Structure of the water-splitting photocatalyst oxysulfide α -LaOInS₂ and *ab initio* prediction of new polymorphs

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SUPPLEMENTARY INFORMATION

S1. EXPERIMENTAL AND THEORITICAL METHODS

Synthesis

A mixture of the precursors $La_2S_3/La_2O_3/In_2S_3$ in the ratio 1:2:3 were mixed and thoroughly grounded in an agate mortar before being pressed into pellets and heated in evacuated sealed quartz tube. The tube was subsequently placed in a tubular furnace and heated up to 800°C at a rate of 100°C/h for 12 hours, and then cooled down at 100°C/h to room temperature.

The powder X-ray diffraction pattern was collected on a Bruker D8 diffractometer equipped with a linear detector Lynxeye ($Cu_{\kappa\alpha}$) in Bragg-Brentano geometry at room temperature.

UV-Visible measurements: The absorbance of the sample was measured from 250 to 800 nm on a Perkin Elmer Lambda 650 device.

The photocatalytic activity was measured on Pt(1 wt %):LaOInS₂. Pt nanoparticles (used as cocatalyst) are directly photo-deposited. $H_2PtCl_6, 6H_2O$ (Sigma Aldrich) precursor was reduce to Pt in presence of ethanol and under irradiation of 100 W Xe lamp for 2 hours in order loaded La-In oxysulfide with 1 wt. % Pt. Then, 50 mg of the catalyst is dispersed in 150 ml of an aqueous solution consisting of a mixture of Na₂S - Na₂SO₃ with a concentration of 10 mM (sacrificial electron donors) and containing 10 vol% of ethanol. The amount of H₂ produced is measured by a gas sensor based on Pt:SnO₂ (Hanwei Electronics Co., LTD) with high sensitivity to hydrogen. In order to avoid parasitic interactions especially with H₂S, a blank test on the reaction mixture without catalyst is carried out and then removed from the measurement with the catalyst.

Mott-Schottky measurements: A potentiostat/galvanostat (Radiometer-Voltalab 4 PGZ 301) was used to carry out the Mott-Schottky measurements. The experimental setup is made up from the LaOInS₂ coated ITO glass as the working electrode, immersed in an electrolyte of an aqueous solution of 0.1 M of Na₂SO₄. A platinum electrode and a standard Ag/AgCl electrode were used as counter electrode and as a reference electrode, respectively. The LaOInS₂ film was elaborate by the drop-casting method from sample/ethanol mixture with 1:10 ratio. The coated area was fixed at 1x1.5 cm and then dried at 100°C overnight.

X-ray photoelectron spectroscopy (XPS) experiments were performed using an AXIS Ultra DLD Kratos spectrometer equipped with a monochromatized aluminum source (Al K α = 1486.7 eV) and charge compensation gun. All binding energies were referenced to the C 1s core level at 285 eV. Simulation of the experimental photopeaks was carried out using a mixed Gaussian/Lorentzian peak fit procedure according to the software supplied by CasaXPS. Semiquantitative analysis accounted for a nonlinear Shirley background subtraction.

DFT calculations

DFT calculations were carried out by employing the projector augmented wave (PAW) ¹⁻² method encoded in the Vienna ab initio simulation package (VASP) ³ and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) for the exchange-correlation functionals.⁴ The full geometry optimizations of α -LaOInS₂ were carried out using a plane wave energy cutoff of 550 eV and 16 *k* points in the irreducible Brillouin zone. It converged with residual Hellman-Feynman forces on the atoms smaller than 0.03 eV/Å and led to a good match with the experimental structure, i.e. within a reasonable error expected for the GGA method. The relaxed structure was used for calculations of the electronic structure. For the later, the plane wave cutoff energies of 550 eV and the threshold of self-consistent-field energy convergence of 10⁻⁶ eV were used, with 48 *k* points in the irreducible Brillouin Zone. Phonon density of states was calculated with the PHONOPY code⁵ using the density functional perturbation theory (DFPT).

