

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231642725>

Photoinduced Formation of Defects and Nitrogen Stabilization of Color Centers in N-Doped Titanium Dioxide

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · JULY 2007

Impact Factor: 4.77 · DOI: 10.1021/jp071181v

CITATIONS

69

READS

45

5 AUTHORS, INCLUDING:



Alexei V Emeline

Saint Petersburg State University

75 PUBLICATIONS 2,195 CITATIONS

SEE PROFILE



Nick Serpone

University of Pavia

435 PUBLICATIONS 17,992 CITATIONS

SEE PROFILE

Photoinduced Formation of Defects and Nitrogen Stabilization of Color Centers in N-Doped Titanium Dioxide

A. V. Emeline,^{*,†} N. V. Sheremetyeva,[†] N. V. Khomchenko,[†] V. K. Ryabchuk,[†] and N. Serpone^{*,‡}

V.A. Fock, Institute of Physics, St. Petersburg State University, St. Petersburg 198504, Russia, and Dipartimento di Chimica Organica, Università di Pavia, Via Taramelli 10, Pavia 27100, Italia

Received: February 12, 2007; In Final Form: May 10, 2007

Second-generation photocatalysts based on the metal oxide TiO₂ and doped with various anions (e.g., N, S, and C) and cations have recently been the object of intense scrutiny as a result of the red-shift of the absorption edge of TiO₂ to longer wavelengths, thereby increasing the photocatalytic efficacy based on total UV and visible light absorbed relative to pristine nondoped TiO₂ which can only absorb UV radiation. This article examines the optical behavior (diffuse reflectance spectroscopy) of a nitrogen-doped TiO₂ specimen and explores the photoinduced formation of defects when the N-doped specimen is subjected to oxidative (O₂) and reductive (H₂) stresses relative to vacuum. The resulting absorption spectrum in the visible spectral region (400 nm < λ < 900 nm) of the N-doped TiO₂ consists of overlapping single absorption bands, each one of which reflects absorption by the constituent color centers. Kinetics of formation and accumulation of these color centers (Ti³⁺ centers) have been assessed. The electron nature of the color centers has been unraveled by the effect(s) that hydrogen and oxygen have on the photocoloration of TiO₂ under UV radiation and by the photobleaching of the photoinduced defect states by red light (λ > 610 nm). A model is described that pertains to the stabilization of such color centers by the azide anions through a defect charge compensation effect. Different mechanisms prevail for the physical relaxation of the electronic subsystem and for the chemical pathways when the N-doped metal oxide is subjected to UV-light or to visible-light irradiation.

1. Introduction

Spectral sensitization of the photoactivity of solid photocatalysts by low-energy photons is one of the major challenges facing researchers in heterogeneous photochemistry. An effective solution to this challenge would allow utilization of a sufficient portion of the solar emitted UV–visible wavelengths to irradiate such solids in practical applications. However, this problem must be seen against increasing the activity of photocatalysts, which from a basic point of view typically requires photons of high energy to drive successfully the interfacial processes in heterogeneous systems, thereby denying the utilization of small band gap solids (true semiconductors). For the latter, light absorption is very efficient in the visible spectral region, albeit their photoactivity tends to be negligible or otherwise nonexistent.

Accordingly, some compromise between these two issues must be found to produce the next generation of visible-light-active photocatalysts. A possible solution, prompted by the mechanism of natural photosynthesis, is the formation of intermediate energy states within the band gap of the semiconductor photocatalysts to facilitate multistep excitation to higher energy levels utilizing a smaller fraction (multiphoton) of lower energy quanta. In such solid photocatalysts, the role in forming such intermediate states within the forbidden band gap belongs to intrinsic defects and impurities. In other words, creation of defects within the bulk and/or at the surface with certain

desirable properties makes it possible to excite the photocatalyst to higher energy states with lower energy photons, sufficiently to initiate surface photochemical processes.

The approach to create intermediate energy levels by doping with transition metal ions has been employed in many studies in the last few decades,^{1–3} although without much success mostly because of the added role of such defects to act as recombination centers of photogenerated charge carriers or because of the chemical instability of the metal dopants. However, promising results have been forthcoming with non-metal doping of photocatalysts such as TiO₂ during the past few years. In particular, a successful candidate for a photocatalyst that is sensitive to visible-light activation is N-doped TiO₂.^{4–14} Asahi et al.⁴ reported that N-doping of TiO₂ shifts the absorption edge of TiO₂ in the TiO_{2–x}N_x specimens to lower energies, thereby increasing the photoactivity in the visible-light region through a narrowing of the TiO₂ band gap. Some studies,^{6,8,11,13,15} however, have proposed that electronic transitions in these doped TiO₂ subsequent to visible-light irradiation involves electronic transitions from localized band gap states to the conduction band (CB) of this metal oxide. Since these reports appeared, however, a lively debate in the recent literature^{6,11,13,15} has centered on the causes that lead the absorption onset of TiO₂ to be shifted to the visible region.

Most proposed methods of photocatalyst synthesis are reductive and thus should lead to the formation of corresponding intrinsic defects such as anion vacancies and Ti³⁺ states. Formation of such intrinsic defects is also favorable from a physical point of view to compensate for the excess negative charge brought about by replacement of O^{2–} anions with N^{3–}

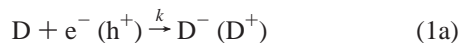
* Corresponding authors. E-mail: emeline_av@hotmail.com (A.V.E.) and nick.serpone@unipv.it or nickser@alcor.concordia.ca (N.S.).

[†] St. Petersburg State University.

