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LETTER TO THE EDITOR

Effects of dopant states on photoactivity in carbon-doped TiO_2

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Abstract
Recently an effective photoresponse in the visible-light region was experimentally observed in carbon-doped TiO_2. We contribute a theoretical understanding of this phenomenon. Our *ab initio* density functional theory investigations show that substitutional carbon dopants incorporated into TiO_2 drastically affect the electronic structure of the material, thus improving its photoactivity. The resulting bandgap of 2.35 eV predicted in this work agrees with the available experimental observations for carbon concentration around 5%. We also address the effects of doping concentration on the photoresponse of this material.

In 1972, Fujishima and Hondo [1] demonstrated that photoexcitation in TiO_2 can be used to chemically split water over TiO_2 to form H_2 and O_2; thus greater possibilities of solar energy conversion through semiconducting materials was conceived. In addition to water cleavage from photoactive TiO_2 as a possible alternate fuel usage, other environmental applications have also attracted extensive interest (for example, see [2–7]). The use of metal oxide semiconductors like TiO_2 in such applications is promising because of their excellent functionality, long-term stability, and nontoxicity [2]. Despite the broad range of applicabilities for TiO_2, only about 3% of the solar spectrum (ultraviolet) can be utilized due to its wide intrinsic bandgap. Therefore, considerable efforts have been made to extend the photoresponse of TiO_2-based systems further into the visible-light region using dopants.

Various transition-metal cation dopants in TiO_2 have been extensively studied [8–11]. However, except for a few cases [9, 10], the photocatalytic activities of cation-doped TiO_2 decrease even in the UV region. This is because the transition-metal-doped TiO_2 suffers from an increase in recombination centres introduced by the dopant-related localized d-states deep in the bandgap of TiO_2 [8]. Anionic nonmetal dopants, such as carbon [12–15], nitrogen [16–21], and sulfur [22–25], may be more appropriate for the extension of photocatalytic activity of TiO_2 into the visible-light region because impurity states are near to the valence band edge, but do not act as charge carriers. Furthermore, their role as recombination centres might be minimized as compared to cation doping. Although doping with S shows a similar bandgap narrowing [23, 25], it would be difficult to incorporate it into the TiO_2 crystal because of its large ionic radius [16]. Doping with both C and N results in about a 50 nm red shift in the absorption spectra [12–16], and produces photoactivity in the visible-light region. Recent results with carbon further demonstrate improved photocatalytic efficiency in water splitting with a total conversion efficiency of up to 11% [13].

Although recent experiments have demonstrated that carbon-doped TiO_2 is a promising photoactive material in chemical reactions, the understanding of the photoresponse mechanisms are rather limited. Light absorption in materials greatly depend on the electronic structures; experimental results [12–19, 23, 25] imply that anionic nonmetal dopants strongly modify the electronic structures of TiO_2 so that it absorbs in the visible-light region. In this work, we explore the electronic properties of carbon-doped TiO_2 using an *ab initio* tight-binding method, called FIREBALL, which is based on density functional theory (DFT) with nonlocal pseudopotentials within the local density approximation (LDA) [26]. Our calculations provide an initial glance into the electronic properties required for acceptable photocatalysis. In the calculations, we choose a minimal basis set for C, O, and Ti, adding a excited p-state for polarization to the Ti ground-state configuration.

Two phases of TiO_2 are considered photoactive—rutile and anatase; both are tetragonal. The tetragonal rutile structure belongs to the space group $P4_2/mnm$ (D_{4h}^{14}), containing 6 atoms per primitive unit cell. The tetragonal anatase structure belongs to the space group $I41/amd$ (D_{4h}^{19}), containing 12 atoms per conventional unit cell. Structural parameters for both rutile and anatase have been determined to a high degree accuracy from the neutron diffraction experiments performed by Burdett *et al* [27]. We calculate the optimal structures by minimizing the total energy of the rutile and anatase TiO_2 with respect to the lattice parameters a and c, and the internal parameter u. Our results of the structural properties in both rutile and anatase structures are in excellent agreement [28], being within 1% of the experimental results of Burdett *et al* [27].

From our theoretically predicted equilibrium lattice parameters, we have calculated the self-consistent electronic band structures for rutile and anatase along the high-symmetry directions of the irreducible Brillouin zone. For the rutile (anatase) structure, the calculated direct bandgap from Γ to Γ of 3.05 (3.26 eV) eV is in agreement with the reported experimental gap of 3.06 eV [29] (3.20 [30] and 3.42 eV [31]). The LDA generally underestimates the experimental bandgap for insulators and semiconductors, and the bandgap obtained from previous *ab initio* planewave calculations for TiO_2 is around 2 eV [32–34]. The underestimating effect of the LDA is compensated in our calculations because we use a local orbital basis set in FIREBALL[1]. We discuss more detailed structural and electronic properties of TiO_2 in [28].

