

## Native defects and hydrogen impurities in $\text{Ag}_3\text{PO}_4$

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(Received 22 March 2012; revised manuscript received 2 June 2013; published 17 June 2013)

Silver orthophosphate ( $\text{Ag}_3\text{PO}_4$ ) exhibits extremely high photocatalytic activity under visible light. Gaining insight into the behavior of point defects would open opportunities for new applications. Our hybrid density-functional calculations show that intrinsic point defects are unlikely to cause carrier trapping. Charge neutrality analysis suggests that  $\text{Ag}_3\text{PO}_4$  possibly behaves as a weak  $n$ -type semiconductor under the O-poor condition and as a weak  $p$ -type semiconductor under the O-rich condition. Unlikely to other oxides, unintentionally incorporated hydrogen does not necessarily lead to strong  $n$ -type conductivity. Migration properties of some Ag-related defects and hydrogen are also discussed.

DOI: [10.1103/PhysRevB.87.245205](https://doi.org/10.1103/PhysRevB.87.245205)

PACS number(s): 61.72.Bb, 61.72.S-, 71.55.Ht

Semiconductor photocatalysis has attracted much attention in recent decades due to its technological importance in clean-fuel production and environmental remediation from solar energy.<sup>1</sup> Photoexcited carriers occurred in photocatalysis are involved in two competing processes: (i) diffusion to the surface such that chemical reactions with adsorbed molecules can occur; and (ii) recombination, which decreases the number of active carriers consumed by chemical reactions on the surface. Therefore, it is important to promote electron-hole separation for the enhancement of photocatalytic activity. Carrier recombination is believed to be accelerated by trapping centers, which are formed by defects in a crystalline semiconductor. In a study of Nb-doped  $\text{TiO}_2$  it was argued that deep states act as recombination centers and degrade the photocatalytic activity.<sup>2</sup> It was also shown that doping anatase  $\text{TiO}_2$  with a high concentration of nitrogen is disadvantageous for photocatalytic efficiency, probably due to defect formation.<sup>3</sup> Recently, Kong *et al.*<sup>4</sup> demonstrated that decreasing the relative concentration of bulk defects with respect to surface defects in  $\text{TiO}_2$  leads to enhanced high photocatalytic performance. These observations underscore the significance of understanding the role of defects in photocatalysts.

The large band gap of  $\sim 3.2$  eV in  $\text{TiO}_2$  implies that the photocatalytic activity is triggered only under ultraviolet light and doping is a common treatment for sensitizing it under visible-light irradiation although external doping is usually accompanied by the creation of recombination centers. In contrast, some silver-based oxides such as  $\text{AgNbO}_3$ ,  $\text{AgAlO}_2$ , and  $\text{AgGaO}_2$  are photosensitive under visible light<sup>5-11</sup> and enable solar energy conversion without the need for doping. Therefore, it is important to understand their intrinsic properties such as the nature of native defects to reveal the origin of their preferred photocatalytic activities.

Recently, it has been reported that semiconductor  $\text{Ag}_3\text{PO}_4$  exhibits extremely high photocatalytic activity with strong oxidation power leading to a high quantum yield of nearly 90% for the production of oxygen from water under visible

light.<sup>6</sup> This is intriguing because most photocatalysts give much poorer quantum yields of  $\sim 20\%$ . The outstanding photocatalytic properties of  $\text{Ag}_3\text{PO}_4$  have triggered theoretical investigations of their origin.<sup>12-14</sup> However, unanswered questions still remain such as why  $\text{Ag}_3\text{PO}_4$  possesses superior quantum efficiency to other photocatalysts. The nature of native defects and unintentionally doped impurities in  $\text{Ag}_3\text{PO}_4$  should have correlations with its unique properties.

