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Synthesis, Structure and Photocatalytic Activity of Layered LaOInS₂

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Indium oxychalcogenides would be attractive semiconductors considering the practical use of indium oxides and sulfides such as indium-tin oxides (ITO) and copper-indium-gallium diselenides (CIGS). In this work, a novel layered indium oxysulfide, LaOInS₂, was synthesized by a metathesis reaction between LaOCl and In₂S₃. Synchrotron X-ray diffraction showed that LaOInS₂ consisted of alternately stacked rocksalt-type In–S and PbO-type La–O layers. InS₆ octahedron had splitting In sites with abnormally large anisotropic atomic displacement factors. LaOInS₂ was found to be a direct semiconductor. Density functional theory calculations exhibited well-dispersed bands composed of In 5s/5p and S 3p/O 2p orbitals with a band gap of ~2.4 eV, which was close to the experimental value estimated by optical absorption (2.64 eV). By responding this visible-light absorption, LaOInS₂ exhibited photocatalytic activity for H₂ and O₂ evolution from water with the aid of Pt and IrO₂ cocatalysts, respectively

Introduction

Oxychalcogenides have been studied extensively because coexistence of ionic oxide anions and chalcogenide anions often adopt both low-dimensional structure and anisotropic electronic structure together with various applications.^{1–5} For instance, Sm₂Ti₂S₂O₅ adopts the layered structure similar to a Ruddlesden–Popper-type layered perovskite oxide, and it acts as a water splitting photocatalyst under visible light.⁶ LaOAgS consists of alternate stacking of La–O and Ag–S layers, and is an excellent ion conductor.⁷ Isostructural LaOCuS has been found to be a p-type semiconductor with a band gap of 3.2 eV.⁸ Some researchers have studied bismuth oxychalcogenides containing Bi–S/Se layer, such as LaOBiS₂ and LaOBi(S,Se)₂, and their superconductive and thermoelectric properties have been examined.^{9–14} The crystallographic structure of LaOBiS₂ can be characterized as a distorted rocksalt-based Bi–S layer sandwiched by La–O blocks. Low-dimensional and covalent Bi–S layers form highly dispersed bands, which acts a

superconductive layer by inducing electronic carrier properties.^{10–12} Abnormally high thermal vibration of Bi–Se layers has been detected in LaOBi(S,Se)₂, which is advantageous for thermoelectric materials.¹³

Indium oxides and chalcogenides, including indium tin oxides (ITO), In–Ga–Zn–O (IGZO)¹⁵ and CuIn_xGa_{1–x}Se (CIGS),¹⁶ are used as transparent conductive layers and solar cells, owing to their excellent optical and electronic properties. Their band edge is composed of In5s and In5p orbitals overlapped with p orbitals of anions, which contribute to the optical absorption and electronic conductivity. The excellent optical and electronic properties of indium compounds are also attractive for photocatalysis. Indeed, In₂S₃ is reportedly used as a photocatalyst in organic compound decomposition.¹⁷ In₂S₃ with layered rocksalt structure is reported as a photocatalyst for H₂ evolution.¹⁸ Ogisu et al. have reported the photocatalytic activity of a lanthanum-indium oxysulfide, LaInS₂O, for H₂ and O₂ evolution.¹⁹ X-ray diffraction peaks of LaInS₂O have been assigned as the orthorhombic cell with *a*=20.5421(6) Å, *b*=14.8490(4) Å, *c*=3.9829(1) Å.²⁰ However its crystal structure has not been solved. In contrast, more complicated lanthanum indium oxysulfides, La₅In₃S₉O₃²⁰ and La₆In₁₀S₉O₁₇²¹, have been synthesized and their crystal structures solved by single-crystal XRD.

In this paper, we report a novel layered indium oxysulfide, LaOInS₂, whose crystal structure is different from the reported orthorhombic LaInS₂O.²⁰ This layered LaOInS₂ is synthesized by a metathesis reaction between LaOCl and In₂S₃ with the formation of NaCl as a byproduct. LaOInS₂ consists of alternately stacked In–S and La–O layers. The characteristic of the In–S plane is the splitting of In sites with abnormally large anisotropic atomic displacement factors. This is a semiconductor with the band gap of ~2.5 eV where In5s/5p–S3p orbitals dominantly contribute to the bands near the band gap. A photocatalytic activity test shows H₂ and O₂ evolution under visible light.

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layered structure, or that NaCl byproducts are not completely removed by the water wash.

