

Double-hole-induced oxygen dimerization in transition metal oxides

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Rather than being free carriers or separated single-hole polarons, **double holes in anatase TiO₂ prefer binding with each other, to form an O-O dimer after large structural distortion.** This pushes the hole states upward into the conduction band and traps the holes. Similar double-hole-induced O-O dimerization (a bipolaron) exists also in other transition metal oxides (TMOs) such as V₂O₅ and MoO₃, which have the highest valence bands composed mainly of O 2*p* states, loose lattices, and short O-O distances. Since **the dimerization can happen in impurity-free TMO lattices,** independent of any extrinsic dopant, it acts as an intrinsic and general limit to the *p*-type conductivity in these TMOs.

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I. INTRODUCTION

Transition metal oxides (TMOs) have been intensively studied for their electronic, spintronic, photonic, and photocatalytic applications [1–5]. Quite often the synthesized wide-gap TMOs have unintentional *n*-type conductivity and poor *p*-type conductivity [6,7]. This has significantly limited the applications of TMOs, especially in *p*-*n* junction devices [8–10]. Traditionally the origin of the poor *p*-type conductivity was attributed to the limited hole concentration: charge-compensating donor defects, such as oxygen vacancies and cation interstitials [11,12], will form spontaneously as the Fermi energy shifts down to near the valence-band maximum (VBM) level, which is low in the wide-gap TMOs [9,13]. This mechanism follows the empirical doping-limit rule [14,15].

Besides the thermodynamic limit to the hole concentration, the limit to the hole mobility can be another possible reason for the poor *p*-type conductivity. A recent density functional theory (DFT) study by Varley *et al.* using hybrid functionals showed that, in the prototypical TMO, TiO₂, the hole carrier will form a self-trapped polaron, and thus has very low mobility [16]. The formation of hole polarons results from the localized nature of the O 2*p* orbitals, so it happens whether the holes are created by *p*-type doping with extrinsic elements (like Al, Ga, In, etc.) [17,18], or injected electrically or by light absorption. The low mobility of hole polarons provides another explanation for the poor *p*-type conductivity, an alternative to the thermodynamic limit to the hole concentration. Because the VBMs of many TMOs are derived from the O 2*p* orbitals, polaron formation might occur widely in many TMOs. Indeed, similar hole polarons have been found in HfO₂, SnO₂, and Li₂O₂ [19–22].

So far study has been focused on **isolated hole polarons** [16–19,23], while the polaron-polaron interaction has been ignored in TMOs. In general, the electronic structure of an isolated single-hole polaron is characterized by a spin-polarized localized state with an energy level in the band gap (Fig. 1). When two or multiple polarons get close to each other,

how do the hole states interact? Intuitively, due to the Coulomb repulsion, one might expect that two polarons will repel each other and thus remain separated. However, **in this paper we will describe a phenomenon where two polarons bind to form a bipolaron pair, even in an impurity-free TMO lattice.** Such a pair pushes **the hole states all the way into the conduction band.** Thus, between the occupied and unoccupied states there is a clean gap, as large as that of the original TMO, and the Fermi energy can be pinned at the middle of the gap (as in an intrinsic semiconductor) despite the existence of the positively charged and localized holes. The rise of the Fermi energy suppresses the spontaneous formation of charge-compensating donor defects, so the conventional mechanism based on the limit to the hole concentration becomes ineffective [14,15]. This phenomenon highlights the complexity of TMO carrier dynamics, showing that it is questionable to use our understanding of the main group of semiconductors to explain the TMO behaviors.

Besides the abnormal electronic structure, there is significant change in the atomic structure near the bipolaron. Its negative binding energy relative to two separated polarons results from **the hybridization of the two hole states plus large O atomic relaxation, which can overcome the Coulomb repulsion.** The large displacements of two O atoms lead to the formation of an O-O bond (dimer) which does not exist in the original TMO lattice. **The O-O bond (dimer) formed traps two holes tightly, which causes a low hole mobility (even lower than that of the single-hole polaron) and limits the *p*-type conductivity.** This effect is found to exist in TMOs with short O-O distances and loose lattices, such as anatase TiO₂, V₂O₅, and MoO₃, independent of any dopants or the formation of defects, so it is an intrinsic and general limit.

