

Supplementary Material
for
Charge carrier dynamics and photocatalytic activity of {111} and {100}
faceted Ag₃PO₄ particles

*Rochan Sinha¹, Dennis Friedrich², Georgios Zafeiropoulos¹, Erwin Zoethout¹, Matteo Parente¹,
Mauritius C. M. van de Sanden^{1,3}, Anja Bieberle-Hütter^{1,*}*

¹Dutch Institute for Fundamental Energy Research (DIFFER), P.O. Box 6336, 5600 HH Eindhoven, the Netherlands

²Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

³Department of Applied Physics, Eindhoven University of Technology (TU/e), P.O. Box 513, 5600 MB Eindhoven, the Netherlands

*Corresponding author. Email: a.bieberle@diffier.nl

Crystallographic properties

Structural characterization was done by X-ray diffraction (see experimental methods in main manuscript for details). XRD was performed in a Bragg-Brentano configuration in the 2θ range from 20° - 72° . The XRD diffractograms (Figure S1) show the presence of polycrystalline Ag_3PO_4 (6.004 \AA , BCC, P_43n, ICSD number: 14000) for both particles. The particles are almost phase pure. The small peak around 38.2° in the tetrahedral spectrum corresponds to Ag (111) and is believed to be related to some reduction of Ag_3PO_4 to Ag at the surface of this sample. XPS analysis (see subchapter "surface composition" in the main text) did in general not detect metallic Ag at the surface of tetrahedral particles. SEM analysis did also not prove metallic Ag at the surface, since this would result in a rough overlayer on the particles.

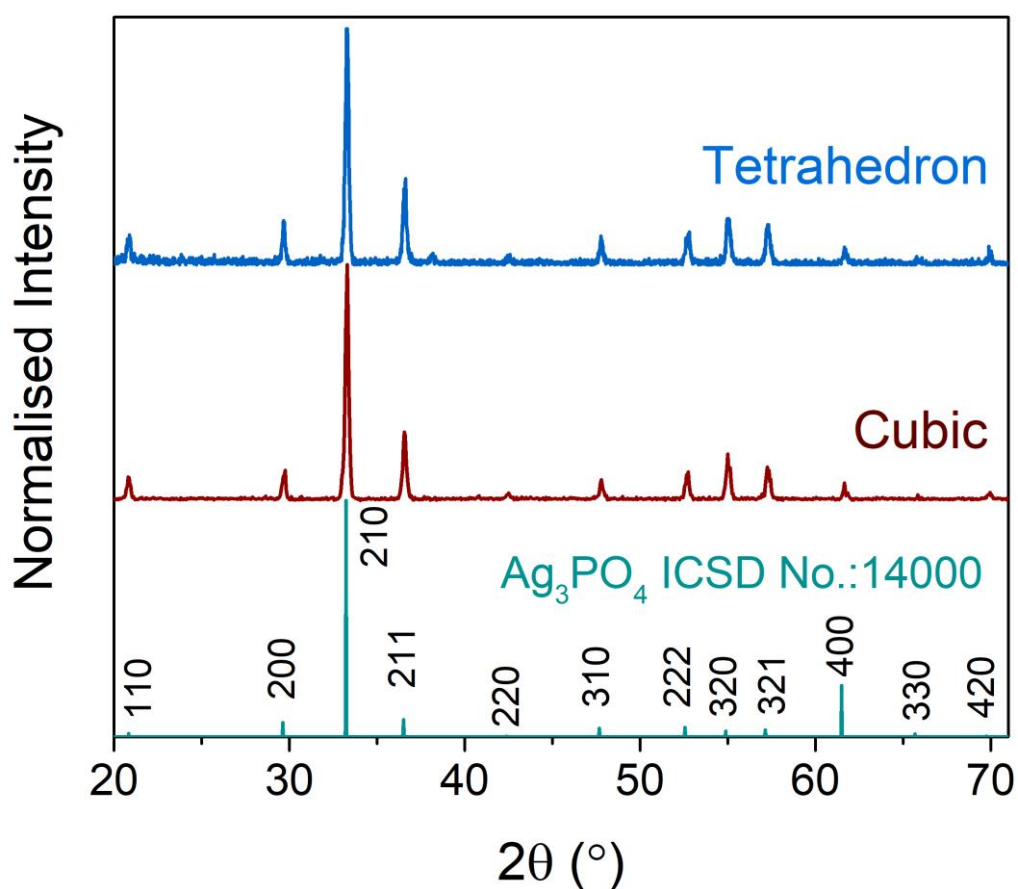


Figure S1 XRD spectra of the cubic and tetrahedral Ag_3PO_4 particles. Peaks are labelled with the corresponding crystallographic orientations according to ICSD catalogue number 14000.

Surface composition

The surface composition was characterized by X-ray photo-electron spectroscopy (XPS) (see experimental methods in main manuscript for details). The survey spectra are shown in the main text. The Ag 3d high resolution XPS spectra are shown in Figure S2. The Ag 3d_{5/2} peak for both cubic and tetrahedral particles is found at a binding energy value of 267.9 eV. This peak position is attributed to the Ag(I) oxidation state and corresponds to Ag⁺ ions in Ag₃PO₄. Reduction to the Ag (0) metal state would result in a shift of the 3d_{5/2} peak to a higher binding energy of 368.6 eV, which is not observed here.