Given the fact that  $\text{Ag}_3\text{PO}_4$  is a semiconductor with a band gap of 2.4 eV and a relatively small effective mass of electron<sup>12</sup> (compared to that of  $\text{In}_2\text{O}_3$ ), it might be applicable to optoelectronic devices. Indeed, crystalline thin film of  $\text{Ag}_3\text{PO}_4$  has been grown and used as photoanode in a photoelectrochemical cell, suggesting that  $\text{Ag}_3\text{PO}_4$  is an  $n$ -type semiconductor.<sup>6</sup> Moreover,  $\text{Ag}_3\text{PO}_4$  is a known ionic conductor in which the transportation of ions is reportedly assisted by defects.<sup>15,16</sup>

Ma *et al.*<sup>13</sup> used the local-density approximation with on-site Coulomb interactions (LDA +  $U$  method) to suggest theoretically that the silver vacancy ( $V_{\text{Ag}}$ ) in  $\text{Ag}_3\text{PO}_4$  is a shallow acceptor. However, there is no unique way to determine the value of  $U$ , and it is very hard to judge whether the adopted  $U$  gives reasonable results for the defect properties under the circumstances that experimental results are still limited. This is especially because the band gap of  $\text{Ag}_3\text{PO}_4$  is largely underestimated in LDA (0.1 eV) compared to the experimental value (2.4 eV), and the position of the gap state associated with a defect, strongly depends on the  $U$  parameter.

Here we perform density-functional calculations using a screened hybrid functional, which has been proven to reliably describe the electronic and structural properties of defects in semiconductors,<sup>17,18</sup> to investigate the influence of native point defects and unintentionally doped hydrogen on the photocatalytic and electrical properties of  $\text{Ag}_3\text{PO}_4$ . Our findings are summarized as follows. (i) It is very unlikely that intrinsic point defects in  $\text{Ag}_3\text{PO}_4$  cause the degradation of the photocatalytic activity or become the source of the electrical conductivity. (ii) Silver vacancies are abundant in as-grown

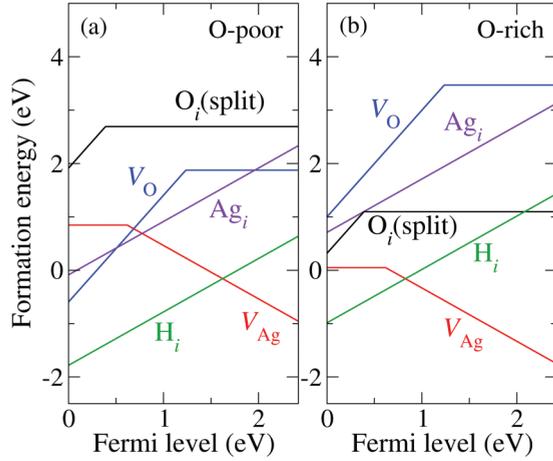


FIG. 1. (Color online) Formation energies as a function of the Fermi level (referenced to the valence-band maximum) of native point defects and interstitial hydrogen in  $\text{Ag}_3\text{PO}_4$ , under (a) O-poor and (b) O-rich growth conditions.

$\text{Ag}_3\text{PO}_4$  and highly mobile, thus are expected to be the origin of ionic conductivity. (iii) Hydrogen, which is often responsible for  $n$ -type conductivity in other oxides, is unlikely to be a main source of electron carriers in  $\text{Ag}_3\text{PO}_4$ .

Our calculations employed the screened hybrid functional proposed by Heyd, Scuseria, and Ernzerhof (HSE),<sup>19</sup> as implemented in the VASP code.<sup>20</sup> The use of 33% of the HF exchange potential yielded a direct band gap of 2.49 eV, in excellent agreement with the experimental value of 2.45 eV.<sup>6</sup> In order to simulate point defects and impurities, we used 128-atom supercells, a shifted  $1 \times 1 \times 1$  Monkhorst-Pack  $k$ -point set for the integration over the Brillouin zone, and a plane-wave basis set with an energy cutoff of 300 eV. The details for calculating formation energies can be found in Supplemental Material.<sup>21</sup>

