Communication

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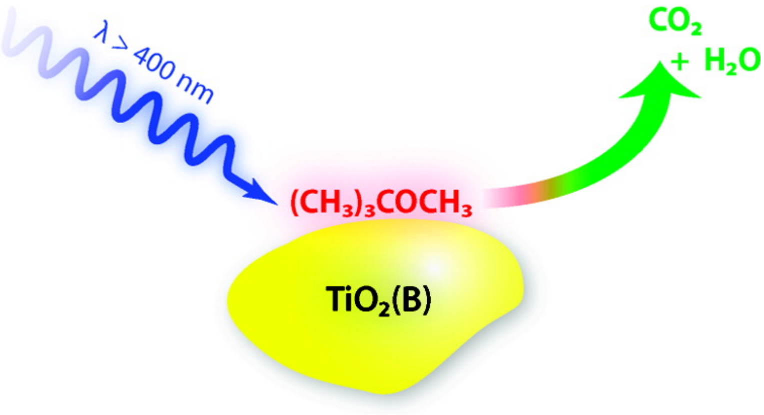

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Effective Visible Light-Activated B-Doped and B,N-Codoped TiO_2 Photocatalysts

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Photocatalytic degradation of organic compounds on semiconductor surfaces under UV irradiation offers a viable approach to the solution of a variety of environmental problems[1a,b] with TiO_2 being the most widely used material because of its stability and low cost. However, a major disadvantage is its ineffectiveness under visible light: the band gap of anatase is 3.3 eV which requires excitation wavelengths of $\lambda < 376$ nm. Given that less than 5% of the solar flux incident at the earth's surface lies in this spectral regime, harvesting sunlight for photocatalytic or photoelectrochemical[1c] purposes would be enormously enhanced by extending the photoresponse of TiO_2 into the visible region.

A promising strategy involves low-level doping of TiO_2 with nonmetals such as N, C, and S [hereafter TiO_2(E), where E is the corresponding dopant], a process that red-shifts its absorption spectrum,[1b−d] though merely inducing visible light absorption does not guarantee photocatalytic activity. Compared to other nonmetals, doping with boron has been much less studied,[2a−d] and the corresponding literature is controversial. Recently Chen et al.[2d] reported that TiO_2(B) had a *larger* band gap than TiO_2, whereas, in contradiction to this, Zhao et al.[2c] found that their samples of TiO_2(B) showed a red-shifted absorption spectrum—although this did *not* result in significant photocatalytic visible light activity.

Here we demonstrate that an optimal level of boron doping, correctly introduced, results in significant absorption of visible light *and* substantial photocatalytic activity, comparable to that of TiO_2-(N).[3] A low-cost, reproducible method for the synthesis of TiO_2-(B) which permits good control of the level of B-doping has been developed. These three attributes are essential if practical applications are to be achieved. A series of TiO_2(B) catalyst precursors with nominal doping levels in the range 1.13−11.9 atom % were prepared by a simple procedure involving the sequential reaction of BH_3 in THF with a calculated small excess of $TiCl_4$ under a dry, O_2-free nitrogen atmosphere, (described in the Supporting Information) followed by stoichiometric reaction of the remaining $TiCl_4$ with an excess of water, then calcination (further details in Supporting Information). The resulting materials were evaluated for visible light activity in the photocatalytic decomposition of methyl tertiary butyl ether (MTBE), a gasoline additive and potential carcinogen that is of increasing concern in regard to public health. By adaptation of our previously published method for the synthesis of TiO_2(N)[3] we also prepared B, N codoped TiO_2 (3.0 and 1.5 atom % each of both N and B). The codoped materials were synthesized in three ways: addition of B first, then N; N first, then B; simultaneous introduction of N and B.

The BET surface areas, crystalline phase, and mean crystallite sizes of these catalysts are given in the Supporting Information, along with reference data for pure anatase, similarly prepared by hydrolysis of $TiCl_4$.

