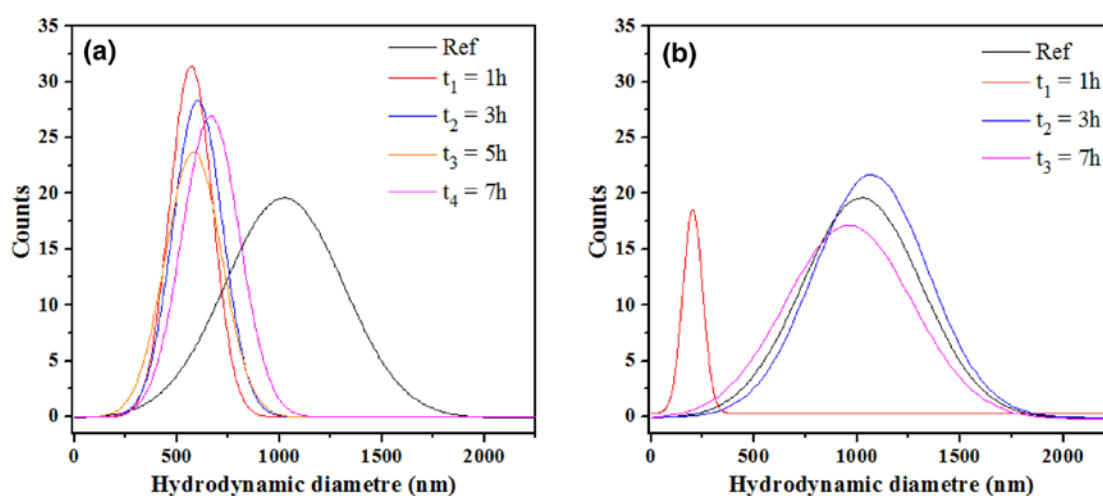


Figure 4. Distribution of the hydrodynamic diameter in an aqueous suspension of milled compounds and reference sample (0.1 g l⁻¹), with $\Omega =$ (a) 200 and (b) 400 rpm.

- Optical properties and electronic structure

Figure 5 displays the diffuse reflectance properties, for commercial (reference sample) and milled TiO₂ NPs at all rotation speeds and milling times. Typical fingerprint of TiO₂ NPs crystallite in the UV range is obtained.

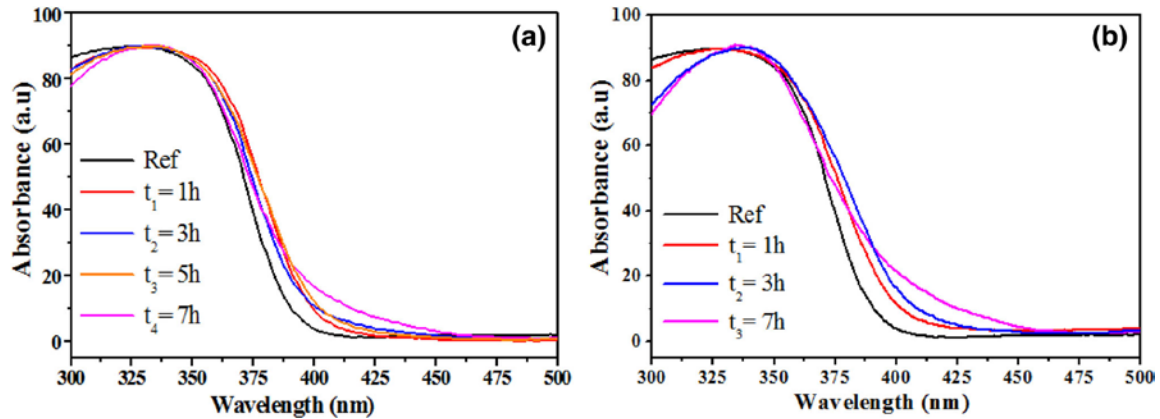


Figure 5. UV–visible spectra for milling time $t = 0$ (reference), 1, 3, 5 and 7h, at $\Omega =$ (a) 200 and (b) 400 rpm. The maximum absorbance obtained at 335 nm for pristine NPs was used as a reference to normalize all of the milled absorbance spectra. For non-normalized spectra, see supplementary figure S3.