[‡] Università di Pavia.

anions.¹⁶ In recent studies, Kuznetsov and Serpone^{17,18} have argued that visible-light absorption by TiO₂ corresponds to absorption by the intrinsic defects regardless of the method of their formation (thermal or photochemical reduction or both, plasma treatment, and metal and nonmetal doping, among others). Consequently, the type and role of impurities and intrinsic defects in visible-light-sensitive N-doped TiO₂ specimens remains uncertain.

One approach that can provide information about defects existing in solids is the examination of photocoloration of such solids.^{19–21} Most metal oxides, including TiO₂, belong to the class of photoresistant solids.^{19,22,23} This means that photoinduced defects are formed as a result of charge carrier trapping by the pre-existing defects (reaction 1), a result of which is the



appearance of new absorption bands corresponding to the photoinduced defects (D^- and D^+) in the absorption spectra of these metal-oxide solids, whereas the absorption features corresponding to the pre-existing defects (D) are bleached. Typically, there are also processes of decay of photoinduced defects (color centers) resulting from different physical processes such as thermo- and photoionization, recombination with a charge carrier of the opposite sign, and tunnel recombination with the complementary defects, among others.

The rate of photocoloration is given by expression 2, whereas the saturation level of photocoloration is illustrated by eq 3.

$$\frac{d[D^-]}{dt} = k[e^-][D] - k_{\text{dec}}[D^-] \quad (2)$$

$$[D^-]_{t \rightarrow \infty} = \frac{k[e^-][D]_{t=0}}{k[e^-] + k_{\text{dec}}} \quad (3)$$

Accordingly, the study of photocoloration of solids provides an opportunity to investigate both pre-existing and photoinduced defects. Moreover, it allows some deductions to be made regarding the mechanisms of their formation and decay. The present article reports the results of a study of photoinduced defect formation in a N-doped titanium dioxide specimen and describes a possible model for the stabilization of the color centers by the nitrogen anionic (azide) dopant.

2. Experimental Section

The powdered N-doped TiO₂ examined was the TP-S201 product obtained from Sumitomo Chemical Ltd., Japan. The specific surface area of this sample (BET method) is $\sim 140 \text{ m}^2 \text{ g}^{-1}$ using the nitrogen gas adsorption protocol; the average crystallite size is $\sim 12 \text{ nm}$ (manufacturer's data). X-ray diffraction (XRD) structural methods confirmed the structure of TiO₂ in the TiO_{2-x}N_x sample to be solely anatase. X-ray photoelectron spectroscopic (XPS) data confirmed the presence of nitrogen in the TiO_{2-x}N_x specimen ($x < 0.01$) and the existence of Ti–N bonds. The XRD (Figure S1) and XPS (Figure S2) data are given in Supporting Information.

A powdered sample of TiO_{2-x}N_x was contained in a quartz cell (loading, ca. 0.5 g; path length of reactor cell, 3 mm; illuminated area, 7 cm²) connected to a high-vacuum setup equipped with an oil-free pumping system. The ultimate gas pressure in the reaction cell was approximately 10^{-7} Pa .

Irradiation of the solid samples (ca. 15 min) was carried out with a 120 watt high-pressure mercury lamp (DRK-120; MELZ, Russia; light irradiance, $\rho \approx 2 \times 10^{16} \text{ photons cm}^{-2}$). Cutoff and bandpass filters from a standard set of colored glass filters (Vavilov SOI) were used to select the spectral regions for sample photoexcitation.

Diffuse reflectance spectra (R) were recorded on a Specord M-40 spectrophotometer equipped with an integrating sphere assembly (Karl Zeiss, Jena, Germany); BaSO₄ was the reference. Data processing was carried out through an interface to a personal computer. In the experiments, the moveable high-vacuum setup/quartz cell system was moved as a single unit between the positions of irradiation and thermal treatment of the sample to a position for recording the spectra; it was anchored at both positions with high precision.

Ubiquitous organic impurities and adsorbed molecules on the sample surface were removed by thermal pretreatment ($T = 700 \text{ K}$) in an O₂ atmosphere ($P = 100 \text{ Pa}$) and in vacuum. The pretreatment procedure was carried out until gas evolution no longer occurred in the reactor during sample heating and spectral changes were no longer observed. The experimental reproducibility of the original absorption spectra was within $\Delta R = \pm 0.001$. A detailed description of the sample treatment is given in Supporting Information. Hereafter, the difference diffuse reflectance is defined as $\Delta R = R_0 - R_{\text{tr}}$, where R_0 is the diffuse reflectance of the initial state of the sample and R_{tr} is the diffuse reflectance of the sample after irradiation (or after some other treatment). Provided that transmittance of the sample $T = 0$ then, $\Delta R = \Delta A = A_{\text{tr}} - A_0$, where A is absorbance (that is, the fraction of light absorbed by the sample). Thus, a positive difference in the absorption spectra ($\Delta R > 0$) refers to the growth of the induced defects (i.e., photocoloration), whereas a negative difference ($\Delta R < 0$) refers to the abatement of the color centers (i.e., photobleaching). Note also that, as demonstrated in our earlier studies,²⁴ $\Delta R = (\text{const}) \times \Delta\alpha$, where $\alpha = \sigma N$ (σ is the cross section of light absorption by the defects, and N is the concentration of defects) is the absorption coefficient of the sample. The latter is correct provided that the photoinduced formation of defects occurs in a thin layer of the powdered sample supported by the scattering media (i.e., noncolored part of the sample).

