

Supporting Information

© Wiley-VCH 2014

69451 Weinheim, Germany

Nanocomposites of Tantalum-Based Pyrochlore and Indium Hydroxide Showing High and Stable Photocatalytic Activities for Overall Water Splitting and Carbon Dioxide Reduction**

*Meng-Chun Hsieh, Guan-Chang Wu, Wei-Guang Liu, William A. Goddard III, and Chia-Min Yang**

anie_201408868_sm_miscellaneous_information.pdf

Supporting Information

I. Experimental Section

Material preparation.....	3
Characterization methods	3
Photocatalytic hydrogen generation and water splitting.....	3
Photocatalytic CO ₂ reduction.....	4

II. Tables

Table S1. Relative molar composition and estimated formula of TIM-x and TIM-x-A ..	5
Table S2. Calculated band energy and band gap by different DFT functionals.....	6
Table S3. Optimized basis sets for Ta, K, In and O	7

III. Figures

Figure S1. XRD patterns of (a) as-prepared and (b) acid-treated samples.....	8
Figure S2. SEM image and EDX results of TIM-190 on large particle (presumably In(OH) ₃) and nanoparticles (presumably pyrochlore).....	9
Figure S3. Solid-state ¹ H MAS NMR spectra of TIM-190 and TIM-190-A.....	10
Figure S4. TGA results of TIM-190 and TIM-190-A.....	11
Figure S5. (a, b) UV–visible diffuse reflectance spectra of selected samples. (c) Corresponding plot of (F(R)hv) ² vs. hv for direct band gap estimation of selected samples.	12
Figure S6. The structure of (a) In(OH) ₃ slab and (b) TP slab..	13
Figure S7. Band dispersion of (a) In(OH) ₃ slab and (b) TP slab.	14

IV. Band structure calculation detail and Optimized atomic coordinates and lattice constants (in the format of CRYSTAL 09)

1. Band structure calculation method.....	15
2. In(OH) ₃ slab	16
3. TP slab.....	18

Experimental Section

Materials preparation

The TIM-x samples were hydrothermally synthesized using $K_8[Ta_6O_{19}] \cdot 14H_2O$ and $InCl_3$ as metal precursors, KOH as a base, and potassium citrate as chelating agent. $K_8[Ta_6O_{19}] \cdot 14H_2O$ was prepared based on the procedure reported by Nyman et al.^[1] Briefly, $TaCl_5$ (5.0 g) was dissolved in the iced H_2O_2 (30 %, 43 mL), and the solution was added subsequently with KOH (4.0 M, 37 mL) and then methanol (150 mL) to obtain white precipitate of $K_3Ta(O_2)_4$. After further washing with methanol, $K_3Ta(O_2)_4$ (4.0 g) together with KOH (3.8 g) and K_3VO_4 (0.14 g) were dissolved in water (10 mL). The solution was hydrothermally heated at 150 °C for 4 h, and the hot solution was filtered and then cooled down to room temperature to allow the crystallization of $K_8[Ta_6O_{19}] \cdot 14H_2O$. For the synthesis of TIM-x samples, an aqueous solution (2.0 mL) of $K_8[Ta_6O_{19}] \cdot 14H_2O$ (0.36 g) was added into the solution prepared by mixing KOH (4.0 M, 1.5 mL) with an aqueous solution (7.0 mL) containing $InCl_3$ (0.12 g) and potassium citrate (0.18 g). The mixture was hydrothermally heated at a temperature x ($x = 170, 190, 205$ or 220 °C) for 4 days. White solid was collected by centrifugation, further washed with water, again collected by centrifugation, and was finally dried at 90 °C. The TIM-x-A samples were prepared by suspending TIM-x samples in 1.0 M HCl for 1 day. The solids were collected, washed with water and then methanol, and were finally dried at 90 °C.

Characterization methods

XRD patterns were recorded on a Bruker D8 diffractometer using Cu K α radiation as X-ray source. SEM image was obtained on JEOL JSM-7000 FESEM equipped with an EDX. TEM images were recorded on a JEOL JEM-2100 electron microscope operating at 200 kV. ICP-MS results were obtained on a Perkin-Elmer SCIEX-ELAN5000 device. TGA-MS was performed on Linseis Pt-1600 thermal analyzer coupled with Pfeiffer VacuumThermostar quadropole mass spectrometer QMS200. UV-vis diffuse reflectance spectra were recorded on a JASCO V-650 spectrophotometer equipped with a diffuse reflection accessory. 1H MAS NMR spectra were recorded with BRUKER AVANCE III 400 spectrometer.

