FEATURE ARTICLE

Is the Band Gap of Pristine TiO$_2$ Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts?

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Second-generation TiO$_{2-x}$D$_x$ photocatalysts doped with either anions (N, C, and S mostly) or cations have recently been shown to have their absorption edge red-shifted to lower energies (longer wavelengths), thus enhancing photonic efficiencies of photoassisted surface redox reactions. Some of the studies have proposed that this red-shift is caused by a narrowing of the band gap of pristine TiO$_2$ (e.g., anatase, $E_{bg} = 3.2$ eV; absorption edge ca. 387 nm), while others have suggested the appearance of intragap localized states of the dopants. By contrast, a recent study by Kuznetsov and Serpone (*J. Phys. Chem. B*, in press) has proposed that the commonality in all these doped titanias rests with formation of oxygen vacancies and the advent of color centers (e.g., **F**, **F**$^+$, **F**$^{++}$, and Ti^{3+}) that absorb the visible light radiation. This article reexamines the various claims and argues that the red-shift of the absorption edge is in fact due to formation of the color centers, and that while band gap narrowing is not an unknown occurrence in semiconductor physics it does necessitate heavy doping of the metal oxide semiconductor, thereby producing materials that may have completely different chemical compositions from that of TiO$_2$ with totally different band gap electronic structures.

Introduction

As a first-generation material, pristine TiO$_2$ has served well in photoassisted degradation and mineralization reactions of a large number of organic substrates in the quest to dispose of environmental contaminants in aqueous and atmospheric (to some extent also in soils) ecosystems.[1] Unfortunately, this metal oxide possesses a wide band gap (anatase, E_{bg} = ca. 3.2 eV; rutile, E_{bg} = ca. 3.0 eV—see Figure 1a) such that its absorption edge occurs below 400 nm, and thus only about 3–5% of the total sunlight can photoactivate this metal oxide to generate charge carriers (CB electrons and VB holes) that ultimately can be exploited to promote reduction and oxidation surface processes. This inherent property of TiO$_2$ curtails the overall efficiency based on the total solar radiation reaching the Earth's surface. Accordingly, many efforts were expended in the late 1980s to develop second-generation titanium dioxides[2] that could bridge both the UV (290–400 nm) and the visible (400–700 nm) radiation and thereby enhance the overall efficiency. The requirement was to red-shift the absorption edge of TiO$_2$ to wavelengths longer than 400 nm. Attempts toward achieving this goal have rested, in part, on photosensitizing this metal oxide with suitable dyes[3] that acted as visible-light-harvesters, which eventually led to their own degradation,[4] and with suitable metal-ion dopants[2] which unfortunately acted either as recombination centers for the photogenerated charge carriers in some cases[5] or were simply ineffective[6] in aiding the surface redox reactions. Recent studies by Anpo and co-workers[7] showed that the metal-ion implantation technique to produce metal-doped TiO$_2$ can enhance photoinduced surface redox reactions even in the

visible-light region, where the wet chemical method to metal-dope TiO$_2$ failed.[2,5]

First reports of anion-doped TiO$_2$ began to appear in the early 1990s,[8,9] but it was not until the 2001 study by Asahi and co-workers[10] in *Science*, which reported a visible-light-active N-doped TiO$_2$, that researchers in heterogeneous photocatalysis considered anion-doping as a prelude to produce second-generation materials that would increase the photoactivity of this metal oxide over the UV and much of the visible-light region. Subsequent studies reported several other visible-light-active N-doped TiO$_2$s,[11–16] together with C-doped TiO$_2$ [10,17–20] and S-doped TiO$_2$ [21–23] materials.

Since these reports appeared, a lively debate in the recent literature[13,16,24,25] has centered on the causes that lead the absorption onset of TiO$_2$ to be shifted to the visible region (for naked anatase TiO$_2$, 387 nm; for rutile, ca. 413 nm—Figure 1a). Asahi et al.[10,11] proposed that N doping of TiO$_2$ shifts the absorption edge of TiO$_{2-x}$N$_x$ to lower energies and increases the photoactivity in the visible light region through narrowing of the TiO$_2$ band gap. Carbon- and sulfur-doped TiO$_2$ displayed similar red-shifts of the absorption edges and increased photo-activity. Some studies,[12,13,16,24,25] however, proposed that electronic transitions in these doped TiO$_2$ subsequent to visible-light irradiation involve transitions from localized states to the conduction band (CB) of this metal oxide (see, e.g., Figure 1b and 1d).