Results and discussion

Synthesis and Crystal Structure

Layered LaOInS_2 was synthesized in the evacuated quartz tube by the reaction of LaOCl with NaInS_2 . At 700 °C, no reaction occurs; only the peaks of LaOCl and NaInS_2 phases are observed in the XRD pattern (Fig. 1). The increase to 800 °C starts to form layered LaOInS_2 phase. The temperature of 850 °C produces the layered LaOInS_2 as the main phase, and NaCl as the by-product. The powder after washing with distilled water shows similar LaOInS_2 peaks but does not show the peaks of NaCl.

The reaction for the formation of LaOInS_2 is below;



Through density functional theory (DFT) calculations using the PBE method, the calculated enthalpy change of the solid-state reaction of eq. (1) at 0 K was slightly endothermic (ca. 0.07 eV); the reaction might be thermodynamically unfavorable. However, above melting point of NaCl (801 °C), the reaction of eq. (1) would be thermodynamically favorable due to NaCl liquid with relatively high entropy. The heating at 850 °C of the mixture of La_2O_3 , La_2S_3 , and In_2S_3 in stoichiometric molar ratio, which did not involve the formation of NaCl, gave no diffraction peaks of LaOInS_2 . Thus, the formation of LaOInS_2 phase above 800 °C from LaOCl and NaInS_2 can be explained by the formation of NaCl liquid as a byproduct. The heating at 900 °C caused the decomposition of the layered LaOInS_2 into unknown phase(s). Thus, this layered LaOInS_2 is a metastable phase which is stable below 900 °C. The diffraction peaks of the product from La_2O_3 , La_2S_3 , and In_2S_3 and unknown phase(s) decomposed from LaOInS_2 were similar to the diffraction patterns of previously reported orthorhombic cell; the structure has not been solved.²⁰

Fig. 2 shows a scanning electron microscopy (SEM) image of LaOInS_2 . Plate crystals 1–10 μm in size and $\sim 1 \mu\text{m}$ in thickness were found. The BET surface area of the crystals was $0.3 \text{ m}^2 \cdot \text{g}^{-1}$. The chemical composition of LaOInS_2 , obtained after washing by water to remove NaCl, is close to the stoichiometric value of LaOInS_2 ; the molar ratio of La:In:S:Na:Cl was 1:0.9:1.8:0.1:0.1, as semiquantitatively determined by energy-dispersed X-ray spectroscopy (EDX). Small amount of Na and Cl were detected; however, the Na amount can be overestimated due to overlapping La and O signals. Thus, we cannot deny the possibility that a small amount of Na and/or Cl is included in the

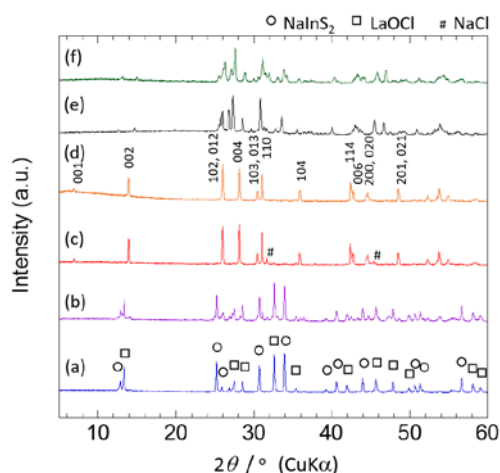


Fig. 1 XRD patterns of the products from the mixture of LaOCl and NaInS_2 heated at (a) 700 °C, (b) 800 °C and (c) 850 °C. (d) XRD pattern of the above mixture heated at 850 °C and subsequent wash by water. (e) XRD pattern of pattern of the mixture of La_2S_3 , La_2O_3 and In_2S_3 heated at 850 °C and (f) the pattern of above mixture of LaOCl and NaInS_2 heated at 900 °C.

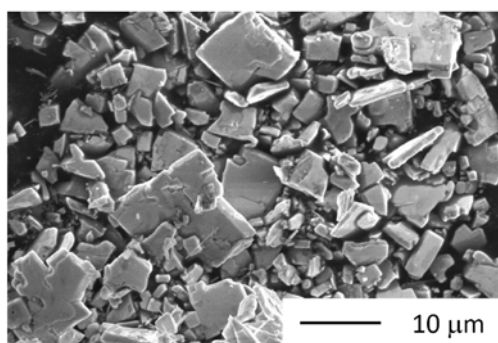


Fig. 2 SEM image of LaOInS_2 powder after washing with water.

