



## Preparation and spectroscopic characterization of visible light sensitized N doped TiO<sub>2</sub> (rutile)

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### ABSTRACT

Nitrogen doped TiO<sub>2</sub> represents one of the most promising material for photocatalytic degradation of environmental pollutants with visible light. However, at present, a great deal of activity is devoted to the anatase polymorph while few data about rutile are available. In the present paper we report an experimental characterization of N doped polycrystalline rutile TiO<sub>2</sub> prepared via sol-gel synthesis. Nitrogen doping does not affect the valence band to conduction band separation but, generates intra band gap localized states which are responsible of the on set of visible light absorption. The intra band gap states correspond to a nitrogen containing defect similar but not coincident with that recently reported for N doped anatase.

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### 1. Introduction

TiO<sub>2</sub> represents one of the most important oxides employed in several fields of photochemistry even though its outdoor applications are partially hampered by the fact TiO<sub>2</sub> adsorbs light with  $\lambda < 387$  nm (UV), light which represents a very small fraction of the incoming solar energy. This drawback is due to the quite large band gap energy value of TiO<sub>2</sub> (3.2 eV for the anatase polymorph and 3.0 for rutile) and for this reason great efforts have been spent until now to improve the oxide performances by shifting the edge of light absorption toward the visible region. Various strategies were followed in the past, for example surface sensitization where electron transfer occurs from an adsorbed dye molecule (antenna) excited by visible light or metal doping of the oxide. During the last decade however a new generation of TiO<sub>2</sub> doped by non-metal elements (p-block) has increasingly attracted the attention of the scientific community [1].

Different non-metal elements (N, C, S, etc.) are employed in this new generation of doped TiO<sub>2</sub>, and among them Nitrogen is certainly the most important one. After the first report by Sato [2] on nitrogen doped TiO<sub>2</sub> (hereafter N-TiO<sub>2</sub>) a considerable number of studies have appeared on the preparation and characterization of this material but, in spite of this fact, many aspects as, for example, the visible light absorption mechanism are still

controversial [3]. A second point of disagreement in the literature is the nature of the active species responsible of the visible light sensitization [4]. In particular atomic nitrogen species have been individuated in the bulk of TiO<sub>2</sub> and their precise nature (substitutional ( $N_s$ ) of interstitial ( $N_i$ ) species) is still under debate. Most paper in the literature are devoted to the anatase phase while few papers only can be found for rutile. Also in the case of our group, recent work on N doped TiO<sub>2</sub> systems was mainly devoted to the anatase polymorph [3,5–7]. With the present paper we report one of the first experimental investigations on polycrystalline N doped rutile prepared by chemical synthesis. Most results available in the literature are in fact theoretical results or experiments on single crystal of titania. The first report on N doped rutile is due to Morikawa et al. [8] who prepared the solid by TiN oxidation and observed a red-shift of the light absorption edge. Later, Di Valentin et al. [9] reported the first theoretical study on both N-doped rutile and anatase based on spin polarized DFT. Di Valentin analysed the effects of nitrogen doping, when N substitutes oxygen in the lattice position, pointing out as in both polymorphs, N ( $2p$ ) localized states are present just above the top of the valence band. At the same time, while the band structure of anatase remains practically unaffected, in the rutile system nitrogen induces a valence band contraction resulting in an overall increase in the optical transition energy. This finding was supported by experimental evidences due to Diwald et al. [10] in a paper devoted to the reactivity of the (110) rutile surface. Materials doped by ion implantation with mixtures of  $N_2^+$  and  $Ar^+$  ions revealed XPS