We reexamine the various claims and argue that the red-shift of the absorption edge is in fact due to the formation of color centers, and that while band gap narrowing is not an unknown occurrence in semiconductor physics it does necessitate heavy doping of the metal oxide semiconductor, thereby producing materials that may have completely different chemical composi-

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Nick Serpone received a B.Sc. (Honors Chemistry, 1964) from Sir George Williams University and a Ph.D. from Cornell University in Physical-Inorganic Chemistry (1968), and then joined Concordia University as Assistant Professor (1968), Associate Professor (1973), and Professor (1980). During this period he spent 4-year leaves in Bologna (1975−76), Lausanne (1983−84), Lyon (1990−91), and Ferrara (1997−98) and was a consultant to 3M's Imaging Sector. He took early retirement from Concordia University as a University Research Professor (1998−2004) and Professor Emeritus (2000). He was Program Director at NSF (1998−2001) and is currently a Visiting Professor at the University of Pavia (2002-). His research interests are in the photophysics and photochemistry of semiconductor metal oxides, imaging science, heterogeneous photocatalysis, environmental photochemistry, and in the photochemistry of sunscreens. He has published over 350 articles and has co-edited four monographs, he was the recipient of the "Best Paper Award" from the Society of Imaging Science & Technology (1997; with Mel Sahyun and Boris Levy), and maintains an active collaboration with researchers at the Institute of Physics of the State University of St. Petersburg (Dr. Ryabchuk, Dr. Emeline, and Dr. Kuznetsov), with Prof. Hidaka (Meisei University), Dr. Horikoshi (Sophia University), and Prof. Albini (Pavia).

tions from that of TiO$_2$ with totally different band gap electronic structures. Among others, these color centers include Ti^{3+} centers, which have been the object of numerous studies as Ti^{3+}-doped oxides are very important in laser materials.[26−31]

The Issue of Band Gap Narrowing

Figure 1b−e illustrates various scenarios of changes that might occur to the band gap structure of TiO$_2$ (Figure 1a) on doping it with nonmetals. Theoretical considerations by Di Valentin et al.[16,32] suggest that for substitutionally N-doped anatase TiO$_2$, the visible light response arises from occupied N

2p localized states located above the valence band edge ($\sim$0.7 eV),[32−35] with interstitial N 2p states lying further up from the valence band.[36] N-doping of TiO$_2$ also creates localized states below the conduction band edge.[33,37] A broad spectral band seen around $410 < \lambda < 535$ nm (3.02−2.32 eV) has been attributed to a set of states centered at $\sim$2.9 eV below the lower edge of the conduction band[12,37] that probably involves color centers associated with oxygen vacancies created during the doping of TiO$_2$.

The presence of localized states near the valence band edge has been said to be at the origin of the visible-light activity of anion-doped TiO$_2$.[10,38−40] This was later supported[32] by EPR evidence of paramagnetic species and DFT calculations, which also inferred the presence of oxygen vacancies sometimes formed in significant number[33] in the nitrogen-doped TiO$_{2-x}$N$_x$. Excitation from such localized states to the conduction band (Figure 1b) would in fact be consistent with the absorption edge shifting to lower energies. However, contrary to implications by some,[10,24,33,41] we argue that this is not band gap narrowing, a point also raised by others.[12,37] The presence of oxygen vacancies correlates with enhanced visible light photoactivity of doped TiO$_2$s,[42,43] with the effect being more evident in TiO$_{2-x}$N$_x$.[10,44,45] For a certain number of oxygen vacancies, a narrow band of defect-derived unoccupied states is produced whose manifestation is experimentally observed at $\sim$2.0−2.5 eV above the valence band edge[46,47] that could be attributed to unoccupied Ti^{3+} states.[36] Other ab initio and DFT calculations by Umebayashi, et al.[22,23] on TiO$_{2-x}$S$_x$ inferred that mixing of S 3p states with O 2p states in the valence band leads to band gap narrowing through a broadening of the valence bandwidth (Figure 1c), a notion also proposed for N-doped TiO$_2$.[10] Such a rigid valence band shift[10,22,23] has recently been questioned,[12,13,25] however.