Photocatalytic hydrogen generation and water splitting

The experiments were carried out in a closed quartz reaction cell. A photocatalyst (0.05 g) was dispersed in aqueous solution of methanol (100 mL, 10 vol%) or deionized water (100 mL). The suspension was magnetically stirred and continuously purged with an argon flow for at least 30 min to remove the dissolved air. The suspension was then irradiated with UV light using a 500 W Hg–Xe arc lamp (Oriel). The power density of UV irradiation ($\lambda < 400$ nm) on reaction cell was 33 mW cm⁻². The evolved gases were analyzed by gas chromatography (GC, Shimadzu GC-2014 with TCD detector and MS-5A column, argon carrier gas). The average rate of H_2 and O_2 evolution was determined by averaging the total amount generated within 3

h. Apparent quantum yields were measured using the same reaction cell and lamp mentioned above, while the lamp was equipped with water filter and attached with a 232 nm band-pass filter (CVI Melles Griot, FWHM: 10 nm). The number of incident photons was measured using a photo-diode head (OPHIRA; 3A-P-SH-V1) and a power monitor (OPHIRA; NOVA-ORIEL). Apparent quantum yield was calculated according to equation (1).

$$\text{Apparent quantum yield (\%)} = \frac{[\text{The number of reacted electrons or holes}]}{[\text{The number of incident photons}]} \times 100 \quad (1)$$

Photocatalytic CO₂ reduction

Photocatalytic reduction of CO₂ was carried out in a closed stainless-steel reactor (volume, ~350mL) with a quartz window on the top of the reactor. The light source was a 500 W Hg–Xe arc lamp (Oriel) equipped with water filter and beam turning mirror (Oriel 66225 Full Reflector Beam Turning Mirror, 200nm - 30μm). The power density of UV irradiation ($\lambda < 400\text{nm}$) on reaction cell was 36 mW cm⁻². The reaction was performed in a gas (vapor)-solid heterogeneous reaction mode. A sample (0.1 g) was dispersed on a glass disk with area of 6.75 cm² and placed on a support below the window in the reactor. Deionized water (~100ml) at the bottom of the reactor was used to maintain saturated water vapor pressure. The reactor was then purged with high purity CO₂ (>99.5%) for 1 h and closed prior to irradiation. The pressure of CO₂ was typically regulated to 0.1 MPa (1atm). The temperature of the reactor was kept at 298 K, and the vapor pressure of H₂O was about 31 kPa. The amount of CO, CH₄, and O₂, were then analyzed by off-line GC equipped with a syn-carbon (ZT-11) column and thermal conductivity detector (TCD). Helium was used as the carrier gas. The average evolution rate of CO and O₂ evolution was determined by averaging the total amount generated within the first 5 hours.

Reference

- [1] a) T. M. Anderson, M. A. Rodriguez, F. Bonhomme, J. N. Bixler, T. M. Alam, M. Nyman, *Dalton Trans.* **2007**, 4517-4522; b) M. Nyman, M. A. Rodriguez, L. E. Shearherwer, J. E. Martin, P. P. Provencio, *J. Am. Chem. Soc.* **2009**, *131*, 11652-11653.

Supporting Tables

Table S1. Relative molar composition and estimated formula of TIM-x and TIM-x-A.

Sample	K ^a	In ^a	Ta ^a	Estimated formula ^b
TIM-170	1.62	0.75	2.00	$H_{0.23}K_{1.62}In_{0.05}Ta_2O_6 \cdot 1.4H_2O / 0.70In(OH)_3$
TIM-190	1.32	0.92	2.00	$H_{0.50}K_{1.32}In_{0.06}Ta_2O_6 \cdot 2.2H_2O / 0.86In(OH)_3$
TIM-205	1.27	1.27	2.00	$H_{0.49}K_{1.27}In_{0.08}Ta_2O_6 \cdot 1.1H_2O / 1.19In(OH)_3$
TIM-220	1.20	1.39	2.00	$H_{0.47}K_{1.20}In_{0.11}Ta_2O_6 \cdot 2.1H_2O / 1.28In(OH)_3$
TIM-170-A	0.43	0.05	2.00	$H_{1.42}K_{0.43}In_{0.05}Ta_2O_6 \cdot 1.4H_2O$
TIM-190-A	0.27	0.06	2.00	$H_{1.55}K_{0.27}In_{0.06}Ta_2O_6 \cdot 0.8H_2O$
TIM-205-A	0.23	0.08	2.00	$H_{1.53}K_{0.23}In_{0.08}Ta_2O_6 \cdot 1.6H_2O$
TIM-220-A	0.17	0.11	2.00	$H_{1.50}K_{0.17}In_{0.11}Ta_2O_6 \cdot 1.5H_2O$

^a Determined by ICP-MS.

^b The formulas were deduced based on the defect pyrochlore ($A_2B_2O_6$) structure. The oxidation states of K, In and Ta are assigned to be 1+, 3+ and 5+. The In-to-Ta ratio of the pyrochlore nanoparticles was assumed to be the same before and after the removal of $In(OH)_3$ by acid treatment. To maintain charge balance, some oxygens in the M_2O_6 moiety must be replaced by hydroxyl (OH^-) groups. For example, the formula of TIM-190-A can be written as $K_{0.27}In_{0.06}Ta_2O_{4.45}(OH)_{1.55}$ or $H_{1.55}K_{0.27}In_{0.06}Ta_2O_6$. The amount of crystallization water was determined by TGA-MS.

Table S2. Calculated band energy and band gap by different DFT functionals.*

DFT functional	In(OH)₃			TP in TIM-190		
	CB ^a	VB ^b	Band gap	CB ^a	VB ^b	Band gap
B3PW91	-0.97	-7.07	6.10	-2.28	-7.61	5.33
B3LYP	-0.62	-6.97	6.35	-2.13	-7.44	5.31
PBE	-1.41	-5.62	4.21	-2.62	-6.30	3.68
PBE0	-0.62	-7.39	6.76	-2.09	-7.85	5.76

* Energy values are relative to the vacuum in unit of voltage.