- 1 G. Kresse, D. Joubert. Phys. Rev. B 1999, 59 (3), 1758–1775.
- 2 P. E. Blöchl, *Phys. Rev. B* 1994, **50** (24), 17953–17979.
- 3 G. Kresse, J. Furthmüller, 2001, Vienna ab-initio simulation package (VASP) Vienna: Vienna University
- 4 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77** (18), 3865–3868.
- 5 A. Togo, I. Tanaka, Scr. Mater. 2015, 108, 1–5

Evolutionary algorithm (EA) first principle structure prediction

The EA code is interfaced with the VASP code for DFT structure relaxation. To ensure an unbiased and complete search, the following parametrization in the USPEX code was used: an initial population of 100 structures was generated randomly and afterward, 60 generations of 80 candidates were generated and considered, energetically worst structures were discarded. These 60 generations were obtained by applying variation operators on

previous structures found, including heredity operations (i.e. combination of slices of two parents lattices, 40%), random symmetric generator (20%), and mutation operators (i.e. random exchange of different atoms, distortion of the crystal lattice, atomic displacements along the softest phonon mode eigenvectors, 20%). Finally, the additional inclusion of known crystal structures yielded an extra generation (20%).

Table S2. Atomic positions and isotropic thermal displacements of LaOInS₂ with unit cell parameters a= 3.9850(2) Å, b= 20.5460(13) Å and c= 14.8477(10) Å and the space group *Pmcn*, V=1215.67(13) Å³

x	У	Z	U _{iso.}
3⁄4	0.4252(5)	0.0422(7)	0.015(5)
1⁄4	0.7425(6)	0.0989(5)	0.024(4)
-1⁄4	0.5943(5)	0.1753(6)	0.016(4)
-3⁄4	0.4038(6)	0.2979(8)	0.027(5)
3⁄4	0.0720(7)	0.0367(9)	0.035(6)
1⁄4	0.2375(8)	0.1775(6)	0.036(6)
-3⁄4	0.4831(16)	0.194(3)	0.026(4)
-3⁄4	0.3614(17)	0.453(2)	0.026(4)
-1⁄4	0.3326(17)	0.231(3)	0.026(4)
3⁄4	-0.008(2)	-0.109(3)	0.026(4)
1⁄4	0.2982(17)	0.040(2)	0.026(4)
3⁄4	0.1509(17)	0.157(3)	0.026(4)
-3⁄4	0.609(4)	0.123(4)	0.005(12)
3⁄4	0.714(3)	0.179(5)	0.005(12)
1⁄4	0.473(4)	0.956(5)	0.005(12)
	X 3/4 1/4 -1/4 -3/4 3/4 1/4 -3/4 -3/4 -1/4 3/4 1/4 3/4 1/4	X Y ¾ 0.4252(5) ¼ 0.7425(6) -¼ 0.5943(5) -¼ 0.4038(6) ¾ 0.0720(7) ¼ 0.2375(8) -¾ 0.4831(16) -¾ 0.3614(17) -¾ 0.3326(17) ¾ -0.008(2) ¼ 0.2982(17) ¾ 0.1509(17) -¾ 0.609(4) ¾ 0.714(3) ¼ 0.473(4)	x y z $\frac{1}{4}$ $0.4252(5)$ $0.0422(7)$ $\frac{1}{4}$ $0.7425(6)$ $0.0989(5)$ $-\frac{1}{4}$ $0.5943(5)$ $0.1753(6)$ $-\frac{1}{4}$ $0.4038(6)$ $0.2979(8)$ $\frac{1}{4}$ $0.0720(7)$ $0.0367(9)$ $\frac{1}{4}$ $0.0720(7)$ $0.0367(9)$ $\frac{1}{4}$ $0.2375(8)$ $0.1775(6)$ $-\frac{1}{4}$ $0.4831(16)$ $0.194(3)$ $-\frac{1}{4}$ $0.3614(17)$ $0.453(2)$ $-\frac{1}{4}$ $0.3326(17)$ $0.231(3)$ $\frac{1}{4}$ $0.2982(17)$ $0.040(2)$ $\frac{1}{4}$ $0.1509(17)$ $0.157(3)$ $-\frac{1}{4}$ $0.609(4)$ $0.123(4)$ $\frac{1}{4}$ $0.714(3)$ $0.179(5)$ $\frac{1}{4}$ $0.473(4)$ $0.956(5)$