True narrowing of the original band gap of the metal-oxide semiconductor would necessitate heavy anion or cation doping, which would require high concentrations of the dopants.[34,35] In the latter case, however, it is questionable whether the metal oxide will retain its original integrity.

Absorption Spectra of Color Centers in Doped TiO$_2$

In a recent study, Kuznetsov and Serpone[48] examined a set of heat-induced and photoinduced absorption spectra of various
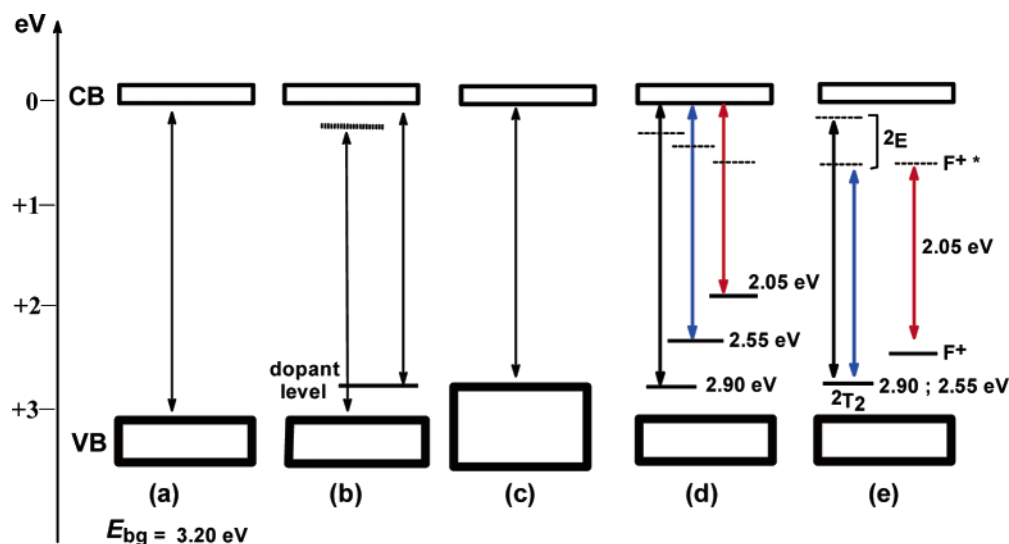

Figure 1. Various schemes illustrating the possible changes that might occur to the band gap electronic structure of anatase TiO$_2$ on doping with various nonmetals: (a) band gap of pristine TiO$_2$; (b) doped TiO$_2$ with localized dopant levels near the VB and the CB; (c) band gap narrowing resulting from broadening of the VB; (d) localized dopant levels and electronic transitions to the CB; and (e) electronic transitions from localized levels near the VB to their corresponding excited states for Ti^{3+} and **F$^+$** centers.
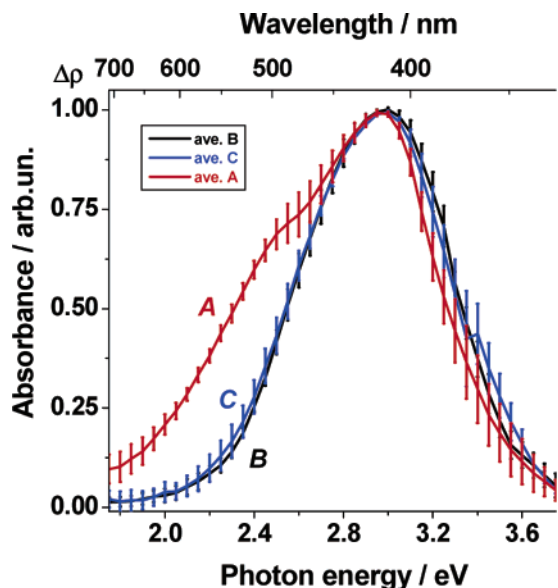
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Figure 2. (A) Mean absorption spectrum of cation-doped TiO_2 from averaging absorption spectra of Fe-doped TiO_2, TiO_2 doped with zinc ferrite, and orange nitrided large $TiO_{2-x}N_x$ clusters. (B) Mean absorption spectrum of the visible-light-active (VLA) TiO_2 obtained from averaging the absorption spectra of Cr-implanted TiO_2, Ce-doped TiO_2, mechanochemically activated N-doped TiO_2, N-doped oxygen-deficient TiO_2, and $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ treated with HNO_3 acid. (C) Average absorption spectrum of various anion-doped titania specimens: N/F-doped TiO_2; N-doped anatase TiO_2; N-doped rutile TiO_2; and yellow nitrided $TiO_{2-x}N_x$ nanocolloids. Adapted from ref 48.
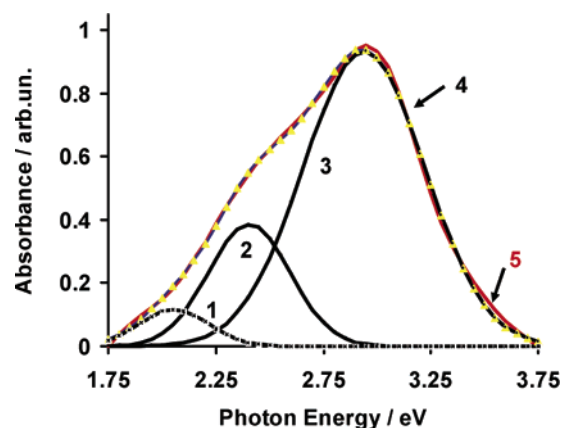