Figure 1 shows the corresponding UV−vis diffuse reflectance spectra from which it is apparent that absorption in the visible region increases with boron content. The insert indicates that spectra for B−TiO_2 (3.23 atom %), N−TiO_2 (3.23 atom %),[3] and B, N−TiO_2 (1.5 atom % of each of N and B) were quite similar.

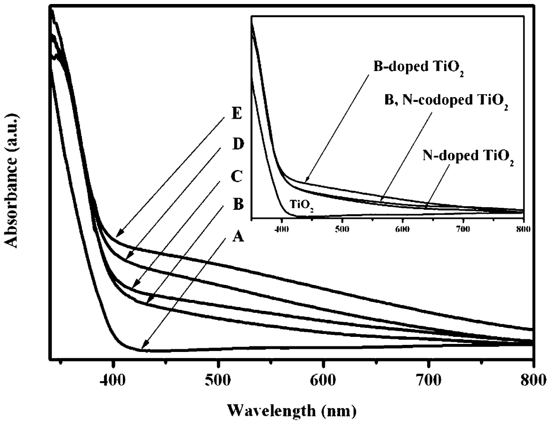

Figure 1. UV−vis absorbance spectra of pure anatase and B-doped TiO_2 for different dopant levels: (a) TiO_2; (b) B(1.13 atom %)-TiO_2; (c) B(3.23 atom %)-TiO_2; (d) B(5.82 atom %)-TiO_2 and (e) B(11.9 atom %)-TiO_2. Inset shows comparison between B-doped (3.23 atom %), N-doped (3.23 atom %), and B, N codoped (1.5 atom % of both N and B) TiO_2 catalysts.

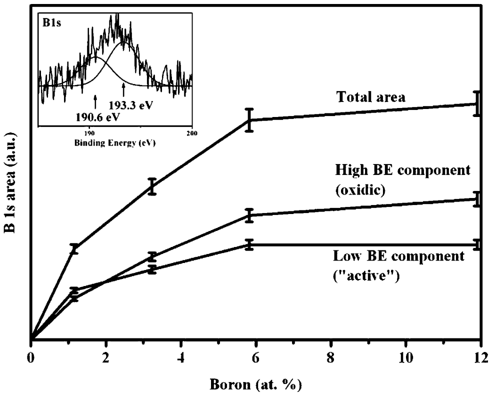

Figure 2. Dependence of B 1s XPS integrated intensities on nominal boron content showing total boron and separate contributions from B_2O_3 and active boron component. Inset shows typical raw data.

XP spectra of the calcined catalysts showed that within the spectroscopic sampling depth (∼6 nm, i.e., of the order of the crystallite size—Supporting Information) the *total* observable boron content increased monotonically, but not linearly, with the expected boron content (Figure 2, top curve). This is at least consistent with the known very limited solubility of B in TiO_2.[2a] The B 1s emission is very broad (fwhm ∼ 6.3 eV) implying the presence of more than one form of boron. Inspection of the data indicates the presence of low and high binding energy (BE) components (Figure 2, inset); spectral fitting procedures are described in the Supporting Information. The high BE component (193.3 eV) is characteristic of B_2O_3

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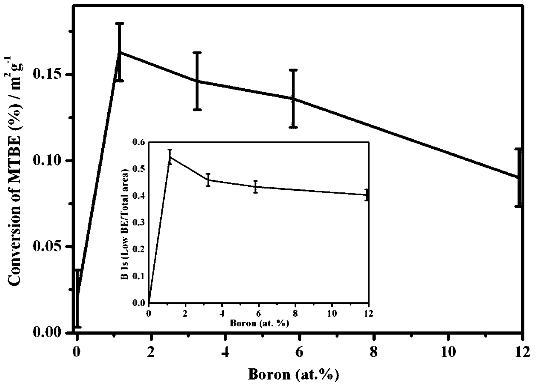

Figure 3. Photocatalytic activity normalized for specific surface area as a function of nominal B content. Inset shows corresponding behavior of ratio of 190.6 eV intensity ("active B") to a total B 1s signal intensity.