Figure 1 shows the formation energies of  $V_{\text{Ag}}$ , oxygen vacancy ( $V_{\text{O}}$ ), silver interstitial ( $\text{Ag}_i$ ), oxygen interstitial ( $\text{O}_i$ ), and interstitial hydrogen ( $\text{H}_i$ ) calculated under the oxygen-poor (silver-rich) and oxygen-rich (silver-poor) growth conditions. Note that the formation energies of  $V_{\text{P}}$ ,  $\text{P}_i$ , and the antisites  $\text{O}_{\text{Ag}}$ ,  $\text{Ag}_{\text{O}}$  are found to be relatively high and thus are not shown in Fig. 1. Other antisite defects which are  $\text{Ag}_{\text{P}}$ ,  $\text{P}_{\text{Ag}}$ ,  $\text{O}_{\text{P}}$ , and  $\text{P}_{\text{O}}$  are not considered here because the ionic radii of the constituents of the antisite are very different. Those antisite defects are expected to have very high formation energies and thus are unlikely to form in a significant amount under thermodynamic equilibrium. The nature of the chemical bonding in  $\text{Ag}_3\text{PO}_4$  suggests that the removal of an Ag atom to form  $V_{\text{Ag}}$  should not cost much energy because it involves the breaking of weak Ag-O bonds. This is reflected by the low formation energy of  $V_{\text{Ag}}$  even under the silver-rich condition. The absence of an Ag atom creates partially occupied states in the band gap [Fig. 3(a)], mostly derived from the  $d$  orbitals of a neighboring Ag atom. These states can accept an additional electron, thus making the  $V_{\text{Ag}}$  a single acceptor. The transition level at which the stable charge state changes from neutral to singly negative  $\varepsilon(0/-)$  is located at 0.62 eV above the valence band maximum (VBM) for  $V_{\text{Ag}}$ , indicating that  $V_{\text{Ag}}$  is a deep acceptor. The method used for calculating defect transition levels is described in Ref. 22. Since  $V_{\text{Ag}}$  is an acceptor,  $V_{\text{Ag}}$

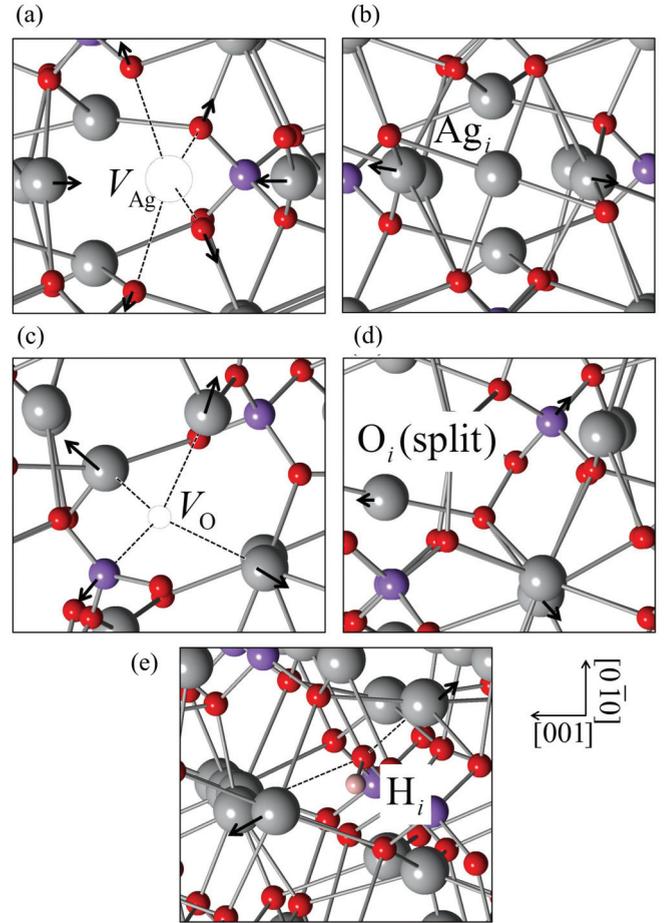


FIG. 2. (Color online) Atomic structures in the vicinity of (a)  $V_{\text{Ag}}^-$ , (b)  $\text{Ag}_i^+$ , (c)  $V_{\text{O}}^{2+}$ , (d)  $\text{O}_i^{\text{(split)}}$ , and (e)  $\text{H}_i^+$ . The directions in which neighboring atoms relax are selectively shown by arrows. The ideal positions of atoms removed to form vacancies are indicated by empty circles.

