Electronic Supplementary Material (ESI) for Energy & Environmental Science
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Supporting Information

Facet engineered Ag_3PO_4 for efficient water photooxidation

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This file includes the following experimental/theoretical methods and figures:

- **Materials Studio figures**
- **Material characterisation (SEM)**
- **Visible light oxygen evolution**
- **XRD**
- **Video: Water photooxidation using a 300 W Xe light source**
- **DFT calculations methodology**

Materials Studio Analysis

A simple 2 x 2 x 2 super-cell was constructed (Figure S1), and then specific crystal planes were cut to give the correct morphology; which was thus verified to be possible. Red: oxygen, pink: phosphorus, blue: silver. (Figure 1, S2).

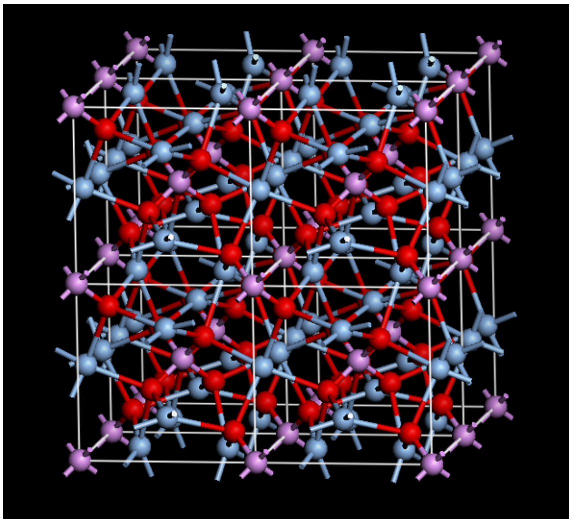
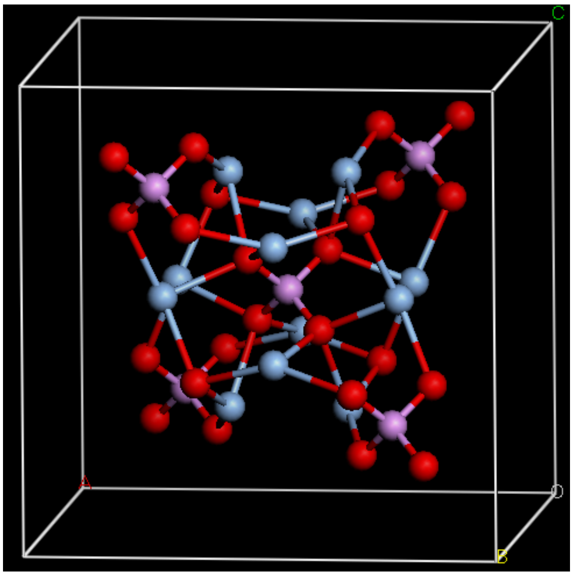
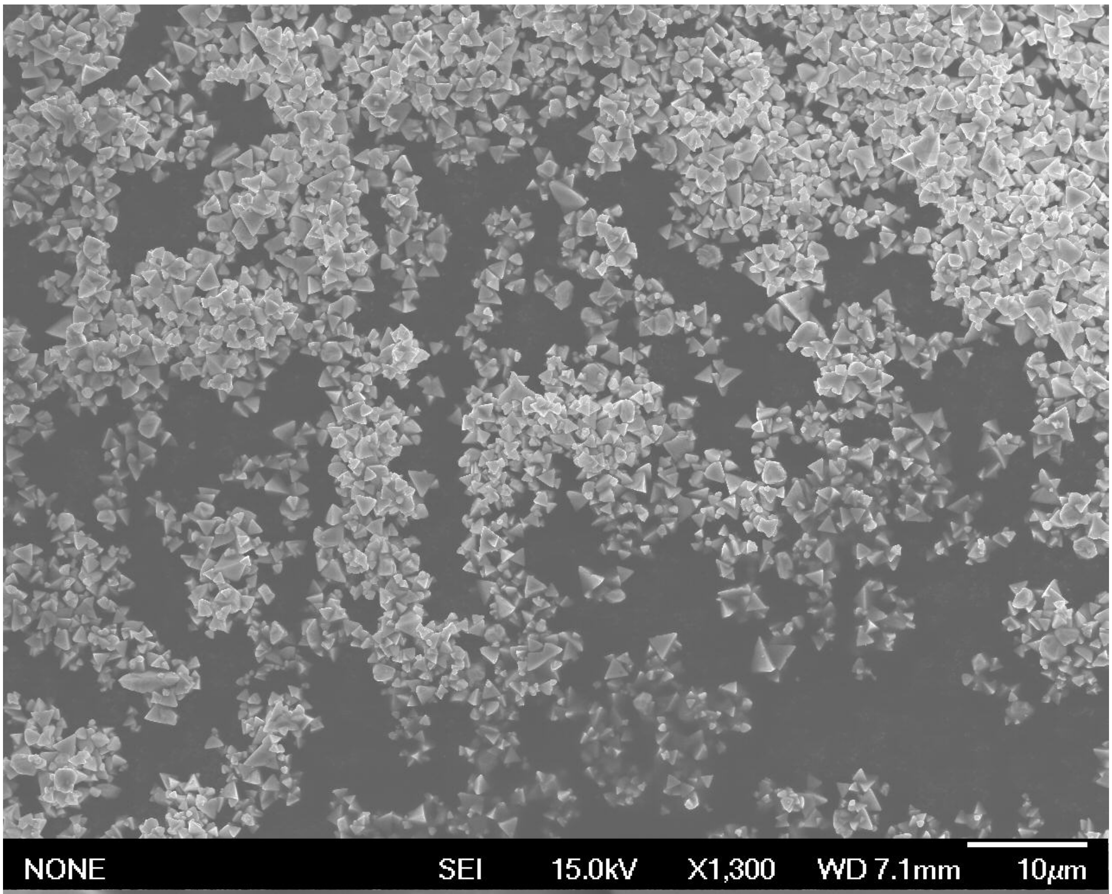


