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# Mechanism of the photoactivity under visible light of N- doped Titanium dioxide. Charge carriers migration in irradiated N- TiO<sub>2</sub> investigated by Electron Paramagnetic Resonance.

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## ABSTRACT

The generation of surface charge carriers in N doped TiO<sub>2</sub> under various types of irradiation has been investigated by EPR using an approach consisting in scavenging surface migrated electrons and holes using oxygen and hydrogen respectively.

N doped TiO<sub>2</sub>, which is moderately active in photocatalytic processes under visible light, forms surface electrons and, at lower extent, surface holes due to the synergistic effect of visible components (around 400 nm) and near infrared ones.

The visible radiation excites electrons from intra band-gap NO<sup>x-</sup> states to the conduction band while NIR frequencies excite electrons from the valence band to the NO<sup>x-</sup> centres. The limited concentration of such centers explains the moderate efficiency of the whole process and, consequently, of the photocatalytic activity of N-TiO<sub>2</sub> in visible light with respect to the case of UV light irradiation. Despite the mentioned limits this material remains a fundamental starting point for a new generation of photocatalytic systems exploiting solar light.

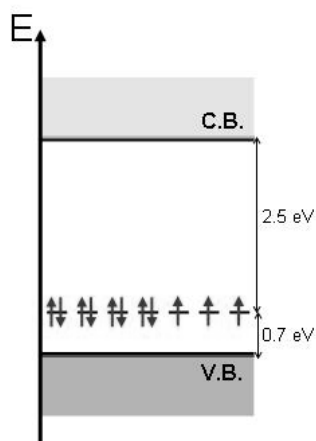
Keywords: Nitrogen doped TiO<sub>2</sub>, visible light photoactivation, Electron Paramagnetic Resonance (EPR), charge carriers

## 1. INTRODUCTION

The photocatalytic decomposition of organic compounds under visible light irradiation in the presence of Nitrogen doped Titanium dioxide (N-TiO<sub>2</sub>) was first reported at the beginning of this century [1]. The interest for this result was immediately very high in the perspective of new photocatalytic processes carried out under solar light. When bare Titanium dioxide is used in photocatalysis, in fact, UV irradiation (whose presence in solar light is relatively low) is required due to the high band gap energy value of the solid (3.2 eV in the case of the anatase polymorph). Since 2001 a huge number of papers have thus been devoted to N-TiO<sub>2</sub> aiming to explore the activity of this new solid in different photocatalytic reactions and to experiment novel routes for its preparation. Nowadays, we are thus facing a long series of results showing, in general, that the photoactivity of N-TiO<sub>2</sub> in visible or solar light is somehow higher than that of the classic P25 TiO<sub>2</sub> (the true benchmark for photocatalytic phenomena) in the same conditions [2,3,4,5,6,7,8,9]. On the other hand the number of experimental papers devoted to understand the reason of the photoactivity and the strategies for improving the photocatalyst's performances are relatively few [2,10,11,12,13,14,15,16,17]. It is not yet clear, therefore, if this new solid will be considered, or not, in the future as a real breakthrough in the history of photocatalytic applications. To go beyond the impasse it is necessary to give more attention to both the electronic properties of N-TiO<sub>2</sub> and to the mechanisms of charge carriers dynamics under irradiation. This should be done also in view of tailoring suitable modifications of the solid aimed to influence its properties.

There is now a general consensus on the electronic structure of N-TiO<sub>2</sub> as most of the Authors agree on the presence of N 2p intra-band gap states some tenths of eV over the Valence Band (VB) limit which absorb visible light in the range 430-450nm [10,18,19,20,21,22]. Actually two types of photoactive centres have been described. The first one is based on substitutional nitrogen (N substitutes O in some lattice position) and forms upon high temperature nitridation treatments of TiO<sub>2</sub> [23,24], the second one (more common as it origins in all wet chemistry preparations of the solid) is based on interstitial N chemically bound to a lattice O ion thus forming a sort of NO group

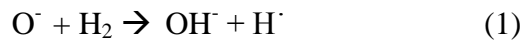
in the bulk of the solid [25]. A fraction of these centres bear one electron in the SOMO and are consequently paramagnetic and EPR active. They can be formally written as  $\text{NO}^{2-}$  and the corresponding EPR spectrum has been widely described in the literature [10,19b,25,26,27,28,29]. The second, larger, fraction is diamagnetic with two electrons in the HOMO ( $\text{NO}^{3-}$ ). Both these centres are responsible of the optical absorption in the visible of N doped titania [30]. A schematic view (actually the energy values of paramagnetic and diamagnetic centers are close one to each other, but not exactly the same) of the energy levels for N-TiO<sub>2</sub>, based on the results reported in ref [19] is reported in Scheme I. In spite of their different chemical features the electronic energy of substitutional and interstitial N centers is very similar [19] so that, to the purposes of the present paper, the distinction between these two forms is not relevant.



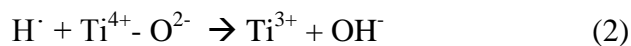
**Scheme I:** Electronic structure of N-TiO<sub>2</sub>.

Despite the agreement on the electronic structure of N-TiO<sub>2</sub>, the behaviour of the system in terms of charge dynamics under visible light irradiation is not yet fully clarified. It should be very important, for instance, to definitely understand whether visible photons are capable to generate charge separation inducing migration of both electrons and holes at the surface. The presence of electrons and holes at the surface is, in fact, essential to entail the redox processes typical of photocatalysis. The dynamics of charge carriers in photocatalytic systems has been mainly investigated, using time resolved spectroscopic techniques, in the case of bare TiO<sub>2</sub>, while relatively few reports are

