

The nature of paramagnetic species in nitrogen doped TiO₂ active in visible light photocatalysis

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Nitrogen doped TiO₂, a novel photocatalyst active in the decomposition of organic pollutants using visible light, contains two different types of paramagnetic centres (neutral NO radicals and NO₂²⁻ type radical ions respectively) which are likely related to specific properties of the solid.

Titanium dioxide is the most important inorganic photocatalytic system for the decomposition of organic pollutants either in gas or in liquid phase because of its high activity and chemical stability. An even wider use of TiO₂, however, is hampered by the fact that the amplitude of its band gap requires the use of UV light during the reaction, thus limiting the possibility of employing solar light in TiO₂ photocatalysis.¹ For this reason a remarkable effort has been made, in the recent past, to obtain band gap narrowing in TiO₂ based materials.² While initial attention was paid to TiO₂ doping by transition metal ions,³ more recent research points to the introduction of non metallic light elements like carbon,⁴ sulfur⁵ and, in particular, nitrogen into the oxide matrix.

After the early report by Sato⁶ a number of papers have appeared concerning different preparations, characterisation and catalytic properties of nitrogen doped TiO₂ (hereafter N-TiO₂) systems active in visible light.⁷⁻¹¹ Nevertheless, the debate on the structural features of N-TiO₂ and on the nature of the centres responsible for the catalytic activity is still in an embryonic state with conflicting hypotheses involving the presence of neutral NO_x species⁶ or nitrogen impurities in substitutional sites.¹² Similarly, controversial ideas exist on the modifications occurring to the electronic structure passing from bare to N doped TiO₂.^{13,14} N-TiO₂ is a yellow material with absorption maximum around 450 nm and peculiar XPS features due to nitrogen doping.¹⁴ In two cases EPR spectra typical of the doped sample were reported without assigning in detail the observed signal.^{15,16}

The present paper confirms that paramagnetic centres in N-TiO₂ are an essential feature of this solid independently from the preparative route and reports their first detailed description and assignment. The role of EPR in the characterization of defects and impurities in the solid state is well known as, in many cases, the defective centres (dangling bonds, trapped electrons, atomic impurities) responsible for various physical properties of the material are paramagnetic.¹⁷ We prepared several N-TiO₂ samples (100% anatase) *via* two different routes *i.e.* sol-gel chemistry and mechanochemistry. In both cases we obtained pale yellow samples with the typical optical absorption centred at about 450 nm and a red shift of the TiO₂ absorption band edge. The solids show catalytic activity in visible light which was monitored according to

the method proposed by Burda.¹⁴ As EPR spectra are satisfactorily reproducible for both preparation methods, we will report the results related to the sol-gel preparation only.

The samples were prepared mixing a solution of titanium(IV) isopropoxide in isopropyl alcohol with a solution of NH₄Cl in water. The gel was left to age for 15 hours at room temperature and subsequently dried at 70 °C for 2 hours. The dried material was eventually calcined in air at 770 K from a minimum of one hour up to a maximum of 15 hours. XRD indicates the exclusive formation of anatase with particle size of about 50 nm.

Two different EPR signals were observed in N-TiO₂ after calcination in air of the xerogel precursor for around 1 hour. The first one (species A, Fig. 1a) is observed at 77 K and disappears on raising the temperature to about 170 K revealing the presence of a second and distinct signal (species B, Fig. 1b). This latter signal is observed also at room temperature while at 77 K it is buried in the more intense trace of species A. The species A signal shows up again on cooling the system at 77 K with unchanged intensity. As easily deduced from the hyperfine structure of the spectra (whose computer simulations are reported in Fig. 1a' and b') both A and B species contain nitrogen atoms and are therefore related to the doping process of the solid. A spin counting performed comparing the intensities of various N-TiO₂ samples with those of freshly prepared DPPH solutions in toluene gave an average value of 10¹⁷ spins (relative to N containing species exclusively) per gram of solid.