Figure 3. Deconvolution of spectrum A (band 5 herein) in Figure 2. Band 4 is the sum of bands 1, 2, and 3.

Figure 4. Deconvolution of spectrum B (band 5 herein) in Figure 2. Band 4 is the sum of bands 1, 2, and 3.

compositions consisting of Degussa P25 TiO_2 and different polymers. Characterization of the reduced TiO_2 in the polymeric media using absorption spectra revealed that the set of absorption spectra could be represented as the sum of individual Gaussian absorption bands with maxima at about 2.05 eV (605 nm; herein referred to as band 1), 2.55 eV (486 nm; band 2), and 2.90 eV (428 nm; band 3). There were no large changes in the spectral positions and bandwidths at half-maximum-amplitude of the absorption bands of TiO_2 reduced in the organic media when compared to TiO_2 specimens reduced in H_2 or CO environments (after O_2 adsorption only)[19,25] and to reduced anatase crystals.[37] Absorption spectra of visible-light-active (VLA) TiO_2 photocatalysts reported in the literature were also analyzed.[48] Where diffuse reflectance spectra $\{\rho(h\nu)\}$ were reported for these VLA TiO_2 systems, they were digitized and their absorption spectra $\{\Delta\rho(h\nu)\}$ calculated,[48] showing that the resulting relatively narrow spectra bore strong similarities to each other and even astonishingly they were independent of the methods with which these visible-light-active TiO_2 samples were prepared. Of particular interest, when some of the spectra were averaged they could also be described reasonably well by the sum of only two Gaussian absorption bands (2 and 3) at the higher energies.

Spectrum A in Figure 2 illustrates averaged absorption spectra[48] of cation-doped TiO_2 from averaging absorption spectra (A(i)) of Fe-doped TiO_2 prepared by oxidative pyrolysis of organometallic precursors in an induction thermal plasma reactor,[49] (A(ii)) of TiO_2 doped with zinc ferrite synthesized by sol−gel methods followed by calcination at various temperatures,[50] and (A(iii)) of orange nitrided large $TiO_{2-x}N_x$ clusters prepared by a procedure otherwise identical to that of yellow N-doped clusters of TiO_2, but with the former consisting of partially agglomerated nanocolloids, i.e., larger $TiO_{2-x}N_x$.[45] Spectrum B illustrates averaged absorption spectra of visible-light-active TiO_2 obtained from averaging the absorption spectra (B(i)) of Cr-implanted TiO_2,[51] (B(ii)) of Ce-doped TiO_2,[52]
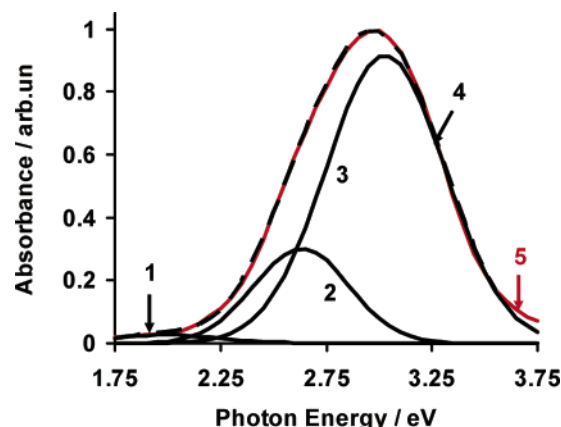
(B(iii)) of mechanochemically activated N-doped TiO_2,[53] (B(iv)) of N-doped oxygen-deficient TiO_2,[44] and (B(v)) of $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ treated with HNO_3 acid[54].