available for N-TiO<sub>2</sub> [31,32]. In these recent studies it has been proposed that the charge separation efficiency for N-TiO<sub>2</sub> under visible light is, as expected, lower than that observed under UV light. In previous work from our lab [30] we were able to show, in the case of N-TiO<sub>2</sub> prepared via sol-gel and using the Electron Paramagnetic Resonance (EPR) technique, that visible light of 437nm is capable to excite electrons from the intra band gap N isolated states to the Conduction Band (CB). EPR is an excellent technique not only to detect paramagnetic impurities in oxides but also to monitor the charge separation processes. This was shown, in the case of bare TiO<sub>2</sub>, by the seminal work of Graetzel and Howe [33,34] who were able to directly monitor the spectral trace of both excited electrons and holes upon irradiation of a colloidal suspension of the oxide in water. Since the direct observation of the charge separation process under vacuum is not always possible and requires monitoring the spectra at very low temperature under continuous irradiation due to the fast recombination of electrons and holes, an alternative approach to make certain the presence of charge carriers at the surface is that of irradiating the solid in the presence of a charge scavenger in the gas phase. This is what done for electrons using oxygen as a scavenger and monitoring paramagnetic adsorbed superoxide ions (O<sub>2</sub><sup>•-</sup>) to prove the occurrence of the photoinduced electron transfer[35,36]. The parallel method to identify surface holes in oxides is based on the reactivity of this carrier with molecular hydrogen. It was in fact shown, in the case of ionic alkali earth oxides [37,38], that a surface hole localized onto an oxygen ion (in chemical terms an O<sup>2-</sup> which becomes an O<sup>•</sup>) reacts with hydrogen generating an OH<sup>-</sup> group and an hydrogen atom:



the latter in turn reacts with the solid leading to a second OH<sup>-</sup> group and a trapped electron. The same process, when the matrix is the reducible titanium dioxide, ends, as shown by Berger et al. [39], with ionization of the H atom and injection of an electron into the solid with formation of Ti<sup>3+</sup>[40]:



The formation of paramagnetic  $\text{Ti}^{3+}$  ions monitored by EPR becomes, therefore, the finger print of the occurrence of reactive holes at the surface of the solid.

In the present work we have systematically applied the described methodologies to investigate the photoinduced charge carrier formation in the case of nitrogen doped titanium dioxide. We have employed in this case a particular type of N- $\text{TiO}_2$ , i.e. a solid we have recently prepared by chemical vapor reaction (CVR) technique (see the experimental section for a detailed description of the method). This technique has the advantage, with respect to the more common sol gel techniques, to avoid the formation into the closed pores of the solid of molecular nitric oxide (NO) as described in previous work of some of us [41,42]. Nitric oxide in fact is paramagnetic and its intense EPR spectrum, particularly observable at low temperature, interferes with those of both superoxide and  $\text{Ti}^{3+}$ . For this reason when we performed the experiments here illustrated with samples prepared via wet chemistry (sol-gel,  $\text{TiCl}_4$  hydrolysis, hydrothermal method) all containing variable amounts of nitric oxide into the pores, the results were not totally unambiguous. In the case of N- $\text{TiO}_2$  prepared via CVR a highly crystalline material with large specific surface area is obtained which has the same optical properties (visible light absorption) and similar photocatalytic behaviour of the more popular systems prepared by wet chemistry methods. On this kind of materials the EPR investigation on the effects of irradiation has been indeed possible without interferences due to nitric oxide.

The present paper has a twofold purpose. We intend to illustrate, first of all, the mechanism of photoexcitation in the case N- $\text{TiO}_2$  showing that migration of both electrons and holes at the surface actually occurs under irradiation with visible polychromatic light, thus corroborating the plethora of results reporting about photocatalytic activity of this system in the same conditions. Additionally we intend to propose the technique here described, and based on simple and easily accessible EPR experiments, as a general method to evaluate the photoinduced charge separation efficiency. Such a method is not limited to  $\text{TiO}_2$  based systems but extensible, in principle, to other photoactive oxide systems.

## 2 EXPERIMENTAL

### 2.1 Synthesis and basic characterisation of the materials

TiO<sub>2</sub> and N-TiO<sub>2</sub> samples were prepared via chemical vapour reaction (CVR) by an home built synthesis apparatus similar to that described by E. Knözinger and coworkers [43] using Ti ethoxide as TiO<sub>2</sub> precursor and urea as N doping agent. The apparatus consists of 2 concentric quartz tubes in which reaction gas (O<sub>2</sub>) and carrier gas (Ar) were respectively flown and two furnaces, one for the vaporisation of the precursors (at 475K) and one for the actual synthesis of the samples (at 1123K). Standard synthesis were carried out starting from 2.5 ml of Ti ethoxide to which were added 2g of urea in the case of N-doped samples. All reactants employed in this work were purchased by Aldrich and used without any further purification treatment. The Ar and O<sub>2</sub> fluxes were optimised through several tries in order to achieve the best synthesis conditions. Bare TiO<sub>2</sub> samples appear of a clean white colour while N doped samples exhibit a yellow shade.

XRD patterns (see supporting Informations) showed the presence of anatase polymorph exclusively in both samples while BET measurements revealed that the bare TiO<sub>2</sub> samples have a 170 m<sup>2</sup>/g surface area, slightly higher than that of N-TiO<sub>2</sub> samples (120 m<sup>2</sup>/g).

### 2.2 Experimental methods

Structural features of the prepared materials have been determined by X-ray Diffraction (XRD) on a Philips 1830 XRD spectrometer using a K $\alpha$  Co source. UV-vis diffuse reflectance (DR UV-vis) spectra were recorded by a Varian Cary 5000/UV-vis-NIR spectrometer using a Cary win-UV scan software to follow the visible absorption enhancement after nitrogen doping.

Electron paramagnetic resonance (EPR) spectra were run using a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation and a temperature controller unit. The measurements were carried out in cells that can be connected to a conventional high-vacuum apparatus (residual pressure <10<sup>-6</sup> kPa). The EPR spectra intensity has

been obtained by double integration of the signal. The evaluation of the intensity of each single component in spectra composed by two or more overlapping species has been derived simulating the whole signal using SIM32 (see S.I.), a program elaborated by Z. Sojka (Jagellonian University, Cracow) [44].

### 2.2.1 Irradiation experiments

All irradiation experiments were carried out after a careful cleaning procedure of the sample surface. The samples were outgased at 773K for 30 min in dynamic vacuum to remove surface contaminants and successively oxidized in 20mbar of pure O<sub>2</sub> at the same temperature in order to get a fully oxidized material.