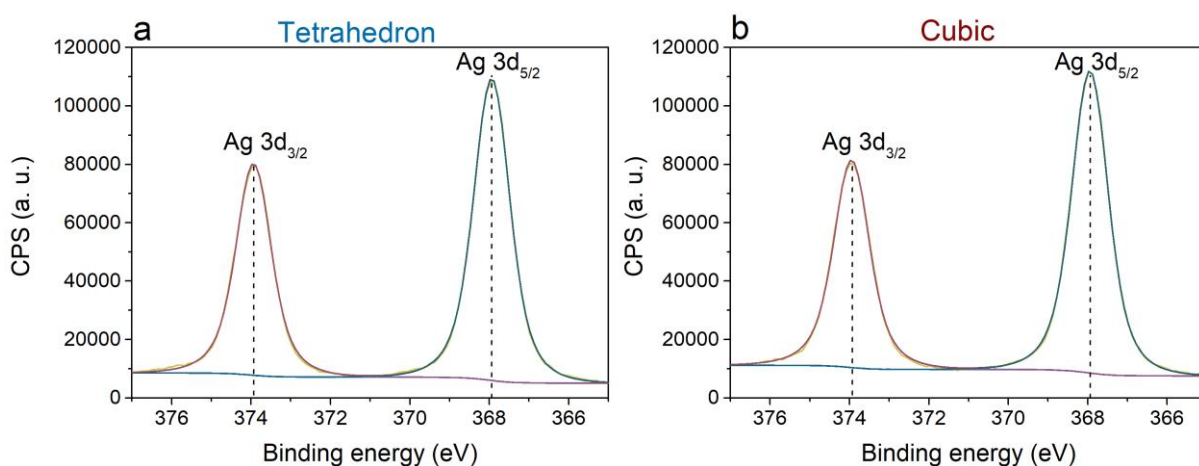


Figure S2 High resolution Ag 3d XPS spectra for (a) tetrahedral particles and (b) cubic particles of Ag₃PO₄.

Time-resolved Microwave Conductivity measurements

Change in the microwave power ($\Delta P/P$) reflected by the cavity upon sample excitation is related to the photoinduced change in the conductance of the sample, ΔG , by the equation²,

$$\frac{\Delta P}{P}(t) = -K\Delta G(t) \quad \text{Eq. S1}$$

where K is the sensitivity factor derived from the resonance characteristics of the cavity and the dielectric properties of the medium (ϵ_r of Ag_3PO_4 is taken as $20^{3,4}$). From the experimentally observed change in the photoconductance, the product of the charge carrier generation yield (ϕ) and the sum of electron and hole mobilities ($\Sigma\mu$) can be obtained from the equation²,

$$\phi\Sigma\mu = \frac{\Delta G}{I_0\beta eF_A} \quad \text{Eq. S2}$$

where I_0 is the incident intensity per pulse, e is the elementary charge, β is the ratio between the inner broad and narrow dimensions of the waveguide, and F_A is the fraction of incident photons absorbed within the sample. The laser pulse intensities were adjusted using calibrated filters and varied from 10^{10} to 10^{14} photons pulse⁻¹ cm⁻².

Calculation of electron and hole mobilities

To calculate the charge carrier mobilities for electrons and holes, we use the following equations⁵:

$$\text{Electron mobility, } \mu_e = \mu_{total} \times \frac{m_h^*}{(m_h^* + m_e^*)} \quad \text{Eq. S3}$$

$$\text{Hole mobility, } \mu_h = \mu_{total} \times \frac{m_e^*}{(m_h^* + m_e^*)} \quad \text{Eq. S4}$$

Here, the sum of the charge carrier mobility (μ_{total}) is taken from Table 2 of the main text and is $0.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for tetrahedral particles and $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for cubic particles. The effective electron and hole masses are $m_e^* = 0.42$ and $m_h^* = 1.53$ for the {111} surface and $m_e^* = 0.41$ and $m_h^* = 1.92$ for the {100} surface.⁶ The calculated individual electron and hole mobilities are shown in Table 2 of the main manuscript.

Calculation of electron and hole diffusion lengths

From the electron and hole mobility values (Table 2 of the main text), the respective diffusion lengths can be calculated using the following equations⁵:

$$\text{Electron diffusion length, } L_{D,e} = \sqrt{D_e\tau_1} \quad \text{Eq. S5}$$

$$\text{where } D_e = (k_b T \mu_e / e) \quad \text{Eq. S6}$$

$$\text{Hole diffusion length, } L_{D,h} = \sqrt{D_h\tau_1} \quad \text{Eq. S7}$$

$$\text{where } D_h = (k_b T \mu_h / e) \quad \text{Eq. S8}$$

Here D is the diffusion coefficient of the charge carriers, k_b is the Boltzmann constant, T is the temperature, and e is the elementary charge. It should be noted that the calculation of the diffusion length assumes that the lifetime (τ_1) is equivalent for the electrons and holes and is taken from the values obtained for the tetrahedral and cubic particles as presented in Table 2 of the main text. The obtained values of the hole and electron diffusion lengths are given in Table S1 below.

Table S1 The electron and hole diffusion lengths calculated using Eq. S5-S8 from the electron and hole mobilities shown in Table 2 of the main text.

Particle type	Hole diffusion length	Electron diffusion length
	$L_{D,h}$ (nm)	$L_{D,e}$ (nm)
Tetrahedral	135	258
Cubic	31	65

References

- ¹ Kubelka and Munk, *Zeit. Für Tekn. Phys.* **12**, (1931).
- ² J.E. Kroeze, T.J. Savenije, and J.M. Warman, *J. Am. Chem. Soc.* **126**, 7608 (2004).
- ³ M. Thomas, S.. Ghosh, and K.. George, *Mater. Lett.* **56**, 386 (2002).
- ⁴ M. Cutroni, A. Mandanici, P. Mustarelli, C. Tomasi, and M. Federico, *J. Non. Cryst. Solids* **307–310**, 963 (2002).
- ⁵ P.Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2010).
- ⁶ N. Umezawa, O. Shuxin, and J. Ye, *Phys. Rev. B - Condens. Matter Mater. Phys.* **83**, 1 (2011).