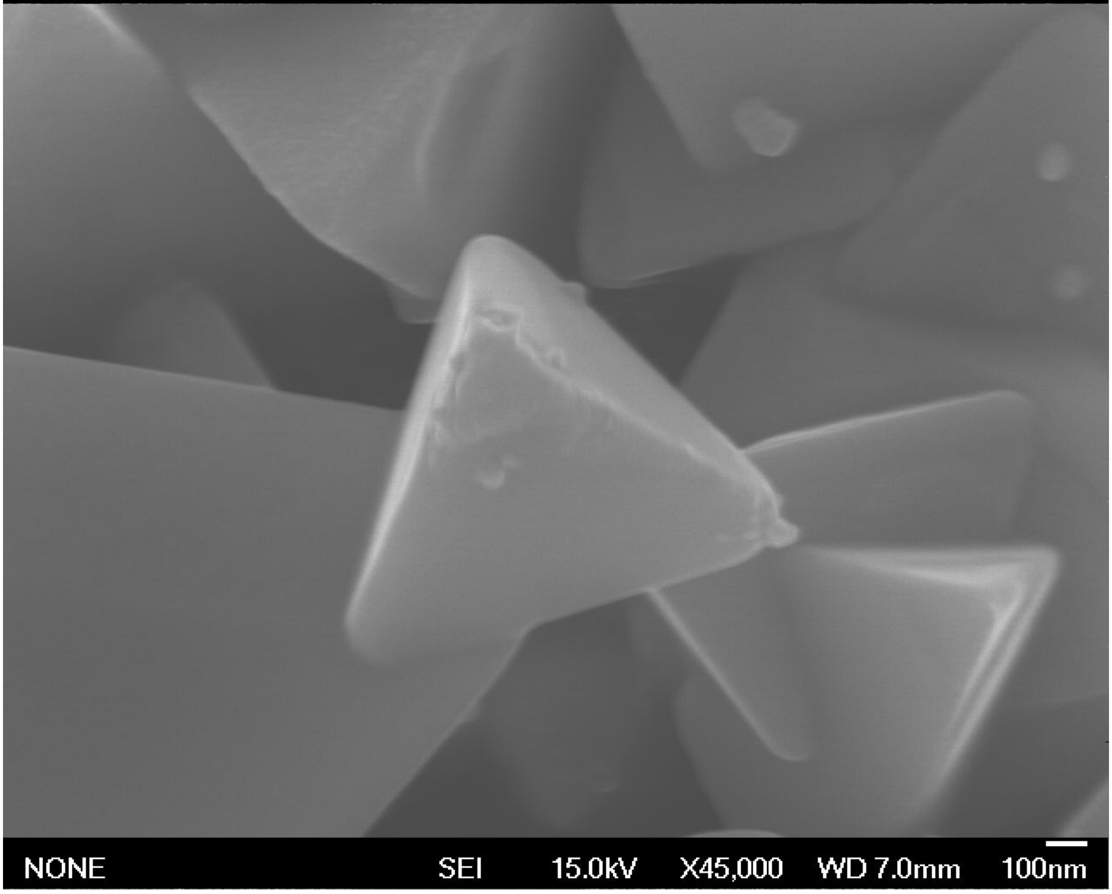
Figure S1: Ag_3PO_4 2 x 2 x 2 supercell

Figure S2 Ag_3PO_4 tetrahedron cell



SEM micrographs of Ag_3PO_4





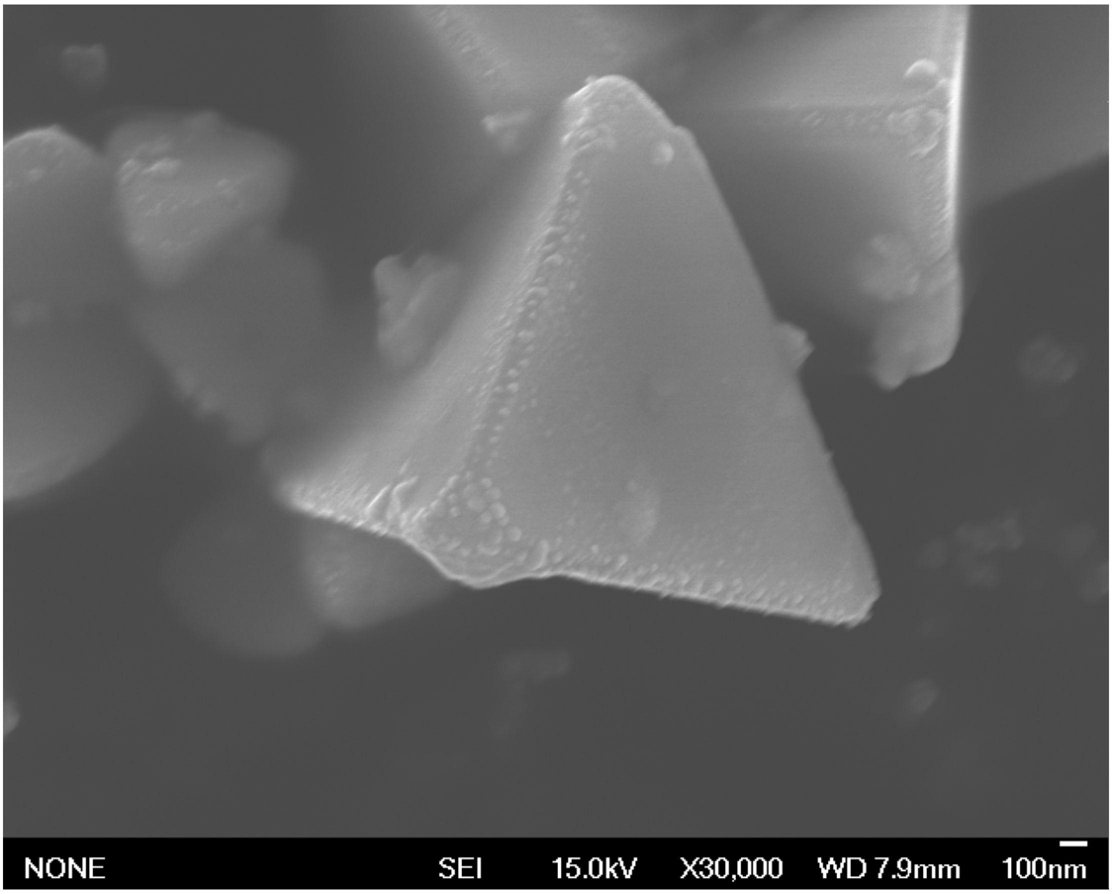