in the negative charge state ( $V_{\text{Ag}}^-$ ) is more easily formed when  $\varepsilon_F$  increases and thus becomes predominant in  $\text{Ag}_3\text{PO}_4$  for  $\varepsilon_F > 0.62$  eV, which is indicated by the very low formation energy under both of the growth conditions shown in Fig. 1. Inward relaxations were observed at the two nearest-neighbor Ag atoms upon the formation of a  $V_{\text{Ag}}$  in both charge states. The distance of the two Ag atoms across the  $V_{\text{Ag}}$  is  $\sim 16\%$  shorter than the equilibrium distance of the corresponding two Ag atoms in the perfect crystal [see Fig. 2(a)]. This indicates the presence of strong attractive interactions between the  $V_{\text{Ag}}$  and the neighboring Ag atoms, possibly leading to high  $V_{\text{Ag}}$  mobility. We investigated this aspect by computing the migration barrier of  $V_{\text{Ag}}^-$ . The calculated migration barrier is very low (0.10 eV), thus a  $V_{\text{Ag}}^-$  is likely to migrate along the path involves the displacement of a nearest-neighbor Ag atom along the [001] direction (see Fig. 2). A barrier of this magnitude can readily be overcome even at room temperature, indicating that although a high concentration of silver vacancies can be formed during growth, they are unlikely to remain as isolated vacancies; they will bind with other defects or impurities, diffuse out of the bulk region, or possibly migrate and become trapped at surface of the  $\text{Ag}_3\text{PO}_4$  particle. Combined with the

fact that it possesses a deep  $\varepsilon(0/-)$  transition level,  $V_{\text{Ag}}$  is unlikely to render  $\text{Ag}_3\text{PO}_4$  a  $p$ -type semiconductor.<sup>23</sup>

Silver interstitial [Fig. 2(b)] favors the tetrahedral site coordinated by four O atoms. Here  $\text{Ag}_i$  acts as a shallow donor, being stable only in  $1+$  charge state such that  $\varepsilon(+/0)$  is located above the conduction-band minimum (CBM). The formation energy of  $\text{Ag}_i$  in  $\text{Ag}_3\text{PO}_4$  is relatively low compared to the corresponding defects in other oxides such as  $\text{Zn}_i$  in  $\text{ZnO}$ <sup>23</sup> and  $\text{Sn}_i$ <sup>24</sup> in  $\text{SnO}_2$  under cation rich condition [Fig. 1(a)]. However, our calculations show that  $\text{Ag}_i$  can readily migrate along the [100] interstitial channel with a low migration barrier of 0.25 eV.<sup>25</sup> This implies that although  $\text{Ag}_i$  might be formed during growth, they are highly mobile even at room temperature. Therefore, it is very unlikely that  $\text{Ag}_i$  cause the  $n$ -type conductivity of  $\text{Ag}_3\text{PO}_4$ .

