Dissimilar anisotropy of electron versus hole bulk transport in anatase TiO$_2$:
Implications for photocatalysis

Donghun Kim,1 Byung Chul Yeo,1,2 Dongbin Shin,3 Heechae Choi,1 Seungchul Kim,1 Noejung Park,3 and Sang Soo Han1,*
1Computational Science Research Center, Korea Institute of Science and Technology, Seoul 02792, Korea
2School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea
3Department of Physics, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea

(Received 17 May 2016; revised manuscript received 24 August 2016; published 19 January 2017)

Recent studies on crystal facet manipulation in anatase TiO$_2$ in photocatalysis have revealed that reduction and oxidation reactions preferably occur on (100)/(101) and (001) facets, respectively; however, a fundamental understanding of their origin is lacking. Here, as a result of first-principles calculations, we suggest that a dissimilar trend in the anisotropy of electron vs hole bulk transport in anatase TiO$_2$ can be a dominant underlying mechanism for the difference in photochemical activity. Photoexcited electrons and holes are driven to different facets, i.e., electrons on (100)/(101) and holes on (001), leading to the observed preference for either reduction or oxidation. This trend of electrons vs holes found in pure TiO$_2$ applies even for cases where a variety of dopants or defects is introduced.

DOI: 10.1103/PhysRevB.95.045209

I. INTRODUCTION

Photocatalysis (PC) has recently attracted a great deal of attentions as it provides a promising pathway for both clean energy (e.g., hydrogen fuel) production [1] and environmental sustainability [2]. Among many candidate semiconductor materials, TiO$_2$, the first prototype material for PC [3], is widely used today because of its advantages regarding desired band-edge positions, long-term photochemical stability, and nontoxicity [1,4]. Two polymorphs of TiO$_2$, i.e., rutile and anatase, are used industrially. Although both polymorphs have been analyzed in great detail [5–7] from the perspective of PC, anatase generally exhibits relatively higher photocatalytic activity than the other due to its favorable electronic properties [7–9]. In the present work, we are mainly interested in anatase TiO$_2$, and thus TiO$_2$ hereafter refers to anatase TiO$_2$ unless otherwise specified.

It has been widely accepted that three low-index facets, (100), (101), and (001), dominate the surfaces of TiO$_2$ particles [10]. It has long been questioned which facet is the most effective for photocatalytic activity. However, in a practical sample, the ratio of a specific facet can hardly be controllable, and thus direct comparison of the photocatalytic activity between different facets has remained challenging. In this regard, the work of Yang et al. [11] is greatly noteworthy: they, for the first time, demonstrated that morphological control was possible using hydrofluoric acid as a shape-controlling agent. This work enables a variety of particle shapes to be tested in PC and to be compared in terms of activities [12–17]. These experiments have led to the interesting consensus that reduction and oxidation reactions preferably occur on different facets, i.e., reductions on (100)/(101) and oxidations on (001), respectively; now, these results require a fundamental understanding of their origin.

There already exist several efforts to reveal this phenomenon on the basis of surface atomic structures [18] or band-edge energies [13,19,20]; however, these efforts are restricted to surface properties, probably because chemical reactions themselves occur at the surfaces of photocatalysts. Unfortunately, little attention is given to the step prior to the actual reactions, namely, bulk transport of photoexcited carriers, despite the fact that about 90% of photogenerated carriers are lost during this step [21]. In this article, considering the phenomenon from the viewpoint of bulk transport, we offer a novel explanation complementing existing explanations.