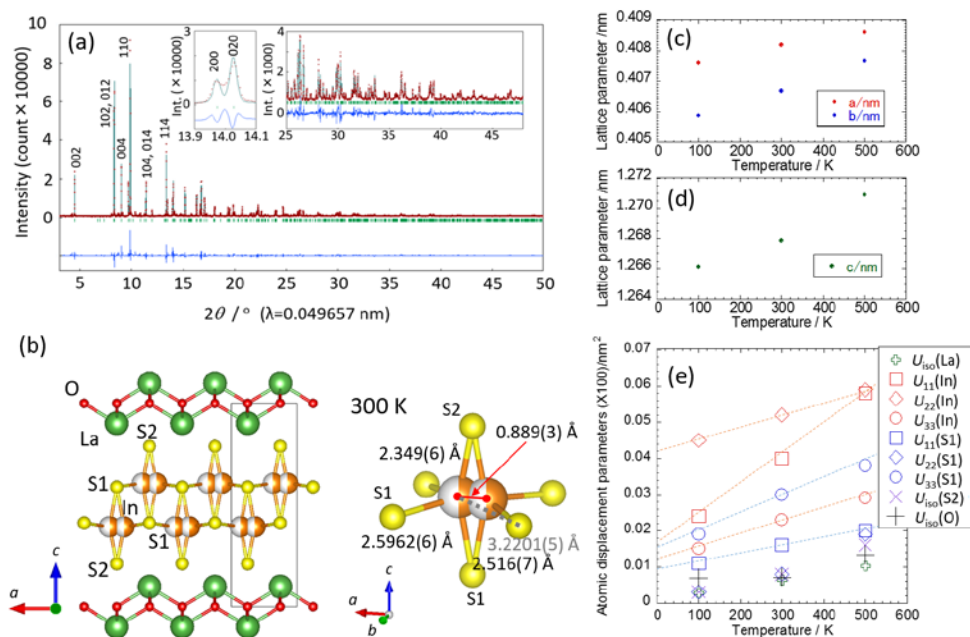


Fig. 3 Crystal structure and Rietveld refinement profile of LaOInS₂. (a) Rietveld profile of synchrotron X-ray diffraction of LaOInS₂ at 300 K. Red dots and black lines indicate experimental and calculated points. Residuals are indicated by blue lines. Insets are expanded profiles of 200 and 020 peaks and high angle regions. (b) Crystal structure model of LaOInS₂ and In-S₆ octahedron. Grey lines indicate the unit cell(c-e) Temperature dependence of lattice parameters and atomic displacement parameters. Anisotropic atomic displacement parameters are refined only for In and S1 (U_{12} , U_{13} , and U_{23} are fixed as zero).

Fig. 3(a) shows the Rietveld profile of layered LaOInS₂ after washing with water. Preliminary refinement using a tetragonal cell isostructural with LaOBiS₂ produced poor fitting: a reliability factor, R_{wp} , was 32.7 %. An obvious peak split for the 200 and 020 peaks were found (inset of Fig.3(a)), suggesting lowering symmetry from the tetragonal cell. The refinements using orthorhombic cells were attempted, but not successful. Thus, we used the monoclinic cell with the space group of $P2_1/m(\#11)$. The refinement of β was 90° within the error, thus it was fixed for further refinements. The refinement with this monoclinic cell using slightly different a and b axes significantly improved the fitting ($R_{wp} = 17.0$ %). However, this refinement converged with an extremely large atomic displacement parameter of In ($U_{iso} = 0.098(2) \text{ nm}^2$). The splitting of the central In site into two sites along the a axis improved the fitting ($R_{wp} = 13.3$ %), and gave a much smaller displacement factor ($U_{iso} = 0.038(2) \text{ nm}^2$). Trial refinements with the structural model containing both center and off-centered sites were not converged with reasonable atomic displacement factors. Through DFT calculations using the PBE method, the energy of the optimized structures of LaOInS₂ with off-centered In site was determined to be more stable by 0.09 eV than one with centered In site. Such splitting in In sites are also found in La₅In₃S₉O₃ and La₆In₁₀S₉O₁₇.^{20, 21} Therefore, we propose a layered LaOInS₂ structure with split In sites in InS₆ octahedron. Final refinement was performed using anisotropic atomic displacement factors of layered In and S1 ($R_{wp} = 13.2$ %).

