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Facet Effects of Ag₃PO₄ on Charge Carrier Dynamics: Trade-Off between Photocatalytic Activity and Charge Carrier Lifetime

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Abstract: Silver phosphate (Ag₃PO₄) is a promising visible-lightdriven photocatalyst with a strong oxidation power and exceptionally high apparent quantum yield of O₂ evolution. Although engineering Ag₃PO₄ facets is widely known to enhance its photocatalytic activity, most studies have explained its facet effect by calculating surface energies. Herein, the charge carrier dynamics in three kinds of Ag₃PO₄ crystals (mixed facets, cubic, and tetrahedral structures) were first investigated using single-particle photoluminescence microscopy and femtosecond time-resolved diffuse reflectance spectroscopy. As a result, we clarified that the disagreement between the photocatalytic activities (dye degradation and O₂ evolution) of different Ag₃PO₄ facets are the consequence of trade-off between catalytic activity and lifetime of photogenerated charge carriers in addition to surface energy.

Silver phosphate (Ag₃PO₄) has emerged as a promising O₂evolving photocatalyst with its bandgap (app. 2.4 eV) and deep valence band (+2.9 V vs. NHE) with an exceptionally high apparent quantum yield of O₂ evolution (over 80% at λ < 480 nm).^[1] Because photocatalytic activity is greatly influenced by surface energy and area, presence of defect sites, and charge carrier lifetime, sophisticated and rational material designs are required to improve its catalytic activity. Among various approaches, crystal facet engineering has been widely applied to many photocatalytic semiconductor materials because surface energy and charge carrier dynamics are greatly influenced by facet and structure.^[2]

There have been great efforts to enhance the Ag_3PO_4 photocatalytic performance. Bi et al. reported the synthesis of Ag_3PO_4 rhombic dodecahedron and cube with sharp corners and edges.^[3] Due to the higher surface energy of the (110) facets, a rhombic dodecahedron shows higher activities of dye degradation than a cube. In addition, Martin et al. reported that the Ag_3PO_4 tetrahedron with (111) facet showed the highest photocatalytic activities for O_2 evolution, followed by mixed facets, cube, and rhombic dodecahedron.^[4] Conversely, Hsieh et al. recently reported that the Ag_3PO_4 tetrahedron was nearly inert for dye degradation, whereas the Ag_3PO_4 cube generated the largest amount of hydroxyl radical ('OH).^[5] Thus, there has been no consensus on which crystal structure of Ag_3PO_4 is advantageous

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as a photocatalyst. Furthermore, a careful investigation of dye degradation and O₂ evolution of Ag₃PO₄ is required, as they cannot be explained by a single factor such as the surface energy of the facet. To the best of our knowledge, there has been no report on the direct monitoring of photogenerated charge carriers of various Ag₃PO₄ crystals, which may have prevented the further development of Ag₃PO₄ as an O₂-evolution catalyst.

In this study, sub-micrometer- to micrometer-sized Ag₃PO₄ crystals with mixed facets (noted Ag₃PO₄ mixed facets later), cubic, and tetrahedral structures are thoroughly investigated to understand their photocatalytic redox activities based on charge carrier dynamics. We first prepared three kinds of Ag₃PO₄ samples (mixed facets, cube, and tetrahedron), as described in the Supporting Information (SI). As shown in Figures 1a-1c, Ag₃PO₄ mixed facets have particle-like morphology with smooth surfaces, whereas Ag₃PO₄ cube and tetrahedron exhibit sharp edges and corners. From a Brunauer-Emmett-Teller (BET) test, the specific surface areas of Ag₃PO₄ mixed facets and tetrahedron are found to be nearly the same (1.18 and 1.10 m² g⁻¹, respectively), whereas that of cube is approximately 3 times smaller (0.38 m² g⁻¹). This result well agrees with the obtained averaged side lengths from SEM images (Table S1). In accordance with previous reports, all three Ag₃PO₄ samples have visible light absorption at over 500 nm (Figure S1a), and the XRD and XPS results well represent the corresponding Ag₃PO₄ structures with high crystallinity (Figure S1b and S2, respectively).