Our results for bulk TiO_2 provide a strong basis for us to explore the electronic properties of the carbon-doped TiO_2 systems. Based on our theoretically determined equilibrium parameters, we constructed supercells of TiO_2 which contain 64 primitive unit cells in both the rutile and anatase structures. In one set of supercells, we substitute one oxygen atom by a carbon, yielding a carbon concentration of 0.26%. In the other set of supercells, we randomly substitute 20 carbons, yielding a 5.20% doping concentration. The electronic density of states (DOS) for the bulk TiO_2 and carbon-doped (called $TiO_{2-x}C_x$) rutile structures are presented in the upper panels of figure 1; the projected DOSs onto carbon and oxygen atoms are also depicted in the lower panels. The scale for the projected DOS onto carbon is ten times larger than the other DOS plots. The dashed lines in the DOS figures indicate the valence band edge in the systems. In this letter, we only present results for rutile but find our results for anatase to be very similar.

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[1] However, the bandgap is not the only criterion to measure an *ab initio* DFT calculation within the LDA. The most important feature of our calculations is that consistent results, not only for the electronic properties but also for the structural properties, are obtained for all three phases of TiO_2 by using our method and basis set.

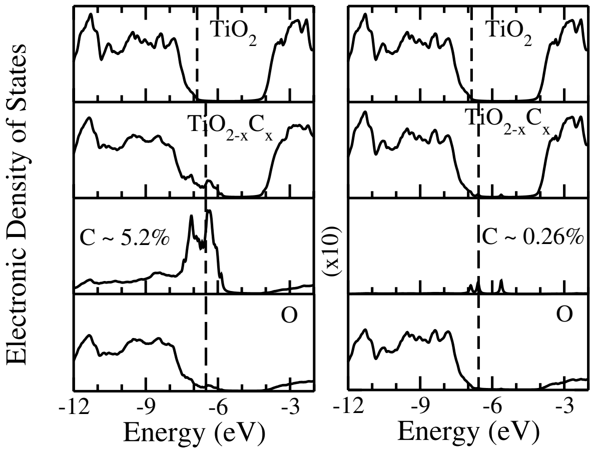

Figure 1. Electronic density of states (DOS) for carbon-doped rutile TiO_2 with 5.2% (left) and 0.26% (right) carbon concentration, respectively. The dashed line indicates the valence band edge in the system. The top panel shows the DOS for bulk TiO_2 as a reference, the second panel shows the carbon-doped ($TiO_{2-x}C_x$) structure, and the third and lowest panels show the projected DOS onto carbon and oxygen atoms, respectively. The scale for the projected DOS onto carbon is ten times larger than the other DOS plots.

Comparing the total DOS of bulk TiO_2 with the corresponding carbon-doped systems, the upper two panels in figure 1 show that the conduction band minimum remains unchanged by carbon doping. This feature confirms that carbon-doped TiO_2 satisfies the photoactive properties required to split water into hydrogen and oxygen [4]. New states close to the valence band edge of the reference TiO_2 are introduced in the carbon-doped systems. Analysis of the projected DOS onto carbon (see the third panels in figure 1) indicates that these states, as well as the states penetrating into the upper valence band of the reference TiO_2 (which is composed of O_{2p} states), are carbon 2p-states, and only about half of these states are filled states. As a result of the substitutional carbon atoms incorporated, the valence band edge shifts to higher energy compared with the reference TiO_2, and the bandgap narrows. Similar phenomena are observed experimentally as several studies reported a red shift in the absorption spectra [12–16]. Irie *et al* [14] and Khan *et al* [13] both show energy levels just above the valence energy of the reference samples which correspond to *substitutional* carbon dopants. They also conclude that the substitutional carbon atoms are responsible for the visible-light absorption.

In the structures containing 5.2% carbon concentration (left panel in figure 1), energy shifts of 0.7 eV are obtained. As a consequence, the corresponding bandgap is narrowed down to 2.35 eV (2.76 eV obtained for the anatase phase). The experiments by Khan *et al* [13] show two optical absorption thresholds, in the visible-light region, at 535 nm (bandgap of 2.32 eV) and 440 nm (bandgap of 2.82 eV) in samples of estimated carbon concentration around 5%. They concluded that these two absorption thresholds result from two different compositions of the carbon-doped TiO_2, i.e., rutile and anatase structures, respectively. Meanwhile, they obtain increased efficiency up to 11% in splitting water, which is a significant improvement over the original Fujishima and Honda experiments [1]. Note that a much lower efficiency was observed by Irie *et al* [14] in carbon-doped TiO_2 samples of estimated carbon concentration around 0.32%.