Lattice parameters and atomic displacement parameters of LaOInS₂ at 100, 300, and 500 K are summarized in Fig. 3 (c-e and Fig. S1). The lattice parameters and the atomic displacement parameters increase with increasing temperature. On the other hand, the asymmetry of a and b axes and anisotropic displacement parameters of U_{11} and U_{22} decrease with increasing temperature. The thermal factors of In and S1 are abnormally high. The extrapolation of the temperature dependence of displacement parameters for In and S1 does not reach zero at 0 K. This indicates the unusual atomic vibrations of the In-S1 layers in the InS₆ octahedron, similar to the structurally related LaOBi(S,Se)₂.¹³

Many oxychalcogenides consisting of alternative PbO-type Ln-O layers (Ln: lanthanoid metals) and MCh₂ layers (Ch: S, Se) with trivalent cations (M: Ga³⁺, In³⁺, Sb³⁺, Bi³⁺) have been reported. Interestingly, there are four-, five-, and six-coordinated MS₂ layers that have been formed within the Ln-O layers (Fig. S2). Simple one is CeOBiS₂, which is crystallized in a tetragonal structure.²² Bi-S layer consists of Bi³⁺-centered square pyramids, and two Bi-S layers are separated by ~3.35 Å due to the lone-pair of Bi³⁺. High displacement factors of in-plane S1 are found, especially parallel to the c -axis. The atomic distances of BiS₅ pentahedron are 2.525(3) and 2.8459(3) Å. The electronic bands near the band edge consist of Bi6p and S3p orbitals, and Bi6s is localized. In the case of LaOInS₂, two In-S layers are strongly bonded (2.48 Å) and form octahedral sites, where in-plane symmetry of the a and b axes breaks. The In site splits into two sites and forms a pseudo-tetragonal structure. Large atomic

displacement parameters of In toward in-plane direction and those of out-of-plane direction of S1 are found. The atomic distances of InS_6 octahedron range from 2.349(6) Å to 2.5962(6) Å. LaOGaSe_2 is crystallized in an orthorhombic structure and is composed of GaSe_2 corner-sharing tetragonal chalcogenide layers.²³ Although the a and b axes are not symmetric, no site-splitting sites of Ga are found. The interlayer distance is close (2.29 Å). The atomic distances of GaSe_4 are in the narrow range from 2.440(6) Å to 2.320(6) Å. Therefore, upon changing from CeOBiS_2 through LaOInS_2 to LaOGaSe_2 , the interlayer distances, deviation of bond length, and average distance are decreased.

These structural changes of chalcogenide layers would be related to lone pairs, ionic radii, and electronegativity. Cations with lone pairs of s orbitals, such as Bi^{3+} , forms two well-separated layers since they need the space for occupying their lone pairs. Structural analyses of LnOBiCh_2 ,^{22, 24} $\text{Ln}(\text{O},\text{F})\text{BiCh}_2$,⁹⁻¹³ and $\text{Ln}(\text{O},\text{F})\text{SbS}_2$ ²⁵ show the same trends. On the other hand, for cations without a lone pair, such as Ga^{3+} and In^{3+} , the two chalcogenide layers are strongly bonded. The coordination change from InS_6 octahedron to GaSe_4 tetrahedron can be understood by the ratio of ionic radii²⁶ and the difference of electronegativity.²⁷ Employing six-coordinated Shannon ionic radii, the ratio of $\text{In}^{3+}/\text{S}^{2-}$ (0.435) is higher than the critical radius ratio of a six-coordinated species (0.4142) in three-dimensional structures while that of $\text{Ga}^{3+}/\text{Se}^{2-}$ (0.319) is lower than the critical radius ratio. Employing the difference in electronegativity²⁸ and the structural map proposed by E. Mooser and W.B. Pearson,²⁷ the difference in the electron negativity, $\Delta\chi$, of both In–S and Ga–Se are located near the boundary of four- and six-coordinated structures. Nonetheless, slightly larger difference can be found in In–S ($\Delta\chi = 0.80$) than Ga–Se ($\Delta\chi = 0.74$); thus, more ionic character and greater preference for six coordination are expected for the In–S layer. Therefore, structural changes of chalcogenide layers in two-dimensional LnOMCh_2 follow the common structural rules based on three-dimensional structures.

Light-absorption property and electronic band structures

Photograph and optical absorption spectrum of the LaOInS_2 powder are shown in Fig. 4. LaOInS_2 powder is yellow, indicating optical absorption of visible light. The band gap of LaOInS_2 , using a Tauc plot and assuming a direct transition, is 2.64 eV.