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spectra with N (1s) features at 396.6 eV generally attributed to substitutional nitrogen ( $N_s$ ). The N-doped crystals containing this substitutional ions only, exhibited a blue shift (0.2 eV) in the photo threshold energy. At variance N-doped  $TiO_2$  rutile single crystal obtained by treatment in  $NH_3/Ar$  atmosphere at about 600 °C exhibited photo activity using photons of 2.4 eV, that is, 0.6 eV below the band gap energy of rutile (3.0 eV) [11]. The active dopant state of nitrogen responsible for this effect showed a N 1s binding energy at 399.6 eV attributed by the authors to a form of interstitial nitrogen likely bound to H, distinctively different from that of substitutional nitrogen (396.7 eV). In a recent theoretical elaboration Yang et al. [12], modelling both the interstitial and substitutional case, found that in the case of rutile no significant band gap modification occurs and, as reported by Di Valentin [9], some N (2p) states lie above the valence band resulting again in a overall lowering of optical transition energy. In another theoretical paper Graciani et al. [13] evaluated the effect of nitrogen doping at the (110) rutile surface in different positions showing that the presence of nitrogen favours the formation of oxygen vacancies and that nitrogen can exist both in doubly charged form  $N^{2-}$  and as  $N^{3-}$  species due to the interplay with electrons left by oxygen vacancies. The same electronic interaction was predicted in other cases [5,14–16]. Furthermore in the case of the interstitial site in ground state ( $N_i^{2-}$ ) a band gap blue shift occurs but due to the interplay with oxygen vacancies the new states associated to  $N_i^{3-}$  centre appear causing a simultaneous recovering of the original  $TiO_2$  band gap value.

The present paper reports an experimental characterization of N doped polycrystalline rutile  $TiO_2$  prepared via sol-gel synthesis. As it will be shown later in this case doping causes the appearance of a pronounced absorption in the visible region but no shift of the band gap energy. The material has been characterized by XRD and optical absorption. A fine characterization of the N based defects and their interaction with visible light was performed using electron paramagnetic resonance (EPR).

## 2. Experimental

All reactants employed in this work were purchased by Aldrich and used without any further purification treatment.  $TiO_2$  has been synthesized via sol-gel method from the reaction of a solution of titanium(IV) isopropoxide in isopropyl alcohol (molar ratio 1:4) with water (molar ratio between water and alcohol 1:10) performed under constant stirring at room temperature. The gel so obtained has been aged overnight at room temperature to ensure the complete hydrolysis and subsequently dried at 343 K. The dried material was heated at 773 K in air for 1 h (heating rate  $\sim 200$  K/min). The same procedure was adopted to prepare N- $TiO_2$ , the only difference consisting in the addition of a nitrogen source ( $NH_4Cl$ ) in the hydrolysis water. X-ray diffraction (XRD) was performed by a Philips 1830 diffractometer using a  $K\alpha(Co)$  source and a X'Pert high-score software for data handling. Diffuse reflectance UV-Visible spectra (DR-UV-Vis) were recorded by a Varian Cary 5 spectrometer using a Cary win-UV/scan software. EPR spectra were run on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation and computer simulation of the spectra were obtained using the SIM32 programme [17]. The effect of visible light on EPR spectra was investigated directly irradiating the sample into the EPR cavity using a 500W mercury/xenon lamp (Oriol instruments) equipped with a IR water filter and a grating monochromator with a transmission range between 500 and 180 nm.