Reproduction of the original state of the samples between experiments was achieved by heating the samples in oxygen for approximately 1 h before each experiment. Reproduction was considered satisfactory when the difference between the spectra of the initial state of the sample in each set of experiments was not greater than the experimental error ($\Delta R = \pm 0.001$). In other words, the initial state (before irradiation) of the sample always displayed the same DRS spectrum as that illustrated in Figure 1, a spectrum that is typical of N-doped TiO₂ systems.

3. Results

3.1. Photoinduced Defect Formation in Vacuum. Irradiation of the pretreated N-doped TiO₂ sample in vacuum at different wavelengths causes changes in the sample absorption. The resulting absorption spectra of photoinduced color centers are depicted in Figure 2a, and the corresponding kinetics of photocoloration on irradiation at different wavelengths in vacuum are presented in Figure 2b. Note that the time range between the time of termination of irradiation and the time of spectra recording varied from 5 to 15 min giving the reproducible absorption spectra. This means that irradiation in vacuum creates the stable photoinduced defects.

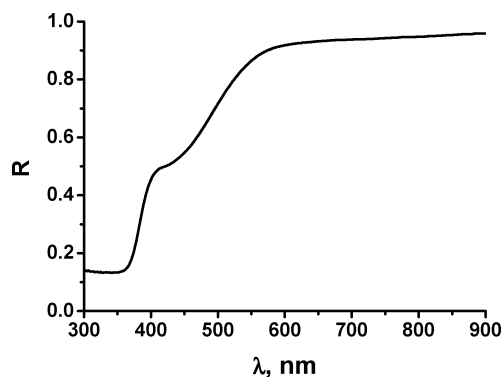


Figure 1. DRS spectrum of the initial state (before irradiation) of the pretreated sample.

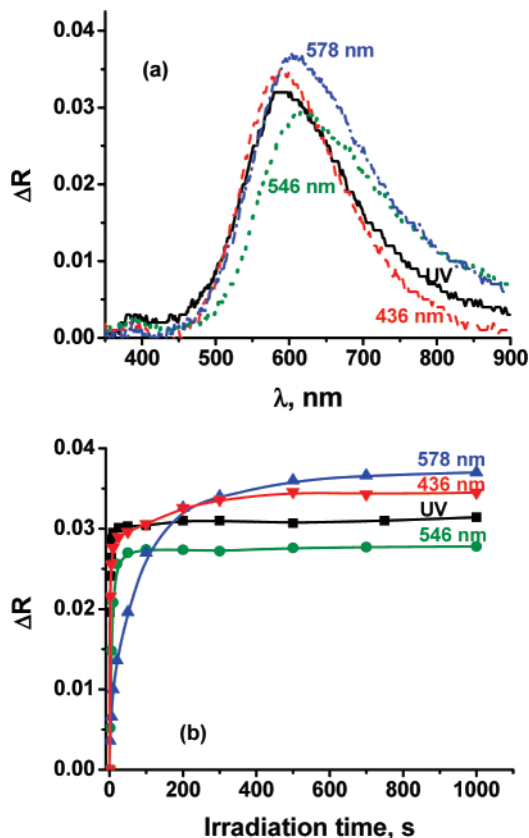


Figure 2. (a) Absorption spectra of N-doped TiO₂ after pre-irradiation in vacuum for 15 min at the indicated different wavelengths. (b) Corresponding kinetics of photocoloration of the N-doped TiO₂ at the different wavelengths in vacuum (monitored at $\lambda = 595$ nm).

The spectroscopic results clearly show some similarities in the observed spectral changes after pre-irradiation in vacuum. However, the position of the band maxima and the band shapes are affected by the irradiation wavelengths of the incident actinic light. This infers that the absorption spectra of newly formed photoinduced color centers are complex and result from an overlap of single absorption bands and that the mechanisms of sample photoexcitation are different at different wavelengths. That is, photocoloration of N-doped TiO₂ is a spectrally selective process. This inference is also confirmed by the kinetics of photocoloration reported in Figure 2b, which display rapidly rising curves to a saturation level, with the ultimate level of saturation depending on the wavelength of the actinic light.

In general, the saturation level of photocoloration of the metal oxide at the longer irradiation wavelengths is expected to increase should the mechanism of photocoloration be the same

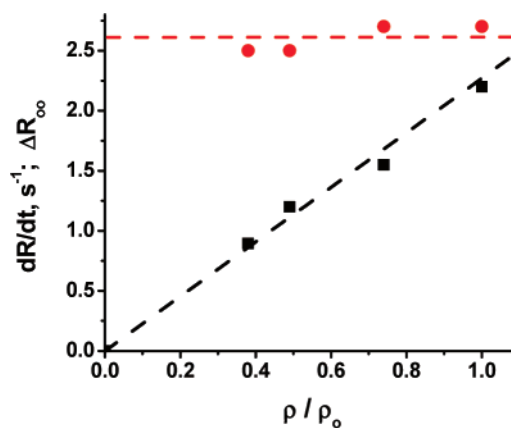


Figure 3. Initial rate (solid squares) and saturation level of photocoloration (ΔR_{∞} ; solid circles) of N-doped TiO₂ under UV photoexcitation at different light irradiances (monitored at $\lambda = 595$ nm).

at all wavelengths. Indeed, in accordance with the diffuse reflectance spectrum of N-doped TiO₂ (see Figure 1), at the longer irradiation wavelengths, a smaller fraction of the incident light is absorbed by the sample, and thus, a larger volume of the powdered sample is irradiated by the light wavelengths at which the photoinduced color centers are formed. Consequently, the ultimate number of photoinduced color centers is expected to be greater at the longer wavelengths, if their formation does not depend on the incident light irradiance. Germane to this expectation, Figure 3 illustrates the dependence of the initial rate and the saturation level of photocoloration on the intensity of the incident actinic light under UV photoexcitation. A similar behavior was observed at other selected irradiation wavelengths. Thus, as evident from the kinetic manifestations in Figure 2b, the expected tendency in the saturation level of photocoloration is observed for the set of wavelengths UV (365 nm), 436 and 578 nm, but not for the 546 nm wavelength which is off the expected trend. This points to a significant difference in the mechanism of defect formation. The latter demonstrates a certain spectral selectivity of photoinduced formation of defects.