Figure S3, S4, S5 (above) – SEM micrographs of tetrahedral Ag_3PO_4

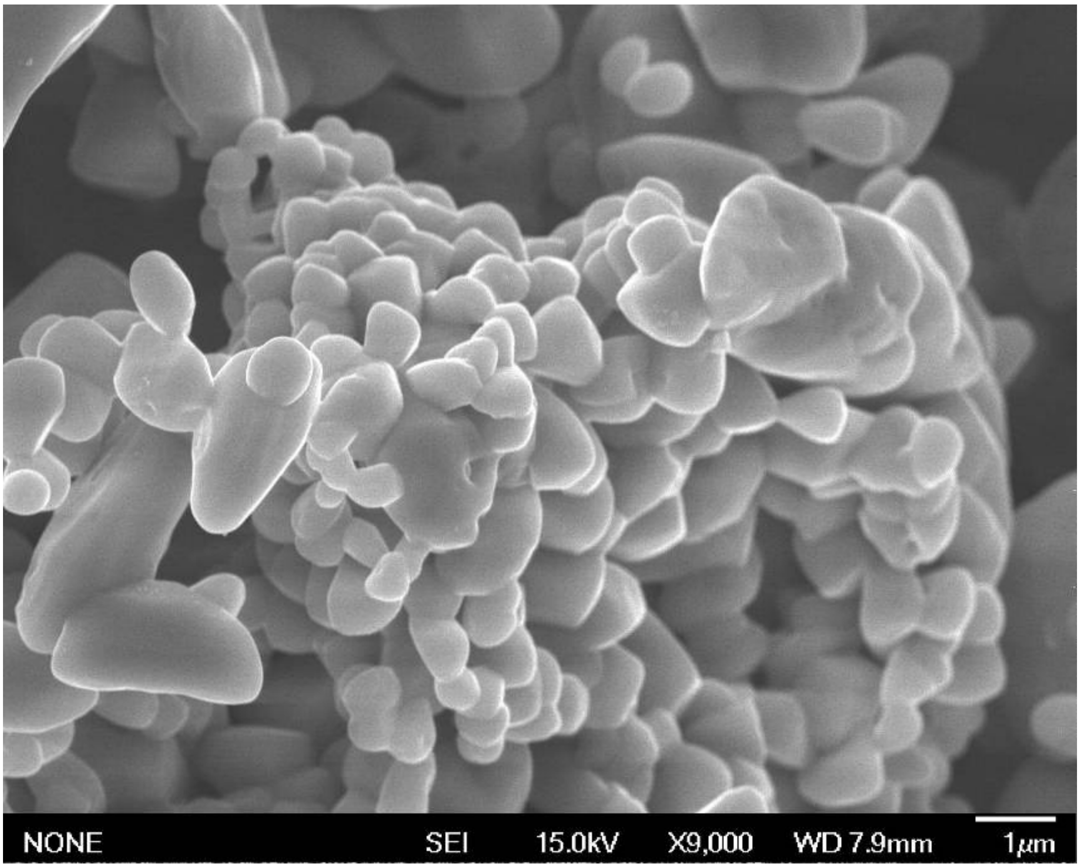


Figure S6 – SEM micrographs of mixed faceted Ag_3PO_4

Oxygen evolution under visible light (S7)