Oxygen vacancy in  $\text{Ag}_3\text{PO}_4$  has a relatively high formation energy (Fig. 1) compared to  $V_{\text{Ag}}$  and  $\text{Ag}_i$  because the strong P-O bond must be broken to remove an O atom. The transition level  $\varepsilon(2+/0)$  is located at 1.12 eV below the CBM indicating that  $V_{\text{O}}$  is a very deep donor. The  $V_{\text{O}}$  presents in the  $2+$  charge state when  $\varepsilon_F$  is near the VBM, at which the  $V_{\text{O}}$ -related states, are empty and located close to the CBM. When  $\varepsilon_F$  is located near the CBM, the  $V_{\text{O}}$  is energetically stable in charge neutral, and gives rise to fully occupied states near the VBM. The  $1+$  charge state is unstable for the entire range of  $\varepsilon_F$  considered here, indicating “negative- $U$ ” behavior in which  $\varepsilon(2+/+)$  lies above  $\varepsilon(+/0)$ . This behavior arises from large differences in the local atomic relaxations for  $V_{\text{O}}$  in different charge states. It is interesting to note that the  $V_{\text{O}}$ -related states in  $\text{Ag}_3\text{PO}_4$  possess the characteristic of the valence band, mainly derived from O and P  $p$  orbitals, and Ag  $d$  orbitals,<sup>21</sup> in contrast to other metal oxides such as ZnO,  $\text{SnO}_2$  where the  $V_{\text{O}}$ -related states are mainly derived from metal  $s$  orbital, having the characteristic of the conduction band.

Another relatively low energy defect is interstitial oxygen. We find that extra oxygen atoms are energetically favorable in the split-interstitial configuration,  $\text{O}_i(\text{split})$ .<sup>23</sup> Here the calculated O-O bond length is 1.45 Å, compared to 1.20 Å for the isolated  $\text{O}_2$  molecule, indicating that the  $pp\pi^*$ -like molecular orbital of the  $\text{O}_i(\text{split})$  is filled by two electrons from neighboring P and Ag atoms. The  $\text{O}_i(\text{split})$  is electrically inactive (neutral) for the most values of  $\varepsilon_F$  considered, and gives rise to an occupied state just above the VBM [Fig. 3(a)]. When the Fermi level is located very close to the VBM,  $\text{O}_i(\text{split})$  can occur in the  $2+$  charge state (Fig. 1) although such conditions are unlikely in  $\text{Ag}_3\text{PO}_4$  as discussed below.

As discussed above, native point defects are unlikely to be responsible for an intrinsic conductivity of  $\text{Ag}_3\text{PO}_4$ , while an  $n$ -type character was observed in the previous report.<sup>6</sup> Therefore, it is worth investigating the influence of an unintentionally doped impurity, hydrogen, which is ubiquitous and regarded as a potential donor in oxides.<sup>26</sup> In addition, precursors for synthesizing  $\text{Ag}_3\text{PO}_4$  usually contain hydrogen, and they are possibly left in a bulk. Neither experimental nor theoretical studies for hydrogen-related impurities in  $\text{Ag}_3\text{PO}_4$  have been reported elsewhere.

We investigated interstitial hydrogen in three charge states: positive, neutral, and negative. Similar to other oxides,<sup>24,26,27</sup>  $\text{H}_i^+$  favors sites close to oxygen [Fig. 2(e)] where a strong O-H bond of length 0.96 Å is formed, the same as the calculated

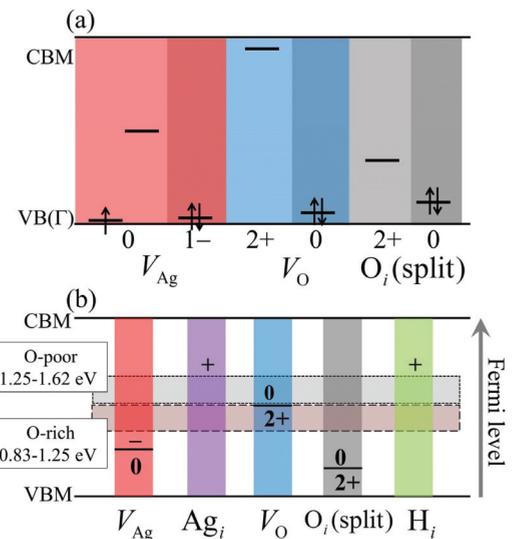


FIG. 3. (Color online) (a) Single-particle energy levels introduced in the band gap by native point defects. The arrows indicate the electron occupation. (b) Thermodynamic transition levels for native point defects and interstitial hydrogen in  $\text{Ag}_3\text{PO}_4$ . The shaded landscape-oriented belts indicate the possible range of Fermi level associated with the two extreme growth conditions (O-rich and O-poor) of  $\text{Ag}_3\text{PO}_4$ .