As it has been unclear whether the dominant carrier transport mechanism is bandlike or polaronic in anatase TiO$_2$, we carried out two largely different sets of ab initio density functional theory (DFT) calculations in this work. In Sec. III A, assuming that carriers in anatase TiO$_2$ prefer a free-carrier state, we focus on a carrier transport property, namely, the carrier’s effective mass ($m^*$). We investigate the anisotropy of the electron ($m^*_e$) and hole ($m^*_h$) effective masses in TiO$_2$ and discover that the anisotropic behavior is the opposite between an electron and a hole. With a particular interest in directions perpendicular to dominant facets, we find that electrons can be transported toward the (100)/(101) facets up to 3.95 times faster than holes can ($m^*_e/m^*_h = 3.95$), whereas holes are driven to the (001) facet 3.8 times faster than electrons are ($m^*_h/m^*_e = 0.26$), resulting in the (100)/(101) and (001) facets exhibiting different reductive and oxidative natures. To unveil the origin of this interesting trend, we thoroughly analyze orbital hybridizations near the conduction- and valence-band (CB and VB) edges along selected $k$ directions (i.e., [100] and [001]), where nearest-neighbor hybridizations between Ti 3$d$ and O 2$p$ orbitals dominate only in the [100] direction for the CB and act oppositely in the [001] for the VB. Because it is very likely that imperfections such as dopants or defects exist in a practical sample, we demonstrate that the above observations can further be expanded to TiO$_2$ with dopants or intrinsic defects. In Sec. III B, motivated by polaronic features in this material, we have expanded our study to cases where polaron hopping is the dominant transport mechanism. Our polaron model presents dissimilar anisotropic manners of electron versus hole bulk transport and still supports the preferred accumulations of electrons on the (100)/(101) facets and holes on the (001) facet.
II. METHODS

DFT calculations were performed using the plane-wave basis VASP code [22] with an energy cutoff of 400 eV and fast-Fourier-transform grid spacing of 0.2 Å in each lattice direction. The projector-augmented-wave method was adopted to describe the potential from the ionic core [23]. For Ti, 3p (semicore), 3d, and 4s states were treated as valence states (3p64s23d2 scheme). Integrations over the Brillouin zone were performed using a Monkhorst-Pack k-point sampling of 8 × 8 × 4 after convergence tests. The geometry is fully relaxed until the maximum Hellmann-Feynman forces are less than 0.01 eVÅ⁻¹ [24]. The hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) is used [25]. In order to match the Kohn-Sham gap with the known one (3.2 eV), 20% of the exchange energy is substituted with the Hartree-Fock exact free-ion levels. On the CB side, Ti 3d and O 2p orbitals, instead of O 2p orbitals, are also needed. The directional dependence of the effective mass (m*) is calculated by fitting parabolic functions to the CB and VB edges with particular interest in their anisotropy [28]. As shown in Fig. 1(b), orbitals for the electron case and to O 2p for the extra hole case, respectively. After extensive tests to find appropriate U parameters, we conclude that, for both the extra electron and the extra hole cases, the U value of 5 eV is the most suitable and, thus, is selected (see the Supplemental Material [46]).

III. RESULTS AND DISCUSSION

A. Anisotropy of bandlike transport in TiO2

The TiO2 in anatase polymorph can be described by four Ti and eight O atoms in a tetragonal unit cell, as shown in Fig. 1(a). The calculated lattice parameters (a = 3.77 Å and c = 9.44 Å) are in a good agreement with the experimentally measured values [26]. We and a previous theoretical work [8] have identified the nature of the indirect band gap. As shown in Fig. 1(b), one can observe that the CB minimum (CBM) occurs at the Γ point, whereas the VB maximum (VBM) occurs at k = [000] (δ ≈ 0.44). It is important to examine orbitals forming the edges of the CB and VB since the E-k dispersion is highly dependent on orbital hybridizations. As shown in the orbital-resolved projected density of states (PDOS) in Fig. 1(b), the lowest CB primarily consists of Ti 3d orbitals, while the highest VB is predominantly contributed by O 2p [8,27]. In solids, however, the crystal field splits the degenerate free-ion levels. On the CB side, Ti 3d and O 2p orbitals, instead of O 2p orbitals, are also needed. The directional dependence of the effective mass (m*) is shown separately for electron [Fig. 2(a)] and hole [Fig. 2(b)], where m* is calculated by fitting parabolic functions to the CB and VB edges with particular interest in their anisotropy [28]. Because the (100), (110), and (001) crystalline planes are well known to be the dominant surface facets in TiO2 particles, carrier transport along directions perpendicular to these three facets, i.e., [100], [1,0,0.15], and [001], respectively, are of particular interest to us. It is important to note that both an electron and a hole exhibit significant anisotropy but in an extremely dissimilar manner. For the electron case, the effective mass is a maximum (3.70m0) in the [001] direction, i.e., z direction, and a minimum (0.59m0) in the [100] or [010] direction, i.e., x or y direction. However, for the hole case, a completely opposite trend is observed: the effective mass...
The aforementioned anisotropy in the effective masses can be related to the photocatalytic activities of facets of TiO₂. Figure 2(c) shows an exemplary schematic of a TiO₂ particle, which resembles those used in previous experiments [13–16,18]. The ratio between the electron and the hole effective mass, defined as \( R = m_e^*/m_h^* \), is calculated for an arbitrary crystal direction on the \( xz \) plane. Given an inversely proportional relationship between transport mobility and effective mass, \( R \) greater than unity (\( R > 1 \)) means that holes can be transported more rapidly than electrons in a specific direction, whereas \( R \) less than unity (\( R < 1 \)) means the opposite. It is found that electrons tend to move toward and accumulate on the (100)/(101) facets much more rapidly (0.26 \( \leq R \leq 1 \)) than holes do, which makes these two facets much more effective for reduction reactions compared to oxidation reactions. However, for the (001) facet, the opposite would occur: holes would be transported toward the (001) facet much more rapidly than electrons would (1 \( \ll R \leq 3.95 \)), resulting in this facet’s possessing a highly oxidative nature.