Spectrum C represents the averaged absorption spectrum of various anion-doped titania specimens, namely, (C(i)) N/F-doped TiO_2 prepared by a spray pyrolytic method,[55] (C(ii)) N-doped anatase TiO_2 and N-doped rutile TiO_2 prepared by a solvothermal process,[56] and (C(iii)) yellow nitrided $TiO_{2-x}N_x$ nanocolloids synthesized in short time at ambient temperatures using a nanoscale exclusive direct nitridation of TiO_2 nanocolloids with alkylammonium compounds.[45]

The averaged absorption spectra in Figure 2 have been deconvoluted using a PeakFit software, which allowed the half-maximum peak width to vary and the first band (3) located on the high energy side. Figures 3 and 4 illustrate the reasonably good fit of the deconvoluted spectra A and B of Figure 2; the fitting parameters are reported in Table 1. Spectrum A required three bands 1, 2, and 3 to obtain a good fit (correlation coefficient, 99.85%) as witnessed by comparing the sum of these three bands (curve 4) with the averaged spectrum A (curve 5).

By contrast, although fitted by three bands, spectra B and C could also have been fitted reasonably well with only bands 2 and 3 as evident in Figure 4 and as seen by the amplitude of the bands expressed as percent area in Table 1. Note that band 1 in Figure 4 provides a somewhat negligible contribution to the overall spectral envelope on contrasting its presence (2% area; Table 1) with the uncertainties in the spectra reported in Figure 2 in the lower energy region. Nonetheless, its inclusion did improve the fit somewhat as was evident from the correlation coefficients.

TABLE 1: Summary of Spectral Features and Parameters of Deconvoluted Spectra in Figure 2

spectrum	band	$\Delta\rho_{max}$ eV	λ_{max} nm	area %	fwhm eV	r of fit %
A	1	2.1	590	14	0.66	99.85
	2	2.40 ± 0.05	517	12	0.41	
	3	2.93 ± 0.02	423	74	0.72	
B	1	2.0	620	2	0.59	99.95
	2	2.63 ± 0.06	471	20	0.53	
	3	3.03 ± 0.04	409	78	0.66	
C	1	$1.7-1.8$	$730-690$	2	0.65	99.94
	2	2.52 ± 0.11	492	5	0.53	
	3	2.97 ± 0.03	417	93	0.78	

Also of interest in the tabulated data are the three bands centered around 1.7−2.1 eV (729−590 nm; band 1), at ca. 2.4−2.6 eV (517−477 nm; band 2), and around 2.9−3.0 eV (428−413 nm) for band 3, in good accord with the band positions reported by Kuznetsov and Serpone[48] for the reduction of TiO_2 in polymeric media (see above). The congruence of the bands in the absorption spectra of such disparate TiO_2 systems is remarkable when considering the large variations in the experimental conditions, which points to the notion that the absorption bands must all share the same origin.

Calculations of densities of states of various anatase $TiO_{2-x}D_x$ specimens (dopant D is carbon, nitrogen, fluorine, phosphorus and sulfur) led Asahi and co-workers[10] to propose that substitutional doping of N for O was most effective (apparently) because the N 2p states mix with O 2p states in the valence band and improve the photoactivity through a narrowing of the inherent band gap of TiO_2 (Figure 1c). This increased activity was tested by the photodegradation of methylene blue and gaseous acetaldehyde. Results showed that the photoactivity of $TiO_{2-x}N_x$ under visible irradiation was greater than for undoped TiO_2. However, no significant changes in photoactivity were seen when $TiO_{2-x}N_x$ and TiO_2 specimens were both subjected to UV radiation,[10] contrasting a recent study by Hashimoto et al.[13] who found significant differences in quantum efficiencies in the photodegradation of gaseous 2-propanol upon UV versus visible light irradiation, and this regardless of the extent of N-doping. Torres et al.[37] reported similar observations in their photoelectrochemical studies. In this context, Mrowetz and co-workers[57] report that N-doped TiO_2 failed to oxidize $HCOO^-$ to $CO_2^{-\bullet}$ and NH_3-OH^+ to NO_3^- under visible illumination, and any band gap narrowing through N-doping attributed to formation of occupied states above the valence band of TiO_2 with the oxidizing species formed on photoactivation of such states by visible wavelengths being unable thermodynamically or kinetically to oxidize such weak donors as the formate ion, despite the creation of (oxygen) vacancies at +2.0 eV by the (2.48 eV) 500-nm photons. Related studies by Kisch et al.[24,58] report negligible band gap narrowing (0.03−0.08 eV) for N-doped TiO_2 specimens; as well, the N dopant was converted into hyponitrite, nitrite, and nitrate species, whereas the carbon in C-doped titania was transformed into carbonate species.[17]