bond length in  $\text{H}_2\text{O}$  (0.96 Å). In the negative charge state,  $\text{H}_i^-$  prefers sites, closer to the cations ( $\text{Ag}^+$  in our case).<sup>27</sup> However, the high formation energy of  $\text{H}_i^-$  results in the  $\varepsilon(+/-)$  transition level being located well above the CBM, implying that  $\text{H}_i^+$  is stable for the entire range of  $\varepsilon_F$  values in the band gap ( $\text{H}_i^0$  is never stable). Therefore,  $\text{H}_i$  should act as a shallow donor in  $\text{Ag}_3\text{PO}_4$ . In addition,  $\text{H}_i^+$  has low formation energy as shown in Fig. 1. In order to reveal whether  $\text{H}_i$  remains active as donor at the temperature of interest, we investigate the migration of  $\text{H}_i$  for the two diffusion paths.<sup>21</sup> The diffusion along the path involved forming new O-H bond with the next-nearest neighbor O atom yield migration barrier of  $\sim 0.32$  eV, which is lower than those in  $\text{ZnO}$ <sup>28</sup> and  $\text{SnO}_2$ .<sup>24</sup> This implies that  $\text{H}_i$  is highly mobile even below room temperature and therefore can diffuse out of the sample or bind with other defects. This does not reflect that O-H bond in  $\text{Ag}_3\text{PO}_4$  is weaker than those in ZnO and  $\text{SnO}_2$  as evident from the calculated O-H bond length of 0.96 Å. In addition, our Bader analysis<sup>29</sup> shows that an O atom in bulk  $\text{Ag}_3\text{PO}_4$  possesses  $-1.49$  electron, more than those in ZnO ( $-1.13e$ )<sup>30</sup> and  $\text{SnO}_2$  ( $-1.26e$ ).<sup>31</sup> This implies that O-H bonds in  $\text{Ag}_3\text{PO}_4$  are more ionic than those in ZnO and  $\text{SnO}_2$ . In fact, the migration barrier of  $\text{H}_i$  is influenced by many factors such as the local atomic environment around the diffusion path. The complete picture of H diffusion in  $\text{Ag}_3\text{PO}_4$  could be complex and is beyond the scope of this study.

We also found that hydrogen acts as a shallow donor when substituted for oxygen ( $\text{H}_\text{O}$ ). At these sites a strong P-H bond is formed with a length of 1.40 Å, whereas no bond is formed with the three Ag atoms (the Ag-H distance is 2.84 Å). This is in contrast to the case of  $\text{H}_\text{O}$  in binary oxides such as ZnO and  $\text{SnO}_2$ , where multicenter bonds are formed leading to an  $n$ -type conductivity.<sup>24,32</sup> In  $\text{Ag}_3\text{PO}_4$ , however,  $\text{H}_\text{O}^+$  can easily

be dissociated to  $V_O^0$  and  $H_i^+$  due to their low binding energy of 0.34 eV. Combined with the fact that the formation energy of  $H_O^+$  is higher than that of  $H_i^+$  by 1.50 eV even under the O-poor growth condition, we can exclude the possibility that  $H_O$  is predominant in  $Ag_3PO_4$  under thermodynamic equilibrium.