The effects of UV, visible and IR light on EPR spectra were investigated irradiating the samples with different light sources which are: a) 300W polychromatic lamp (Osram ultra-vitalux) emitting in a wide range of frequencies including UV, Vis and NIR and equipped with different filters ( $\lambda > 420\text{nm}$  and  $\lambda > 850\text{nm}$ ) to select the needed wavelengths range; b) a 1600W mercury lamp (Newport instruments) equipped with a IR water filter and a grating monochromator with a transmission range between 500 nm and 180 nm for monochromatic visible light irradiation. In both cases irradiation was carried out at low temperature (liquid nitrogen temperature, (77K) using a quartz finger-Dewar in order to avoid sample overheating. Irradiation time was 1h in case a and 30 minutes in case b.

c) A GSD Renas laser emitting pulses in the infra-red ( $1550\text{nm} \pm 5\text{nm}$ ) was adopted for monochromatic IR irradiation.

In the case of pulsed IR irradiation was performed for 1.5 minutes at RT monitoring the sample overheating by a thermocouple (max temperature reached  $\sim 325\text{K}$ ). Molecular oxygen and hydrogen were used in the irradiation experiments at a pressure of 50mbar. Most irradiation experiments have been performed into a dark box and the EPR spectra recorded at the end of irradiation (*ex-situ*

irradiation). In few cases, as specified in the text, irradiation was conducted directly into the EPR resonant cavity (*in-situ* irradiation)

Irradiance was measured in all experiments by a Deltahom instrument equipped with two different detectors for the UV range (315-400nm) and for the Vis-NIR range (400-1050nm). In Table 1 the irradiation conditions of each experiment are reported.

| Irradiation Source | Irradiation and Filtering           | Irradiance (W/m <sup>2</sup> ) |                       |
|--------------------|-------------------------------------|--------------------------------|-----------------------|
|                    |                                     | UV (315-400 nm)                | Vis-NIR (400-1050 nm) |
| Osram 300W         | no filter                           | 200                            | 2000                  |
|                    | $\lambda > 420$ nm                  | $1 \cdot 10^{-2}$              | 1500                  |
|                    | $\lambda > 850$ nm                  | $1 \cdot 10^{-3}$              | 400                   |
| Newport 1600W      | Monochromator ( $\lambda = 437$ nm) | $1 \cdot 10^{-3}$              | 12                    |
| GSD Renas Laser    | $\lambda = 1550$ nm                 | 4700                           |                       |

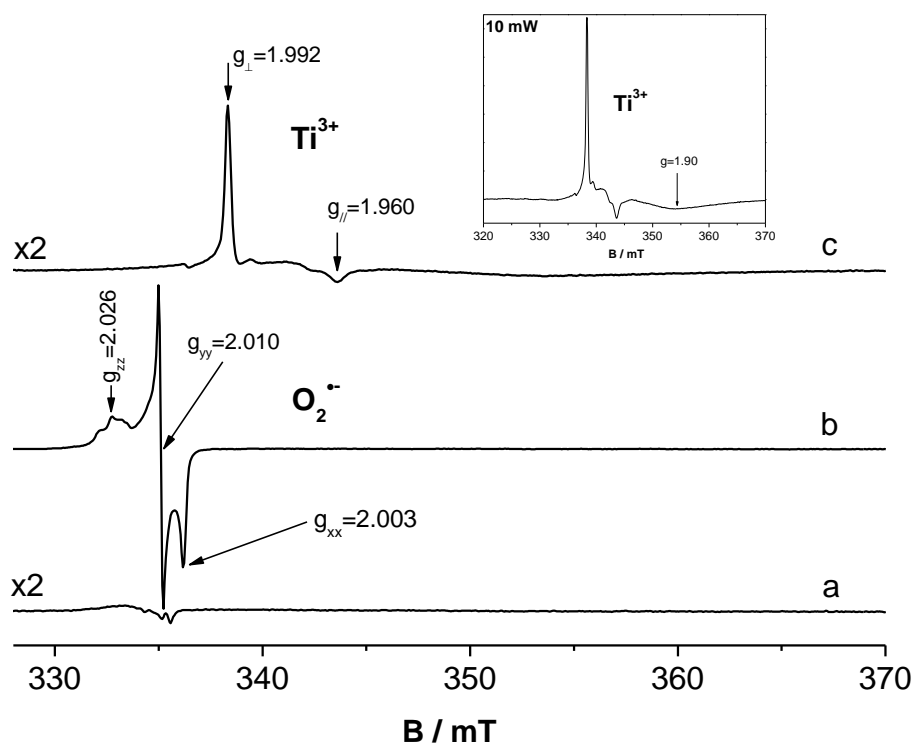
**Table 1:** Irradiance for the difference irradiation conditions adopted in the present work.

### 3. RESULTS AND DISCUSSION.

#### 3.1. UV-Vis Irradiation

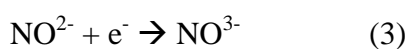
To test our method of carriers scavenging at the surface, a preliminary experiment (Fig. 1) was conducted on bare TiO<sub>2</sub> (produced with the same CVR apparatus adopted to prepare N-TiO<sub>2</sub> materials) irradiating the solid with the unfiltered emission of the 300W UV lamp respectively under oxygen (Fig. 1b) and under hydrogen (Fig. 1c). It is well known that the UV components higher than 3.2 eV cause the excitation of electrons from the valence band to the conduction band of the oxide and that electrons and holes so formed migrate at the surface. Fig. 1a shows the EPR spectrum of the starting material with a tiny concentration of impurities slightly perturbing the baseline. In Fig.1b the typical spectrum of adsorbed superoxide ions is observed with values of the various  $g_{zz}$  components (ranging from 2.027 and 2.019) indicating that O<sub>2</sub><sup>•-</sup> radical ions are

adsorbed on surface  $\text{Ti}^{4+}$  cations and confirming that photoexcited electrons are scavenged by oxygen in the gas phase [45]. The spectrum in Fig. 1c (irradiation under  $\text{H}_2$ ) shows features all due to  $\text{Ti}^{3+}$  centres formed according reactions (1) and (2). The two signals which compose the spectrum are amenable, as shown in a recent paper by some of us [40] to reduced  $\text{Ti}^{3+}$  centers in regular position of the lattice (narrow signal with  $g_{\perp}=1.992$  and  $g_{\parallel}=1.960$ ) and to  $\text{Ti}^{3+}$  centres in a disordered environment corresponding to the crystals surface (broad signal at high field better visible in the inset). Spectrum 1c demonstrates that holes are scavenged at the surface by  $\text{H}_2$  molecules and that the electrons resulting from reaction (2) are injected in the solid and stabilized by titanium ion of the lattice either in bulk or at the surface. Fig.1 validates the methodology here adopted for electrons and holes detection and will be used for comparison in the more complex case of N- $\text{TiO}_2$ .