Figure 1. SEM pictures of Ag₃PO₄ mixed facets (a), cube (b), and tetrahedron (c) (scale bar: 1 μ m). Photocatalytic formation of resorufin (d) and O₂ evolution (e) in aqueous solution using Ag₃PO₄ mixed facet (black, circle), cube (red, square), and tetrahedron (blue, triangle). All tests were conducted under visible light irradiation (λ > 420 nm, 480 mW cm⁻²). Five-percent methanol was added in the oxidation test of amplex red to decelerate resorufin formation and dye degradation (b). To improve photostability of Ag₃PO₄ without an electron

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scavenger (50 mM AgNO_3), we employed the phosphate buffer condition containing sufficient [PO_4]^-[6]

Amplex red was employed to evaluate the photocatalytic 'OH formation by three Ag₃PO₄ samples (Figure S3).^[7] Pink-colored resorufin was formed by the oxidation of amplex red chromophore by 'OH (Figure S3), which can be detected by the appearance of absorbance at around 572 nm (Figure S4a). Under visible light irradiation (λ > 420 nm), it was revealed that the Ag₃PO₄ tetrahedron induced amplex red oxidation the fastest, whereas the Ag₃PO₄ mixed facet and cube oxidized amplex red 5 times slowly (Figure 1d). Furthermore, O2 evolution tests were performed for three Ag₃PO₄ samples under visible light irradiation. Contrary to the amplex red assay, the rates of photocatalytic O₂ generation of Ag₃PO₄ mixed facets, cube, and tetrahedron did not differ significantly regardless of the presence of an electron scavenger (50 mM silver nitrate, Figure 1e). During our repetitive experiments, the overall trends were not altered by elongated irradiation (Figure S5).

As previously reported, Ag₃PO₄ tetrahedron has been considered as a highly active photocatalytic crystal due to its higher surface energy than that of Ag₃PO₄ cube and rhombic dodecahedron.^[4] Nonetheless, our results indicate that surface energy cannot solely explain the disagreement between the photocatalytic activities of Ag₃PO₄ samples. Previously, we did reveal that the (001) facet of TiO₂ is a more active site for photocatalytic reduction than the (101) facet although the (101) facet exhibits higher surface energy.^[2a] Furthermore, the enhancement in photocatalytic activity by sharp corners and edges^[8] was not observed in our study, as the Ag₃PO₄ mixed facets showed similar activities as those of the Ag₃PO₄ cube and tetrahedron (Figure 1e). Therefore, several factors that may affect the photocatalytic activities of Ag₃PO₄ should be considered together on the basis of time-resolved spectroscopic measurements.

In Figure 2, the transient absorption spectra of three Ag₃PO₄ samples upon 400-nm excitation were measured in the near-infrared (NIR) region using femtosecond time-resolved diffuse reflectance (TDR) spectroscopy. Considering the broad spectral shapes and energy of the transient species,^[9] we assigned the observed transient species to the photogenerated electrons in Ag₃PO₄. The decay of the charge carriers was well fitted with a double-exponential function, as summarized in Table 1. Ag₃PO₄ mixed facets, cube, and tetrahedron underwent a rapid relaxation ($\tau_1 = 37.7, 50.8, \text{ and } 19.1 \text{ ps}, \text{ respectively}$) followed by slower decays in the sub-ns time scale ($T_2 = 584.6$, 837.3, and 434.9 ps. respectively). The observed relaxation processes cannot be explained by bimolecular charge recombination between hole and electron, which usually follow power law kinetics. Because photocatalytic reactions such as water oxidation are reported to occur in the millisecond time scale.^[10] the observed kinetics represent complicated relaxation processes such as charge trapping and recombination before diffusionlimited reactions occur. When the three decay profiles were compared together (Figure 2d), the Ag₃PO₄ tetrahedron exhibited the fastest relaxation pathway of the photogenerated electron (19.1 ps, 39%). The proportion of the remaining electrons at over 1 ns was the largest for cube, followed by mixed facet and tetrahedron (58.5, 34.8, and 27.5%, respectively). This result agrees with the results of Hsieh et al. that the highest barrier for electron transport exists on the (111) crystal facet of the Ag₃PO₄

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tetrahedron, leading to faster charge recombination than that of $\mathsf{cube}^{[\mathbf{5}]}$



Figure 2. TDR spectra of Ag₃PO₄ mixed facets (a), cube (b), and tetrahedron (c) taken after 5, 20, 46, 106, 206, 506, and 1046 ps of a femtosecond-pulse excitation (λ_{ex} = 400 nm). (d) Normalized TDR decays of Ag₃PO₄ mixed facets (black), cube (red), and tetrahedron (blue) monitored at around 950 nm. Green lines show results of double-exponential fitting. The fitting parameters are summarized in Table 1.

Table 1. TDR fitting	parameters ^[a]
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	A1 / %	<i>т</i> ₁ / ps	A2/%	<i>τ</i> ₂ / ps	A3/%
Mixed facets	33 ± 1	37.7 ±	37 ± 1	584.6 ±	28 ± 1
		2.5		55.4	
Cube	16 ± 2	50.8 ±	35 ± 2	837.3 ±	47 ± 3
		9.2		9.2	
Tetrahedron	39 ± 1	19.1 ±	33 ± 1	434.9 ±	23 ± 1
		1.1		31.2	

[a] Three decay profiles (Figure 2d) were well fitted by a double exponential function; $y = A1exp(-x/r_1) + A2exp(-x/r_2) + A3$.