Fig. 5 shows the band structure and projected density of states pDOS of LaOInS_2 with off-centered In sites calculated by the HSE06 method. The band structure of LaOInS_2 is composed of dispersed conduction and valence bands in the in-plane direction, which is characteristic of layered compounds. At the G and Z points, the band gap is close to minimum, and it is a direct band gap of ~2.4 eV, which is close to the band gap estimated by optical absorption (2.64 eV). This valence-band top is mainly attributed to the S 3p and O 2p orbitals. The bottom of the conduction band consists of In 5s and In5p orbitals. Presence of more dispersed states for In and S than for La and O suggests more covalent character of the In–S layer, as expected. **The calculated absorption coefficient under visible light is below 10^4 cm^{-1} , which is not high as InP and CdS.**²⁹

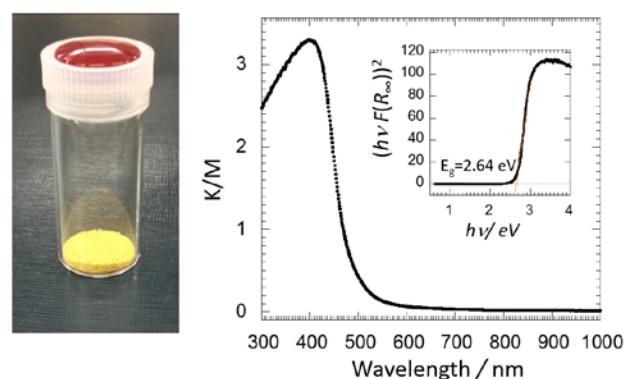


Fig. 4 Photograph and optical absorption of LaOInS_2 powder. Inset shows the Tauc plot.

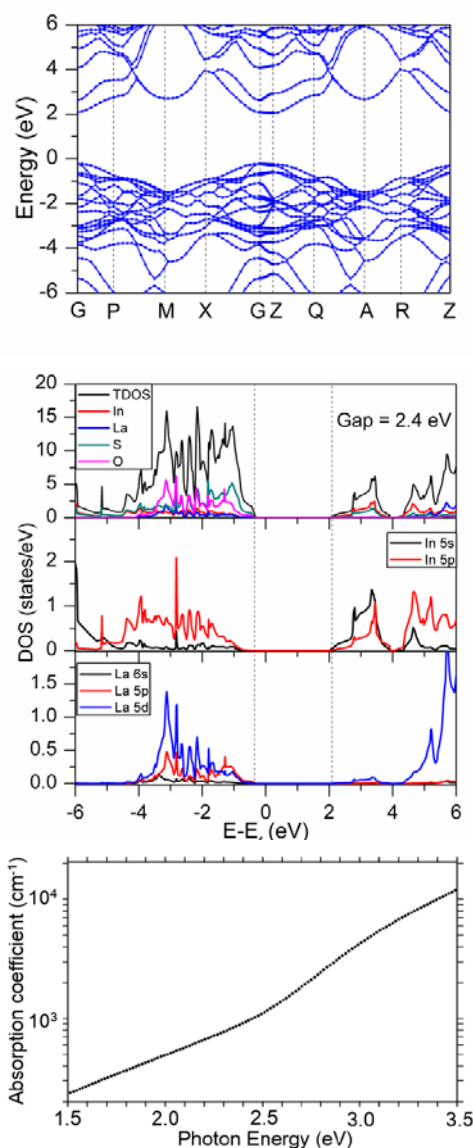


Fig. 5 Computationally calculated band structure, pDOS and absorption coefficient of LaOInS_2 .