3.3. Influence of Photostimulated Adsorption of Gases on Photocoloration. The major objective here was to examine the photostimulated formation of defects in the presence of gaseous hydrogen and oxygen and, consequently, explore the effect(s) of photostimulated adsorption of these gases on the photocoloration of TiO₂ in the N-doped sample. Oxygen is a typical electron-acceptor molecule, whereas hydrogen represents a typical electron-donor molecule, both of which are often used to identify the nature of the color centers.

Figure 4a illustrates the absorption spectra of photoinduced color centers in N-doped TiO₂ formed during irradiation with UV light in vacuum and in the presence of oxygen and hydrogen ($p_0 = 100$ Pa). The corresponding kinetics of photocoloration are displayed in Figure 4b. Evidently, the photostimulated adsorption of oxygen causes a slight decrease in the saturation level of photocoloration compared with the level in vacuum, whereas the presence of molecular hydrogen increases the saturation level of photocoloration relative to that seen in vacuum. This is a typical behavior of electron-type color centers also observed earlier in other metal oxide specimens.^{19,25}

The experimental results suggest that the photoinduced color centers formed in UV light irradiated N-doped TiO₂ samples either are located mostly in the bulk or else are relatively inactive toward both hydrogen and oxygen adsorption at the TiO₂ surface, as no significant spectral changes were observed following the introduction of the gases into the reactor and thus at the surface of the pre-irradiated samples.

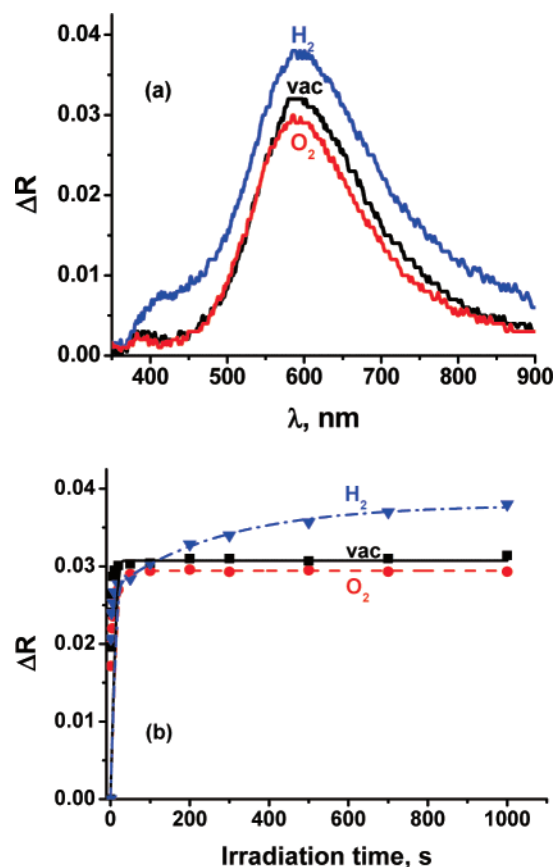


Figure 4. (a) Absorption spectra of UV-induced color centers in N-doped TiO₂ obtained after pre-irradiation in vacuum and in the presence of oxygen and hydrogen. (b) Corresponding kinetics of the UV-induced coloration of N-doped TiO₂ during irradiation in vacuum and in the presence of oxygen and hydrogen (monitored at $\lambda = 595$ nm).

The effect of the presence of oxygen and hydrogen on the photostimulated formation of defects on irradiation of TiO_{2-x}N_x with visible light at 546 nm is displayed in Figure 5a; the corresponding kinetics of formation and accumulation of photoinduced color centers are illustrated in Figure 5b. Similar behaviors were also observed on irradiation at the wavelengths 436 and 578 nm. While the influence of hydrogen on photocoloration under irradiation at 546 nm is nearly the same (Figure 5a,b) as under UV irradiation (Figure 4a,b), that is, the number of photoinduced defects increases, the consequence of the photostimulated adsorption of oxygen is the exact opposite to that seen under UV irradiation. In other words, the saturation level of photocoloration in the presence of oxygen is increased considerably under 546 nm irradiation relative to the level in vacuum and relative to what is observed under UV-light irradiation (see Figure 4a,b). This infers that the mechanism of photoexcitation and surface photoreaction under visible-light excitation of the TiO_{2-x}N_x specimen in the presence of oxygen differs from those processes that take place under UV irradiation.