II. STABILIZATION MECHANISM

We will first take the anatase TiO₂ as an example system to show why the double-hole-induced O-O bipolaron is stable vs free holes or separated single-hole polarons. When free hole carriers are present in the lattice, there is no structural distortion and the holes stay at the energy level of the VBM state (Fig. 1). When a single-hole polaron is formed, one Ti-O bond will be elongated by 0.2 Å, as shown in Fig. 2(b). Meanwhile the hole wave function becomes localized on one

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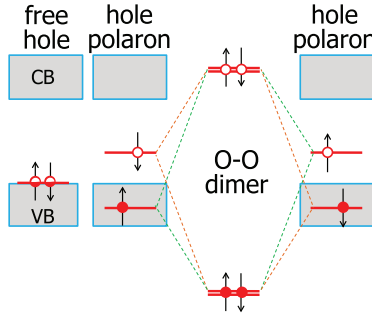


FIG. 1. (Color online) The band diagram of TMOs with a free hole near the VBM (left), and two single-hole polarons binding to form an O-O dimer bipolaron (right). The dashed lines show how the coupling between two single-hole polaron states induces the formation of an O-O dimer.

O atom with the energy level shifting up into the gap, as shown schematically in Fig. 1 (right) and quantitatively in Fig. 3(b) where the calculated partial density of states is projected on the displaced O atom (the calculation details are given in Sec. V). The hole polaron state is about 1.8 eV above the VBM, which traps the holes to the localized O 2p orbitals, and on the opposite-spin side the polaron also induces a localized state -5.3 eV lower than the VBM.

When there are two holes in the system, intuitively we may expect that they will form two separated hole polarons due to

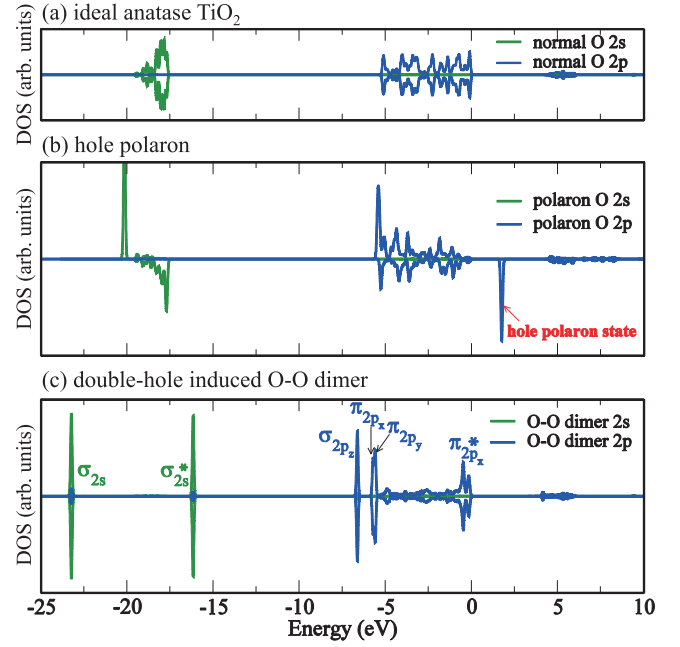


FIG. 3. (Color online) The calculated partial density of states (DOS) projected on (a) a normal O atom in the anatase TiO₂ lattice, (b) the polaron O atom, as shown by the green ball in Fig. 2(b), and (c) the O-O dimer as shown in Fig. 2(c). The energy is relative to the VBM eigenenergy. The top and bottom panels show the spin-up and spin-down DOSs, respectively.