It is important then to recognize that, in all cases, the absorption features displayed by TiO_2 specimens in the visible spectral region are likely the result of formation of color centers in all the doped TiO_2s (or otherwise) that originate from the reduction of TiO_2 after some form of heat treatment or photostimulation process, as suggested by Kuznetsov and Serpone.[48] Hence, the absorption spectra of N-, C-, and S-doped TiO_2 (or otherwise) in the visible spectral region originate from the existence of such color centers rather than from a narrowing of the original band gap[45] of TiO_2 ($E_{BG} = 3.2$ eV; anatase) through mixing of oxygen and dopant states, as claimed by some.[11,12,36,46,47]

Band gap narrowing through changes in the electronic structure of valence and conduction bands is not a novel concept in semiconductor physics.[59,60] However, observation of such narrowing necessitates high concentrations of dopants and strong interactions between dopant states and the relevant states of the valence and conduction bands. If band gap narrowing does occur on heavy doping of TiO_2 (and other metal oxides), one must question whether the resulting doped TiO_2 remains as TiO_2 with all its inherent properties, or whether a new oxide forms having an entirely different chemical composition from TiO_2 with accompanying new electronic band gap structures.

The debate on band gap narrowing is fueled further by a 2006 report by Wang and Lewis[61] on the band gap structure of C-, N-, and S-doped TiO_2 (anatase and rutile) using an ab initio electronic-structure method. The study also examined the effects of dopant concentration on the localization properties of the valence band edge. For C-doped anatase TiO_2, density-of-states calculations showed a significant overlap of the C 2p states with O 2p states for 5.20% carbon concentration structures, whereas at lower C loadings (0.26%) the states introduced by the C dopant were quite distinct and highly localized on the single carbon dopant state. By contrast, both high and low dopant concentrations lead to a red-shift of the valence band edge by ∼0.7 eV in C-doped rutile TiO_2. In N-doped rutile TiO_2 there was no significant energy shift (<0.05 eV) of the valence band edge at high N loadings (5.2%), contrary to the significant shift seen at lower N dopant concentration (0.52%) resulting in a narrowed band gap of 2.55 eV. On the other hand, an energy red-shift of ∼0.44 eV occurred in N-doped anatase TiO_2 at both high and low concentrations of dopant yielding a band gap of 2.82 eV. For S-doped TiO_2, no significant shift of the valence band edge occurred at low dopant concentration (0.26%), whereas a significant red-shift of the valence band edge occurred at the higher dopant concentration (5.20%) in both rutile and anatase titanias; the corresponding band gaps narrowed to 2.3 and 2.2 eV, respectively. An added significant result of these ab initio calculations is the observation that the red-shift of the valence band edge depends not only on the nature and concentration of dopant impurities but also on the crystalline phase of the metal oxide TiO_2 (rutile versus anatase).

The picture that emerges from the above discussion is that the calculations of density-of-states in TiO_2 provide little assistance in understanding the band gap electronic structure since they do not seem to agree among each other, and there is scant direct experimental evidence for the narrowing of the band gap which has been based mostly on the discrepant ab initio and DFT calculations. Despite these uncertainties, however, the large body of evidence that exists points to oxygen vacancies and to the ensuing color centers as the most likely cause for the red-shift of the absorption edge. Accordingly, we now describe what the nature of these color centers might be.
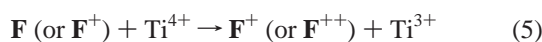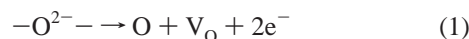
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TABLE 2: Spectroscopic Assignments of Absorption Spectral Bands Observed in Various Metal Oxides