However, the milling process induced a slight shift of the absorption edge towards higher wavelength, regardless of the speed. Consequently, as MM generates different type of defects (such as surface, lattice strain, vacancy, interstitial, dislocation, grain boundary, etc.), additional states appear within the band gap of TiO₂, create band tails extending of the valence and conduction band edges⁶⁰. Two important parameters are naturally impacted by this physical situation, namely the optical gap (E_g) and the Urbach energy (E_u) pointing to changes in the electronic structure (doping, disorder, etc.). To assess E_g and E_u , the absorption coefficients $F(R)$ are deduced from the reflectance curves, according to the Kubelka–Munk equation^{61–63}:

$$F(R) = (1 - R)^2 / 2R \quad (2)$$

where R is the reflectance, and $F(R)$ is equivalent to the absorption coefficient (α). The band gap, E_g is evaluated through the Tauc plot on the linear part of $(\alpha hv)^n \propto hv - E_g$ (where $n = 1/2$ for indirect band gap) for $(\alpha hv)^{1/2} = 0$ (see figure 6).

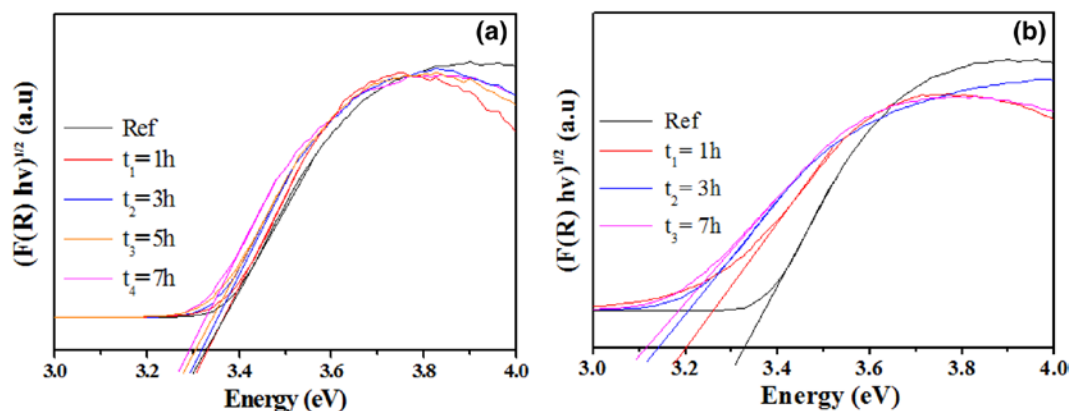


Figure 6. Variation of the band gap (E_g) according to Kubelka–Munk approach for milled TiO₂ NPs at $\Omega =$ (a) 200 and (b) 400 rpm, E_g is estimated by the intercept of the Tauc plot of $(\alpha hv)^{1/2} \propto hv - E_g$ and the energy axis.

The Urbach energy, E_u is given by the following phenomenological relation ⁶⁴, where α_0 and E_0 are constants related to the studied material:

$$\alpha = \alpha_0 \exp (h\nu - E_0 / E_u) \quad (3)$$

Figure 7a and b represent the respective variations of E_g and E_u as a function of milling time for both the values of Ω . It is observed that as expected, E_g and E_u have opposite evolution curves. Nevertheless, the more the value Ω of is high, the more its influence is obvious for E_g , rather than for E_u . Finally, the influence of grain size on the variations of the Urbach energy, E_u and the optical band gap, E_g is highlighted in figure 7c and d. Although the displayed results are rather scattered, they show clear trends in the evolution of these parameters: for both speeds, E_g and E_u have regular and opposite behaviours.