Photocatalytic activity

The well-dispersed valence and conduction bands, as well as visible light absorption of LaOInS_2 , are attractive for use as a photocatalyst. Photocatalytic activity of LaOInS_2 was thus evaluated with respect to H_2 and O_2 evolution from water. Pt nanoparticle was deposited as a cocatalyst for proton reduction. Fig. 6 shows that LaOInS_2 was capable of producing H_2 from water containing sacrificial electron donors (Na_2SO_3 and Na_2S) under visible light irradiation of $420 < \lambda < 800$ nm. The H_2 evolution activity was improved with an increase in the loading amount of Pt, reaching a maximum at 0.75 wt%, beyond which it began to drop (Fig. S3). TEM observation for the optimized sample indicated that the deposited Pt was in the form of nanoparticles having ca. 2 nm in size (Fig. S4). Apparent quantum yield of the optimized sample for H_2 evolution was determined to be 0.2% at 420 nm (Fig. S5). It was also confirmed that the H_2 evolution was driven by light absorption of LaOInS_2 . Even under $500 < \lambda < 800$ nm irradiation, H_2 evolution was clearly observed while no H_2 was evolved under $580 < \lambda < 800$ nm irradiation (Fig. S6). This change in the H_2 evolution activity is consistent with the optical absorption of LaOInS_2 . No significant degradation of LaOInS_2 phase after the H_2 evolution was confirmed by XRD data (Fig. S7). XPS showed no significant change in the peak positions of La3d, In3d, S2p and O1s signals, indicating the surface of LaOInS_2 (at least partially) sustained after the photocatalytic test (Fig. S8). However, the shoulders of In3d signals at lower binding energy appeared, suggesting the partial reduction of indium. The signal of S2p became broader, which implied the generation of different S species on the surface, although the detailed structure was still unclear.

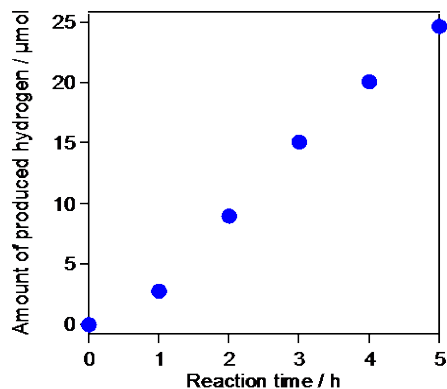


Fig. 6 Time course of H_2 evolution on 0.75 wt% Pt/ LaOInS_2 under visible light irradiation ($420 < \lambda < 800$ nm). Reaction conditions: catalyst, 50 mg; aqueous methanol solution (10 vol%, 140 mL); light source, xenon lamp (300 W) with cutoff filter; reaction vessel, Pyrex top-irradiation type.

It is known that water oxidation into O_2 by sulphide-based photocatalysts is generally difficult because the valence band of sulphides is formed by S3p orbitals that are more susceptible to oxidation than water.³⁰ On the other hand, the valence band of oxysulfides consists of hybridized orbitals of S3p and O2p, which may lead to stable photocatalytic behaviour in water oxidation.⁶ Thus, we examined photocatalytic O_2 evolution activity of LaOInS_2 in the presence of AgNO_3 an electron acceptor and La_2O_3 as a pH buffer.^{5,6} While no O_2 was evolved using unmodified LaOInS_2 ,

modification of LaOInS_2 with colloidal IrO_2 as a water oxidation cocatalyst resulted in clearly observable O_2 evolution under visible light ($420 < \lambda < 800$ nm), as shown in Fig. 7. This result indicates that LaOInS_2 satisfies the thermodynamic potential to oxidize water into O_2 as well as to reduce water to H_2 . The rate of O_2 evolution decreased with time due to the deposition of metallic Ag, which hinders light absorption by LaOInS_2 and blocks active sites for redox reactions, as the result of reduction of Ag^+ .⁶ The deposition of metallic Ag was confirmed by XRD analysis (Fig. S9). It is also clear that the peaks of LaOInS_2 phase after the O_2 evolution were sustained after O_2 evolution. However, detailed XPS analysis of the reacted photocatalyst was difficult, because of mixing of La(OH)_3 , which resulted from the La_2O_3 buffer. We could not remove the La(OH)_3 residue by a conventional acid treatment,^{5,42} due to chemical instability of LaOInS_2 in an acidic solution.

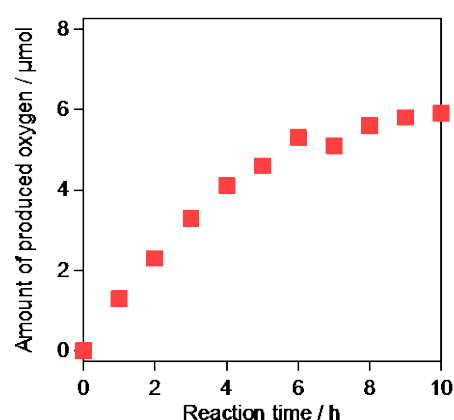


Fig. 7 Time courses of O_2 evolution on 0.5 wt% IrO_2 / LaOInS_2 under visible light ($420 < \lambda < 800$ nm) from silver nitrate solution containing 200 mg of La_2O_3 . Reaction conditions: catalyst, 50 mg; reactant solution, aqueous silver nitrate solution (10 mM, 100 mL); light source, xenon lamp (300 W) with cutoff filter; reaction vessel, top-irradiation type.