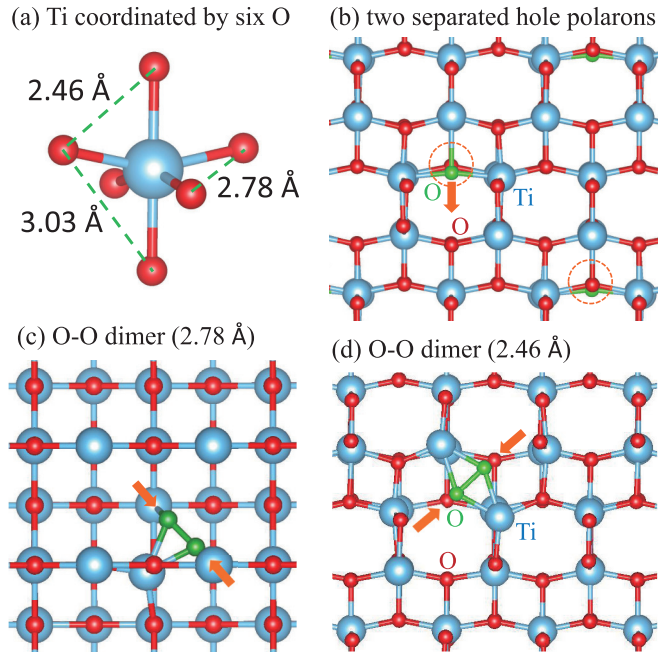


FIG. 2. (Color online) Structural plots for (a) one Ti cation coordinated by six O anions in the anatase TiO₂ lattice, (b) an anatase supercell with two separated single-hole polarons, and (c), (d) an anatase supercell with formation of two different O-O dimers. The red and light blue balls show the O and Ti atoms without displacement, respectively, and the green balls show the O atoms displaced from their ideal positions. The dashed lines in (a) show the distances between the O atoms. (c) is the top view along the c axis while (b) and (d) show the side view along the b axis.

the Coulomb repulsion. However, if the coupling between the two hole polaron states is considered, we find that there is a possibility for two hole polarons to bind with each other and induce an O-O dimerization. This can be understood according to a simple band-coupling model, which is plotted in Fig. 1 (right). When two hole polarons get close to form an O-O dimer, the two spin-up polaron states will couple, as will the two spin-down states. As a result, the two bonding states are pushed down into the valence band and two antibonding states are pushed up into the conduction band. Despite the large energy level separation between the initial spin-up and spin-down states, the final spin-up and spin-down bonding (and antibonding) states are degenerate, so the system becomes non-spin-polarized. At the final stage, there is no state in the band gap and the two electrons in the bonding states have significantly lowered energies, thus gaining total energy for the system. If the energy gain is larger than the strain energy of the structural distortion plus the hole-hole Coulomb repulsion, the O-O dimerization is stabilized relative to the two separated polarons.

To show whether this O-O dimerization is more stable than two separated hole polarons, a direct calculation of their total energy has been carried out (details are given in Sec. V). Here we follow Varley *et al.*'s methods and define a self-trapping energy for two holes as [16]

$$\Delta E_{ST} = E(\text{distorted}, 2h^+) - E(\text{ideal}, 2h^+) + 2\Delta V, \quad (1)$$

where $E(\text{ideal}, 2h^+)$ is the total energy of a 108-atom anatase TiO₂ supercell with two delocalized free holes (no structural distortion), and $E(\text{distorted}, 2h^+)$ is the total energy of the

same supercell with two holes trapped by structural distortion [either two separated polarons as shown in Fig. 2(b), or an O-O dimer, as shown in Fig. 2(c) or Fig. 2(d)]. Since the supercell is charged with two holes, we follow the procedure of Varley *et al.* and include a term $2\Delta V$, where ΔV is the electrostatic potential difference between the free-hole supercell and the trapped-hole supercell, calculated at a region far from the structural distortion [16,24]. As the supercell size becomes larger, ΔV will approach zero, but for finite-size supercells, the inclusion of $2\Delta V$ will make the calculated ΔE_{ST} converge faster depending on the supercell size [24]. A negative ΔE_{ST} means the self-trapped holes are more stable than the free holes. If ΔE_{ST} of the O-O dimerization is lower than that of two separated hole polarons, the O-O dimerization is energetically more favorable, and their difference gives us the polaron-polaron binding energy.