In order to determine the Fermi level of  $Ag_3PO_4$ , we have self-consistently satisfied the condition of charge neutrality  $\sum_i q_i c(X_i^{q_i}) - n + p = 0$ , where the first term is a sum over concentration of all point defects considered in charge state  $q_i$ .  $n$  is the concentration of electrons in the conduction band and  $p$  is concentration of holes in the valence band. The detailed procedure for determining the Fermi level from the charge neutrality condition is described in Ref. 21. The defects with the lowest formation energies (highest concentration) essentially dominate in the charge neutrality. Let us consider the two extreme cases in which the realistic situation may fall somewhere in between. For the first case, all highly mobile defects which are  $H_i^+$ ,  $Ag_i^+$ , and  $V_{Ag}^-$  are considered to be annealed out or be passivated by counter charge defects and thus become electrically inactive.<sup>23</sup> In this case, the concentration of the charge neutrality is satisfied among electron and hole carriers in the same way as an intrinsic semiconductor leading to the Fermi level pinned at 1.25 eV above the VBM for both O-poor and O-rich conditions. For the second case, all defects shown in Fig. 1 are taken into account for the calculation of Fermi level, which is estimated to be about the intersections of two lines for  $H_i^+$  and  $V_{Ag}^-$ , which are about 1.62 and 0.83 eV above the VBM for the O-poor and O-rich conditions, respectively. We thus expect the realistic pinned Fermi level, is in between the two extreme cases, which is reasonably far away from the band edges. At this Fermi level,  $n$  and  $p$  are negligible and thus  $Ag_3PO_4$  is intrinsically insulating. The analysis above also suggests that  $Ag_3PO_4$  possibly behaves as a weak  $n$ -type semiconductor under the O-poor condition and as a weak  $p$ -type semiconductor under the O-rich condition. This behavior of an intrinsic  $Ag_3PO_4$  is in contrast to the typical photocatalyst  $TiO_2$  which usually shows  $n$ -type conductivity under an oxygen poor condition.

The calculated single-particle energy levels and thermodynamic transition levels associated with native point defects and hydrogen impurities are summarized in Fig. 3. Based on these levels, we now provide insight into the photocatalytic and electrical properties of  $Ag_3PO_4$ . The remarkably high quantum efficiency of nearly 90% implies that most of the photoexcited carriers participate in the photocatalytic reactions and that electron-hole recombination is suppressed. One origin of this property might be the large difference in the effective masses of electrons ( $m_e^*$ ) and holes ( $m_h^*$ ).<sup>12</sup> Moreover, silver-based oxides possess the characteristic that the top of the VB is composed both of  $Ag d$  and  $O p$  orbitals.<sup>12</sup> This promotes carrier hopping between cation and anion sites and is thus advantageous for hole transfer.<sup>33</sup> However, these features alone cannot explain the unique properties of  $Ag_3PO_4$ . Recombination due to traps induced by defects or impurities is known as Shockley-Read-Hall (SRH) recombination and is promoted more by midgap defect levels than the near-edge levels.<sup>34</sup> Our results suggest that native point defects are unlikely to cause carrier recombination in  $Ag_3PO_4$ . Under the O-poor condition, where the Fermi level is pinned at  $\sim 1.25$ – $1.62$  eV above the VBM, the thermodynamically stable charge states of relevant

defects are  $V_{Ag}^-$ ,  $V_O^0$ , and  $O_i^0$  (split) [Fig. 3(b)] of which occupied single-particle levels (hereby referred as “defect levels”) lie close to the VB edge [Fig 3(a)]. Under the O-rich condition, where the Fermi level is pinned at  $\sim 0.83$ – $1.25$  eV above the VBM, the defect levels in their thermodynamically stable charge states  $V_{Ag}^-$ ,  $V_O^{2+}$ , and  $O_i^0$  (split) still lie close to the band edges. This indicates that there is no plausible carrier recombination centers associated with native defects under a realistic Fermi level of as-grown  $Ag_3PO_4$ , which partly explain the high photocatalytic activity of  $Ag_3PO_4$  observed in Refs. 6 and 35. We note that the defect levels associated with  $Ag_i^+$  and  $H_i^+$  lie above the CBM and are thus unlikely to cause the carrier recombination. The absence of the deep states in  $Ag_3PO_4$  is one of the reasons for its superior quantum efficiency to other photocatalysts.