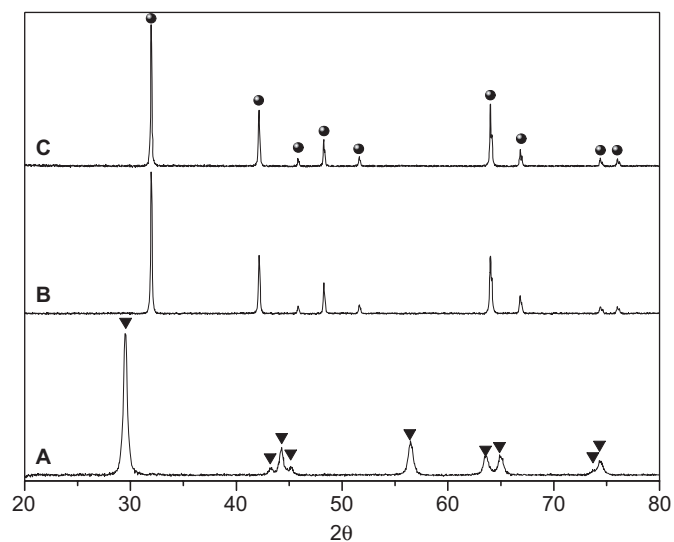
## 3. Results

The sol-gel synthesis followed by calcination in air leads to two different crystallographic phases in the case of bare and doped N- $TiO_2$ . In the former case, calcination at 773 K ( $\sim 200$  K/min) leads to a solid characterized by anatase structure (spectrum A in Fig. 1). The doped material, calcined in the same condition, is characterized by the rutile structure (spectrum B in Fig. 1) and by a vivid yellow colour. An undoped rutile sample was also prepared upon calcination of the gel at 1073 K for 1 h (spectrum C in Fig. 1). The presence of N compounds in the system kinetically favours, therefore, the formation of the rutile phase.

In Fig. 2 the DR-UV-Vis spectra of pure and doped rutile samples are reported. Pure material shows the typical absorption of rutile with an intense transition in UV region with an absorption edge around 400 nm due to electron promotion from valence band to conduction band (spectrum A in Fig. 2).

The doped sample shows the same behaviour of bare rutile in the UV region overlapped with an absorption shoulder at around 430 nm (2.9 eV), typical of N- $TiO_2$  systems [2,18] (spectrum B in Fig. 2).

The N doped rutile sample shows a complex EPR spectrum (Fig. 3A) which can be interpreted as the superimposition of the signals of two distinct paramagnetic centres. In Fig. 3 the simulation of the EPR spectrum (Fig. 3B) and its deconvolution in two signals are also reported. The former signal (Fig. 3B') is isotropic ( $g = 2.002$ ) and can be assigned to carbon radical impurities [19] formed during the calcination of the gel and labelled with  $C^\bullet$ . The second species (spectrum B'' in Fig. 3) is characterized by orthorhombic  $g$  tensor ( $g_1 = 2.007$ ,  $g_2 = 2.005$ ,  $g_3 = 2.004$ ) and by a triplet of hyperfine lines due to the interaction of the unpaired electron with a single N nucleus (the nuclear spin is  $I = 1$  for  $^{14}N$ ). The hyperfine tensor elements are  $A_1 = 0.6$  G,  $A_2 = 4.4$  G,  $A_3 = 32.8$  G with a Lorentzian line shape. A signal very similar to the one here described has been reported by other authors [20–23] and by some of us [3,5–7,24] in the case of N doped anatase. In the above cited papers from our group the N based paramagnetic species was labelled as  $N_i^\bullet$ . For the sake of clarity this label is also employed for the analogous species in rutile here described.



**Fig. 1.** XRD patterns of bare and doped  $TiO_2$ . (A) Bare  $TiO_2$  calcined at 773 K (200 K/min), (B) nitrogen doped  $TiO_2$  calcined at 773 K (200 K/min) and (C) bare  $TiO_2$  calcined at 1073 K (200 K/min).  $\blacktriangledown, \bullet$  symbols indicate anatase and rutile polymorphs, respectively.

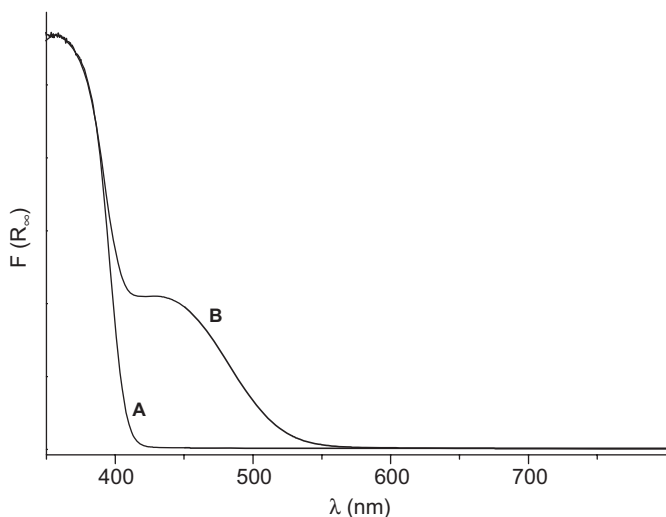


Fig. 2. DR-UV-Vis spectra of rutile (A) and N doped rutile (B).