Three different configurations of O-O dimers in anatase TiO_2 are considered. They are formed through moving the O atoms together, starting from three O-O pairs which have original separations 2.46, 2.78, and 3.03 Å, as shown in Fig. 2(a). After local structural relaxation, the O-O dimers formed from the 2.78 and 2.46 Å O-O pairs are stabilized at O-O distances of 1.45 and 1.49 Å, respectively [shown in Figs. 2(c) and (d)] with negative $\Delta E_{ST} = -1.50$ and -1.18 eV per hole pair (-0.75 and -0.59 eV/hole). However, the dimer formed from the 3.03 Å O-O pair is unstable after relaxation. It should be noted that it is the double holes that stabilize the O-O dimer, and when there are no holes, all the O-O dimers are unstable.

We have also calculated ΔE_{ST} for two separated polarons, as shown in Fig. 2(b). The corresponding ΔE_{ST} is -0.96 eV per hole pair (-0.48 eV/hole). To test the convergence of our calculation, we have also calculated ΔE_{ST} when there is only one polaron in the 108-atom supercell; the corresponding result is -0.53 eV/hole. The difference is only 0.05 eV/hole. No matter which value is used, the energy of separated polarons is higher than that of the O-O dimers. Relative to two separated polarons in the supercell, the polaron-polaron binding energies are -0.54 eV and -0.22 eV per hole pair for the Fig. 2(c) and Fig. 2(d) O-O dimers, respectively [25]. The geometry of the O-O dimerization is rather like that of the dopant-dopant binding (e.g., N-N, C-S, C-O in anatase TiO_2) as found interestingly by Yin *et al.* [2] In contrast with the dopants (impurity atoms) which are locally charge neutral when not ionized, the hole polarons are positively charged, so it is unexpected that the strong Coulomb repulsion can be overcome and the polaron-polaron binding is favored.

III. ELECTRONIC STRUCTURE

In Fig. 3(c), we plot the calculated partial density of states (DOS) projected on the O-O dimer. It is obvious that the O-O dimer produces localized electronic states in the lattice, as demonstrated by the high peaks in the DOS, which can be likened to the O_2 molecular orbitals. For an isolated O_2 molecule (or O-O bonds in peroxides [22]), the hybridization of $2p$ atomic orbitals produces the bonding states σ_{2p_z} , π_{2p_x} , and π_{2p_y} , and the antibonding states $\pi_{2p_x}^*$, $\pi_{2p_y}^*$, and $\sigma_{2p_z}^*$. As labeled in Fig. 3(c), the three highest peaks of the O-O dimer $2p$ DOS can be attributed to four O_2 molecular orbitals, whose

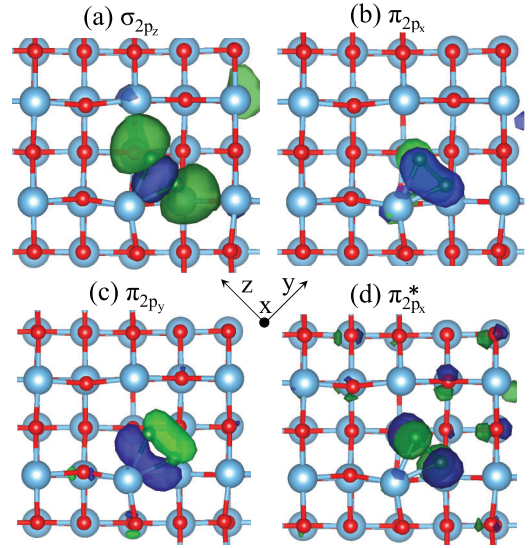


FIG. 4. (Color online) The wave functions of four electronic states localized on the O-O dimer, which produce the three highest peaks of the partial DOS as plotted in Fig. 3(c). In the xyz coordinate system shown here, these four states correspond to the σ_{2p_z} , π_{2p_x} , π_{2p_y} , and $\pi_{2p_x}^*$ orbitals of the O_2 molecule.