The origin of the effective mass anisotropy can be attributed to orbital hybridizations near the CB and VB edges. To start with the CB side, in Fig. 3(a), the lowest CBs along the [100] vs [001] \( k \) direction are shown with a comparison of orbital constitutions (O 2\( \pi \)/Ti 3\( d_{xy} \) ratio). Within the range near the CBM of \( |k| \leq 0.03 \) (2\( \pi \)/Å), orbital constitutions along the [100] vs [001] direction turn out to be very different: for the [100] direction, O 2\( \pi \)/Ti 3\( d_{xy} \) increases with \( |k| \) [8.3% at \( |k| = 0.03 \) (2\( \pi \)/Å)], whereas the ratio is constantly 0 for the [001] direction. This is also shown in Figs. 3(b) and 3(c) of the square of wave functions (i.e., partial charge densities) at the selected \( k \) points in the CB. In Fig. 3(b), one can see that the contributions of O 2\( \pi \) exist along the [100] \( k \) direction: strong \( d_{xy}-p_{\pi} \)-hybridizations between neighboring Ti and O ions lead to the highly dispersive band. However, in Fig. 3(c), we observe that O 2\( \pi \) orbitals do not emerge at all along the [001] \( k \) direction: relatively much weaker \( d_{xy}-d_{xy} \) interactions between Ti ions dominate, resulting in the flatlike band.

Let us now move to the VB side: in Fig. 3(d), the highest VBs along the [100] and [001] \( k \) directions are compared around the VBM. Unlike the CB side, because the VB primarily consists of O 2\( \pi \) orbitals, we now trace the emergence of Ti 3\( d \) orbitals along both directions. Interestingly, the ratio Ti 3\( d \)/O 2\( \pi \) remains negligibly low along the [100]; contrary to this, the ratio increases with \( |k| \) along [001] [6.7% at \( |k| = 0.03 \) (2\( \pi \)/Å)]. These results can visually be confirmed from partial charge density plots at the selected \( k \) points in the VB [Figs. 3(e) and 3(f)]. It can be seen that O 2\( \pi \) solely contributes to the VB along the [100] \( k \) direction, whereas Ti 3\( d \) appears along the [001] \( k \) direction. As a consequence, unlike the CB case, the VB is more dispersive in the [001] direction, due to the presence of stronger \( p_{\pi}-d_{xy} \)-hybridizations between neighboring Ti and O ions than in the [100] case, where relatively much weaker \( p_{\pi}-p_{\pi} \) bonding interactions between O ions dominate.

Thus far, we have investigated the anisotropy of carrier effective masses in pure TiO₂. In photocatalytic applications,
FIG. 3. Origin of opposite anisotropy of electron vs hole effective mass. (a) The lowest CBs along the [100] or [010] (circles) and [001] (triangles) \( k \) directions. The color code indicates the ratio \( \frac{O_2p\pi}{Ti 3d_{xy}} \). (b, c) Two-dimensional cross sections of the square of wave functions of the CBs at \( k = CBM + (0.03, 0, 0) \) (2\( \pi/\AA \)) (b) and \( k = CBM + (0.0, 0.03, 0) \) (2\( \pi/\AA \)) (c). (d) The highest VBs along the aforementioned directions in (a). The color code indicates the ratio \( \frac{Ti 3d}{O_2p\pi} \). (e, f) The square of wave functions of the VBs at \( k = VBM + (0.03, 0, 0) \) (2\( \pi/\AA \)) (e) and \( k = VBM + (0, 0.03, 0) \) (2\( \pi/\AA \)) (f). Red and black dots in a unit cell indicate Ti and O atoms in the cross sections, respectively. The isosurface value is 0.002 \( e/\AA^3 \).