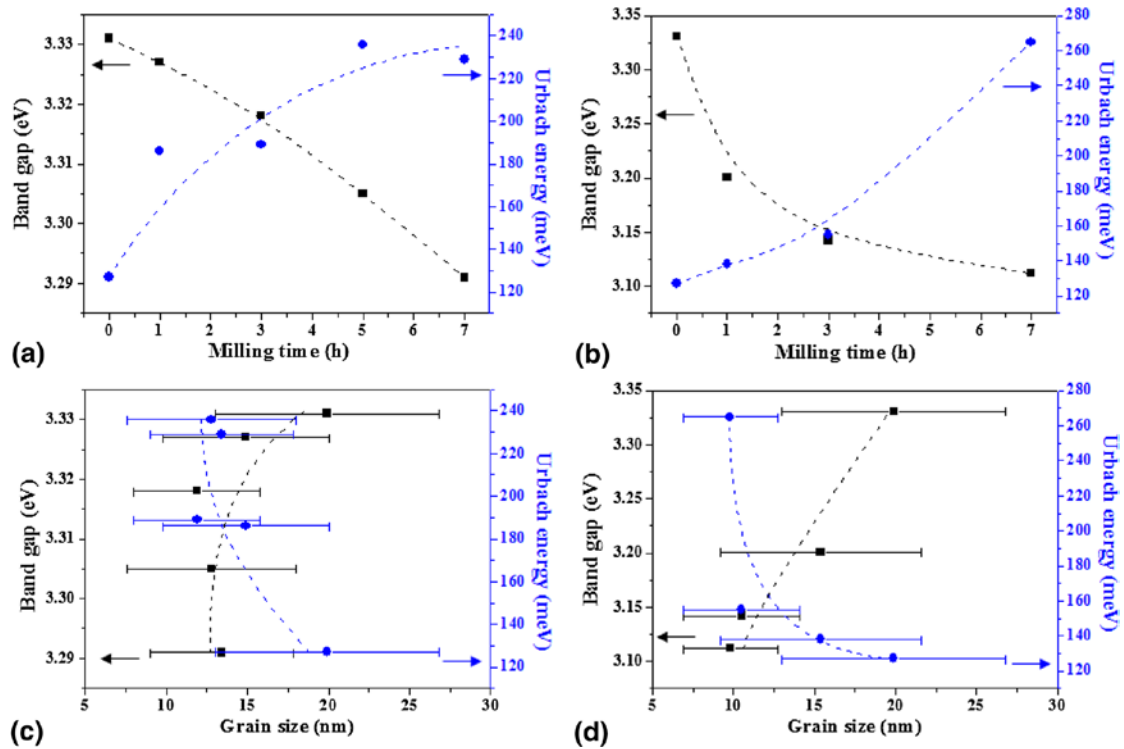
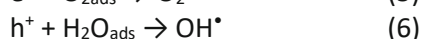
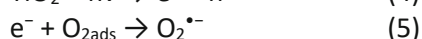
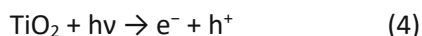


Figure 7. Variations of the band gap (E_g , black square) and Urbach energy (E_u , blue circle) with the milling time (upper panel) and resulting grain size (lower panel) for the two milling speeds: (a and c) 200 and (b and d) 400 rpm. Dashed lines are indicated as guide for the eyes.

In summary, regardless of the applied speed, the milling of TiO_2 powder affects the light absorption properties of the powder. Furthermore, it is shown in figure 5 that from about 400 nm, the absorption curves are more spread out toward higher wavelength as the milling time increases. This is attributed to the formation of novel electronic states in the band gap at the TiO_2 nanoparticles surface ⁶⁵, in agreement with the observed increase of Urbach energy together with the milling time. In TiO_2 , Ti^{4+} is surrounded by six oxygen ions forming the TiO_6 octahedral⁶⁶, high energy ball milling alters the arrangement of oxygen ions around Ti^{4+} leading to either oxygen vacancies, while breaking the Ti–O bonds⁶⁷, or phase changes. This broadens the valence and conduction band edges, decreasing the gap energy, while increasing the Urbach energy⁶⁸. As indicated by the XRD and HRTEM data comparison, it can be assumed that this process starts at the particle surfaces and propagate increasingly to the NP core as a function of energy.