Our results also suggest that native defects cannot be responsible for the electrical conductivity of  $Ag_3PO_4$ . From the thermodynamic transition levels shown in Fig. 3(b), it is apparent that  $V_{Ag}$  is a deep acceptor, and its capability of generating hole carriers is limited. In addition, the low migration barrier of  $V_{Ag}$  implies that it will not remain as isolated defect, and thus cannot act as compensating center for  $n$ -type doping. These properties of  $V_{Ag}$  are very contrast to that of cation vacancies in other oxides, in which the formation energy of cation vacancies and their migration barriers are relatively high. The presence of  $V_{Ag}$  in the bulk at very low temperatures might be detected by positron annihilation spectroscopy (PAS), which was successfully performed to detect  $V_{Zn}$  in ZnO.<sup>36</sup> Given that  $V_{Ag}$  is highly abundant, can be negatively charged, and has high mobility, we suggest that  $V_{Ag}$  could be responsible for the ionic conductivity observed in  $Ag_3PO_4$ .<sup>16</sup> We also find that native defects are unlikely to cause  $n$ -type conductivity. Although  $Ag_i$  shows the characteristic of a shallow donor, it is highly mobile.  $V_O$  and  $O_i$  (split) are very deep donors and have very high formation energies [Fig. 3(b)]. Surprisingly, unlike other oxides, the unintentionally incorporated hydrogen cannot cause  $n$ -type conductivity, either. This is because  $H_i^+$  is highly mobile and does not successfully generate electron carriers, while  $H_O^+$ , which is known as a source of  $n$ -type conductivity in many oxides, has a high formation energy and can easily be dissociated into  $V_O^0$  and  $H_i^+$ , indicating that  $H_O^+$  is unlikely to be the primary donor. Hence, the origin of the  $n$ -type characteristic observed in a  $Ag_3PO_4$  thin film in Ref. 6 was not identified in the present study. However, as we discussed above, under the O-poor condition  $Ag_3PO_4$  can behave as a weak  $n$ -type semiconductor.

Since there is no potential compensating center for donors and the position of the CBM is relatively low (which implies that the donor ionization level can be very close or even above the CBM), we expect that external doping for  $n$ -type  $Ag_3PO_4$  is feasible with high carrier concentration. Such an  $n$ -type  $Ag_3PO_4$  is required for an electrode in the photoelectrochemical cell and other applications. Our results suggest that shifting the Fermi level towards the conduction band, or in other words  $n$ -type conditions, likely enhance the photocatalytic activities in  $Ag_3PO_4$ . Sulfur is a possible candidate for  $n$ -type doping when substituted for P, as in the case of S-doped GaP which exhibits  $n$ -type conductivity.<sup>37</sup> Last but not least, our results also reveal that the behaviors

of point defects in  $\text{Ag}_3\text{PO}_4$  are different<sup>21</sup> from those in metal oxides such as ZnO, and lead to a deep understanding of the electronic and photocatalytic properties of Ag-based oxides.

In summary, we have investigated the influence of native point defects and hydrogen impurities in  $\text{Ag}_3\text{PO}_4$  using hybrid-functional calculations. We find that native point defects are unlikely to degrade the photocatalytic activity or be responsible for the electrical conductivity. The charge neutrality analysis suggests that  $\text{Ag}_3\text{PO}_4$  possibly behaves a weak  $n$ -type semiconductor under the O-poor condition and as a weak  $p$ -type semiconductor under the O-rich condition. The unintentional incorporation of hydrogen does not necessarily

cause  $n$ -type conductivity in contrast to other oxides. Our results suggest that  $\text{Ag}_3\text{PO}_4$  could feasibly be doped in  $n$ -type fashion.

We would like to thank S. Ouyang and J. Ye for fruitful discussions and advice. N.U. thanks H. Hosono for useful advice. This work was supported by the Japan Science and Technology Agency (JST) Precursory Research for Embryonic Science and Technology (PRESTO) program. P.R. thanks J. T.-Thienprasert for useful discussion. P.R. and N.U. thank the High-Performance Computing Center of California NanoSystems Institute (CNSI, UCSB) and the Synchrotron Light Research Institute (SLRI, Thailand) for their hospitality.

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