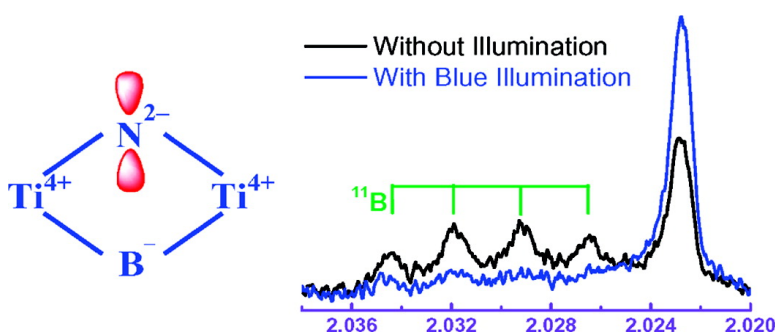## Communication

Chemical State and Environment of Boron Dopant in B,N-Codoped Anatase TiO Nanoparticles: An Avenue for Probing Diamagnetic Dopants in TiO by Electron Paramagnetic Resonance Spectroscopy

Neeruganti O. Gopal, Hsin-Hsi Lo, and Shyue-Chu Ke

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Chemical State and Environment of Boron Dopant in B,N-Codoped Anatase TiO₂ Nanoparticles: An Avenue for Probing Diamagnetic Dopants in TiO₂ by Electron Paramagnetic Resonance Spectroscopy

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With the purpose of utilizing a wider range of the solar spectrum in the photocatalytic application of TiO_2, the role of nonmetal elements in modifying the optical properties of TiO_2 has been the subject of extensive work in the past few years.[1] Among those doped materials, the origin of photoactivity under visible light has been clearly elucidated only for nitrogen doped TiO_2 ($N-TiO_2$),[2] with the help of light dependent electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT) based calculations. While the $N-TiO_2$ system has been widely investigated and a fairly unified conclusion has been reached, little is known about boron-doped TiO_2 ($B-TiO_2$) and the corresponding literature is controversial.[3] Recently, based on the good correspondence between the X-ray photoelectron spectroscopy (XPS) measurements of B 1s emission intensity at 190.6 eV and the visible light photocatalytic activities,[3b] it was shown that substitutional boron in an oxygen vacancy is responsible for the visible light photoactivities. However, this does *not* imply that boron centers are the photoactive centers, and the oxidation state of the boron dopant was virtually unspecified as well (falls between those of B_2O_3 and TiB_2).[3a,b]

To shed light on the microscopic mechanism of the effects of boron doping on the photoactivity, the chemical state and environment of the boron dopant in $B-TiO_2$ need to be unambiguously determined as a prerequisite. Here, to advance toward this goal, we have prepared N/B-codoped anatase TiO_2 ($N/B-TiO_2$) in which nitrogen serves as a paramagnetic probe for EPR investigation.

Undoped, $N-$, $B-$, and $N/B-TiO_2$ nanoparticles were prepared by sol−gel synthesis (Supporting Information). Absorption red shifts were observed in doped samples as compared to undoped samples (Figure S1). For the $B-TiO_2$ sample, refinement of X-ray diffraction data (XRD) (Figure S2) showed an ~0.5% contraction of the c-axis lattice parameter (Table S1) and XPS measurements (Figure S3) showed that the B 1s binding energy is at 191.6 eV, both consistent with earlier reports for substitutional boron at an oxygen site.[3a,b] On the contrary, when boron dopant is weaved into the interstitial site in the form of B^{3+}, an expansion of the unit cell and a broadened band gap were observed.[3c]

The EPR spectrum of $N-TiO_2$ exhibiting a hyperfine pattern caused by a ^{14}N nucleus based paramagnetic center denoted as [N] similar to that which has been reported[2] is shown in Figure 1a. The substitutional boron in an oxygen vacancy denoted as $[B^x]$ in $B-TiO_2$ is EPR silent (Figure 1b) indicating that the oxidation state of boron, "x", should be equal to either −1 or −3 which will be determined later. As deliberately designed, the $N/B-TiO_2$ exhibits two sets of nitrogen based EPR signals (Figure 1c). The first set of signals, identical to that for Figure 1a, is due to isolated [N] centers in $N/B-TiO_2$. The second set of signals is indicative of a nitrogen based center interacting with a ^{11}B ($I = {}^3/_2$, 80.2%) nucleus that further splits each nitrogen hyperfine signal into a quartet; the center is designated as a "B coupled N-center" for now. Simulated spectra
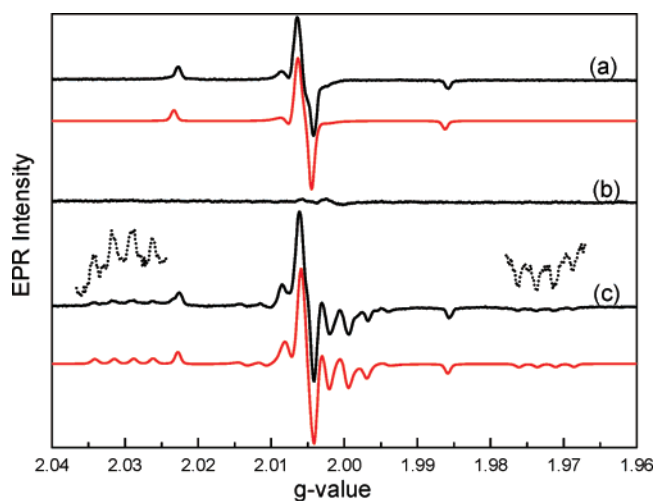