wave functions are also plotted in Fig. 4. (Two O_2 molecular orbitals, the occupied $\pi_{2p_y}^*$ and unoccupied $\sigma_{2p_z}^*$, do not induce high peaks in the partial DOS, since their wave functions hybridize heavily with the Ti $3d$ states.) Although the O-O dimer is in the TiO_2 lattice, these wave functions have obvious characteristics of O_2 molecular orbitals, indicating that an O-O bond is really formed. Therefore the O anions now have a valence of -1 , rather than the valence -2 of normal O anions. This can be considered as a local superoxidation [26] induced by two holes.

The calculated DOS (Fig. 3) of the O-O dimer is in good agreement with the band coupling model as shown in Fig. 1: (i) the σ_{2p_z} energy level of the O-O dimer shifts down relative to the $2p$ levels of the normal O atom or polaron O atom, which lowers the energy of the O-O dimer (contributing to the large and negative ΔE_{ST}); (ii) after the two polarons bind, the system become non-spin-polarized with the same spin-up and spin-down DOSs; (iii) the hole states are pushed up into the conduction band, leaving a clean band gap as large as that of the ideal anatase TiO_2 , so the holes are trapped at states high in the conduction bands and their mobility should be seriously suppressed. This sets an intrinsic limit to p -type conductivity regardless of the hole concentration.

IV. OTHER TRANSITION METAL OXIDES

As well as in the anatase TiO_2 , double-hole-induced O-O dimerization exists in other TMOs. One example is V_2O_5 (shcherbinaite structure [27]) and another is MoO_3 [28]. Their trapping energies ΔE_{ST} for single-hole polarons and double-hole bipolarons (O-O dimer) are shown in Table I. In V_2O_5 , a negative $\Delta E_{ST} = -0.98$ eV/hole is found for the O-O dimer with a separation 1.37 Å (2.98 Å in the nondistorted crystal), which is lower than the trapping energy of the single-hole polaron (-0.85 eV/hole). In MoO_3 , a large

TABLE I. Calculated self-trapping energy ΔE_{ST} (in eV/hole) for the single-hole polaron and the O-O dimers in different TMOs.

	V ₂ O ₅	MoO ₃	Anatase TiO ₂	Rutile TiO ₂
Hole polaron	-0.85	-0.54	-0.53	-0.08
O-O dimer	-0.98	-1.31	-0.75	0.41

negative $\Delta E_{ST} = -1.31$ eV/hole is found for the O-O dimer with a separation 1.37 Å (2.82 Å in the nondistorted crystal), which is much lower than the trapping energy of the single-hole polaron (-0.54 eV/hole). The large negative ΔE_{ST} clearly shows that two polarons in V₂O₅ and MoO₃ prefer to bind together to form O-O dimers. All these TMOs have the top part of the valence bands composed of O 2p states, as in TiO₂, so the stabilization of the O-O dimers can be understood according to the same band-coupling model as shown in Fig. 1.