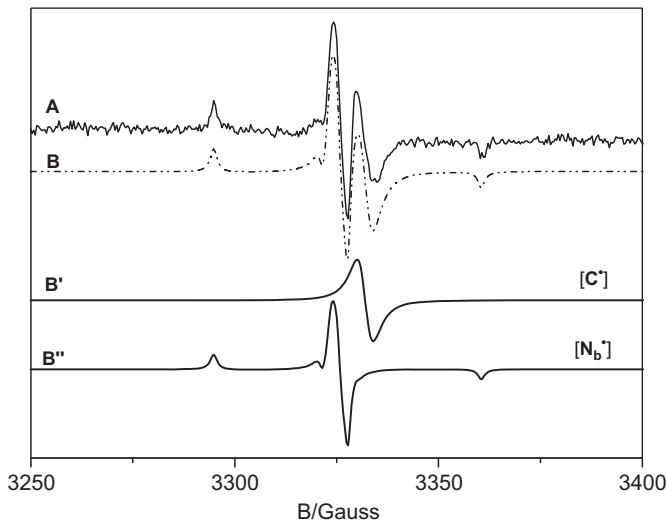


Fig. 3. EPR spectra of nitrogen doped rutile. (A) N-TiO<sub>2</sub>. (B) Computer simulation. (B' and B'') Deconvolution of spectrum B. The spectra have been recorded at room temperature.

N<sub>b</sub><sup>•</sup> species is observed both at RT and at low temperature (77 K) and is located in the bulk of the solid because EPR spectra recorded in presence of adsorbed molecular oxygen do not show any dipolar broadening effect. The behaviour of species N<sub>b</sub><sup>•</sup> under irradiation with visible light is similar to that observed for the analogous species in anatase [7]. Fig. 4 reports the effects of irradiation of N doped rutile using a monochromatic source with  $\lambda = 437$  nm corresponding to the shoulder of the optical absorption (Fig. 2). The intensity of the spectrum recorded in the dark (Fig. 4A) dramatically increases under irradiation (Fig. 4B). The difference spectrum (Fig. 4C) indicated that it is the intensity of N<sub>b</sub><sup>•</sup> that selectively grows under irradiation.

#### 4. Discussion

The sol-gel synthesis used in this work leads to the formation of the N doped rutile polymorph at relatively low temperature. This is due to the coupling of two factors: high heating rate employed during calcination and presence of the nitrogen source

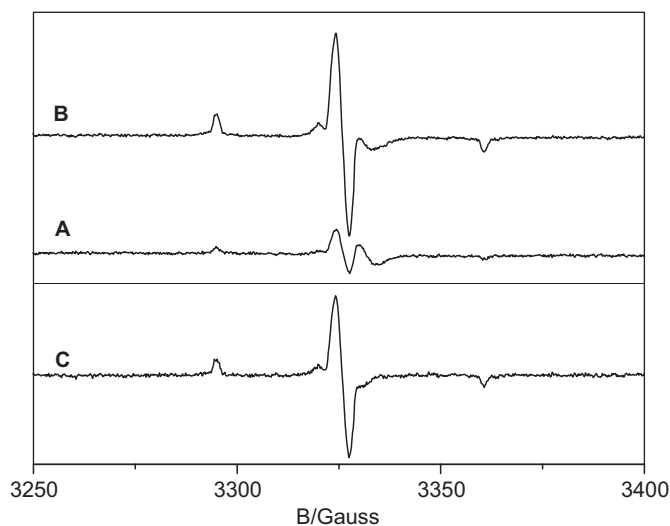


Fig. 4. EPR spectra of species N<sub>b</sub><sup>•</sup> under irradiation in vacuo with monochromatic light ( $\lambda = 437$  nm): (A) in dark and (B) under blue light irradiation. Spectrum C represents the difference between spectra B and A. The spectra have been recorded at room temperature.