Atom	U11	U22	U33	U12	U13	U23
La1	0.019(9)	0.020(8)	0.007(7)	0	0	-0.008(6)
La2	0.033(7)	0.011(7)	0.028(7)	0	0	0.004(7)
La3	0.021(8)	0.009(7)	0.019(6)	0	0	0.008(6)
In1	0.015(10)	0.041(10)	0.025(9)	0	0	0.009(7)
In2	0.002(10)	0.049(11)	0.054(11)	0	0	-0.009(8)
In3	0.033(8)	0.071(13)	0.003(7)	0	0	0.005(8)

Table S3. ADP harmonic parameters

 $\textbf{Table S4.} \ \text{Main distances for } LaOInS_2$

Atom 1 – Atom 2	Distance (Å)	Atom 1 – Atom 2	Distance (Å)
La1-S1	3.23(3)	In1-S1	2.25(4)
La1-S1	3.23(3)	In1-S2	2.46(4)
La1-S3	3.39(4)	In1-S3	2.66(3)
La1-S5	3.28(3)	In1-S3	2.66(3)
La1-S5	3.28(3)		
La1-01	2.55(6)	In2-S2	2.72(3)
La1-O3	2.56(5)	In2-S2	2.72(3)
La1-O3	2.56(5)	In2-S4	2.71(4)
La1-O3	2.09(8)	In2-S4	2.62(3)
		In2-S4	2.62(3)
La2-S2	3.24(3)	In2-S6	2.41(4)
La2-S2	3.24(3)		
La2-S3	3.13(4)	In3-S3	2.90(3)
La2-S5	2.98(3)	In3-S3	2.90(3)
La2-S5	2.98(3)	In3-S5	2.40(4)
La2-01	2.77(8)	In3-S6	2.69(3)
La2-O2	2.39(4)	In3-S6	2.69(3)
La2-O2	2.39(4)	In3-02	2.19(7)
La3-S1	3.04(3)		
La3-S1	3.04(3)		
La3-S6	3.40(3)		
La3-S6	3.40(3)		
La3-O1	2.16(2)		
La3-O1	2.16(2)		
La3-O2	2.46(6)		
La3-O3	2.39(7)		

S5. Comparison of our phase $\alpha\mbox{-LaOInS}_2$ and the reported polymorph \mbox{LaOInS}_2 with a layered structure



Rare mixed anion Indium polyhedra with both S and O around In (heteroleptic environment) 3D structuration

3 different Indium sites

LaOInS₂ (same composition but different structure)





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Figure S6. UV-Visible absorbance measurement for α -LaOInS₂ which is in agreement with previous reports with a band gap found to be ~2.7 eV

S7. Band edges positions

We have estimated the band edge positions using the empirical method based on Mulliken electronegativities proposed by Butler and Ginley [1] and further described by Xu and Schoonen [2].

For comparison with our phase, we have reproduced $LaTaON_2$ photocatalyst band edges positions with this method as reported by Castelli *et al.* [3]. The later study reports such calculations for a bench of photocatalysts. We confirm in our case that the band edges positions encompass the redox potential of water which is required to evolve hydrogen and oxygen.

[1] M. Butler and D. Ginley, "Prediction of flatband potentials at semiconductor-electrolyte interfaces from atomic electronegativities". *Journal of the Electrochemical Society* 125 (1978), pp 228-232.

[2] Y. Xu and M. A. Schoonen, "The absolute energy positions of conduction and valence bands of selected semiconducting minerals". American Mineralogist 85 (2000), pp 543-556.
[3] Ivano E. Castelli *et al. Energy Environ. Sci.*, 2012, 5, 9034



Figure S8. XPS spectra of In3d (left) and of La 3d (right) for α -LaOInS₂ before (black) and after (red) photocatalysis

S9. Mott-Schottky plots for LaOInS₂

The capacitance versus potential (C – V) measurement was used to determine the conduction type, the flat band (E_{fb}) and carrier density (N), which can be determined in a Mott-Schottky (MS) plot ($1/C^2 - V$). Figure 2b within the article shows the MS plot of the LaOInS₂ film performed at 1 kHz. The negative slope observed on the depletion zone indicates to us the behavior of a p-type semiconductor. The E_{fb} is estimated at 1.26 V (*vs.* Ag/AgCl electrode) which correspond to 1.46 V (*vs.* NHE).