^a CB: Bottom level of the conduction band.

^b VB: Top level of the valance band.

Table S3. Optimized basis sets for Ta, K, In and O*

	Ta		K		In		O	
	exponent	coefficient	exponent	coefficient	exponent	coefficient	exponent	coefficient
s	1.6886	1.0000	2.9692	1.0000	0.4734	1.0000	33.8074	0.1602
	1.6116	-1.0209	0.7500	-2.0760	0.4196	-0.9221	8.1487	1.0000
	0.3793	1.0000	0.2960	1.0000	0.1500	1.0000	2.5693	1.0000
	0.3048	1.0000	0.1500	1.0000	-	-	0.8942	1.0000
	-	-	-	-	-	-	0.2700	1.0000
p	2.4848	1.0000	7.8617	1.0000	0.9174	1.0000	33.8074	0.1820
	1.3587	-2.0579	0.9855	-12.2015	0.2620	-0.6087	8.1487	1.0000
	0.5097	1.0000	0.3228	1.0000	0.1500	1.0000	2.5693	1.0000
	0.1500	1.0000	-	-	-	-	0.8942	1.0000
	-	-	-	-	-	-	0.2700	1.0000
d	0.9757	1.0000	-	-	-	-	0.6000	1.0000
	0.3971	1.3652	-	-	-	-	-	-
	0.1500	1.0000	-	-	-	-	-	-

* The basis optimization was carried out with Billy script (Towler, M. CRYSTAL Resources Page. <http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html>). The exponent of outermost shell of bases were fixed at largest possible values without causing basis linear-dependency.

Supporting Figures

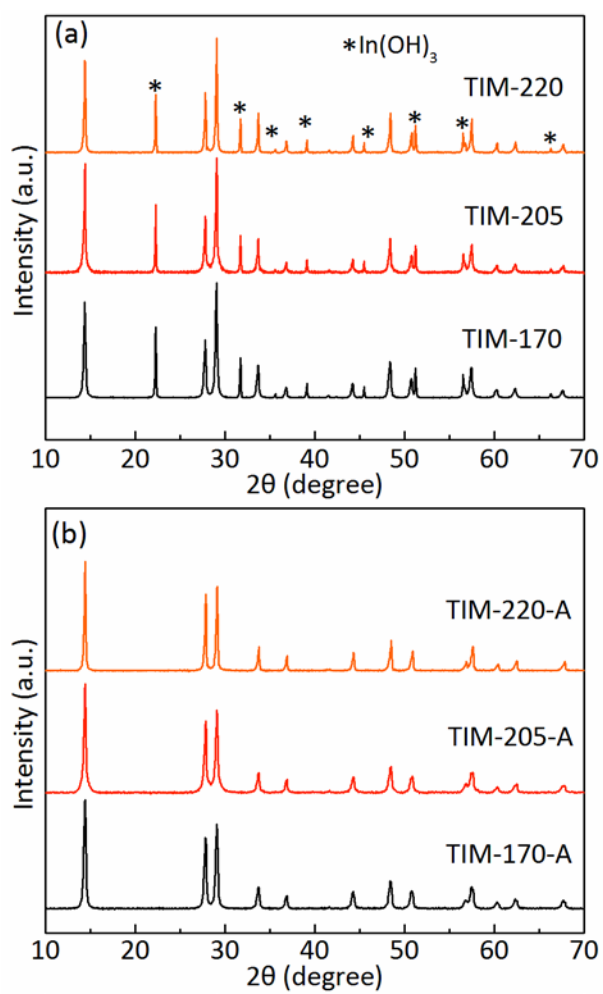


Figure S1. XRD patterns of (a) as-prepared and (b) acid-treated samples.