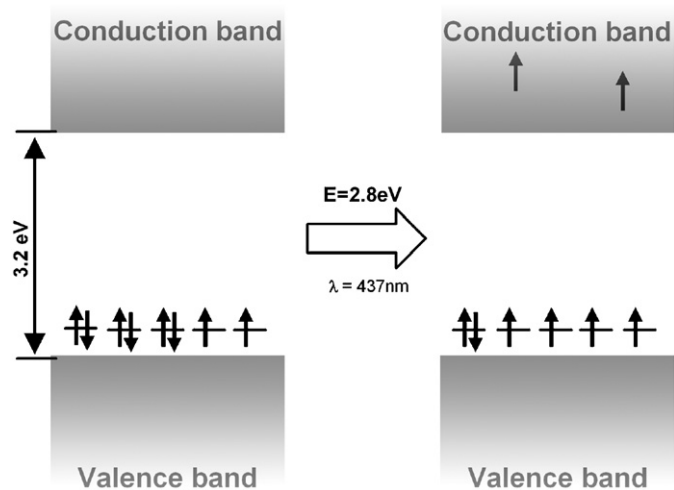


Fig. 5. Scheme of the electronic structure of N-TiO<sub>2</sub> and effect of the irradiation with blue light (427 nm).

(NH<sub>4</sub>Cl) during the synthesis of the doped material. In the case of bare TiO<sub>2</sub>, however, the high heating rate alone is not able to lead to rutile formation. On the other hand, N doped anatase can be easily obtained, as shown by previous work of our laboratory [3,5–7,24], using NH<sub>4</sub>Cl simply reducing the heating rate to about 15 K/min. The EPR spectra reported in Fig. 3 indicate the presence of carbon impurities beside the most important N<sub>b</sub><sup>•</sup> species. Carbon contamination is the consequence of the sol-gel procedure and of the presence of organometallic molecules in this preparation. As mentioned in the previous section the spectrum, of N<sub>b</sub><sup>•</sup> was reported in the case of N doped anatase only. The *g* factor and hyperfine coupling constants of N<sub>b</sub><sup>•</sup> in N doped rutile, although very similar, slightly differ from those observed for anatase [5]. This fact induces two distinct observations: (i) due to the high sensitivity of EPR parameters to the electron density there is no doubt that N<sub>b</sub><sup>•</sup> in anatase and rutile are essentially the same species in terms of chemical nature; (ii) the small differences monitored for the parameters of N<sub>b</sub><sup>•</sup> in the two TiO<sub>2</sub> polymorphs is likely due to a slightly different coordinative

**Table 1**Comparison of experimental Hamiltonian parameters of  $N_5^{\bullet}$  species in  $TiO_2$  polymorphs and computed parameters for both interstitial and substitutional case in anatase

	Par. species	$g_1/\Delta H$ (G)	$g_2/\Delta H$ (G)	$g_3/\Delta H$ (G)	$A_1$ (G)	$A_2$ (G)	$A_3$ (G)	Ref.
Exp.	$N_5^{\bullet}$ (rutile)	2.007/1.6	2.005/1.4	2.004/1.2	0.6	4.4	32.8	a
	$N_5^{\bullet}$ (anatase)	2.005/1.3	2.004/1.2	2.003/1.1	2.3	4.4	32.3	[5]
Comp.	N (interstitial)	–	–	–	0.2	1.8	33.4	[5]
	N (substitutional)	–	–	–	2.5	2.8	38.2	[5]

 $\Delta H$ : line with, a: present work.

environment of the species amenable to the structural differences between anatase and rutile. These are both characterized by tetragonal structure based on connections of octahedra having a different distortion degree.  $TiO_6$  and  $OTi_3$  units are easily individuated in both structures.