The H_2 evolution activity of LaOInS_2 was much lower than that of sulphides, such as CdS , with quantum yields of several tens percent.^{31,32} Although there are some early reports that describe photocatalytic water oxidation by sulfides, recent studies showed that sulfides were essentially inactive for photooxidation of water.⁶ Therefore, this layered oxysulfide, LaOInS_2 , is advantageous over other sulfides in terms of the abilities to reduce and oxidize water.

Conclusions

A novel layered oxychalcogenide, LaOInS_2 , was synthesized by the reaction of LaOCl and NaInS_2 , with the formation of NaCl liquid as a byproduct. Its crystal structure, electronic structure, optical and photocatalytic properties were examined. It exists as a metastable phase, and its crystal structure can be described as alternately stacked Ln–O oxide and In–S chalcogenide layers. This stacking is similar to those in CeOBiS_2 and LaOGaSe_2 , while octahedral coordination of InS_2 layer is different from the five-coordinated BiS_2 layer in CeOBiS_2 and the four-coordinated GaSe_2 layer in LaOGaSe_2 . LaOInS_2 is a semiconductor and its band gap, estimated by optical absorption, is 2.64 eV, which is

close to the computationally predicted value (2.5 eV). The bottom of the conduction band is predominantly composed of In 5s/p orbitals, and the valence band mainly consists of O 2p and S3p orbitals. Hydrogen and oxygen evolution from water was confirmed under band-gap photoexcitation of LaOInS₂. Tunable electronic structure of LaOInS₂ by replacing La, O and S sites suggests that LaOInS₂ can be a start point for exploring new functional materials, similar to extensively studied LaOBiS₂ and related oxychalcogenides³³

Experimental and Computational

Synthesis and structural and compositional analysis

The following chemicals were used without purification: LaCl₃·6H₂O (Wako>97.0%), In(NO₃)₃·nH₂O (Wako 99.9 %) and NaSH·nH₂O (Sigma-Aldrich). First, LaOCl was synthesized by heating ~1 g of LaCl₃·6H₂O at 820 °C in a N₂ flow, similar to the literature.³⁴ NaInS₂ was synthesized by heating ~1 g of In(NO₃)₃·nH₂O and ~2 g of NaSH·nH₂O in a Teflon-lined autoclave at 200 °C. After heating, the precipitate was washed with distilled water to remove excess NaSH and byproducts, and dried at 50 °C. The synthesized LaOCl and NaInS₂ were mixed in Ar atmosphere. This mixture was heated in a vacuumed quartz tube at 700–900 °C for 4 h. To remove NaCl byproduct, the product was washed with distilled water and dried at room temperature. For comparison, the mixture of La₂S₃, La₂O₃, and In₂S₃ in the molar ratio of 1:2:3 was heated at 850 °C in a vacuumed quartz tube.

The crystal structure was examined by powder X-ray diffraction (XRD: Rigaku Miniflex600). Synchrotron XRD was measured using the one-dimensional semiconductor detector (MYTHEN) at the BL02B2 experimental station in SPring-8 (Proposal number of 2016B1078). Rietveld refinements were performed using RIETAN-FP³⁵, and a crystal scheme was drawn using VESTA³⁶. Diffuse reflectance spectrum was obtained using a UV-vis-NIR spectrophotometer (JASCO V-670). Morphology was observed by SEM (JEOL JSM-6510LA) and transmission electron microscopy (TEM: JEOL, JEM-2010), and chemical compositions were semiquantitatively determined by EDX. Surface area was measured by N₂ absorption experiments. Surface of the powders was examined by XPS (JEOL, JPS-9200). The binding energies were corrected by reference to free carbon (284.6 eV).