An interpretation for quantum efficiency given by Asahi *et al* [16], which we support, is that the states in the gap should overlap sufficiently with the O 2p-states to transfer photoexcited carriers to reactive sites at the TiO_2 surface within their lifetime. Our DOS calculations

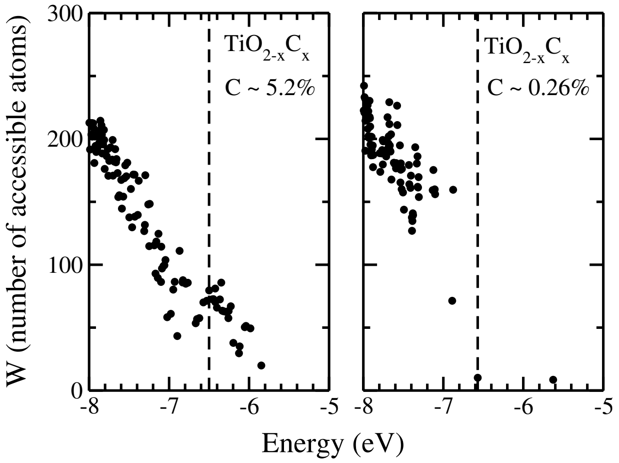

Figure 2. Number of accessible atoms for each electronic state near the valence band edge in carbon-doped rutile TiO_2 with carbon concentration of 5.20% (left) and 0.26% (right), respectively. The dashed line indicates the valence band edge in the system.

(the left panels of the projected DOS into carbon and oxygen atoms) show that there is significant overlap between the carbon states and O_{2p} states for 5.20% carbon concentration. On the other hand, in the lower carbon concentration (the right panels of projected DOS into carbon and oxygen atoms), the states introduced by carbon dopants are quite distinct and highly localized on the single carbon dopants. There is no significant overlap between carbon and oxygen observed for 0.26% carbon concentration. Additionally, the energy shift of the valence band edge is much smaller compared to the energy shift for the higher doping concentration. Consequently, we predict that the photocatalytic performance of the lower concentration samples would be much lower than that of high concentration ones.

To further understand the concentration effects on the photoresponse in carbon-doped TiO_2 systems, we introduce the number of accessible atoms, which describes the spatial extent of the electronic state in the systems, from the electronic state quantum entropy [35]. For a particular state ν, the wavefunction $\Phi(\nu)$ has a Mulliken population $p_i(\nu)$ on atom i, which loosely is considered as the probability that an electron is in state ν and resides on atom i. The populations are normalized, $\sum_i p_i(\nu) = 1$. From probability theory, we define a quantum entropy for state ν as $S(\nu) = -\sum_i p_i(\nu) \ln p_i(\nu)$. From Boltzmann's equation, we can determine the number of accessible atoms $W(\nu)$ for a given electronic state $W(\nu) = \mathrm{e}^{S(\nu)}$. The number of accessible atoms $W(\nu)$ gives a quantitative, and easily calculable, measure of how many atoms a particular electronic state $\Phi(\nu)$ reaches.

Figure 2 presents the number of accessible atoms, $W(\nu)$, for each electronic state near the valence band edge in the carbon-doped TiO_2 (rutile) structure with carbon concentration of 5.20% (left) and 0.26% (right), respectively. The dashed line indicates the valence band edge in the electronic structures. For the lower carbon concentration the top valence band state is very localized, and there is very little overlap with oxygen atoms. As a result, the mobility of a hole created there will be quite poor, and this explains why the photoactive efficiency for the chemical reactions is small for low concentration. The results for higher carbon concentration follow the opposite trend: the valence band edge is quite delocalized, there is significant overlap with oxygen atoms, and hole mobility should be sufficient. Therefore, higher concentration carbon would produce both visible-light absorption with larger photocatalytic efficiency overall.

In conclusion, the electronic properties of bulk and carbon-doped TiO_2 materials are precisely determined using FIREBALL, an *ab initio* electronic-structure method. Our theoretical predictions concerning the photoresponse in carbon-doped TiO_2 are consistent with available experimental results. Concerning available experimental evidences and our theoretical results, we conclude that both bandgap narrowing and the overlap between the O 2p and dopant states introduced by carbon will strongly affect the photoactivity. Our results explain why higher doping concentrations lead to more efficient photoactive reaction in the experimental observations.

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