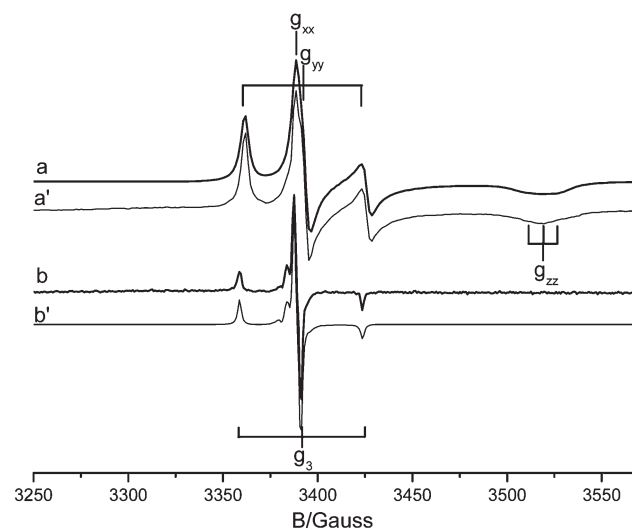


Fig. 1 Experimental (a) and simulated (a') EPR spectra of species A ($T = 77$ K); experimental (b) and simulated (b') EPR spectra of species B ($T = 298$ K).

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Species A was simulated on the basis of a rhombic g tensor ($g_1 = 2.001$, $g_2 = 1.998$, $g_3 = 1.927$) with one value (g_3) pronouncedly lower than the free spin value (2.0023) and an anisotropic N hyperfine tensor ($A_1 = 0$, $A_2 = 32.2$ G, $A_3 = 9.6$ G). Species B was instead simulated in terms of the presence of two akin species (B, B') with slightly different parameters. At variance with species A the g tensor of B has three values very close to one another and to the free spin value ($g_1 = 2.005$, $g_2 = 2.004$, $g_3 = 2.003$).

The largest hyperfine constant is observed in the direction of the smallest g element ($g_3 = 2.0030$, $A_3 = 32.3$ G) while a smaller coupling is observed in one of the other two directions only ($A_1 = 4.9$).

The structure of the species A signal ($g_1 \approx g_2 > g_3$, $A_2 > A_3 > A_1$) is that expected for an $11e^-$ diatomic π radical with configuration $^2\Pi_{1/2}$ and is assigned to nitric oxide (NO). The EPR spectrum of NO is not observed in the spectral region of the free electron unless the degeneracy between the two 2π antibonding orbitals is lifted by the effect of some asymmetric electric field. The unpaired electron is confined, in such a case, in the 2π antibonding orbital with lower energy. This leads to a rhombic g tensor with a particularly low g_{zz} value (z being the direction of the internuclear axis) given by $g_{zz} = g_3 = g_e - 2\lambda/\Delta$ where λ is the spin orbit coupling parameter associated with the investigated radical while Δ is the $2\pi_g^x - 2\pi_g^y$ separation.¹⁸

Spectra very similar to those reported in Fig. 1a were observed in the case of NO adsorbed at the surface of ionic or partially ionic oxides like MgO,¹⁸ ZnO¹⁹ and also TiO₂.²⁰ However in all cases of surface adsorbed NO the molecule is weakly bound to the surface and is readily and irreversibly desorbed on out-gassing the solid at relatively low temperature (from 170 K–200 K onwards)²¹ while, in the present case, both A and B species are not affected by outgassing up to about 470 K. This fact (together with the absence of dipolar broadening when the EPR spectra are recorded in the presence of molecular oxygen) indicates that N containing species are located in the bulk of N–TiO₂ microcrystals. Annealing the N–TiO₂ sample *in vacuo* up to $T = 770$ K induces the well known depletion of oxygen with consequent reduction of the solid and formation of Ti³⁺ centres.²² In such conditions the spectrum of species A is practically unaffected while species B disappears at about 500 K. Interestingly, recovery of the solid stoichiometry (by oxidation at 770 K) completely restores the spectrum of species B, indicating that this latter species is in electronic contact with the solid lattice and involved in its redox chemistry.