To investigate the underlying mechanisms of the facet and the structural effects on photocatalytic activities, single-particle photoluminescence (PL) microscopy was used to monitor the PL properties of Ag₃PO₄. This method can clearly visualize the local active site on the single particle and hidden photocatalytic mechanisms, which are not accessible through ensembleaveraged photocatalytic experiments.^[11] Figures 3a-3c show the representative PL lifetime images of Ag₃PO₄ mixed facets, tetrahedron, and cube, and additional results can be found in Figures S6 and S7. Interestingly, there were common characteristics between the lifetime and energy of Ag₃PO₄ singleparticle PL; as the PL energy increases (i.e., blue-shifted emission spectra), the PL lifetime becomes shorter. As shown in Figure 4, the maximums of the PL spectra with short ($\tau < 0.2$ ns) and long lifetime (2.5 ns $< \tau < 5.0$ ns) were approximately 460 and 750 nm, respectively. Considering the band-gap energy of Ag₃PO₄ (app. 2.6 eV, Table S1), the former represents band edge emission, and the latter represents NIR emission, which is presumably induced by the relaxation of charge trapping states. Such heterogeneity in PL lifetime/energies was most apparent in Ag₃PO₄ mixed facets (Figures 3 and S6). On careful comparison of single-particle PL



Figure 3. Representative single particle PL lifetime images of (a) Ag_3PO_4 mixed facet, (b) cube, and (c) tetrahedron (λ_{ex} = 405 nm) taken in air and (insets) corresponding SEM pictures (scale bar: 1 µm). (e-f) Single particle PL spectra measured at the points indicated by arrows in (a) and (b) or at the center of a single Ag_3PO_4 tetrahedron (c). Incomplete spatial matching between SEM and PL images is due to photocorrosion or slight displacement of Ag_3PO_4 samples under the vacuum condition of SEM measurement.

lifetime and SEM images, the sites with short PL lifetime were found to be located on the defect-like surfaces or grain boundaries. This spatial correlation implies that the photogenerated electron in the Ag₃PO₄ mixed facets in the structural defect undergoes rapid charge recombination. Besides, the charges on the smooth surfaces of Ag₃PO₄ mixed facets are slowly relaxed, resulting in charge recombination in the nanosecond time scale.

On the other hand, we initially supposed that the sharp corners of the Ag_3PO_4 cube and tetrahedron would be strongly emissive because the corners and edges of the semiconductor have intrinsically more defect sites and act as reactive sites and charge recombination centers of the photocatalyst. As shown in Figures 3b and 3c, however, strong PL of the Ag_3PO_4 cube PL was detected at certain sites on the planes and edges, whereas the entire plane of the Ag_3PO_4 tetrahedron was emissive without a particular spatial dependency. Another noteworthy finding is that the PL intensities and spectra of the Ag_3PO_4 cube were largely heterogeneous by particles, which was not evident in the Ag_3PO_4 tetrahedron; the PL intensity, lifetime, and spectrum of the Ag_3PO_4 tetrahedron did not deviate based on sites or particles.

To elucidate the observed properties of Ag_3PO_4 , we propose that there are two types of surface trapped holes (STH) in Ag_3PO_4 depending on its facets: a hole either in a short-lived and reactive 'shallow trap' or in a relatively more stable and less reactive 'deep trap' (Figure 4). It has been reported that the conduction and valence bands (CB and VB, respectively) of Ag_3PO_4 are composed of Ag 5*s*5*p* with a small quantity of P 3*s* orbitals and Ag 4*d* with O 2*p* orbitals, respectively.^[1] Thus, upon photoirradiation, we expect charge separation (eq 1) and subsequent formation of STH (eq 2) in Ag_3PO_4, as given below.

 $Ag_3PO_4 + hv \rightarrow Ag_3PO_4 + h^+ + e^-$ (1)

$$[Ag_2=O-Ag]_{suff} + h^+ \rightarrow [Ag_2=O\cdots Ag]_{suff}^+,$$
(2)

where the phosphorus-oxygen bond is omitted in eq 2. In light of the previous study, the Ag atoms on the (100) surface are coordinatively saturated, whereas the Ag atoms on the (111) surface are located at three-coordinated sites with one dangling bond.^[12] Thus, the STH residing on the (111) surface ([Ag₂=O•••Ag]_{surf}⁺ in eq 2) would be less stable than those on the fully coordinated (100) surface. Consequently, the hole on the (111) facet has a greater tendency to recombine with photogenerated electron or oxidize nearby substances than that on the (100) facet.