However, in a practical sample, it is likely that a variety of imperfections exist. Thus, to have a broader impact, we expand this study to cases where either dopants or defects are introduced. For doped TiO\(_2\), we selected four transition-metal cation dopants, i.e., W \[30\], Nb \[31\], Zr \[32\], and Y \[33\], all of which are widely used in PC experiments. These dopants (M) are well known to be incorporated by substituting the Ti ion of the charge state +\( q \) (i.e., M\(^q+\)Ti), rather than being an interstitial: W\(^{2+}\)Ti, Nb\(^{1+}\)Ti, Zr\(^{4+}\)Ti, and Y\(^{3+}\)Ti \[34–36\]. For intrinsic defects, we chose the three V\(^{2+}\)O, O\(^{2-}\), and Ti\(^{4+}\) \[37–39\], all of which are well known to be dominant defect types.

Here, the following key question is of interest to us: Is the opposite anisotropic behavior of electron vs hole in pure TiO\(_2\) preserved even when either dopants or defects are introduced? In Fig. 4, we compare the effective mass ratio of the [001] to [100] direction, \( \frac{m^*_{[001]}}{m^*_{[100]}} \), of pure TiO\(_2\) and other cases and find that any imperfections introduced in the present study do not change the qualitative trend in the effective mass anisotropy, though they do affect the quantities. For the electron, the ratio \( \frac{m^*_{[001]}}{m^*_{[100]}} \) is much larger than unity (7.58–10.04), whereas, for the hole, the ratio is smaller than unity (0.10–0.48), indicating that the opposite trend of anisotropy holds for all cases. The preservation of the trend can be rationalized by the fact that the orbital hybridization does not change much upon the introduction of dopants or defects (see the Supplemental Material \[46\]).

B. Anisotropy of polaronic transport in TiO\(_2\)

It is still under debate whether the dominant carrier transport mechanism is bandlike or polaronic in anatase TiO\(_2\). In Sec. III A, we have assumed that carriers in anatase TiO\(_2\) prefer a delocalized free-carrier state, mainly based on several recent studies \[9,40\] revealing that polaron formation is rather difficult. However, motivated by polaronic features captured in other studies \[41,42\], we have performed extensive DFT + \( U \) calculations to investigate the direction dependence of polaron hopping transport (both excess electron and excess hole).

Polaron mobility (\( \mu \)) in metal oxides is typically modeled within the framework of Marcus/Holstein theory \[42–45\], where polarons undergo thermally activated hopping from site to site. The formula for the mobility is

\[
\mu = \frac{eD}{k_B T} \left( 1 - c \right) v_0 \exp \left( -\Delta G / k_B T \right),
\]

where \( D \) is the diffusion constant of carriers, \( 1 - c \) is the probability that a neighboring site is available for hopping, \( \Delta G \) is the activation energy for polaron hopping, \( v_0 \) is the optical phonon frequency, \( k_B \) is Boltzmann’s
constant, T is the absolute temperature, and \( a \) is the hopping distance.

One can see that the mobility (\( \mu \)) is proportional to \( \exp(-\Delta G / k_B T) \). Noting that other factors in the above equation have relatively minor impacts on the mobility, we focus on only \( \Delta G \) values. The polaron transfer process involves initial, transition, and final states. In the initial state, polaron is mainly localized on a single atom, and in the final state, it is localized on a neighboring atom with the same coordinative environment. In this case, the transition state should occur midway between these two states. The activation energy for polaron hopping (\( \Delta G \)) can be estimated by calculating the potential energy changes as the polaronic lattice distortions are displaced from the initial to the final geometry. We investigate how \( \Delta G \) differs by hopping directions of our interests for both electron and hole polarons.

As shown in Figs. 5(a) and 5(b), an excess electron in anatase creates a polaron state within the band gap (lying 0.7 eV below the CBM). This extra electron becomes self-trapped at a Ti site, making itself Ti\(^{3+}\) instead of Ti\(^{4+}\). It turns out that each bond between Ti\(^{3+}\) and neighboring O anions elongates by 3.09% and 3.72%, respectively, compared to the neutral case. Likewise, as shown in Figs. 5(d) and 5(e), the extra hole creates a polaron state within the band gap (lying 0.8 eV higher than the VBM). This excess hole becomes localized at a selected O site, making itself O\(^{1-}\) instead of O\(^{2-}\). Each bond between the O\(^{1-}\) anion and neighboring Ti cations increases in length by 0.05%, 0.36%, and 2.16%.