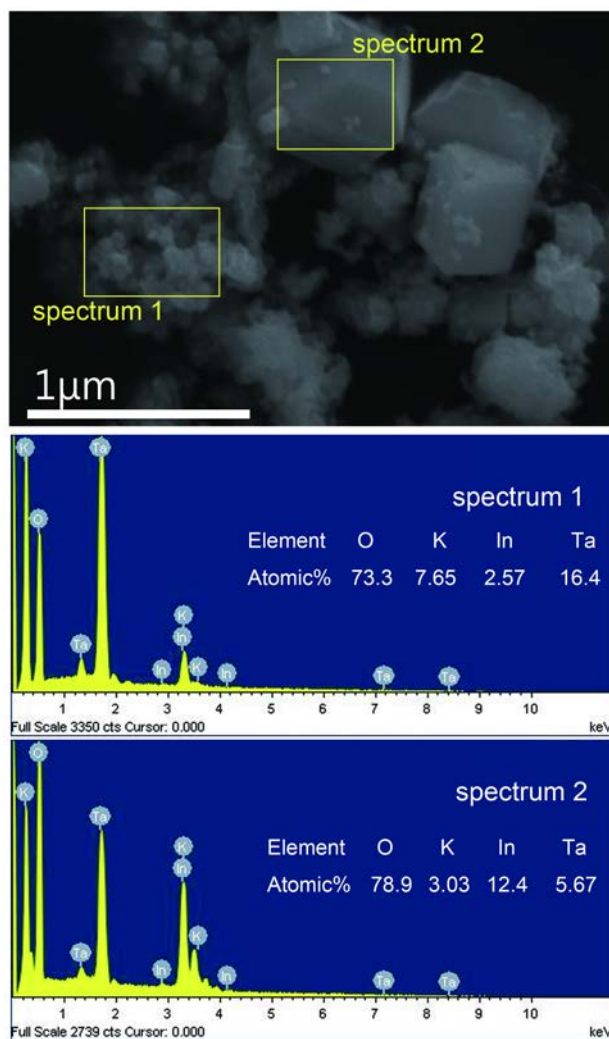


Figure S2. SEM image and EDX results of TIM-190 on large particle (presumably $\text{In}(\text{OH})_3$, spectrum 1) and TP nanoparticles (spectrum 2).

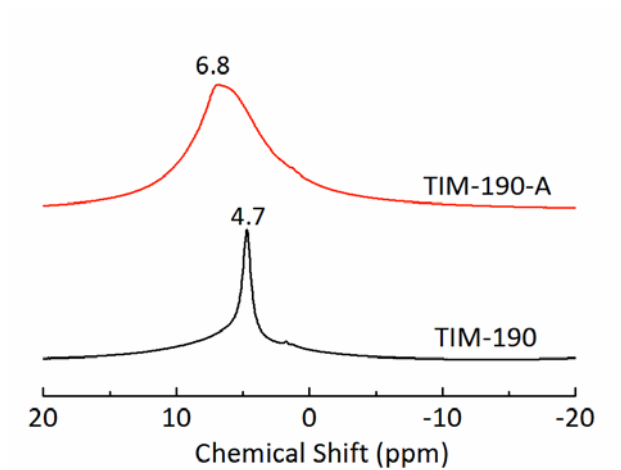


Figure S3. Solid-state ^1H MAS NMR spectra of TIM-190 and TIM-190-A. The line at 4.7 ppm may be attributed to the crystallization water. The exchanged protons in TIM-190-A may be associated to the broad signals in the spectrum.

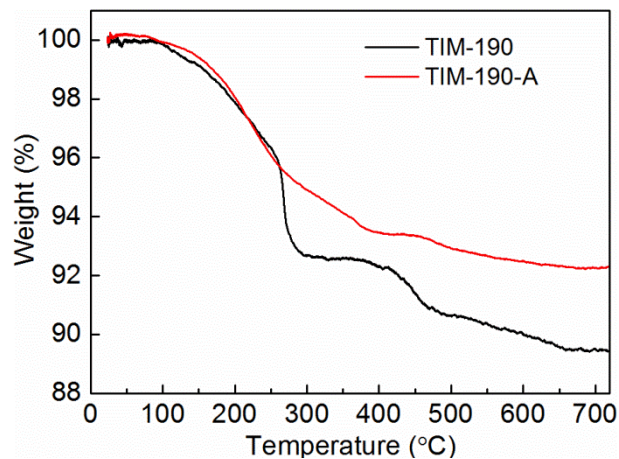


Figure S4. TGA results of TIM-190 and TIM-190-A. The weight loss during 200-700 °C could be mainly associated with the loss of crystallization water (and the dehydration of $\text{In}(\text{OH})_3$ at 260 °C), which could be confirmed by MS signal at $m/z = 18$ at corresponding temperature.