However, not all TMOs will form O-O dimers when two holes are present. In TMOs like zinc-blende ZnO or even rutile TiO₂, the O-O dimers are unstable. More specifically, in ZnO the O-O dimer breaks up after structural relaxation, while in rutile TiO₂ the O-O dimer is metastable with positive $\Delta E_{ST} = 0.41$ eV/hole. (In contrast, single-hole polarons have negative ΔE_{ST} , which is consistent with the experimental identification of single-hole polarons in rutile TiO₂ [23].) The reason is twofold: (i) In anatase TiO₂, V₂O₅, and MoO₃, there is a large void space around the O-O pairs, which can tolerate the structural distortion with low strain energy. But in ZnO or rutile TiO₂ the crystal structure is relatively compact without such a large void, which makes large structural distortion costly. (ii) The shortest O-O distance in ZnO (3.21 Å) or rutile TiO₂ (2.54 Å) is larger than that in anatase TiO₂ (2.46 Å), so the formation of an O-O dimer needs larger structural distortion and more strain energy. Although the present study considered only a limited number of TMOs due to the computational expense, we expect that double-hole-induced O-O dimerization exists in other TMOs, as long as there are large voids and loosely bonded O atoms around such sites and the initial O-O distance is short. The band-coupling model of O-O dimerization is general for all TMOs with the highest valence bands consisting of localized O 2p states.

V. CALCULATION METHODS AND ANALYSIS

All the above calculations are performed within the DFT formalism as implemented in the Vienna Ab-initio Simulation Package (VASP) code [30]. Projector augmented-wave pseudopotentials [31] and an energy cutoff of 400 eV were used in all cases. The hybrid exchange-correlation functional Heyd-Scuseria-Ernzerhof (HSE) [29] is used with one-quarter ($\alpha = 0.25$) of exact electron exchange mixed into the generalized gradient approximation (GGA) [Perdew-Burke-Ernzerhof (PBE)] functional. The supercell size is 108 atoms for anatase TiO₂, 216 atoms for rutile TiO₂, 144 atoms for MoO₃, 84 atoms for V₂O₅, and 96 atoms for ZnO. To ensure the proper occupation of the free-hole state, only the Γ point is included in the Brillouin-zone integration, following the procedure of Varley *et al.* [16]. Test calculations with a larger supercell (216 atoms) and more k points for anatase TiO₂

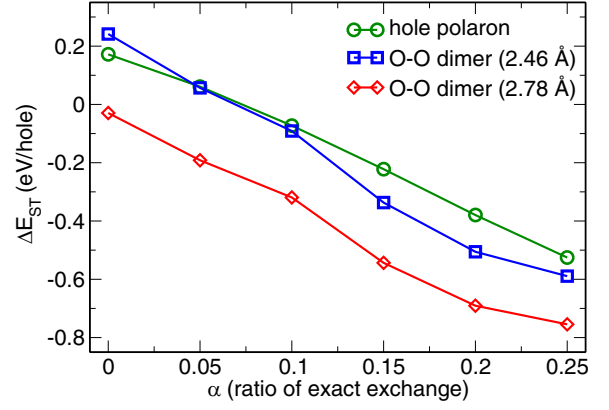


FIG. 5. (Color online) The dependence of the calculated self-trapping energy ΔE_{ST} on the α parameter of the hybrid functional for holes trapped by polarons or two O-O dimer bipolarons in anatase TiO₂.

showed that the error in the calculated self-trapping energy is less than 0.05 eV/hole.

Besides the hybrid functional HSE, we also tested our calculations using different functionals. As we know, DFT calculations with the local density approximation (LDA) or GGA tend to delocalize electron wave functions of 2p states due to an erroneous self-interaction energy [32], which makes the formation of polarons unlikely in the first place. The HSE functional largely corrects this problem, but nevertheless the result might depend on the mixing parameter α of the hybrid functional, which determines the percentage of the exact exchange mixed into the GGA functional [29]. It is thus necessary to test the dependence of our results on this mixing parameter, and ensure that the phenomena we found exist for the whole plausible parameter range.