(193.0 ± 0.4).[4a,b] Given the large band gap of B_2O_3 (~6.3 eV)[4c] it therefore seems plausible that this high BE component corresponds to inclusions of boric oxide-like material that do not contribute to the observed visible light activity of our TiO_2(B). The inference is that the lower BE component at 190.6 eV corresponds to boron actually incorporated within the TiO_2 lattice thereby inducing the unprecedented visible light photocatalytic activity of TiO_2(B) that we detail below. The B 1s BEs of elemental boron and TiB_2 are both 187.5 eV[4d] implying that the extent of B → Ti charge transfer in the latter is small. Accordingly, the higher value of 190.6 eV associated with the active B incorporated with the TiO_2 is at least consistent with substitutional B occupying O sites where, compared to TiB_2, B → Ti charge transfer should be enhanced by the presence of the five remaining oxygen atoms adjacent to the Ti site. This reasoning does of course neglect possible final state relaxation effects that inevitably accompany the process of photoemission; however, it is the kind of argument that is commonly used in rationalizing chemical shifts.

The dependence of the amounts of "active" and inactive or oxidic boron on the nominal composition of the precursor materials is also shown in Figure 2, to be discussed below.

Photocatalytic measurements were carried out in a single-pass reactor at ambient temperature under visible light irradiation from an appropriately filtered source. MTBE destruction and CO_2 production were monitored by gas chromatography and nondispersive infrared spectrometry, respectively.[3]

Figure 3 shows visible light photocatalytic activity as a function of nominal boron content. The results are presented as % conversion of MTBE normalized with respect to catalyst specific surface area. Undoped TiO_2 anatase showed negligible activity, as expected, whereas boron doping resulted in very significant activity that maximized at 1.13 atom % boron (nominal). This set of results was reproduced using repeated de novo preparations starting with fresh batches of precursors. The insert to Figure 3 shows the ratio of the XPS emission intensity from the active component to the total B 1s intensity. Notice the correspondence between this quantity and the visible light photocatalytic activity; in particular both properties exhibit a maximum at 1.13 atom % B (nominal). *Why* maxima occur in Figure 3 is a question that cannot be answered on the basis of the data presented here. There are too many unknowns, including the morphology of the B_2O_3 inclusions and their effect on electron/hole creation and recombination rates. The latter effect[4e] may account for the eventual decrease in activity that accompanies increasing visible light absorption (Figure 1). What seems clear is that the 190.6 eV boron component, likely present substitutionally, is responsible for the red-shifted optical absorption *and* the visible light photoactivity.

We explored the possibility of synergistic effects by testing B, N codoped TiO_2, prepared as described above, and found that within the experimental error, nominal precursor compositions of 1.5 atom % N + 1.5 atom % B and 3.0 atom % N + 3.0 atom % B gave normalized visible light photocatalytic activites comparable to those of the best N-only and B-only catalysts (see Supporting Information).

Finally, we may ask why our TiO_2(B) is an effective visible light photocatalyst whereas ostensibly similar material prepared by others[2c,d] is not. A clue is provided by a very recent theoretical study[5] on TiO_2(N) in which it was found, perhaps unsurprisingly, that the mode of N incorporation depends on the prevailing oxygen activity. A similar effect may operate in the case of boron doping—it's not just what you do but how you do it.

In summary, effective *visible light-active* photocatalysts have been prepared by a low-cost synthetic method that allows controlled and reproducible doping of TiO_2 with boron, thus opening the door to large scale preparation. Maximum activity occurs at 1.13 atom % B associated with an "active" boron component probably present substitutionally at oxygen sites. Inactive boron is also present as boric oxide-like material. The visible light photoactivities of B, N codoped materials were similar to those with the same level of B-only doping: the absence of synergy is itself an interesting phenomenon that awaits further investigation.

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Supporting Information Available: Experimental procedures for boron doping and catalyst testing; supplementary catalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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