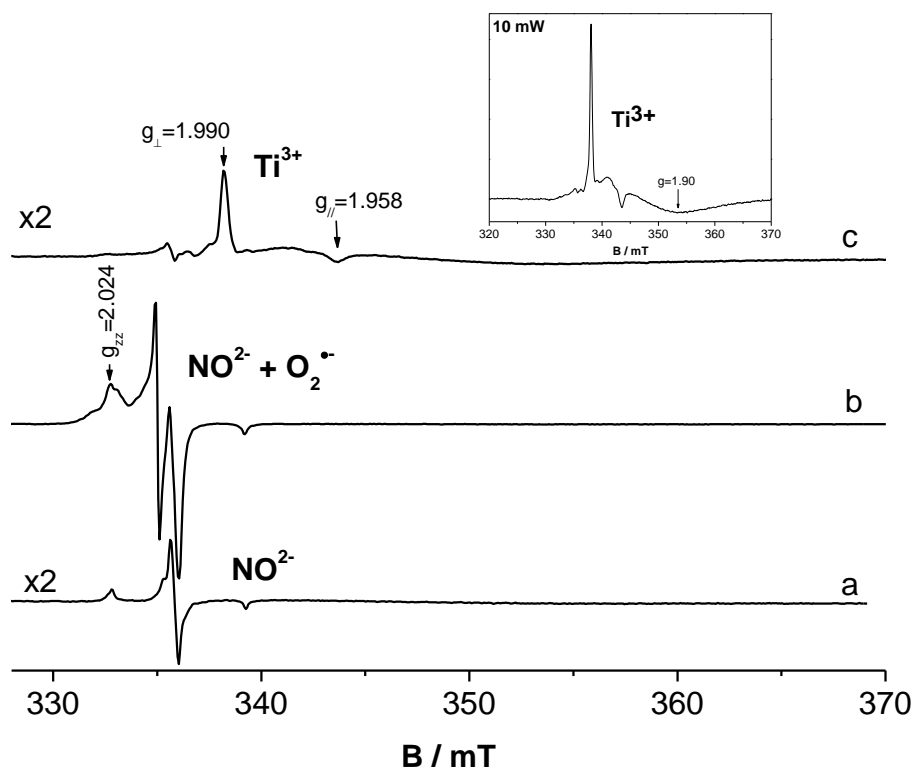


**Fig. 1:** EPR spectra recorded at 77K and 1mW of bare  $\text{TiO}_2$  prepared by CVR. a) spectrum recorded in dark; b) after irradiation (unfiltered UV lamp) under  $\text{O}_2$ ; c) after the same irradiation under  $\text{H}_2$ . The inset reports the spectrum corresponding to 1c) and recorded at 10mW to evidence the second  $\text{Ti}^{3+}$  signal around  $g=1.90$ . Irradiation source: 300W Lamp.

The N-doped sample prepared via CVR is pale yellow and its optical spectrum differs in fact from that of undoped TiO<sub>2</sub> because of a band centred at about 440nm (see S.I.) and responsible of the visible light absorption. The same irradiation (full lamp) adopted for TiO<sub>2</sub> in Fig. 1 was performed using N-TiO<sub>2</sub> (Fig. 2). In this case (Fig. 2a) the EPR spectrum baseline is not flat and show the presence of the well-known signal due to the interstitial form of N in TiO<sub>2</sub>. These centers, containing one unpaired electron, can formally be written as NO<sup>2-</sup> [25] and, as mentioned in the introduction, are responsible of the visible absorption of the material. Beside them, diamagnetic two-electrons centres are also present (formally NO<sup>3-</sup>). [19,30] Irradiation with the UV lamp under oxygen (Fig. 2b) causes the appearance of a spectrum which is the overlap of the superoxide signal reported in Fig. 1b with that of the NO<sup>2-</sup> centres of the background. Irradiation in H<sub>2</sub> produces a spectrum (Fig. 2c) due to Ti<sup>3+</sup> similar to that in Fig. 1b and also characterized by the almost complete disappearance of the NO<sup>2-</sup> background spectrum. The two spectra (2b,2c) indicate that the VB → CB (or Ti 3d ← O 2p) excitation due to UV irradiation for N doped TiO<sub>2</sub> works in the same manner than for undoped TiO<sub>2</sub>. The almost complete disappearance of the NO<sup>2-</sup> background signal in the case of irradiation under H<sub>2</sub> (Fig. 2c) is due to an additional electron scavenging effect by these low energy centers which efficiently compete with Ti<sup>4+</sup> in the capture of electrons (Reaction 2) injected in the system by H atoms.



The results in Figs 1 and 2 show thus that bare TiO<sub>2</sub> and N-TiO<sub>2</sub> behave in the same manner when irradiated with light having a dominant UV component, the main photophysical process being excitation from valence band to conduction band.