The calculated trapping energies ΔE_{ST} as functions of α are shown in Fig. 5 for the single-hole polaron and two O-O dimers in anatase TiO₂. They decrease almost linearly with α . With a larger α ratio, more exact exchange is mixed in the hybrid functional, and the O 2p states become more localized. That means the polaron and bipolarons (O-O dimers) become more stable as the O 2p states become localized. As a result of the linear dependence, the ΔE_{ST} differences between the single-hole polaron and the O-O dimers are almost independent of α . Within the whole plausible range of the α parameter from 0 (equivalent to a pure GGA functional in PBE form) to 0.25 (the standard HSE functional), ΔE_{ST} of the most stable O-O dimer [shown in Fig. 2(c)] is always negative and lower than that of the single-hole polaron. Thus, it is rather safe to say that such an O-O dimer is the stablest configuration regardless of what α is used. This is also true for the lowest-energy O-O dimers in V₂O₅ and MoO₃. Therefore our conclusion is independent of the specific approximations to the functionals used.

On the other hand, as discussed above, the σ_{2p_z} energy level of the O-O dimer shifts down relative to the 2p levels of the normal O atom or polaron O atom, which lowers the energy of the O-O dimer (contributing to the large and negative ΔE_{ST}). If the splitting between the bonding σ_{2p_z} and antibonding $\sigma_{2p_z}^*$ levels is exaggerated in DFT (PBE or HSE) calculations, ΔE_{ST} will be overestimated (more negative

than the real value). However, our test calculations of the O_2 molecular orbital energy levels show that the σ_{2p_z} and $\sigma_{2p_z}^*$ splitting is underestimated by about 2.2 eV in the GGA (PBE) calculation and by about 0.5 eV in the hybrid (HSE) functional calculation relative to the experimental splitting [33]. Because the electronic states of the O-O dimer bipolaron are analogous to the O_2 molecular orbitals, the σ_{2p_z} and $\sigma_{2p_z}^*$ splitting and thus the ΔE_{ST} of the O-O dimer bipolaron are underestimated in our DFT calculations. Therefore the formation of the O-O dimer bipolaron is unlikely to be caused by the bonding-antibonding splitting error of DFT calculations.

VI. KINETIC BARRIERS

Although the double-hole bipolaron is thermodynamically more stable than two separated single-hole polarons, it should be noted that its formation in real materials also depends on the specific synthesis kinetics. If we assume the free holes are generated during the ionization of acceptor defects or dopants, the formation of polarons or bipolarons depends on the transition barrier from free holes to them. Following the method in Ref. [16], we calculated the barrier for (1) the transition from one free hole (ideal lattice with no distortion) to an isolated single-hole polaron (the value is 0.01 eV/hole), (2) the transition from two free holes to the lowest-energy O-O bipolaron (the value is 0.05 eV/hole), and (3) the transition from two separated single-hole polarons to an O-O bipolaron (the value is 0.41 eV/hole). These values indicate the following: (i) if the holes are generated by optical excitation, and hence will recombine with electrons within a nanosecond time period, most hole carriers will be trapped into single-hole polarons rather than bipolarons; (2) if the holes are permanent, generated via acceptor doping, then they will likely be trapped

into single-hole polarons first, and then eventually change into bipolarons (within the time scale of seconds or hours due to the 0.41 eV barrier height; the time is also dependent on the hole carrier concentration). This is the case at room temperature. At high temperature (e.g., during synthesis with temperature >600 K), the holes can stay as free carriers without falling into single-hole polarons, and directly form bipolarons.

VII. CONCLUSIONS

In conclusion, two holes in anatase TiO_2 are found to induce the formation of an O-O dimer (bipolaron), which is more stable than two free holes or two single-hole polarons. The formation of the O-O dimer pushes the hole states up into the conduction band, which traps the holes and sets an intrinsic limit to the p -type conductivity. According to the band-coupling model, we explained the stabilization mechanism of the double-hole-induced O-O dimerization. A similar phenomenon is also found in other TMOs with the highest valence bands composed of O $2p$ states, loose lattices, and short O-O distances, such as V_2O_5 and MoO_3 , so it could be a general phenomenon in a series of TMOs.

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with each other to form O-O bipolarons, but different O-O bipolarons prefer to stay separated from each other to reduce the strain and Coulomb energy.

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