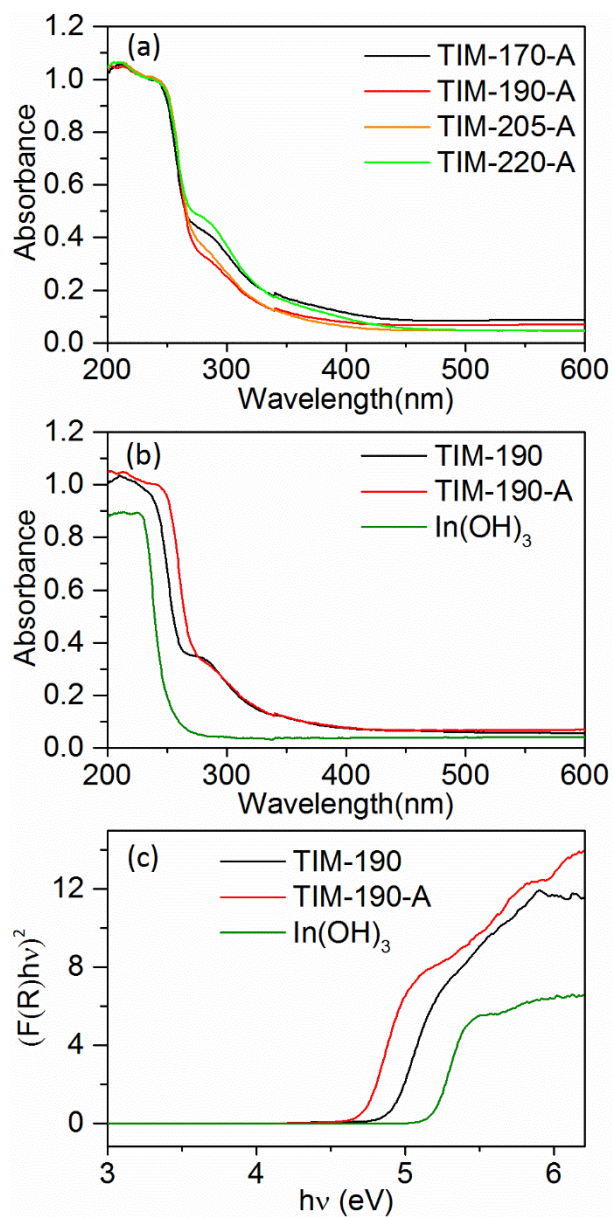


Figure S5. (a, b) UV–visible diffuse reflectance spectra of selected samples. (c) Corresponding plot of $(F(R)h\nu)^2$ vs. $h\nu$ for direct band gap estimation of selected samples. $F(R) = (1-R)^2/2R$ where R is the reflectance, and $F(R)$ is proportional to the extinction coefficient (α).

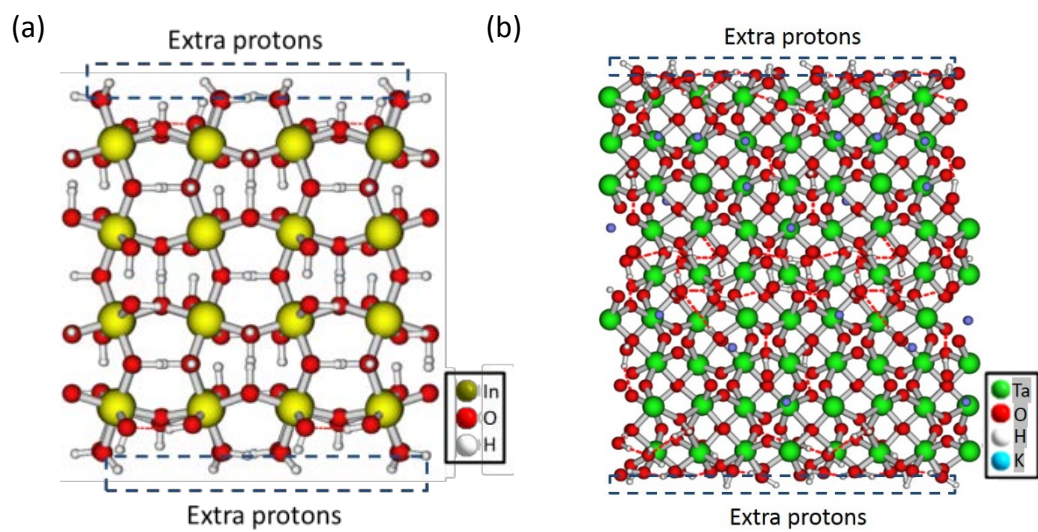


Figure S6. The structure of (a) $\text{In}(\text{OH})_3$ slab and (b) TP slab.

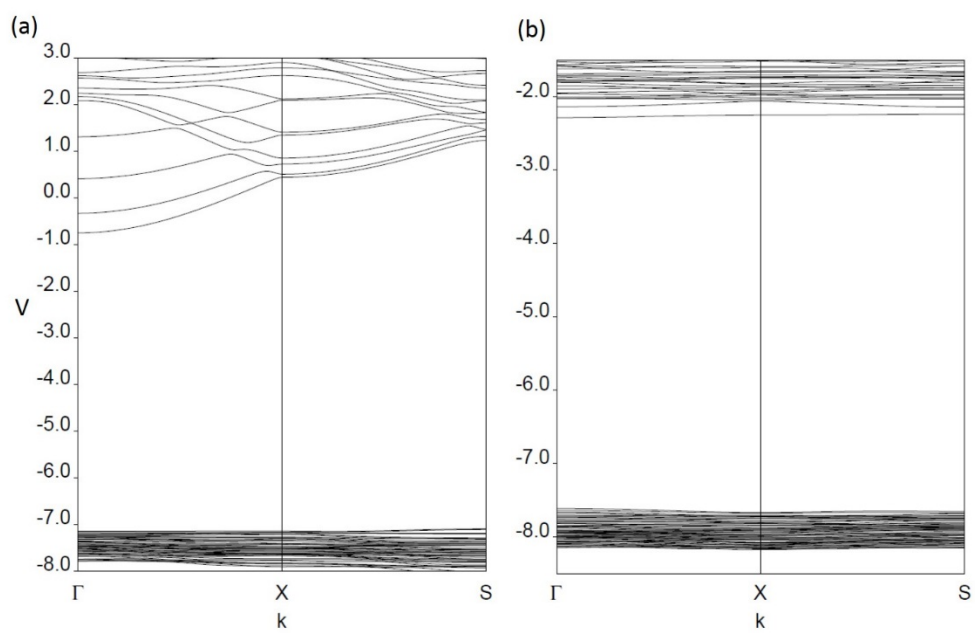


Figure S7. Band dispersion of (a) $\text{In}(\text{OH})_3$ slab and (b) TP slab.