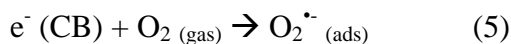


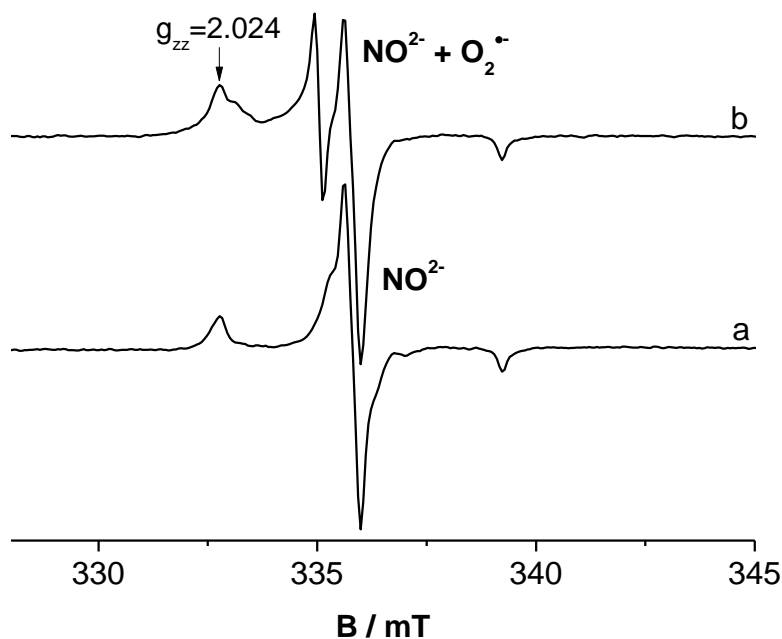
**Fig. 2:** EPR spectra (77K, 1mW) of N-TiO<sub>2</sub>. a) in dark b) after 1h unfiltered UV lamp irradiation in O<sub>2</sub> c) after 1h irradiation in H<sub>2</sub>. The inset reports the spectrum corresponding to 1c) and recorded at 10mW to evidence second Ti<sup>3+</sup> signal around g=1.90. Irradiation source: 300W Lamp.

The two experiments shown in Fig. 1 and Fig. 2 were performed independently using two distinct samples. However they can be also performed in consecution, that is on the same sample alternating the irradiation in oxygen and in hydrogen (or vice versa). We show in the supporting information an ad-hoc experiment to demonstrate this point. Once generated, say, superoxide by irradiation in oxygen the gas was removed and substituted by hydrogen. A new irradiation causes disappearance of the superoxide signal and appearance of the Ti<sup>3+</sup> one (Fig. SI6). An analogous result is observed inverting the procedure and starting from irradiation in hydrogen followed by irradiation in oxygen.

### 3.2 Visible light irradiation.

To understand the efficiency of visible light in the promotion of charge carriers at the surface we have performed irradiation of both TiO<sub>2</sub> and N-TiO<sub>2</sub> materials using either a monochromatic source at 437nm (the wavelength corresponding to the maximum of the visible absorption for N-TiO<sub>2</sub>) or the same polychromatic source of the experiment in Fig. 1 and 2 with a cut-off at 420nm in order to exclude all UV components. Fig. 3 reports the effect of irradiation with visible light having  $\lambda = 437$  nm (blue) on N-TiO<sub>2</sub> under O<sub>2</sub> atmosphere. The effect of this visible wavelength on O<sub>2</sub>/TiO<sub>2</sub> is negligible. As opposite irradiation with the same monochromatic light under oxygen of N- TiO<sub>2</sub> (Fig. 3b) causes the formation of surface adsorbed superoxide ions similarly to what already observed for sol gel prepared materials [30]. The spectrum (Fig.3b) is similar, though less intense, to that reported in Fig.2b which is related to UV irradiation of the same material. The spectrum in Fig. 3b is composed, as shown by the computer simulation reported as Supporting information (S.I.3) by two overlapped signals respectively due to O<sub>2</sub><sup>•-</sup> and NO<sup>2-</sup>. The main process monitored in the experiment is the excitation in the conduction band of electrons coming from the diamagnetic, two electrons NO<sup>3-</sup> centres which become NO<sup>2-</sup> paramagnetic ones (Ti (3d)  $\leftarrow$  N(2p) ). This is followed by the electron transfer onto the scavenger (O<sub>2</sub>). In chemical terms the described process can be written as:





**Fig.3** EPR spectra (77K, 1mW) of N-TiO<sub>2</sub>. a) in dark b) after 1h of monochromatic visible light irradiation ( $\lambda=437\text{nm}$ ) in O<sub>2</sub>. Irradiation source 1600W Lamp.

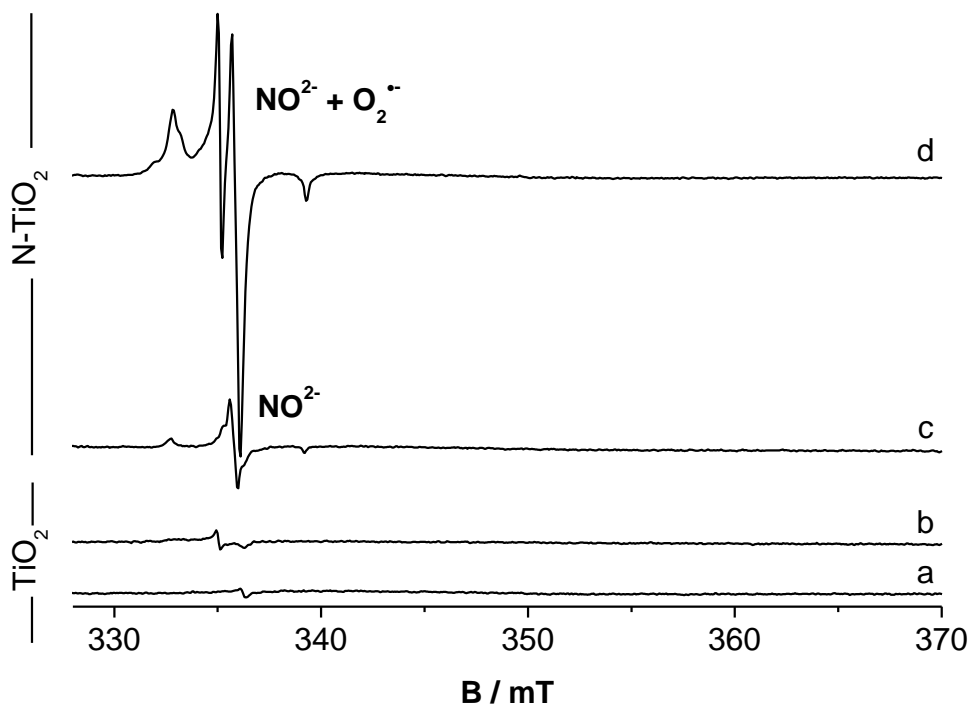
Evidence of the former step (Eq 4) is reported in S.I.4. For visible wavelengths definitely higher than 437 nm, the described effect is not observed.