- Photo-catalytic properties and ROS generation

As already mentioned, the radical photo-generation is related to surface reactions. Therefore, the morphology of the NPs, the crystal phase as well as the surface states are the major parameters influencing the generation rate of the photomediated ROS. Semiconductors in aqueous suspension are known to generate reactive species upon illumination with photon energy equal or higher to the energy band gap. The photo-generated electrons and holes oxidize and reduce rapidly the molecular oxygen and water as shown in the following equations (5–7)⁶⁹, allowing the ROS generation such as $O_2^{\bullet-}$ and HO^{\bullet} , whose rate competes with the electron– hole recombination (equation (6)).



Remarkably, other ROS can arise from the reactions described above (equations (5–7)), such as hydrogen peroxide and singlet oxygen^{70,71}. Oxidation and reduction processes occur at the particle surface/solvent interface. The average lifetime of the photo-generated ROS being extremely short (from ns to μ s at room temperature) when compared to the time of experiment, their evolution rate was estimated following two indirect methods: (i) the study of the degradation of the MO using UV–visible spectroscopy and (ii) spin-scavenging EPR technique using TEMPOL as paramagnetic probe. Figure 8 shows the decay of the normalized absorbance ($A(t)/A_0$) recorded at $\lambda = 480$ nm for the reference sample and for all milled samples at the different speed and time conditions.

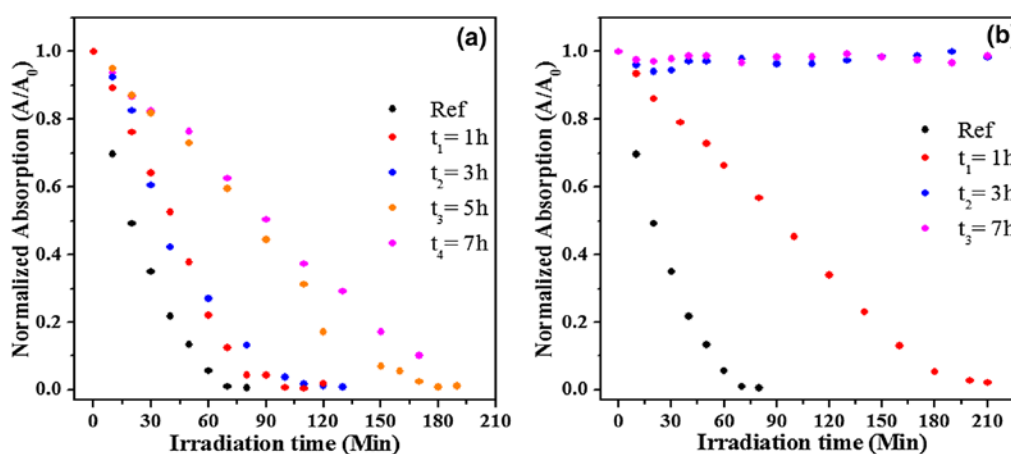


Figure 8. Photo-catalytic degradation, over time, of methylene orange in aqueous solution in the presence of TiO_2 NPs, for the milling times: $t = 0$ (reference), 1, 3, 5, 7 h at $\Omega =$ (a) 200 and (b) 400 rpm.

We notice that for both milling speeds, the normalized MO kinetic of degradation ($A(t)/A_0$) slows down when the milling time increases. Interestingly, no photo-catalytic activity is detected (up to 210 min of illumination) for the highest energy milling ($\Omega = 400$ rpm) and for a milling time of 3 h and more (figure 8b).