The effect of photobleaching of the photoinduced color centers by red light at wavelengths longer than 610 nm in vacuum and in the presence of oxygen and hydrogen is demonstrated in Figure 6. The experimental data show that no significant changes in the absorption of photoinduced color centers occur during photoexcitation in vacuum and in the presence of hydrogen. By contrast, the presence of oxygen significantly increases the effect of photobleaching of the UV-induced defects, a typical behavior of electron-type color centers.^{19,21}

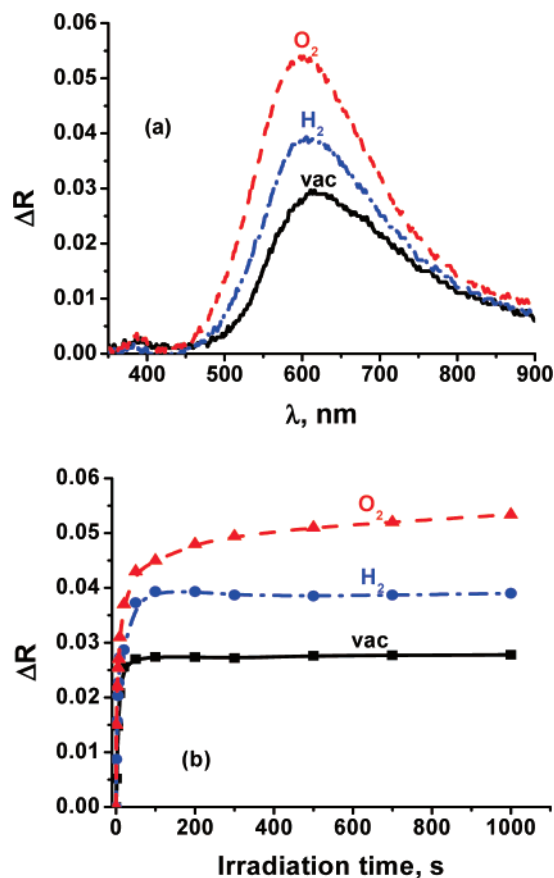


Figure 5. (a) Absorption spectra of photoinduced color centers in N-doped TiO₂ obtained after pre-irradiation at 546 nm in vacuum, in the presence of oxygen, and in the presence of hydrogen. (b) Corresponding kinetics of photoinduced coloration in N-doped TiO₂ during irradiation at 546 nm in vacuum and in the presence of oxygen and hydrogen (monitored at $\lambda = 595$ nm).

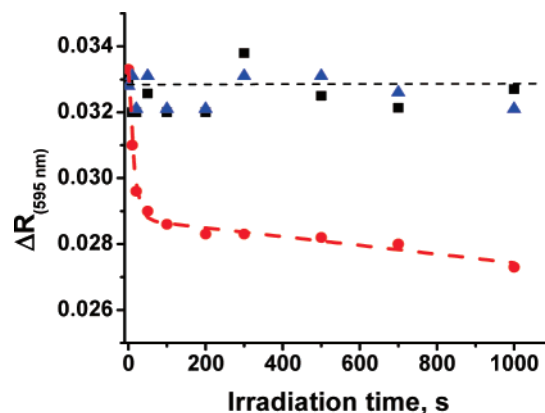
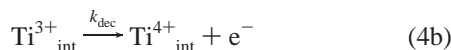
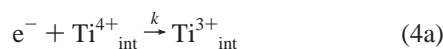


Figure 6. Kinetics of photobleaching (recorded at $\lambda = 595$ nm) of photoinduced color centers on irradiation of TiO_{2-x}N_x by the red light wavelengths ($\lambda > 610$ nm) in vacuum (■), in the presence of oxygen (●), and in the presence of hydrogen (▲).

4. Discussion

In earlier studies,^{19,21,25} we reported that the major mechanism of photoinduced formation of defects (color centers) in metal oxides is a process that implicates trapping of photogenerated free charge carriers by pre-existing lattice defects such as, for example, anion (V_a) and cation (V_c) vacancies, interstitially located cations (Ti⁴⁺_{int}), and impurities, among others. The absorption band of photoinduced color centers observed in N-doped TiO₂ after irradiation in vacuum is attributed to electronic Ti³⁺ states^{26,27} formed as a result of the trapping of

electrons by disordered cations such as titanium(IV) interstitials $\text{Ti}^{4+}_{\text{int}}$ (reaction 4a); reaction 4b expresses the decay of the color center.



To the best of our knowledge, this is the very first observation of stable photoinduced Ti^{3+} defects in titanium dioxide. Such defects are typically short-lived and can only be observed by time-resolved fast spectroscopic techniques.^{28,29} We deduce that this stabilization of Ti^{3+} states is caused by the N-doping and originates from a compensation effect of the nitrogen localized band gap states on the intrinsic defects in TiO_2 .

As evidenced earlier by the experimental data, the absorption spectra of photoinduced color centers are complex. A numerical analysis performed according to the Alentsev–Fock method³⁰ shows that these spectra are formed by an overlap of (at least) two bands with maxima at 1.80 eV (687 nm) and 2.08 eV (594 nm); the corresponding widths at half-maximum amplitude are 0.50 and 0.46 eV, respectively. Photoexcitation of the N-doped TiO_2 at different wavelengths in the visible spectral range alters the ratio between these two absorption bands. This infers that the two bands belong to two different defect states that probably differ in the surrounding environment. Ultimately, the environment also determines the dominant process of photoexcitation, which leads to the favorable formation of a certain type of defects, a manifestation of the spectral selectivity of photo-stimulated formation of defects.

Equation 3 that described the saturation level of photocoloration can be rewritten in the case of the formation of photoinduced Ti^{3+} states as,

$$[\text{Ti}^{3+}]_{t \rightarrow \infty} = \frac{k[\text{e}^-][\text{Ti}^{4+}]_{t=0}}{k[\text{e}^-] + k_{\text{dec}}} \quad (5)$$

Equation 5 can also be obtained from the rate of formation of photoinduced Ti^{3+} states, as given by expression 6, on the basis

$$\frac{d[\text{Ti}^{3+}]}{dt} = k[\text{e}^-][\text{Ti}^{4+}] - k_{\text{dec}}[\text{Ti}^{3+}] \quad (6)$$

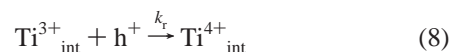
of reactions 4a and 4b and on application of the steady-state approach to the formation of Ti^{3+} and from considerations that $[\text{Ti}^{4+}] = [\text{Ti}^{4+}]_0 - [\text{Ti}^{3+}]$.