Computational calculation

Band structure, density of electron states, and optical absorption coefficient were calculated by density functional theory (DFT) employing the VASP package^{37, 38} with HSE06 method^{39, 40}. The electron-ion interaction was described by the projector augmented wave (PAW) method with energy cutoff of 400 eV⁴¹. The convergence criteria for all calculations were set for the electronic self-consistent iterations and forces with 10^{−5} eV and 0.02 eV/Å respectively. The Gamma-point-centered Monkhorst–Pack (MP) (5×5×2) k-mesh scheme⁴² was used for structure optimization and density of states (DOS) and dielectric function calculations. The high asymmetry k-points were chosen for band structure calculations. About the optical

properties, the imaginary part ($\epsilon_{\text{Im}}(\omega)$) of the frequency dependent dielectric matrix (ϵ) is determined by a summation over empty states using the converged ground state as following formula,

$$\epsilon_{\text{Im}}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \times \langle u_{ck} + e_{\alpha} q | u_{vk} \rangle \langle u_{ck} + e_{\beta} q | u_{vk} \rangle^*$$

where the indices c and v refer to conduction and valence band states respectively, ω is the photon energy, and u_{ck} is the cell periodic part of the orbitals at the k-point, k. The real part ($\epsilon_{\text{Re}}(\omega)$) of the dielectric tensor is obtained by the Kramers-Kronig transformation.

$$\epsilon_{\text{Re}}(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\epsilon_{\text{Im}}(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega'$$

Then, the adsorption coefficient ($\alpha(\omega)$) was obtained from the dielectric function by the expression:

$$\alpha(\omega) = \sqrt{2\omega} \sqrt{\epsilon_{\text{Re}}^2(\omega) + \epsilon_{\text{Im}}^2(\omega) - \epsilon_{\text{Re}}(\omega)}$$

More details can be found in the work of Gajdoš et al.⁴³

Deposition of IrO₂ cocatalysts for photocatalytic water oxidation

Colloidal IrO₂ having 1–2 nm in size was prepared according to the same method reported previously.⁴⁴ Because direct adsorption of the prepared IrO₂ colloids onto LaOInS₂ was unsuccessful, LaOInS₂ (200 mg) was in prior modified with Ca(OH)₂ (28 mg, ≥96.0%, Wako Pure Chemical Co.) by an impregnation method in methanol (2 mL, ≥ 99.8%, Kanto Chemical Co.).⁶ After drying the suspension, the resulting solid (Ca(OH)₂/LaOInS₂) was subject to heating at 573 K for 1 h under a flow of N₂ (100 mL min^{−1}). Then, the heated sample was dispersed in colloidal IrO₂ (0.5 wt%) aqueous solution overnight. This procedure allowed for quantitative adsorption of IrO₂ onto Ca(OH)₂/LaOInS₂. For simplicity, the as-prepared material will be represented hereafter as IrO₂/LaOInS₂.

Photocatalytic H₂ and O₂ evolution reactions

Photocatalytic activity was evaluated at room temperature in a top-irradiation-type reaction cell connected to a closed gas circulation and evaluation system. The details of the reaction setup can be found elsewhere.⁴⁵ For H₂ evolution, LaOInS₂ powder synthesized at 850 °C (50 mg) was suspended in 140 mL of an aqueous solution containing 10 mM Na₂S (≥98.0%, Wako Pure Chemical Co.) and 10 mM Na₂SO₃ (≥95.0%, Wako Pure Chemical Co.) as electron donors. Pt (0.1~1.0 wt%) was loaded on LaOInS₂ by an in-situ photodeposition method using H₂PtCl₆·6H₂O (Kanto Chemical Co., 98.5+%) as the precursor. For water oxidation to O₂, 50 mg of IrO₂/LaOInS₂ was dispersed in 100 mL of an aqueous AgNO₃ (≥99.8%, Wako Pure Chemical Co.) solution (10 mM) containing 200 mg of La₂O₃, which buffers reaction pH (8–8.5) during the reaction.⁶ La₂O₃ (≥99.9 %, Tokyo Chemical Industry Co., Ltd.) was calcined at 1273 K for 2 h in air to remove carbonate and/or hydroxide phases prior to use. The suspension was thoroughly degassed and then exposed to argon (5 kPa). The suspension was irradiated using a Xe lamp (300 W, output current 20 A) fitted with a cold mirror (CM-1) and a cutoff filter to eliminate UV light. The evolved gases were

analyzed by online gas chromatography. When wavelength dependence was examined, a different cutoff filter was used with 10 A output current of the Xe lamp.

The apparent quantum yield (AQY) for H₂ evolution was estimated as

$$\text{AQY(\%)} = (A \times R/I) \times 100$$

where *A*, *R*, and *I* represent coefficients based on the reactions (H₂ evolution, 2), the H₂ evolution rate, and the rate of incident photons, respectively. The total number of incident photons (6.8 mW) was measured using a powder meter.

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