Band structure calculation detail and Optimized atomic coordinates and lattice constant in the format of CRYSTAL 09

1. Band structure calculation method

The atomic coordinates of heavy atoms of $\text{In}(\text{OH})_3$ and pyrochlore were taken from experimental structures determined by X-ray crystallography. The structures were then optimized with the addition of H atoms with B3PW91 functional,^[1] which has been demonstrated to reproduce experimental bandgaps for semiconductors.^[2] For K, In and Ta, Los Alamos angular momentum-projected effective core potentials^[3] were used with split-valence (double-zeta) type basis sets. Since the negatively charged O determines the position of valence band, a highly flexible 6-2111* type basis set was used to ensure O is able to fully respond to the change of chemical environment. The basis set optimization was carried out on KTaO_3 (for K, Ta and O) and In_2O_3 (for In). The basis set of H is taken from Pople's basis set.^[4] All calculations were carried out with CRYSTAL09.^[5] (Results in Table S3 and part IV in SI)

Reference

- [1] Becke, A. D. *The Journal of Chemical Physics* **1993**, 98 (7), 5648-5648.
- [2] Xiao, H.; Tahir-Kheli, J.; Goddard, W. A., *The Journal of Physical Chemistry Letters* **2011**, 2 (3), 212-217.
- [3] Hay, P. J.; Wadt, W. R., *The Journal of Chemical Physics* **1985**, 82 (1), 299-299.
- [4] Binkley, J. S.; Pople, J. A.; Hehre, W. J., *Journal of the American Chemical Society* **1980**, 102 (3), 939-947.
- [5] R. Dovesi, V. R. S., C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, and M. Llunell, CRYSTAL09 University of Torino: Torino, 2009

2. In(OH)₃ slab

2			
7.9743	7.9743	90	
62			
249	-2.483097750431E-01	-2.506729261157E-01	1.936061450668E+00
249	2.458129329016E-01	2.461747584623E-01	5.829128591044E+00
249	-2.554712583762E-01	-2.592678044474E-01	5.783411666795E+00
249	2.529426175298E-01	2.513236517440E-01	1.928984411725E+00
249	-2.558547052589E-01	2.483024677001E-01	5.823473810400E+00
249	2.489000762944E-01	-2.491669888469E-01	1.951724985584E+00
249	-2.509459990586E-01	2.488207606801E-01	1.946629628404E+00
249	2.437330336427E-01	-2.509128036411E-01	5.828685754992E+00
8	-3.243399069380E-01	4.995725970537E-01	2.493922450966E+00
8	3.183829626321E-01	4.979125238128E-01	5.275036618036E+00
8	-1.709540293911E-01	-3.476033683421E-01	7.716061097513E+00
8	-3.279159208446E-01	-1.747270688702E-01	3.897336282768E+00
8	3.222892293306E-01	1.738360669742E-01	3.860635910453E+00
8	-3.354872781148E-01	4.947345465682E-01	5.295212251754E+00
8	3.280485093938E-01	-4.966025574135E-01	2.439750130813E+00
8	-3.169647632118E-01	1.686668080514E-01	3.882455128316E+00
8	3.168967832025E-01	-1.710913786986E-01	3.905766076684E+00
8	-1.832868102150E-01	-1.119251525913E-02	6.369459794553E+00
8	1.757087980975E-01	2.838255576753E-03	1.388841780142E+00
8	-1.717983448323E-01	-1.089810823835E-03	1.457035318228E+00
8	1.708837850638E-01	-1.767114372710E-03	6.242885917420E+00
8	-1.783802905805E-01	3.244983563693E-01	7.716663399394E+00
8	1.771404082478E-01	-3.255138510940E-01	-4.270721026447E-04
8	-7.291609167929E-03	-3.259714456452E-01	5.182734437853E+00
8	2.387512335711E-03	3.206865632245E-01	2.516026770824E+00
8	4.938966050308E-01	1.870443648319E-01	6.452014223311E+00
8	4.999004312290E-01	-1.779649567005E-01	1.363385765376E+00
8	4.630166255963E-04	-3.117906817015E-01	2.535273361555E+00
8	-5.666493406572E-03	3.076945564095E-01	5.217759329871E+00
8	4.975960500899E-01	-2.063944333655E-01	6.559806257208E+00
8	-4.970142501415E-01	1.873454710503E-01	1.328637582078E+00
8	1.657982885485E-01	-3.326587212439E-01	7.709785604418E+00