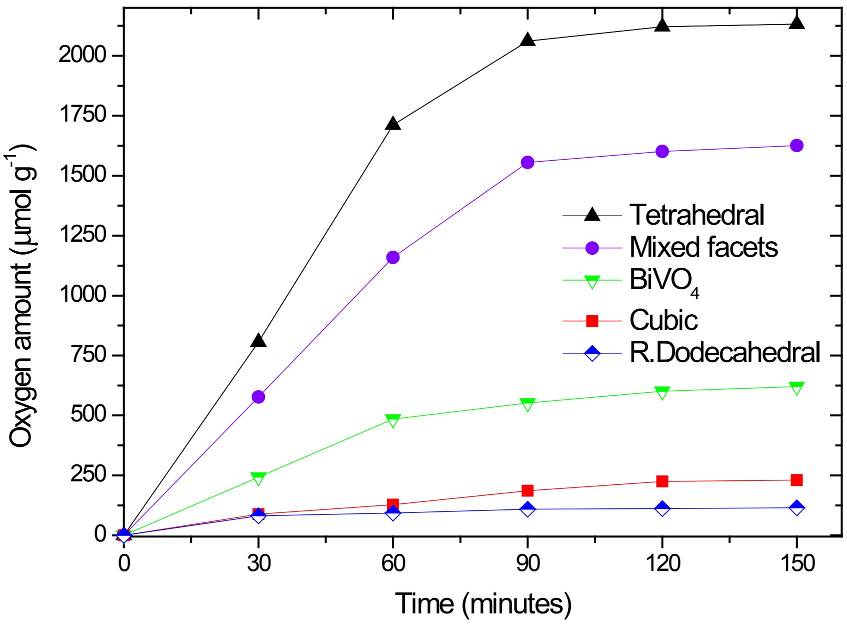


Figure S7 - Oxygen evolution of tetrahedral crystals using a 300W Xe lamp fitted with 420 nm long pass filter, $AgNO_3$ was used as an electron scavenger (0.85g). $BiVO_4$ was synthesised according to a previously reported recipe[25]

XRD patterns before and after photooxidation of water

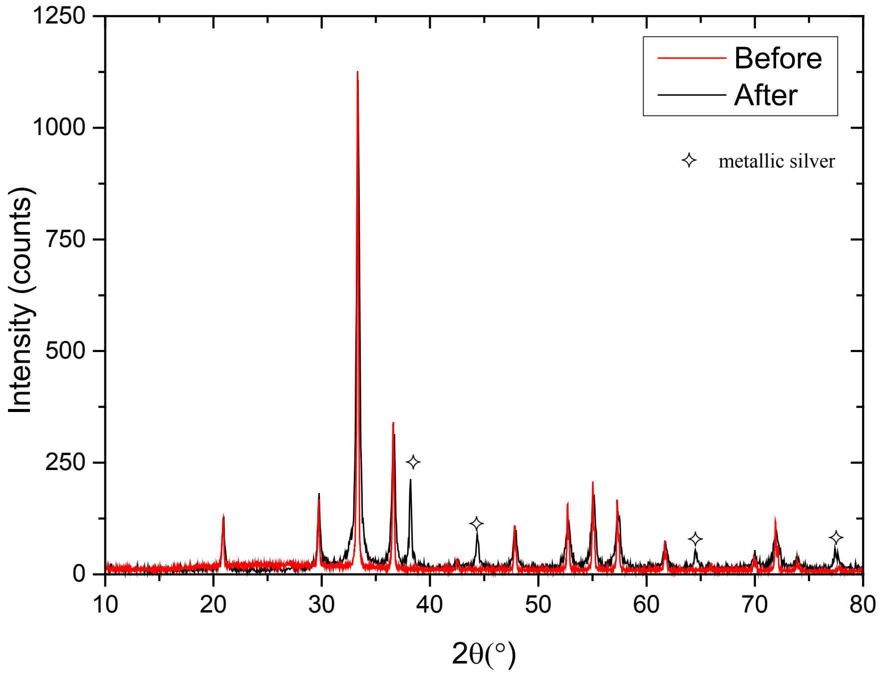


Figure S8: XRD pattern before and after photocatalyst. $AgNO_3$ was used as a scavenger, and thus deposited on the surface.

Video (S9)

The video demonstrates of oxygen evolution using tetrahedral Ag_3PO_4 particles. A 300 W Xe lamp was used during the video, fitted with a 420 nm band pass filter. A black opaque cardboard slide was used to intermittently block incoming radiation (as shown in captions in the video); doing this avoided intensity fluctuations caused by turning the lamp on and off.