Taken together, eqs 5 and 6 imply that if the decay constant k_{dec} were of the monomolecular type, that is, the decay of color centers were spontaneous (as might be caused by thermooxidation), the initial rate of photocoloration would then scale linearly (see also below) with light irradiance ρ , as observed in Figure 3.

Both $[\text{e}^-] = g_e \tau_e$ and $[\text{h}^+] = g_h \tau_h$ scale linearly with light irradiance ρ (that is, $g \propto \rho$), where g is a function of the photogeneration of free charge carriers and τ is their lifetime. Accordingly, since the electron concentration scales linearly with light irradiance, that is, $[\text{e}^-] = \text{const} \times \rho$, eq 5 can then be rewritten as expression 7

$$[\text{Ti}^{3+}]_{t \rightarrow \infty} = \frac{a\rho[\text{Ti}^{4+}]_{t=0}}{a\rho + k_{\text{dec}}} \quad (7)$$

(where a is a constant) indicating that the saturation level of Ti^{3+} depends on light irradiance (provided k_{dec} is irradiance independent). Clearly, the saturation level of photocoloration would then be described by a sublinear growth to saturation with an increase in light irradiance, ρ , as deduced from eq 7. However, the latter inference contrasts with the experimental results reported in Figure 3. The experimental behavior finds an explanation on the assumption that the decay of photoinduced Ti^{3+} states may be caused by the recombination of the trapped electrons with the photoholes h^+ (reaction 8). With this premise,



k_{dec} effectively becomes $k_{\text{dec}} = k_t[\text{h}^+]$ and $k_{\text{dec}} = (b\rho)$ considering that the concentration of h^+ also depends linearly on ρ . The initial rate still scales linearly with light irradiance (eq 9; note

$$\frac{d[\text{Ti}^{3+}]}{dt} = (a[\text{Ti}^{4+}] - b[\text{Ti}^{3+}])\rho \quad (9)$$

the lack of a power dependence on ρ), but the saturation level of photocoloration is then independent of light irradiance (eq 10) in line with observations reported in Figure 3.

$$[\text{Ti}^{3+}]_{t \rightarrow \infty} = \frac{a\rho[\text{Ti}^{4+}]_{t=0}}{(a + b)\rho} \quad (10a)$$

$$[\text{Ti}^{3+}]_{t \rightarrow \infty} = \frac{a[\text{Ti}^{4+}]_{t=0}}{(a + b)} \quad (10b)$$

Thus, the decay of photoinduced color centers in N-doped TiO_2 during irradiation is due to the trapping (recombination) of free holes by photoinduced Ti^{3+} states (trapped electrons). This mechanism is rather typical in solid-state physics as it describes a simple model of the behavior of deep traps in solids.

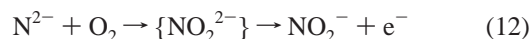
Surface photochemical reactions are closely associated with photophysical processes in the photocatalysts as they affect the electronic subsystems of the solids. This connection is manifested by the influence that surface photoreactions have on the photocoloration of solids. A detailed analysis of this effect and its general mechanism was presented earlier.^{19–21} It suffices to note that, for electron-type color centers, the number of these defects is expected to increase for a photoreaction involving electron-donor molecules (e.g., hydrogen) and to decrease for a surface photoreaction involving electron-acceptor molecules such as molecular oxygen.^{19,21} The influence of the photoadsorption of hydrogen and oxygen on the photocoloration of TiO_2 observed under UV-light photoexcitation conforms completely to the expectations about the electron type of photoinduced color centers (viz., Ti^{3+} centers) examined experimentally in the present study. A simple interpretation of such behavior can be deduced in light of eq 5.

Surface photochemical reactions involve free charge carriers and therefore change the corresponding probabilities of formation and decay of photoinduced color centers. In particular, the photostimulated adsorption of oxygen causes a decrease in the concentration of free electrons, whereas photoadsorption of hydrogen leads to a decrease in the concentration of photoholes. Consequently, a decrease of the electron concentration caused by the photoreduction of oxygen results in a decrease of the saturation level of accumulation of Ti^{3+} states, whereas a decrease of the concentration of holes induced by the photo-

adsorption of hydrogen leads to the effective decrease of k_{dec} and thus to an increase in the ultimate number of photoinduced color centers. Note also that hydrogen photoadsorption causes an increase of the absorption around 400 nm (Figure 4a) revealing yet another type of photoinduced defect of the electron-type in N-doped TiO_2 . This absorption was ascribed earlier^{17,26} to being associated with oxygen vacancies. The increase in absorption of the ~ 400 nm band impacts negatively on earlier reported inferences that light absorption in the visible spectral range induced by N-doping of TiO_2 is the result of band gap narrowing of TiO_2 in $\text{TiO}_{2-x}\text{N}_x$ samples⁴ or the result of formation of subbands of nitrogen states in $\text{TiO}_{2-x}\text{N}_x$,¹² since in both scenarios these states are completely occupied by electrons.