8	-1.867466187621E-01	-3.307783674564E-01	1.296755855694E-02
8	1.614967272419E-01	3.383033821986E-01	7.743305650283E+00
1	2.350904291975E-04	-3.094452159921E-01	3.531773969136E+00
1	-5.184334295942E-03	3.024221359917E-01	4.225771737629E+00
1	-4.756934895412E-02	-1.762956149768E-03	1.515104940242E+00
1	4.763841389870E-02	-8.934277353464E-04	6.233132571174E+00
1	-3.114443993800E-01	4.447920240265E-02	3.868014015037E+00
1	3.076855504303E-01	-4.680859532679E-02	3.919586520389E+00
1	-1.808996365549E-01	-9.357830192182E-03	7.336824021823E+00
1	1.782731741597E-01	1.169702151841E-03	3.995421526170E-01
1	-4.521065845953E-01	-1.793471307267E-01	3.866003151491E+00
1	4.460642930309E-01	1.778606103569E-01	3.888311948992E+00
1	-3.564790828663E-03	-4.497838021172E-01	5.243677662770E+00
1	5.978044844618E-04	4.443775088294E-01	2.476144487750E+00
1	4.928450200654E-01	6.731455642103E-02	6.656985515013E+00
1	4.989004744184E-01	-5.414594823626E-02	1.404226269030E+00
1	-3.237004056102E-01	4.996810352589E-01	3.484244739862E+00
1	3.157839419461E-01	4.968801277746E-01	4.285212063489E+00
1	-1.841612055289E-01	-4.749029002165E-01	7.757477041720E+00
1	5.339519822610E-02	-3.211601882120E-01	-1.178265445463E-02
1	4.973695498889E-01	-2.522277257614E-01	7.457079185064E+00
1	-4.987161380813E-01	1.921248607995E-01	3.349019027991E-01
1	3.824945168176E-02	3.186199205769E-01	7.841574989815E+00
1	-4.598779330895E-01	4.962732988757E-01	5.358820534691E+00
1	4.522656982924E-01	-4.983934853027E-01	2.383318867825E+00
1	-4.558886651338E-02	-3.308155510793E-01	7.755860376674E+00
1	-1.926606937731E-01	-4.550992583323E-01	-1.219295297715E-03
1	1.764073891529E-01	4.635037966023E-01	7.832909990034E+00
1	2.001612781710E-01	-2.580135671575E-01	8.418930009162E+00
1	-2.562882576389E-01	2.902850572673E-01	8.405118507155E+00

3. TP slab (Ta₁₆O₄₈H₈K₈•6H₂O slab)

2			
10.64248593	10.70134497	90.247671	
127			
273	5.000000E-01	-5.000000E-01	0.000000E+00
273	-4.876667E-01	4.974535E-01	1.042771E+01
273	4.998934E-01	2.969897E-03	5.416129E+00
273	-2.279395E-03	-4.998705E-01	5.262679E+00
273	0.000000E+00	0.000000E+00	0.000000E+00
273	2.640769E-02	-8.970391E-03	1.069499E+01
273	-4.921416E-01	-2.647904E-01	2.602436E+00
273	-4.914163E-01	2.594794E-01	7.823346E+00
273	1.482110E-02	-2.526866E-01	7.900162E+00
273	2.911300E-03	2.625743E-01	2.613980E+00
273	-2.413939E-01	-2.590800E-01	1.043939E+01
273	2.668666E-01	2.495514E-01	1.186071E-01
273	2.551404E-01	2.385246E-01	1.053068E+01
273	2.472973E-01	-2.476314E-01	5.221429E+00
273	-2.407528E-01	2.359654E-01	5.221769E+00
273	-2.472335E-01	4.932764E-01	2.701175E+00
273	2.588104E-01	-4.916765E-01	7.760032E+00
273	2.494837E-01	1.253637E-02	2.846423E+00
273	-2.347760E-01	-1.626046E-02	7.760142E+00
8	4.396822E-01	-3.759959E-01	1.315163E+00
8	4.445565E-01	-3.557378E-01	1.171456E+01
8	-4.258120E-01	3.750866E-01	9.248265E+00
8	-1.153946E-01	-3.147942E-01	9.216626E+00
8	1.317394E-01	3.109763E-01	1.264087E+00
8	1.300337E-01	3.041811E-01	1.182003E+01
8	3.797418E-01	-2.933081E-01	3.900588E+00
8	-3.638345E-01	3.046677E-01	6.607242E+00
8	-1.802406E-01	-3.634847E-01	1.307404E+00
8	-1.891454E-01	-3.639730E-01	1.191625E+01
8	1.845292E-01	3.792048E-01	9.249833E+00
8	-1.189221E-01	-4.380915E-01	3.924025E+00
8	1.341028E-01	4.394942E-01	6.561152E+00