Indeed, the decay of photogenerated electron was the fastest in the Ag₃PO₄ tetrahedron, and no spatially preferential charge recombination was observed. This phenomenon can be explained by the short-lived and reactive STH on the (111) facets. Once the photogenerated charge carriers are trapped on the (111) facets, most of them probably undergo charge recombination, which conversely prevents photocorrosion (Figure S8).^[13] From single-particle PL measurements, these shallow traps are found to have comparable energies of the Ag₃PO₄ bandgap. It should be emphasized that we did not observe any NIR emission from the Ag₃PO₄ tetrahedron; hence, the deep trap is not dominant on the (111) facets. When considered together, the charge recombination kinetics of a few tens and hundreds of picoseconds obtained in the TDR measurements represent the process of charge carrier migration to the surface and trapping in the 'shallow traps' (k_{CR1} and k_{CR2} in Figure 4b, respectively). In addition to the charge carrier dynamics described above, the (111) facets exhibit over-abundance of dangling phosphorusoxygen bonds, which act as oxidation sites, thus further contributing to the strong photocatalytic oxidation ability of the Ag₃PO₄ tetrahedron.^[14]

Meanwhile, the 'deep traps' are considered to be mostly located on the fully saturated Ag. As shown in single-particle PL

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Figure 4. Charge carrier kinetics and different types of traps depending on the Ag₃PO₄ facets revealed in this study. ST and DT denote shallow and deep traps, respectively. k_{CR} indicates the rate constant of charge recombination obtained from the TDR measurements, whereas $k_{DT,r}$ and $k_{ST,r}$ are the rate constants of the radiative recombination processes of the deep and shallow traps, respectively, calculated from single-particle PL measurements.

images, long-lived deep traps were populated on the smooth surfaces of Ag₃PO₄ mixed facets and cube samples. From their spatially distinguished NIR emissions, the energy of the photogenerated charge carriers in the deep traps would be approximately 0.6–1.0 eV smaller than in the Ag₃PO₄ bandgap. Because the Ag₃PO₄ mixed facets and cube enable the same photocatalytic oxidation reaction as that of the tetrahedron, we expect that the energy level of the deep trap should be sufficient for water oxidation. Thus, 0.6-1.0 eV smaller energy originates from both trap sites of electron and hole, as depicted in Figure 4a. Based on the results of the TDR measurements, a few hundreds of picosecond kinetics represents the trapping of charge carriers in less reactive deep traps (k_{CR2} in Figure 4a). On the other hand, short-lifetime and band-edge PL was observed in the defect sites and grain boundaries of Ag₃PO₄ mixed facets and cubes, indicating that the STH in the imperfect crystalline region (analogous to shallow traps of (111) facets) undergo rapid charge recombination (k_{ST,R} in Figure 4a). While the role of grain boundaries in the charge carrier lifetime are varied depending on the photocatalyst materials,^[15] the grain boundaries of Ag₃PO₄ mixed facets accelerated the charge recombination process.

We further claim that the long-lived photogenerated charge carriers make Ag₃PO₄ vulnerable to photocorrosion, as implied by the initiation of surface roughening from the smooth surfaces of the mixed facets (Figure S8). In particular, Ag₃PO₄ cubes exhibiting (100) facets on the surface were more photocorroded when compared with the Ag₃PO₄ mixed facets. Facilitated charge migration in Ag₃PO₄ cube suggested by Hsieh et al.^[5] may accelerate sequential bond cleavages on (100) facets, formation of defect sites, and concentrated charge recombination, finally

resulting in significant photocorrosion. Such surface roughening has been reported in rutile TiO_2 , induced by nucleophilic attack of an H_2O molecule on the STH.^[16] Interestingly, we did observe fluctuation of single-particle PL intensity of Ag_3PO_4 mixed facets and shortening of single-particle PL lifetime, indicating *in situ* formation of defect sites and shallow traps on the smooth surface due to the cleavage of the coordination bonds of Ag (Figure S10).

conclusion, we have thoroughly investigated In photocatalytic activities, kinetics of photogenerated charge carriers, and single-particle PL behaviors of Ag₃PO₄ depending on its facets. Here, we first demonstrated the presence and distribution of different trap sites on the (100) and (111) facets of Ag₃PO₄. The different photocatalytic activities of the (111) and (100) facets to generate 'OH and O₂ (Figures 1d and 1e) can presumably be attributed to the proportion of shallow traps with a higher oxidation ability since 'OH formation requires higher oxidation potential than O2 evolution (2.83 and 1.23 eV vs NHE, respectively).^[17] Nonetheless, STH on the (111) facets are less stable, resulting in facile charge recombination. These results indicate a trade-off relationship between charge carrier lifetime and photocatalytic activity; long-lived charge carriers are sometimes too stable to react. The obtained insights will contribute toward improving the photostability of Ag₃PO₄, which is a major drawback of Ag₃PO₄ in practical applications, and designing more sophisticated photocatalysts to trigger a selective oxidation process for biological and medical applications (e.g., selective O₂ evolution during water oxidation with negligible 'OH formation).

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