The same experiment of light irradiation with  $\lambda = 437$  under H<sub>2</sub> has no consequences both on TiO<sub>2</sub> and N-TiO<sub>2</sub> spectra. Summarizing the results of the experiments reported in this section, it can be concluded that the monochromatic light corresponding to the maximum of the visible absorption is capable of producing surface reactive electrons but is incapable to symmetrically produce surface reactive holes. This is because the electrons are not excited from the valence band but, rather, from intraband gap states (see Scheme I), so that each hole generated in this way is not mobile, but still associated to the localized state. In other words the additional NO<sup>2-</sup> centers produced by irradiation (Equation 4) can be seen in terms of a hole localization onto NO<sup>3-</sup> ones.

Irradiating the solid with polychromatic light, obtained by a lamp cut-off at 420 nm which excludes UV components, things are different. It is worth noticing that in these conditions the light interacting with the solid encompasses all visible frequencies and some frequencies in the near infra-red (NIR, see Table 1). Fig. 4 and Fig. 5 report the results of this kind of irradiation under

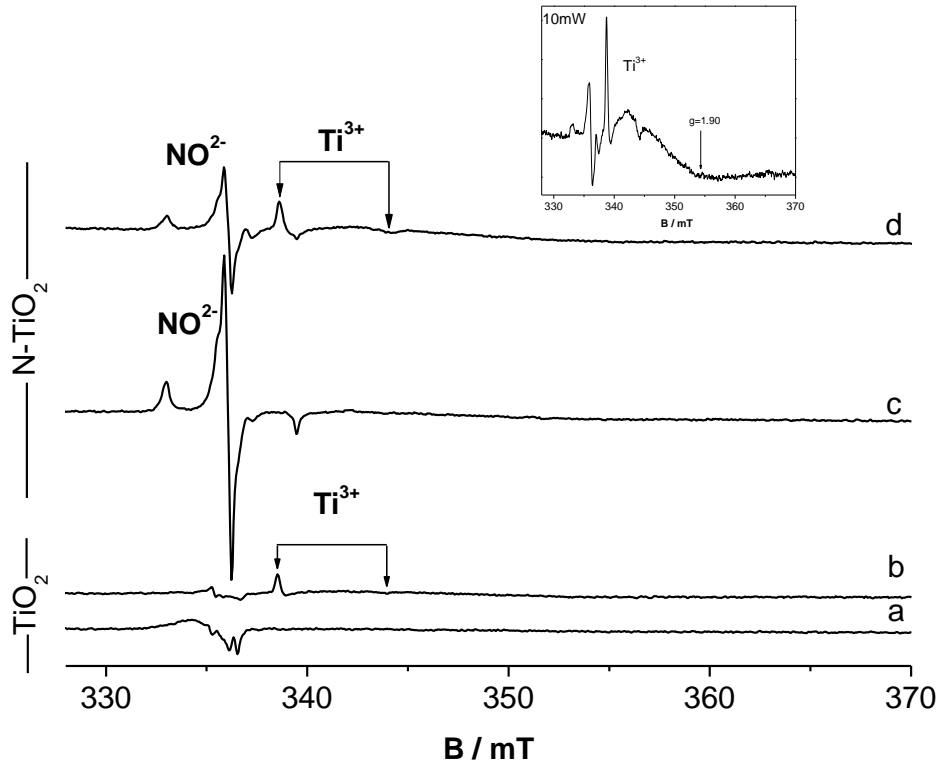
oxygen and hydrogen respectively, comparing the spectra observed for  $\text{TiO}_2$  and  $\text{N-TiO}_2$ . Irradiation under oxygen leads, for  $\text{N-TiO}_2$ , to a result quite similar (Fig. 4d) to that reported in Fig.3d (monochromatic visible light) confirming, via  $\text{O}_2^{\cdot-}$  formation, that excitation of electrons in CB is basically due to the blue component of the visible irradiation.

Fig. 5 reports the spectra obtained by the polychromatic irradiation under  $\text{H}_2$ . Once again the effect of the irradiation on undoped  $\text{TiO}_2$  is small, and visible in terms of formation of a tiny  $\text{Ti}^{3+}$  signal (Fig.5b). On the other hand the same irradiation has a two fold effect on  $\text{N-TiO}_2$  consisting in the appearance of  $\text{Ti}^{3+}$  traces ( also seen in the 10mW spectrum reported in the inset which evidences the formation of the broad  $\text{Ti}^{3+}$  signal at  $g=1.90$ ) accompanied by a decrease of the  $\text{NO}^{2-}$  signal intensity ( Fig. 5d). This result is parallel to that observed using the full lamp emission (Fig. 2) although the intensity variations monitored in this case (from 5c to 5d) are lower.



**Fig. 4:** EPR spectra (77K) of  $\text{TiO}_2$  and  $\text{N-TiO}_2$  samples under polychromatic light irradiation ( $\lambda > 420$  nm) in 50mbar  $\text{O}_2$ . a)  $\text{TiO}_2$  in dark b)  $\text{TiO}_2$  after 1h irradiation c)  $\text{N-TiO}_2$  in dark d)  $\text{N-TiO}_2$  after 1h irradiation. Irradiation source: 300W Lamp.

In spite of this fact, the results in Fig.4 and 5 have an high importance as they show that, coupling polychromatic visible light to N doped  $\text{TiO}_2$ , both types of charge carriers needed to entail photocatalytic phenomena definitely form and migrate to the surface.