The flat band potential reflects the position of the Fermi level [L. Lin, J. M. Lin, J. H. Wu, S. C. Hao, Z. Lan, Mater. Res. Innovations, 14 (2010) 370-374]. In the p-type semi-conductor, the Fermi level lies close to the Valance Band (VB). This measured value is in good agreement with VB obtained by modeling.

Table S10. Optimized structure of LaOInS₂, the relaxed unit cell parameters and volume are (their evolution with respect to the experimental structure is indicated): a= 4.0013 Å (+0.4%), b= 20.7344 Å (+0.9%) and c= 15.1681 (+2.2%) Å in *Pmcn*, V= 1258.40 Å³ (+3.5%), 12 LaOInS₂ F.U./unit cell)

Atom	x/a	y/b	z/c
La1	0.75000	0.42598	0.03955
La2	0.25000	0.74073	0.10071
La3	0.75000	0.59370	0.17380
In1	0.25000	0.40175	0.29783
In2	0.75000	0.07151	0.03262
In3	0.25000	0.23578	0.17659
S1	0.25000	0.48252	0.18197
S2	0.25000	0.35886	0.45199
S3	0.75000	0.33333	0.23942
S4	0.75000	0.99503	0.89520
S5	0.25000	0.30336	0.04253
S6	0.75000	0.15274	0.16554
01	0.25000	0.62952	0.10530
02	0.75000	0.71619	0.18176
03	0.25000	0.45607	0.96521

Table S11. Atomic positions of predicted model 1 (most stable), space group $P2_1/m$ with a=7.9991Å, b=3.8424Å, c=13.8647Å and β =104.315°, V=412.91 Å³ (4 F.U. LaOInS₂/unit cell)

Atom	Wyck.	x/a	y/b	z/c
In1	2e	0.31152	1/4	2/3
In2	2e	0.32062	1/4	1/6
La1	2e	0.09740	1/4	0.86951
La2	2e	0.10736	1/4	0.36966
01	2e	0.04770	1/4	0.68963
02	2e	0.05726	1/4	0.18920
S1	2e	0.64281	1/4	0.18878
S2	2e	0.78075	1/4	-0.03983
S3	2e	0.63390	1/4	0.68854
S4	2e	0.78735	1/4	0.45949

Atom	Wyck.	x/a	y/b	z/c
ln1	4e	0.18493	0.74574	0.33257
La1	4e	0.60322	0.25556	0.86956
01	4e	0.55236	0.25584	0.69000
S1	4e	0.86345	0.75950	0.81232
S2	4e	0.71158	0.74788	0.04084

Table S12. Atomic positions predicted model 2, space group $P2_1/c$ a=8.0246 Å b=3.8405 Å c=13.8578 Å β=104.6805°, V= 413.13 Å³ (4 F.U. LaOInS₂/unit cell)

Table S13. Atomic positions predicted model 3, the NCS structure in $P2_12_12_1$ with a=3.8400 Å, b=8.8079 Å and c=11.3588 Å, V= 384.18 Å³ (4 F.U. LaOInS₂/unit cell)

Atom	Wyck.	x/a	y/b	z/c
In1	4a	0.01124	-0.08366	0.53035
La1	4a	0.02073	0.29178	0.64461
01	4a	0.52061	0.34996	0.54114
S1	4a	-0.00936	0.00235	0.17749
S2	4a	0.50808	0.85635	0.38163

Table S14. Atomic positions predicted model 4, space group *Pnma*, a=8.7991 Å b=3.8405 Å c=11.3649 Å, V= 384.05 Å³ (4 F.U. LaOInS₂/unit cell)

Atom	Wyck.	x/a	y/b	z/c
ln1	4c	1/3	1/4	0.47077
La1	4c	-0.04182	1/4	0.35535
01	4c	0.09987	1/4	0.54193
S1	4c	0.24951	1/4	0.82424
S2	4c	0.60512	1/4	0.38089

Figure S15. Total Density of States (DOS) and Projected Density of States (PDOS) on La1 superposed with its surrounding O1 states; In1, In2 and In3 states, as well as anions surrounding the heteroleptic In3S₅O, *i.e.* O2, S5 and S6.