A curious behavior is observed in the effect that surface photoreactions have on photocoloration under photoexcitation of $\text{TiO}_{2-x}\text{N}_x$ in the visible spectral region. While the effect of hydrogen photooxidation induced by visible light is similar to the effect observed under UV-light photoexcitation, in accord with the proposed model, the influence of the photoadsorption of oxygen is entirely the opposite. That is, under visible-light irradiation, the photoadsorption of oxygen increases the number of photoinduced Ti^{3+} color centers (Figure 5). In terms of a revised model, the only possible explanation is that different pathways of physical and chemical relaxation of the heterogeneous system prevail under visible-light photoexcitation compared with pathways that prevail under UV-light irradiation. To the extent that the influences of oxygen and hydrogen on photocoloration are similar, we deduce that in both cases the origin(s) of the effect is the same, namely, the effective decrease of k_{dec} caused by a decrease in the concentration of photoholes. In turn, this means that the hole states generated by UV- and visible-light excitation must be different and display different reactivities toward molecular oxygen. Under typical experimental conditions, the surface-localized hole states are of the O_s^- types. These hole states are very active toward the photooxidation of hydrogen. By contrast, interaction of these hole states with molecular oxygen yields O_3^- surface complexes that are typically observed only at low temperatures. Accordingly, we need to look elsewhere for the nature of the hole states.

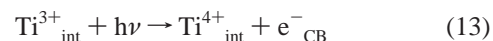
In the N-doped TiO_2 specimen, nitrogen anionic (N^{3-}) dopants potentially play the role of hole traps (reaction 11) because of the excess negative charge in comparison with oxygen anions O^{2-} . Considering that under our experimental conditions the possible interaction of N^{2-} species with molecular oxygen may produce NO_2^{2-} or equivalent species (reaction 12), we should then observe an effect of the photoadsorption of oxygen on the photocoloration of the metal oxide, in



complete accord with experimental observations. Relevant to this inference, Kisch and co-workers¹³ reported formation of hyponitrite at the surface of $\text{TiO}_{2-x}\text{N}_x$ along with nitrite and nitrate species (also in the bulk). At the same time, this also points to a distinct possibility that different chemistries might occur under visible-light excitation relative to those that take place under UV-light irradiation. Related experimental studies in this area are currently in progress and will be reported elsewhere.³¹

Photobleaching of photoinduced electron-type color centers in metal oxides demonstrates that light absorption in the corresponding absorption band implicates photoionization through

electronic transitions from the defect energy levels to the conduction band (reaction 13),^{19,21} albeit this needs confirmation by photoconductivity and other similar studies.¹⁸ A similar mechanism was proposed by Komaguchi et al.³² for the



photobleaching of Ti^{3+} sites in thermally reduced pristine nondoped TiO_2 samples. In this case, the effective decay rate constant (reaction 1b) is given by $k_{\text{dec}} = \sigma\rho$, where σ is the cross section of the photoionization of the defect (color center). Komaguchi et al.³² also noted that the EPR signal of the photobleached Ti^{3+} sites is restored fairly rapidly after termination of the irradiation, even at low temperatures. This accords with our observations of negligible photobleaching in vacuum. Consequently, we can infer that electron trapping by Ti^{4+} cations in defect positions (interstitials) is a very efficient process. Oxygen interaction with surface electrons precludes back electron trapping by the Ti^{4+} states and therefore increases the rate of photobleaching of the defects (color centers), whereas hydrogen has no effect on photobleaching. This behavior is consistent with our assignment of the absorption spectra (Figures 2a, 4a, and 5a) to electron-type color centers. A more detailed description of the effect of surface photoreactions on the photobleaching of color centers was given earlier.^{20,21}

5. Concluding Remarks

Three major results obtained in this study are worth summarizing. First, the visible-light absorption induced by N-doping of TiO_2 is complex and is formed by an overlap of at least two (or more) single absorption bands that correspond to different electronic states with different mechanisms of photoexcitation. This conclusion is supported by the demonstration of the spectral variation of photocoloration as a function of wavelength of the actinic light. The appearance of an additional absorption band in a wide spectral range with maximum at approximately 400 nm during the photocoloration in the presence of hydrogen also infers that the N-doping induced visible absorption belongs to different localized electronic states. Accordingly, the shift of the absorption edge of N-doped TiO_2 to longer wavelengths cannot be attributed to band gap narrowing or to the formation of bands of nitrogen delocalized states within the band gap. Following the conclusions reached by Kuznetsov and Serpone¹⁷ and by Serpone,¹⁸ we find that these states likely correspond to such intrinsic defects in TiO_2 as anion and oxygen vacancies (i.e., F^{++} , F^+ , and F centers). The role of N-doping thus lies in the stabilization of these defects (color centers) as a result of the defect charge compensation effect. Second, photoexcitation of N-doped TiO_2 in the UV and/or visible spectral regions can also lead to the generation of photoinduced defects (color centers) that can be ascribed to Ti^{3+} states formed by electron trapping by Ti^{4+} cations located in defect sites. The electron nature of these color centers is demonstrated by the observed effect of hydrogen and oxygen on photocoloration under UV irradiation and by the photobleaching of photoinduced defects by red light at wavelengths longer than 610 nm. Third, the effect of oxygen photoadsorption on the photocoloration induced by visible-light irradiation suggests that different mechanisms of physical relaxation and different chemical pathways must prevail under visible light relative to UV irradiation. In particular, we expect different interactions between oxygen and the surface of N-doped TiO_2 samples photoexcited at different wavelengths. That is, we expect to see spectral photochemical selectivity.

Acknowledgment. The work in Pavia was supported by the Ministero dell'Università e Ricerca (MUR, Roma to N.S.). We also wish to thank Dr. V. N. Kuznetsov of the State University of St. Petersburg, Russia, for his kind help with the numerical analysis of the absorption bands of photoinduced defects.