We are particularly interested in their mobility along several directions, which can be indirectly assessed by calculating the activation energies for the hopping (\( \Delta G \)). For the electron polaron case, we selected three directions, i.e., [100], [001], and [201], as these are (quasi-) perpendicular to three dominant facets of anatase particles, i.e., (100), (001), and (101), respectively. It turns out that \( \Delta G \) is direction dependent [Fig. 5(c)]: \( \Delta G \) is similar and small along the [100] and [201] directions (\( \Delta G = 0.24 \) eV for the [100] direction and \( \Delta G = 0.23 \) eV for the [201] direction), whereas \( \Delta G \) is much larger along the [001] direction (\( \Delta G = 0.51 \) eV). This implies that polarons can hop much faster along the [100] and [201] directions, compared to the [001] direction. Moving on to the excess hole case [Fig. 5(f)], we compared \( \Delta G \) values of two directions, i.e., [100] and [001]. Unlike the extra electron case, the \( \Delta G \) values along these two directions are almost the same: \( \Delta G \) is 0.37 eV along the [100] direction, and \( \Delta G \) is 0.39 eV along the [001] direction. In order to check whether this trend is independent of \( U \) parameters, we have repeated all calculations at an extreme \( U \) value (i.e., \( U = 10 \) eV). Comparing the results between the \( U = 5 \) eV and the \( U = 10 \) eV cases (see the Supplemental Material [46]), we observe that absolute \( \Delta G \) values increase with the \( U \) term, however, their relative order between different directions is preserved in all cases.

Key results are as follows: (i) electrons are transported much more rapidly toward the (100)/(101) facets than the (001), and (ii) almost-isotropic transport is predicted for holes, dissimilarly to the bandlike transport case. It is important to note that, despite the quasi-isotropic hole polaron mobility, our polaron model still supports the preferred accumulations of electrons on the (100)/(101) facets and holes on the (001) facets. This is because the identification of reductive and oxidative facets should be based on the relative order between electron and hole transport mobility. For an example of the (001) facet, \( \Delta G \) along the [001] direction for an electron (0.51 eV) is much larger than the value for a hole (0.39 eV), which indicates that holes that will survive to the surface will outnumber electrons; as a result, holes would remain on this facet. Likewise, for the (100) facet, \( \Delta G \) along the [100] direction for an electron (0.24 eV) is much smaller than the value for a hole (0.37 eV), which leads to the conclusion that electrons would remain on this facet. To sum up, despite the isotropic hole polaron mobility, our polaron model also supports the experimental finding, i.e., preferred accumulations of electrons on the (100)/(101) facets and holes on the (001) facets.

IV. CONCLUSION

In summary, using first-principles calculations and assuming bandlike transport, we discover that the anisotropic behavior of electron and hole bulk transport in anatase TiO\(_2\) is the opposite. Meticulous analyses of orbital hybridizations were followed to explain this trend. This finding sheds a new light on the observed reduction/oxidation separations on different facets of TiO\(_2\) particles. For a broader impact, we additionally demonstrate that the opposite trend in anisotropy of electrons vs holes is widely applicable to TiO\(_2\) with dopants or defects. Motivated by the polaronic features in this material,
we expand the study to the case where polaron hopping is the dominant transport mechanism. Our polaron model also predicts dissimilar anisotropic behavior of electron vs hole bulk transport and supports the observed facet dependence of the photochemical activity of anatase TiO₂.

ACKNOWLEDGMENTS

This work was supported by the Creative Materials Discovery Program through the National Research Foundation of Korea (NRF-2016M3D1A1021140) and KIST institutional project (No. 2E26130). The authors thank KISTI for providing computational resources (Project No. KSC-2015-C2-033).

[28] Effective mass is calculated according to

$$m^* = \pm \hbar^2 \left( \frac{d^2 E}{dk^2} \right)^{-1},$$

where $\hbar$ is the reduced Planck constant, and $E$ is the band energy as a function of the wave vector $k$. The fitting range is $|k| < 0.1 \text{ Å}^{-1}$.