system	optical bands (eV)	assignments	refs
TiO_2	2.81; 2.55	oxygen vacancies	62
N,F-codoped TiO_2	>2.25	(i) F and F^+ centers	63
		(ii) energy state of unknown origin	
		(iii) N-atom energy state	
rutile TiO_2	1.63	F^+ center	66
	0.73	F center	
TiO_2 nanowires	2.92 (PL)[a]	self-trapped exciton	67, 68
	2.67 (PL)[a]	F center	
	2.34 (PL)[a]	F^+ center	
rutile TiO_2	1.78	F^+ center	69
	1.02	F center	
rutile TiO_2	2.88; 1.70	Ti^{3+} $3d^1$ bands	83
Ti^{3+}-doped $YAl_3(BO_3)_4$	2.41; 2.15	$^2T_2 \rightarrow {}^2E$ (J–T split)	87
Ti^{3+}-doped $GdAl_3(BO_3)_4$	2.38; 2.12	$^2T_2 \rightarrow {}^2E$ (J–T split)	87
Ti^{3+}-doped $YAlO_3$	2.86; 2.52	$^2T_2 \rightarrow {}^2E$ (J–T split)	88
Ti^{3+}-doped Al_2O_3	2.01	$^2E(t) \rightarrow {}^2E(e)$	89
Ti^{3+}-doped Al_2O_3	2.54; 2.20	$^2T_2 \rightarrow {}^2E$ (J–T split)	96
Ti^{3+}-doped Al_2O_3	2.48	$^2T_{2g} \rightarrow {}^2Eg$	103
Ti^{3+}-doped α-Al_2O_3	2.01	$^2T_2 \rightarrow {}^2E$	102
Ti^{3+}-doped $LiNbO_3$	~1.8	$^2T_2 \rightarrow {}^2E$	90
Ti^{3+}-doped $LiNbO_3$	2.65 ± 0.25	Ti^{3+} $3d^1$ bands	95
	1.62 ± 0.08		
photoinduced Ti^{3+}-doped $LiO/Al_2O_3/SiO_2$ glass	2.54; 2.42 (sh)	Ti^{3+} $3d^1$ bands	91
thermally induced Ti^{3+}-doped $LiO/Al_2O_3/SiO_2$ glass	2.43 (sh); ~2.24	Ti^{3+} $3d^1$ bands	91
Ti^{3+} in Titanite (Ti^{3+} in tetragonally distorted octahedron)	2.00	$^2B_{2g} \rightarrow {}^2A_{1g}$	92
	1.70	$^2B_{2g} \rightarrow {}^2B_{1g}$	
	0.89	$^2B_{2g} \rightarrow {}^2E_g$	
Ti^{3+}-doped Na_2O/B_2O_3 glass	2.48	$^2B_{2g} \rightarrow {}^2B_{1g}$	93
Ti^{3+}-doped Na_2O/P_2O_5 glass	1.74	$^2B_{2g} \rightarrow {}^2A_{1g}$	
Ti^{3+}-doped $SrTiO_3$	0.50	$3d^1$ band	94
	(no 2.48 band seen)		
γ-ray induced Ti^{3+} in TiO_2	2.30	Ti^{3+} $3d^1$ band	84
Ti^{3+}-doped BeO	2.50; 2.27	Ti^{3+} $3d^1$ bands	96, 101
Ti^{3+} in silicate glass	2.48; 2.17	Ti^{3+} $3d^1$ bands	97
TiO_2	2.30; 1.88	Ti^{3+} $3d^1$ bands	85
Ti^{3+} in pyropes	2.76; 2.00	$^2T_{2g} \rightarrow {}^2E_g$ (J–T split)	98
thermal reduction of $KTiOPO_4$	2.12	$^2T_2 \rightarrow {}^2E$	99
Ti^{3+} in $CaYAlO_4$	2.30	Ti^{3+} $3d^1$ band	100
Ti^{3+} in quartz glass	2.82; 1.77	Ti^{3+} $3d^1$ bands	104
	2.43	O atom related color center	

[a] PL is photoluminescence.