The intensity of  $N_5^{\bullet}$  intensity under irradiation is explained with the same arguments used in the case of N doped anatase [5,7] namely the presence, beside the paramagnetic  $N_5^{\bullet}$ , of a diamagnetic (EPR silent)  $N_5^-$  species. It is the photoexcitation of electrons from  $N_5^-$  which, under irradiation, causes the promotion of electrons in the conduction band according to



with consequent increase of  $N_5^{\bullet}$  EPR intensity.

Both  $N_5^{\bullet}$  and  $N_5^-$  species correspond to isolated intra band gap energy states located above the valence band (see scheme in Fig. 5). The position of the isolated states in the band gap is compatible with the energy (2.8 eV) associated to photons at 437 nm.

Carbon doping is an alternative way to dope  $TiO_2$  [25] but, as the signal intensity due to carbon impurity ( $C^{\bullet}$ ) remains unchanged during irradiation, it can be inferred that, in our case, carbon impurities are not involved in visible light sensitization. The above discussed model is parallel to that previously reported for N doped anatase. The presence of isolated N states in the band gap is accompanied by the onset of optical absorption in the visible. No appreciable shift of the typical band gap absorption edge is observed in agreement with the theoretical results of Graciani [13].

A final comment is devoted to the nature of  $N_5^{\bullet}$  species. A systematic theoretical investigation has found only two possible models for stable centres involving one N atom in the bulk of  $TiO_2$  [5,26] namely the interstitial ( $N_i^{\bullet}$ ) and substitutional ( $N_s^{\bullet}$ ) species reported in Table 1. In the case of  $N_s^{\bullet}$  a nitrogen atom substitutes an oxygen one in the lattice while  $N_i^{\bullet}$  is based on a N interstitial atom which tends to stick to an  $O^{2-}$  ion of the lattice forming a chemical bond with the latter and originating a sort of  $NO^{2-}$  species with the unpaired electron shared by the  $\pi$  orbitals of the two atoms [5]. Amazingly the EPR parameters calculated for both species are quite close one to the other and also similar to the experimental data for  $N_5^{\bullet}$ . This fact limits a totally unambiguous assignment of  $N_5^{\bullet}$  to one of these two models. There are however two reasons that allow one to indicate the interstitial Ni species as the most suited assignment for  $N_5^{\bullet}$ . The first one is that the spin-Hamiltonian parameters calculated for Ni are definitely closed to the experimental values. The second one concerns the preparation adopted for the system which takes place in quite mild conditions (the maximum temperature reached in the preparation is of 773 K). During calcinations  $NH_4^+$  is oxidized to NO [6] which likely tend to be stabilized in the vacancies available during the transformation of the material from a gel to a crystalline oxide. In such conditions the energy needed to form N atoms and to substitute with them lattice oxygen are not easily available. We think therefore that  $N_5^{\bullet}$  is very likely the interstitial species described in Ref. [5].

## 5. Conclusion

Summarizing we have shown that N-doped rutile can be prepared by sol-gel technique just controlling the rate of temperature increase during calcination of the gel. The solid has a vivid yellow colour indicating absorption of visible light. As found for N doped anatase, a single N photosensitive species is present in the bulk of N doped rutile which is responsible of visible light absorption and which has been characterized by EPR showing parameters close but not exactly equal to those found for the same species in anatase. The photoactivity of this species, i.e. its ability to harvest visible light corresponding to blue, was been monitored in term of variation of the EPR spectral intensity under irradiation. The species is, most probably, an interstitial atom stick to a  $O^{2-}$  lattice ion as the alternative for such a model (a N substituting  $O^{2-}$  in the lattice) seems less probable in the relatively mild conditions of the sol-gel preparation. Doping with N populates the band gap at isolated energy states but does not influence the valence band to conduction band transition.

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