8	-2.902955E-01	-1.287016E-01	9.175031E+00
8	3.118699E-01	1.199549E-01	1.351374E+00
8	3.227988E-01	1.171468E-01	1.176542E+01
8	-3.071613E-01	3.733974E-01	3.926268E+00
8	3.221991E-01	-3.695153E-01	6.561880E+00
8	1.878987E-01	-1.217523E-01	3.942245E+00
8	-1.804987E-01	1.219960E-01	6.566053E+00
8	-1.456721E-01	-1.022396E-01	7.146517E-01
8	-1.150881E-01	-1.317072E-01	1.138482E+01
8	1.349314E-01	1.217944E-01	9.858039E+00
8	-1.189339E-01	3.819317E-01	1.900302E+00
8	1.399768E-01	-3.702144E-01	8.546976E+00
8	3.790544E-01	-1.153194E-01	1.866705E+00
8	-3.726309E-01	1.215028E-01	8.649352E+00
8	1.178352E-01	-7.548744E-02	1.404628E+00
8	1.447392E-01	-6.485479E-02	1.180160E+01
8	-1.200797E-01	6.488873E-02	9.204755E+00
8	-3.710106E-01	4.519195E-01	1.307292E+00
8	-3.838949E-01	4.517852E-01	1.197653E+01
8	3.838580E-01	-4.513219E-01	9.201833E+00
8	1.305419E-01	-3.704376E-01	4.648110E+00
8	-1.180968E-01	3.727481E-01	5.860672E+00
8	-3.671076E-01	-3.753104E-01	9.832476E+00
8	3.838759E-01	3.700333E-01	7.428988E-01
8	3.789315E-01	3.789534E-01	1.133611E+01
8	-3.778374E-01	-1.879810E-01	1.285476E+00
8	-3.809646E-01	-1.859917E-01	1.169156E+01
8	3.775508E-01	2.092618E-01	9.200379E+00
8	-3.670754E-01	-3.716717E-01	3.286701E+00
8	3.842927E-01	3.785796E-01	7.214138E+00
8	-4.303467E-01	-1.115630E-01	3.832698E+00
8	4.391297E-01	1.254901E-01	6.656467E+00
8	6.914111E-02	3.785096E-01	3.899496E+00
8	-4.985000E-02	-3.738705E-01	6.576446E+00
8	5.638961E-02	-1.222443E-01	9.204787E+00
8	-4.551711E-02	1.307666E-01	1.194118E+00
8	-5.403885E-02	1.222664E-01	1.182073E+01
8	3.764209E-01	6.764201E-02	4.008046E+00

8	-3.733117E-01	-6.096138E-02	6.623283E+00
8	3.814610E-01	-1.210419E-01	5.931271E+00
8	-3.703981E-01	1.215082E-01	4.638764E+00
8	1.360893E-01	-1.848141E-01	6.624291E+00
8	-1.214183E-01	1.919000E-01	3.841720E+00
8	1.272163E-01	1.306301E-01	3.283842E+00
8	-1.157483E-01	-1.281654E-01	7.133230E+00
8	-2.977318E-01	9.994632E-02	1.043821E+00
8	-2.265291E-01	2.708025E-01	1.098500E+01
8	4.857642E-01	-2.065367E-02	1.020331E+01
1	-3.110408E-01	1.157546E-01	9.189812E-02
1	-2.953639E-01	2.357271E-01	1.046061E+01
1	-4.629721E-01	-7.609507E-02	1.077921E+01
1	-2.151299E-01	1.380287E-01	1.234301E+00
1	-1.742919E-01	2.038479E-01	1.143374E+01
1	4.344561E-01	3.040309E-02	1.081649E+01
8	-6.525486E-02	4.334727E-01	9.653244E+00
8	7.401765E-02	-4.084581E-01	8.239044E-01
8	2.836164E-01	-2.291190E-01	1.039326E+01
1	-7.453297E-02	-4.764207E-01	9.802110E+00
1	7.144209E-02	-4.996335E-01	8.786257E-01
1	-1.193618E-01	3.883858E-01	1.028978E+01
1	9.819162E-02	-3.919675E-01	-1.142641E-01
1	2.264308E-01	-2.857293E-01	9.911764E+00
8	4.387779E-01	4.047961E-01	4.446614E+00
8	-4.178287E-01	-3.786600E-01	6.055187E+00
1	-4.698557E-01	4.113802E-01	4.323587E+00
1	4.918049E-01	-3.893069E-01	5.932997E+00
1	4.306017E-01	4.172080E-01	5.413017E+00
1	-3.857850E-01	-3.674297E-01	5.147262E+00
219	-2.530931E-01	-4.895867E-01	7.661675E+00
219	2.576140E-01	-4.916021E-01	2.691952E+00
219	-4.710799E-01	2.291046E-01	2.433410E+00
219	4.966316E-01	-2.364588E-01	8.119092E+00
1	4.343752E-01	-6.209225E-02	1.343200E+00
1	-4.232209E-01	6.923613E-02	9.301946E+00
1	-1.643990E-01	1.303452E-01	9.681571E+00
1	1.257017E-01	-1.657725E-01	1.390336E+00

1	2.306583E-01	-1.749674E-01	1.097115E+01
1	-8.890999E-02	-3.737027E-01	1.140668E+00
1	-2.490678E-01	-4.271228E-01	1.223824E+01
1	1.031637E-01	4.109245E-01	9.590313E+00
1	-3.745318E-01	-5.936003E-02	3.304882E+00
219	2.507651E-01	2.510434E-01	5.275693E+00
219	-8.243423E-02	-1.771827E-01	4.342176E+00
219	-8.733795E-04	2.517797E-01	7.881954E+00
1	-2.112316E-01	-4.160218E-02	1.009302E+00
219	2.821646E-01	-2.657821E-02	8.313169E+00
1	3.732899E-01	-3.082027E-01	1.125345E+01
1	-3.256012E-01	3.814830E-01	1.186931E+01
1	-4.874328E-01	-2.905156E-01	1.186555E+01
1	2.644943E-01	5.036967E-02	1.207354E+01
1	1.171724E-01	3.885804E-01	1.212149E+01
1	6.243257E-03	1.897034E-01	1.204875E+01
1	-3.531521E-01	-1.552294E-01	1.255029E+01
1	4.039513E-01	3.622406E-01	1.225097E+01
1	-8.839295E-02	-1.706583E-01	1.221428E+01