Figure 1. Room-temperature EPR spectra of (a) N−TiO₂, (b) B−TiO₂, and (C) N/B−TiO₂ along with simulations (red) for (a) and (c). The quartet structures in the high and low field portions are enlarged by a factor of 12 (dotted lines). Instrument settings: microwave frequency, 9.51 GHz; microwave power, 3.16 mW; modulation amplitude, 2 G at 100 kHz.

are also shown in Figure 1, and the derived spin-Hamiltonian parameters are given in Table S2.

We have calculated the nitrogen and boron contributions to the semioccupied molecular orbital by comparing their isotropic and anisotropic hyperfine interactions with estimates for Hartree−Fock−Slater wavefunctions (Supporting Information).[4] For the B coupled N-center, our estimates of spin densities in N(2s), N(2p₁), and N(2p₂) are 3.3%, 78%, and 10%, and in B(2s) and B(2p), they are 0.4% and 5.1%, respectively. The total spin density thus amounts to 91.3% on the N and 5.5% on the B. In total the spin density on N and B sums up to 96.8% equivalent to one unit of unpaired spin indicating that the unpaired electronic wavefunction does not extend beyond the center. The calculation also shows that the predominant site of the unpaired spin is on a single p orbital of the nitrogen atom. A preliminary model for the B coupled N-center can now be developed based on the following arguments and will be fully developed when light dependent EPR data are incorporated.

(a) First, Zhao et al.[3a] have carried out DFT calculations for three systems: O substituted by B, Ti substituted by B, and interstitial B doping. Their results showed that it is energetically favored for B to substitute O. Second, DFT calculations[2,5] and transmission electron microscopy[6] experiments both suggested that nitrogen doping is likely accompanied by formation of oxygen vacancies. In our case, that means N doping could facilitate B dopants into the oxygen vacancies when B and N are codoped. Third, from the anisotropic hyperfine constant "b" for boron, if we assume that is solely due to a dipole−dipole interaction with $b = (1/h)[g_e\beta_e][g_B\beta_B](1/R^3)$, we obtain an electron−boron distance R of ~2 Å suggesting
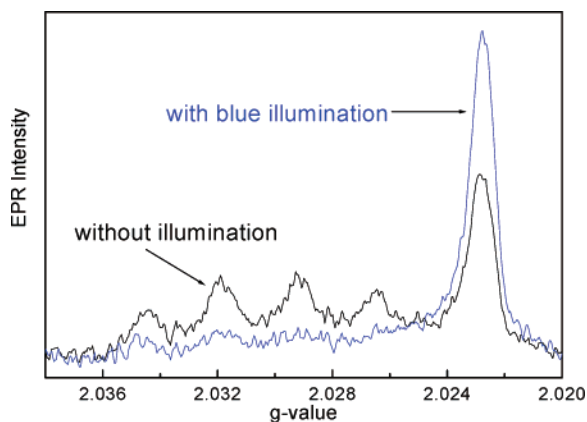
Figure 2. Room-temperature EPR signals of [N] and [N^{2-}B$^-$] centers in N/B-codoped TiO$_2$ before and after blue light irradiation. Only the low field portion of Figure 1c is shown for clarity.

that nitrogen and boron appear as proximal neighbors in the anatase lattice. Together, these results suggest that the geometric structure of the B coupled N-center is a divacancy consisting of two nearest neighbor oxygen vacancies in which one is substituted by a nitrogen and the other is occupied by a boron. Further, the estimated distance R is compared with the crystallographic distance of 2.4 Å suggests that the boron atom may undergo a large relaxation toward the nitrogen atom; i.e., boron occupies an off-center position in the oxygen vacancy.