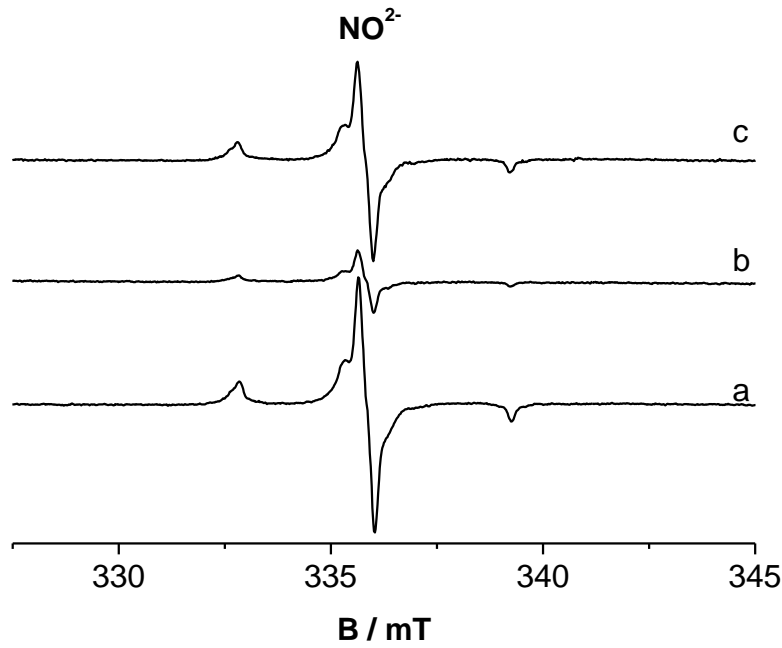


**Fig. 5:** EPR spectra (77K) of  $\text{TiO}_2$  and N- $\text{TiO}_2$  samples under polychromatic light irradiation ( $\lambda > 420$  nm) in 50mbar  $\text{H}_2$ . a)  $\text{TiO}_2$  in dark b)  $\text{TiO}_2$  after 1h irradiation c) N- $\text{TiO}_2$  in dark d) N- $\text{TiO}_2$  after 1h irradiation. The inset reports the spectrum corresponding to 5d) and recorded at 10mW. Irradiation source 300W Lamp.

### 3.3 Infra-Red irradiation.

The reason of the different behaviour of monochromatic (blue) and polychromatic visible light has to be searched in the effect of other frequencies present in the lamp emission. In particular it has to be recalled that the energy difference between the localized N states and the VB limit is around 0.7eV [19] which corresponds to photons belonging to the Near Infra Red ((NIR) region. It is therefore essential to investigate whether NIR frequencies have some effect on the electron population of the system. This has been done irradiating a N- $\text{TiO}_2$  sample, under *vacuo*, either using a lamp cut-off at  $\lambda = 850\text{nm}$  (polychromatic light with  $\lambda > 850\text{nm}$ , See S.I.5) or a series of lasers

pulses at 1550nm (Fig. 6). The results in the two cases are very similar. The starting spectrum of the  $\text{NO}^{2-}$  centres reduces its intensity after 1 hr of NIR irradiation by a factor of about one order of magnitude. This is due to a  $\text{N}(2p) \leftarrow \text{O}(2p)$  transition with electrons excited from the valence band to the intraband gap  $\text{NO}^{2-}$  paramagnetic states. In other terms



**Fig.6:** EPR spectra (77K) of N-TiO<sub>2</sub> after irradiation in vacuo with monochromatic IR light ( $\lambda=1550\text{nm}$ ). a) In dark b) immediately after IR light irradiation and c) after 1h at RT. Irradiation source: GSD Renas Laser.

The excitation of VB electrons by means of infrared irradiation is reversible but the decay of excited electrons is not fast. The EPR spectrum in fact recovers its original intensity after about one hour. The same experiment of IR irradiation was conducted under hydrogen to verify the occurrence, in such conditions, of reaction 2 indicating a detectable concentration of reactive holes at the surface. The reaction was not observed either with  $\lambda > 850\text{nm}$  nor using the laser source at 1550nm. This point will be discussed in the following Section. Nonetheless the importance of the experiment in fig. 6 is very high as it definitely shows that I.R. frequencies are active in promoting electrons from the valence band to the  $\text{NO}^{2-}$  intra-band gap states. The energy difference between

these latter states and the VB limit is, according to theoretical calculations[19] , of about 0.8eV, an energy indeed corresponding to NIR photons.

### 3.4 Photoformation of charge carriers in N-TiO<sub>2</sub>.

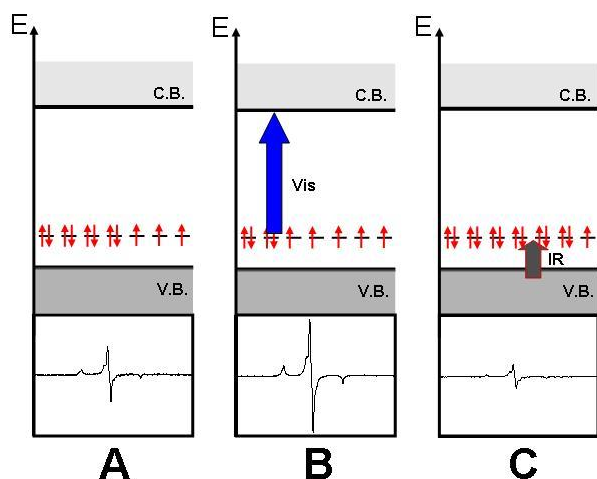
The methodology for investigating the photoformation of surface carriers proposed in the present work is based on two independent redox reactions respectively suited to scavenge surface electrons ( $O_2 \rightarrow O_2^{\bullet -}$ ) and surface holes ( $H_2 \rightarrow Ti^{3+}$ ). The experiments reported before involving the two scavengers have essentially a qualitative value and it could be misleading to compare the absolute values of spectral intensities observed in the two cases. This is because: i) the efficiency of each scavenging process is unknown; ii) the concentration of surface sites active in the two types of reaction is also unknown and is not, in principle, the same in the two cases.