Nature of the Color Centers

Upon the loss of an O atom in a metal oxide the electron pair that remains trapped in the cavity V_O (reaction 1) left behind gives rise to an **F** center (reaction 2), whereas a positively charged **F^+** center is equivalent to a single electron associated with the O vacancy (reaction 3). The electron-pair deficient oxygen vacancy, also known as an anion vacancy V_A, is referred to as a doubly charged **F^{++}** center (reaction 4). Thus, the color centers associated with oxygen vacancies are the **F**, **F^+**, and **F^{++}** centers in TiO_2 [62–73] and other metal oxides.[74–82] The electrons left in the V_O cavity can also interact with adjacent Ti^{4+} ions to give Ti^{3+} centers (reaction 5).[83–85]

$$-O^{2-}- \rightarrow O + V_O + 2e^- \qquad (1)$$

$$V_O + 2e^- \rightarrow F \qquad (2)$$

$$V_O + e^- \rightarrow F^+ \qquad (3)$$

$$-O^{2-}- \rightarrow --\{\equiv V_A \equiv F^{++}\} \qquad (4)$$

$$F \text{ (or } F^+) + Ti^{4+} \rightarrow F^+ \text{ (or } F^{++}) + Ti^{3+} \qquad (5)$$

Extensive experimental and theoretical studies of **F** centers in MgO[86] have shown that the ground state of the **F** center lies above the O 2p valence band but well below the conduction band, whereas the ground state of the **F^+** center probably lies closer to the valence band levels (note that the **F^{++}** center is silent in absorption and EPR spectroscopy). Table 2 summarizes studies that examined the electron paramagnetic resonance (EPR) features and absorption spectral characteristics of **F** centers and of Ti^{3+} present through thermal or radiation-induced processes.[62,63,66–69,83–85,87–104] Interestingly, in only a few of these[62,63,66–69] were the absorption bands attributed to the **F/F^+** centers, with the remaining large number of studies attributing the absorption spectral features to electronic transitions deriving from the Ti^{3+} color centers. In this regard, it is relevant to point out that in many cases the EPR features correlated with the absorption behaviors, thereby confirming the nature of the color centers. Our earlier study[48] was silent in this regard. Nonetheless, on the basis of the data reported in Table 2 it is tempting to attribute bands 3 and 2 (Figures 3 and 4, and Table 1) seen in the range 2.9–3.0 eV (428–413 nm) and 2.4–2.6 eV (ca. 517–477 nm), respectively, to Jahn–Teller split $^2T_2 \rightarrow {}^2E$ transitions of Ti^{3+} centers–centers that were recently confirmed by electron paramagnetic resonance in N-doped TiO_2 specimens calcined at various temperatures.[105] Band 1 seen in the 1.7–2.1 eV region (729–590 nm) is tentatively assigned to a transition from the

ground state of the F^+ center to its corresponding excited F^{+*} state.[66,69] The transition from the singlet ground-state S_o of the F center to the first F^* excited singlet state ($S_o \rightarrow S_1$) likely occurs at much lower energies.[66,69] Confirmation of such assignments will have to await rigorous systematic studies that will examine anion- and cation-doped TiO_2 specimens by diffuse reflectance spectroscopy, and by electron paramagnetic resonance techniques and photoconductivity methods. They should allow for a delineation of the schemes illustrated in Figure 1d and 1e.

Concluding Remarks

It has been argued that visible-light activation of TiO_2 specimens (anion-doped or otherwise) implicates defects associated with oxygen vacancies that give rise to color centers displaying these absorption bands, and not to a narrowing of the original band gap of TiO_2 ($E_{BG} \approx 3.2$ eV; anatase) through mixing of dopant and oxygen states, as has been suggested recently in the literature. While the absorption bands have been attributed to formation of defects associated with oxygen vacancies (color centers), the mechanistic details of the photo-activation of TiO_2 by light absorption into these absorption bands have yet to be fully unraveled.[106] It is evident that additional studies into band gap narrowing are required, paying particular attention to determine the actual chemical composition of the metal-oxide specimens when heavily doped, and suitable crystals must be grown for X-ray structural determinations to ascertain the actual positions of the dopant atoms (substitutionals versus interstitials). As well, if anion-doped TiO_2s are to be used as potential photocatalysts in a variety of synthetic and environmental applications, their photostability or -instability must also be addressed, as we discovered with the metal-ion doped TiO_2 materials produced with wet chemical methods.[2] Thorough photoconductivity studies, together with electron paramagnetic resonance and diffuse reflectance spectroscopic examinations of these doped titanias, should aid in delineating the two scenarios displayed in Figures 1d and 1e.

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