To confirm this result, EPR spin-scavenging investigation was achieved^{50,72}. The experiment was performed for the TiO_2 NPs, for the reference sample and for all the milling conditions. Figure 9 shows the decay of the EPR-normalized intensity $I(t)/I_0$ of TEMPOL as a function of the illumination time.

Similar to the MO degradation experiment, TEMPOL concentration decays as a function of UV-exposure time and the respective kinetics slow down when the milling time and/or speed is increased. The reduction of TEMPOL into EPR silent byproducts is mainly attributed here to HO^{\bullet} , H^{\bullet} and/or e^{-50} . At the highest milling speed and above 1 h of milling time, $I(t)/I_0$ curve remains flat despite 90 min of UV exposure in the presence of TiO_2 NPs. When compared to the XRD investigation presented in this work, the degradation of the photo-catalytic properties coincides with the apparition of the

amorphous phase of TiO₂ and surface states modification. Hence, neither the shift of the hydrodynamic diameter towards lower values (as shown in the DLS investigation, figure 4) nor the appearance of brookite phase (see XRD pattern of figure 1) influence neither the MO degradation nor the TEMPOL reduction.

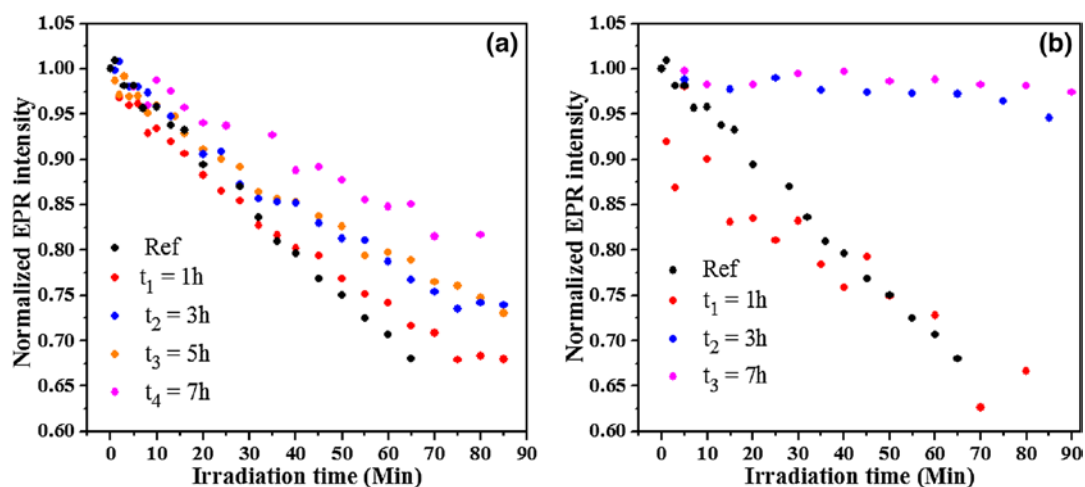


Figure 9. Evolution of TEMPOL-normalized EPR intensity, $I(t)/I_0$ as a function of time exposure to UV-light for the TiO₂ NPs aqueous suspension (0.1 g l^{-1}), I_0 being the intensity obtained prior to illumination. The data presented illustrate different milling speeds $\Omega =$ (a) 200 and (b) 400 rpm and milling times (1, 3, 5 and 7 h) as well as non-milled NPs (reference).

In several studies, the amorphous phase is defined as a catalytically photo-inactive^{47,73,74}, due to a higher e^-/h^+ recombination rate³⁶. However, even in the most altered structure investigated in this study (i.e., 7h milling at $\Omega = 400 \text{ rpm}$), TiO₂ NPs do not appear fully inactive. Indeed, when supplementing the aqueous suspension of NPs with a sacrificial electron donor (such as EDTA), significant reduction of TEMPOL is observed (figure 10), yet delayed when compared to non-supplemented experiment (figure 9). The presence of such electron donor will neutralize the photogenerated holes, limiting e^-/h^+ recombination rate and therefore, increasing the lifetime of the photogenerated electrons available for TEMPOL reduction through direct pathway or indirect one (H^* , HO^*)⁵⁰. Considering the EPR kinetics, with or without EDTA, it appears that the MM does not hamper the overall generation of excitons, but rather drastically increases the recombination rate through newly generated electron traps. These new electronic levels arise from a modification of the electronic level distribution due to the presence of amorphous phase and thus, prevent the formation of reactive species and lead to the degradation of the photo-catalytic properties.