In particular the neutral NO molecule could be segregated in some imperfection of the structure. The spectrum is observed at $T < 170$ K as, in such conditions, NO interacts more tightly with the crystal structure loosening the degeneracy of the π^* orbitals. At $T > 170$ K the molecule, simply trapped in the defective site, has an unperturbed electronic structure and its EPR spectrum is no longer observed.

The assignment of species B and B' is more puzzling. However some important considerations can be proposed on the basis of the structure of the hyperfine nitrogen tensor which can be written and deconstructed as follows:

$$A = \begin{vmatrix} 0 & & & & & \\ & \pm 32.3 & & & & \\ & & \pm 4.5 & & & \\ & & & & & \\ & & & & & \\ & & & & & \end{vmatrix} = a_{\text{iso}} + \begin{vmatrix} -b & & & & \\ & 2b & & & \\ & & -b & & \\ & & & & \\ & & & & \end{vmatrix} + \begin{vmatrix} 2b' & & & & \\ & -b' & & & \\ & & -b' & & \\ & & & & \\ & & & & \end{vmatrix}$$

According to the choice of signs for the hyperfine elements, which cannot be deduced from powder spectra, one obtains slightly different values for a_{iso} , b and b' . Using the reported atomic value²³ of the dipolar ^{14}N constant $B^{\circ} = 4/5g_N\beta_n \langle r^{-3} \rangle_{2p} = 39.62$ G the spin density on the nitrogen 2p orbitals can be calculated by direct comparison of the experimental b (b') values according to the well known formula $\rho_{2p} = 2b/B^{\circ}$. This gives a spin density value ranging from 0.50 to 0.58 mainly due to one single 2p (b) orbital with a minor contribution of a second one (b'). The isotropic Fermi contact term has to be compared with the atomic isotropic hyperfine constant, A°_{iso} (N) = 646.2 G. In this case one has $\rho_{2s} = a_{\text{iso}}/A^{\circ}$ which can range from 0.014 to 0.019. The total spin density on the N atom of species B is thus essentially due to a nitrogen 2p orbital. This result and the g values of the species are compatible with the properties of an oxo-nitrogen radical ion like NO_2^{2-} , a 19-electron bent species with the unpaired electron confined to a $2b_1$ antibonding orbital mainly involving a p orbital of the central nitrogen atom and two parallel p orbitals of the oxygen atoms.²⁴ Such a species was first observed in irradiated KNO_3 and its formation in the present case suggests a complex chemical interaction between N compounds and the oxide phase during the preparation. The spin Hamiltonian parameters of species B could, however, be compatible also with similar nitrogen based species deeply interacting with the oxide lattice. Further experiments and elaborations are needed to reach a complete understanding of the nature and structure of this centre.

In conclusion we have shown that N–TiO₂, an intriguing photocatalytic system active in visible light, contains in its bulk two types of radical centres formed during the synthesis of the material. The two centres are stable at high temperature (770 K), indicating that they are non transient species, well stabilized in the oxide matrix. The first one is molecular NO permanently trapped in the crystal and the second one is a nitrogen based paramagnetic centre (here described in terms of a NO_2^{2-} radical anion) deeply interacting with the oxide and with more than half of its spin density in a p orbital of the nitrogen atom. There is no conclusive evidence, at the present state of the investigation, that A and/or B species are directly responsible for the alteration of catalytic properties observed passing from bare to N-doped TiO₂. However the systematic observation of such species in materials with peculiar optical and catalytic properties and their intimate, previously discussed, interaction with the lattice are rather strong clues to take them into account in future investigations and debates about the properties of N–TiO₂.

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