Supporting Information Available: X-ray diffraction pattern (XRD) illustrated in Figure S1, the X-ray photoelectron spectrum (XPS) of the N-doped TiO₂ specimen given in Figure S2, and a detailed procedure of the sample treatment and the absorption spectrum (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Serpone, N.; Lawless, D.; Disdier, J.; Herrmann, J.-M. *Langmuir* **1994**, *10*, 369.
- (2) Gracia, F.; Holgado, J. P.; Caballero, A.; Gonzalez-Elipse, A. R. *J. Phys. Chem. B* **2004**, *108*, 17466.
- (3) Mattsson, A.; Leideborg, M.; Larsson, K.; Westin, G.; Osterlund, L. *J. Phys. Chem. B* **2006**, *110*, 1210.
- (4) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- (5) Sakthivel, S.; Kisch, H. *Chem. Phys. Chem.* **2003**, *4*, 487.
- (6) Irie, H.; Watanabe, Y.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 5483.
- (7) Yin, S.; Yamaki, H.; Komatsu, M.; Zhang, Q.; Wang, J.; Tang, Q.; Saito, F.; Sato, T. *J. Chem. Mater.* **2003**, *13*, 2996.
- (8) Lindgren, T.; Mwabora, J. M.; Avendano, E.; Jonsson, J.; Granqvist, C.-G.; Lindquist, S. E. *J. Phys. Chem. A* **2003**, *107*, 5709.
- (9) Torres, G. R.; Lindgren, T.; Lu, J.; Granqvist, C.-G.; Lindquist, S.-E. *J. Phys. Chem. B* **2004**, *108*, 5995.
- (10) Diwald, O.; Thompson, T. L.; Zubkov, T.; Goralski, E. G.; Walck, S. D.; Yates, J. T. *J. Phys. Chem. B* **2004**, *108*, 6004.
- (11) Nakamura, R.; Tanaka, T.; Nakata, Y. *J. Phys. Chem. B* **2004**, *108*, 10617.
- (12) Mrowetz, M.; Balcerski, W.; Colussi, A. J.; Hoffmann, M. R. *J. Phys. Chem. B* **2004**, *108*, 17269.
- (13) Sakthivel, S.; Janczarek, M.; Kisch, H. *J. Phys. Chem. B* **2004**, *108*, 19384.
- (14) Fu, H.; Zhang, L.; Zhang, S.; Zhu, Y. *J. Phys. Chem. B* **2006**, *110*, 3061.
- (15) Di Valentin, C.; Pacchioni, G.-F.; Selloni, A. *Phys. Rev. B* **2004**, *70*, 085116.
- (16) Di Valentin, C.; Pacchioni, G.-F.; Selloni, A.; Livraghi, S.; Giamello, E. *J. Phys. Chem. B* **2005**, *109*, 11414.
- (17) Kuznetsov, V. N.; Serpone, N. *J. Phys. Chem. B* **2006**, *110*, 25203.
- (18) Serpone, N. *J. Phys. Chem. B* **2006**, *110*, 24287.
- (19) Emeline, A. V.; Kataeva, G. V.; Litke, A. S.; Rudakova, A. V.; Ryabchuk, V. K.; Serpone, N. *Langmuir* **1998**, *14*, 5011.
- (20) Emeline, A. V.; Petrova, S. V.; Ryabchuk, V. K.; Serpone, N. *Chem. Mater.* **1998**, *10*, 3484.
- (21) Emeline, A. V.; Kataeva, G. V.; Ryabchuk, V. K.; Serpone, N. *J. Phys. Chem. B* **1999**, *103*, 9190.
- (22) Ryabchuk, V. K.; Burukina, G. V. *Sov. J. Phys. Chem.* **1991**, *65*, 1621.
- (23) Defects and Impurity Centers in Ionic Crystals: Optical and Magnetic Properties, Part 1. *J. Phys. Chem. Solids* **1990**, *51*, Issue No. 7.
- (24) Burukina, G. V.; Vitkovsky, G. E.; Ryabchuk, V. K. *Vestn. Leningr. Univ., Ser. 4: Fiz., Khim.* **1990**, *25*, 93.
- (25) Emeline, A. V.; Kataeva, G. V.; Panasuk, A. V.; Ryabchuk, V. K.; Sheremetyeva, N.; Serpone, N. *J. Phys. Chem. B* **2005**, *109*, 5175.
- (26) Sekiya, T.; Ichimura, K.; Igarashi, M.; Kurita, S. *J. Phys. Chem. Solids* **2000**, *61*, 1237.
- (27) Lu, T.-C.; Wu, S.-Y.; Lin, L.-B.; Zheng, W.-C. *Physica B* **2001**, *304*, 147.
- (28) (a) Serpone, N.; Lawless, D.; Khairutdinov, R.; Pelizzetti, E. *J. Phys. Chem.* **1995**, *99*, 16655. (b) Sahyun, M. R. V.; Serpone, N. *Langmuir* **1997**, *13*, 5082.
- (29) (a) Colombo, D. F.; Bowman, R. M. *J. Phys. Chem.* **1996**, *100*, 18445. (b) Bahnemann, D. W.; Henglein, A.; Lilie, J.; Spanhel, L. *J. Phys. Chem.* **1984**, *88*, 709.
- (30) Fock, M. V. *Proc. Phys. Inst. Acad. Sci. U.S.S.R.* **1972**, *59*, 3.
- (31) Emeline, A. V.; Ryabchuk, V. K.; Sheremetyeva, N. V.; Serpone, N., work in progress.
- (32) Komaguchi, K.; Nakano, H.; Araki, A.; Harima, Y. *Chem. Phys. Lett.* **2006**, *428*, 338.