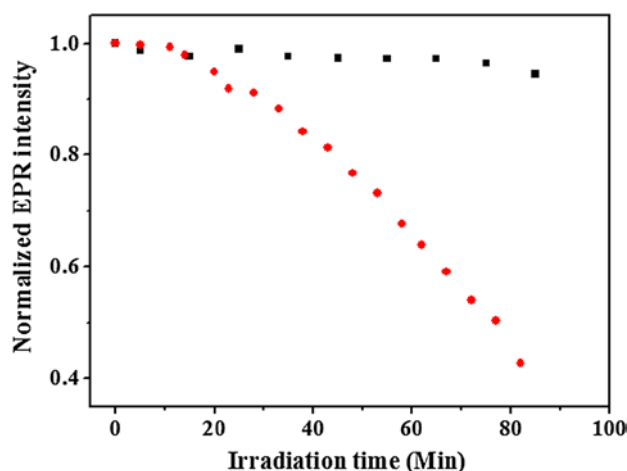


Figure 10. Evolution of normalized TEMPOL EPR intensity, $I(t)/I_0$ as a function of UV exposition time for the TiO₂ NPs (milled at 400 rpm for 7 h) in aqueous suspension (0.1 g l^{-1}), where I_0 is the EPR intensity obtained prior to illumination: with (filled circle) or without (filled square) sacrificial donor EDTA at 0.1 M, pH = 6.5.

Finally, low temperature EPR ($T = 25\text{K}$) was also used to confirm how MM induces structural alteration of the NPs. On one hand, the EPR fingerprint of nano-TiO₂ in its anatase form⁷⁵⁻⁷⁷ in the $g = 2$ region appears severely affected by MM (see supplementary figure S4) and is attributed to an increase in the amorphous phase and to induced disorder during milling. On the other hand, EPR spectra with larger sweep range (see supplementary figure S5) exhibit: (i) signals at $g = 4.31$ testimony of metallic high spin state attributed to Fe(III), and (ii) broad line ascribed to metallic contamination⁷⁸. Noteworthy, each of such tampering hallmarks is increasing with milling time and speed.

Conclusion :

Structural consequences of planetary ball-milling process on TiO₂ NPs are manifold. Significant amorphization of TiO₂ related to the milling time and speed was demonstrated by TEM and XRD, while a weak phase transformation from anatase to brookite was observed. Such phase transformations play in favour of a degradation of the photo-catalytic activity. The diminution of grain size as a function of milling time and speed were characterized by TEM, while the hydrodynamic diameters obtained in aqueous suspension by DLS were determined. These later appear smaller at $\Omega = 200$ rpm and unchanged *ca.* at $\Omega = 400$ rpm. Such evolutions would suggest an increase in the photo-mediated generation of radicals for the lowest milling speed by increasing their respective available surfaces and an equivalent yield for the highest speed. However, the photogeneration activity assessed by MO degradation and EPR spin-scavenging are unquestionable and point toward a drastic degradation of the photo-catalytic activity concluding that no detectable activity for higher milling speed and milling time ≥ 3 h. The photo-catalytic activity seems to be affected much earlier than the occurrence of structural changes. However, the use of a sacrificial electron donor allows restoration of the activity, thus, pointing e^-/h^+ recombination as the limiting process. Finally, EPR at low temperature illustrated the disruption of anatase phase fingerprint as a function of both milling speed and time, and points towards metallic contamination.

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