Density Functional Theory (DFT) calculations

Electronic structure calculations were based on the density-functional theory (DFT) +*U* approach [1]. The exchange-correlation energy functional was represented by the generalized-gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) [2]. Projector-augmented wave pseudo-potentials were employed as implemented in the VASP code [3,4]. The valence configurations of the pseudo-potentials are $4d^{10}5s^1$ for Ag, $2s^22p^4$ for O, and $3s^23p^3$ for P. We used an energy cut-off of 500 eV in the plane-wave basis set expansion. Monkhorst-Pack *k*-point sets of 4×4×4 was used for a 16-atom unit cell of cubic Ag_3PO_4 (space group $P\bar{4}3n$). The on-site Coulomb repulsion (Hubbard *U*) was applied both for Ag *d* and O *p* states. First, we estimated *U* for a single Ag^+ ion by subtracting atomic total energies E_{tot} of three different occupations of *d* states [5]: U_{ion} (Ag^+ *d*) = ($E_{tot}(d^{10})$ - $E_{tot}(d^9)$) – ($E_{tot}(d^9)$ - $E_{tot}(d^8)$) = 13.92 eV where the self-interaction correction was taken into account with the scheme propsed by Perdew and Zunger [6]. Similarly, U_{ion} for a single O^{2-} ion was given by U_{ion} (O^{2-} *p*) = ($E_{tot}(p^6)$ - $E_{tot}(p^5)$) – ($E_{tot}(p^5)$ - $E_{tot}(p^4)$) = 9.5 eV. We then multiply a common parameter □with U_{ion} both for Ag and O to describe the screening effect in bulk Ag_3PO_4. The optimum value of the parameter □= 1.15 was determined so as to reproduce an indirect band gap of Ag_3PO_4 (2.36 eV), which leads to U_{bulk}(Ag *d*)= 16.01 eV and U_{bulk}(O *p*)= 10.93 eV. The band gap correction is important in our calculations because the computational band from PBE significantly underestimates the experimental value. The cell volume and atomic positions of the unit cell were relaxed until the total energy difference converged to less than 0.001 eV. The obtained lattice constant from PBE+*U* was *a*= 5.98 Å in comparison with an experimental value (6.005 Å).

Model construction. The relaxed unit cell was extended to construct the surface models shown in Fig.1. In the case of {100} facet, a 48-atom slab model was created by extending the 16-atom unit cell along the z-direction by three times. Two oxygen atoms on one side are moved to the other side of the slab to satisfy the stoichiometry on each side of the slab. It was then expanded by 2×2 in the x-y plane to construct the 192-atom slab model including 10 Å thickness of a vacuum region (L_{vac}). Thus, the lattice vectors of the super-cell can be described as $\mathbf{A}_1 = 2\mathbf{a}_1$, $\mathbf{A}_2 = 2\mathbf{a}_2$, and $\mathbf{A}_3 = (3 + L_{vac}/a)\mathbf{a}_3$ where $\mathbf{a}_1 = a\boldsymbol{x}$, $\mathbf{a}_2 = a\boldsymbol{y}$, and $\mathbf{a}_3 = a\boldsymbol{z}$ are the lattice vectors of the 16-atom unit cell. For modelling {110} surface, we have created a slab with the lattice vectors described as $\mathbf{A}_1 = -\mathbf{a}_1+\mathbf{a}_2$, $\mathbf{A}_2 = -2\mathbf{a}_3$, and $\mathbf{A}_3 = (3+L_{vac}/|\mathbf{a}_1+\mathbf{a}_2|)(\mathbf{a}_1+\mathbf{a}_2)$. Four atoms each of Ag and O on one side of the slab were moved to the other side for the stoichiometry reason. Similarly, the slab of the {111} surface was created by $\mathbf{A}_1 = -2\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3$, $\mathbf{A}_2 = -\mathbf{a}_2+\mathbf{a}_3$, and $\mathbf{A}_3 = (2+L_{vac}/|\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3|)(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)$. These surface structures were fully relaxed until the residual forces were converged to less than 0.02 eV/Å where the mid layer of each slab was fixed to represent a bulk region. The *k*-points were sampled at 2×2×1 Monkhorst-Pack sets.

References

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