(b) First, the N hyperfine splitting associated with the B coupled N-center is larger in magnitude than that of the nitrogen-only center (Table SII) suggesting that their nitrogen electronic configurations could be different from each other. Second, spin-density analysis shows that the unpaired electron spin is mainly localized on the nitrogen, 91.3% for N vs 5.5% for B, indicating that the formal oxidation state of boron in the coupled center is either −1 or −3, the same as the case for isolated boron center. Third, the higher Pauling electronegativity of N ($\chi = 3.0$) as compared to boron ($\chi = 2.0$) requires that the valence state of nitrogen be more negative than that of boron. Together with the geometric structure of the B coupled N-center, we thus denote its paramagnetic form as [N^{2-}B^x] and diamagnetic form as [N^{3-}B^x] with x equals to −1 or −3. The assignments are further supported by light dependent EPR data (vide infra). Also, a recent report[6] showed that substitutional N present in a N^{3-} valence state facilitates the formation of oxygen vacancies in N−TiO$_2$ lending support to our assignments.

Now, the bulk centers relevant to light dependent EPR investigation in N/B−TiO$_2$ are paramagnetic [N] and [N^{2-}B^x] centers and their diamagnetic counterparts [N$^-$] and [N^{3-}B^x], respectively. Under blue light irradiation (Figure 2), the [N] signal increases described by the photoconversion[2] between [N$^-$] and [N] centers, and the [N^{2-}B^x] signal decreases due to the formation of diamagnetic product [N^{3-}B^x]. More importantly, the [N^{2-}B^x] signal cannot be recovered once eliminated indicating that its diamagnetic counterpart [N^{3-}B^x] is a stable center, from which the oxidation state of boron can be determined. N^{3-} ion substitution for an O^{2-} ion creates a site with an effective local charge of −1 which has to be compensated by the boron at a neighboring oxygen vacancy in the form of B^{1-} (local charge = +1), creating a moiety with overall charge neutrality. Since this [N^{3-}B$^-$] center possesses local electrical neutrality, requiring no charge compensation, it would not liberate or trap any electrons under illumination (350−600 nm). On the other hand, the overall effective charge for [N^{2-}B$^-$] is +1, which would prefer to capture one electron making itself a charge neutral and stabilized [N^{3-}B$^-$] center, where the source of free

electrons in this case comes from promotion of electrons from [N$^-$] centers to the conduction band during blue light irradiation. As a consequence, the [N^{2-}B$^-$] EPR signal decreases upon blue light irradiation and cannot be restored. The following charge-transfer processes are thus established:

$$[N^-] + h\nu \text{ (blue)} \rightarrow [N] + e^-$$

$$[N^{2-}B^-] + e^- \rightarrow [N^{3-}B^-]$$
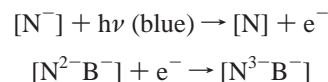
We note that $[NB^{3-}] + e^- \rightarrow [N^-B^{3-}]$ could also satisfy the charge neutrality concern and light dependent EPR data; however, it does not satisfy the electronegativity concern and XPS data.

Finally, through the identification of a stable [N^{3-}B$^-$] center in N/B−TiO$_2$ which satisfies charge neutrality and electronegativity concerns and its paramagnetic counterpart [N^{2-}B$^-$] satisfies spin-Hamiltonian analysis and light dependent EPR data, we could infer that boron enters the oxygen vacancy substitutionally in the form of B^{1-} in B−TiO$_2$ as well. This inference is consistent with the EPR silence of the B−TiO$_2$ sample and with results from XPS[3a,b] suggesting that the oxidation state of boron in B−TiO$_2$ falls between those of B$_2$O$_3$ and TiB$_2$. In analogy to the scenario proposed for N^{-1} in N−TiO$_2$,[2] we propose that boron doping also favors formation of an oxygen vacancy with two excess electrons, which would further reduce two Ti^{4+} ions to form Ti^{3+} cations. Since Ti^{3+} lies higher in the band gap, electron transfer from Ti^{3+} ions to boron is energetically favored and results in the formation of diamagnetic [B$^-$] and reoxidized Ti^{4+} ions. As a result, [B$^-$] is energetically favored in B−TiO$_2$.

In summary, our results are significant in two aspects: (1) We concluded that boron fills an oxygen vacancy in the form of B$^-$ in B−TiO$_2$. Definite assignment of the boron oxidation state will contribute to the preparation, characterization, and understanding of B−TiO$_2$ visible light photoactivity. (2) We demonstrated that nitrogen could serve as a paramagnetic probe for the geometric and electronic structure of other dopants that are present in the lattice as diamagnetic species. However, the synergistic effect of codoping on photocatalytic efficiency is another subject that needs to be subjected to further scientific inquiry.

Supporting Information Available: Experimental procedures for boron doping, UV−vis reflectance spectra, XRD analysis, EPR simulation parameters, spin density analysis, and XPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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