We will limit therefore ourselves to a simple qualitative interpretation of the observed phenomena which is sufficient, however, to propose a general description of the photochemical mechanisms operating when N-TiO<sub>2</sub> is employed as a photocatalyst in visible light. The basic observation reported before can be resumed as follows:

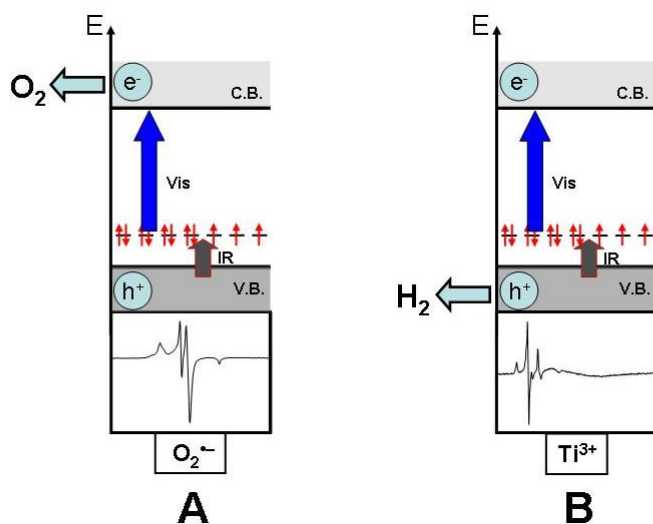
- a. The behavior of N-TiO<sub>2</sub> under UV irradiation (unfiltered UV lamp) is strictly similar to that of bare anatase.
- b. In N-TiO<sub>2</sub> under visible polychromatic light also containing IR frequencies ( $\lambda > 420\text{nm}$ ), electrons are excited from  $NO^{3-}$  intraband gap states to the C.B. (Fig.4 c,d) becoming available for  $O_2$  reduction to  $O_2^{\bullet -}$ . Responsible of this excitation is a very narrow range of frequencies corresponding to blue light (Fig.3, Scheme II B) which, is not, *per se*, capable of producing surface reactive holes.
- c. The same polychromatic light with  $\lambda > 420\text{nm}$ , produces surface reactive holes (Fig. 5 c,d)
- d. Infra red frequencies ( $\lambda = 1550$  or  $\lambda > 850$ ) are able to excite electrons from V.B. to intra-bandgap states reducing  $NO^{2-}$  to  $NO^{3-}$  (Fig. 6, Scheme II C).

The findings reported at point c and Fig.5 are sufficient to explain the continuously increasing number of results reporting photocatalytic activity under visible or solar light using N-TiO<sub>2</sub>. Both surface electrons and holes, necessary to entail a photocatalytic process, are in fact produced by a polychromatic light excluding UV frequencies, though at a lower extent than in the case of UV irradiation. Charge carriers formation is related to the presence of intra-bandgap NO<sup>x-</sup> states which are located some 0.7-0.8 eV over the VB edge. The limited number of these centers limits, in its turn, the efficiency of the charge separation process which remains lower than in the case of UV irradiation which directly transfer electrons from V.B. to C.B. drawing electrons from energy regions with high density of states. The entire mechanism of charge separation is ensured by a synergistic effect between two types of frequencies, namely the visible photons with  $\lambda$  of about 440nm (responsible of the NO<sup>3-</sup> → C.B electron excitation) and the NIR frequencies capable of refilling the intra-bandgap centres via V.B. → NO<sup>2-</sup> electron transfer (Scheme II). The missing direct observation of holes upon IR irradiation under H<sub>2</sub> (see Section 3.3) is very likely due to the fact that the number of holes produced in that way is rather low and that the system properly works in dynamic conditions only, with the simultaneous presence of both types of frequencies as in the case of polychromatic irradiation (Fig.5). The existence of the NO<sup>x-</sup> intra-bandgap states allows the system to draw the needed quantum energy for moving electrons from V.B to C.B from two distinct steps rather than from a direct single step. The nature of localized states, typical of NO<sup>2-</sup> and NO<sup>3-</sup>, limits the range of frequencies employable for the described double excitation process (Scheme III) and explains the limited efficiency of photocatalytic processes in visible light with comparison to those performed under UV irradiation. In the light of the present results, however, tailoring novel photocatalysts with higher concentration of N intraband gap states and taking into account the wavelength selectivity here described while selecting the irradiation technique, possible improvements of the photocatalytic performance of this photocatalyst active in visible light can be predicted.

The method here proposed to indirectly monitor the formation of surface electrons and holes, and based on simple EPR measurements after irradiation, is relatively simple and is based on the accumulation of stable adducts at the surface overcoming the difficulties of direct measurements of charge carriers formation in real time. The method is easily extendible to semiconducting oxide systems different from  $\text{TiO}_2$ .



**Scheme II:** Effect of the visible and Infra Red wavelengths on the intra band gap states ( $\text{NO}^{\text{x-}}$ ) population. A) Dark condition. B) Visible light ( $\lambda = 437\text{nm}$ );  $\text{NO}^{2-}$  population increases. C) IR light; ( $\lambda > 850\text{nm}$ ),  $\text{NO}^{2-}$  population decreases.



**Scheme III:** Indirect detection of photoformed electrons and holes in N- $\text{TiO}_2$  system by specific scavengers under irradiation including visible and NIR components. A) electrons scavenging by  $\text{O}_2$  (formation of  $\text{O}_2^{\bullet-}$ ) B) holes scavenging by  $\text{H}_2$  (formation of  $\text{Ti}^{3+}$ ).

## Conclusions.

The capability of N-TiO<sub>2</sub> to origin surface electrons and holes under visible light irradiation is due to the combined effect of a narrow range of visible frequencies (roughly corresponding to blue light) and of components in the NIR region. The mechanism is based on the presence of the well known NO<sup>x</sup> isolated states few tenths of eV over the limit of the valence band. The visible component excites electrons from NO<sup>x</sup> levels to the conduction band. Simultaneously the intra band gap states receive electrons excited from the valence band by NIR photons. In the presence of both types of radiation we have observed the generation of both surface reactive electrons and holes. The findings here reported rationalize the mechanism of the observed activity of N-TiO<sub>2</sub> in photocatalytic reactions under visible or solar light.

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**Supporting Information Available:** X-ray Diffraction, Diffuse Reflectance UV-Vis spectroscopy, more EPR spectra and EPR simulations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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