Supplementary information (ESI)

Mixed–Halogen Layer Approach of Band Engineering and Anisotropic Charge Migration in X1X2 Sillén Nanosheets Boost Cocatalyst-free Photocatalytic Hydrogen Evolution

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Fig. S1. P-XRD data of synthesized Sillén phases, (a) BiOCl, (b) BiOBr, and (c) SrBiO₂Cl.



Figure S2. Rietveld Refinement profile of SrBi₃O₄Cl₃ (SBOCI).

Table S1. Rietveld Refined Lattice Parameters, Reliability Factors, Positional (x, y, z) and Occupancy Parameters for SrBi₃O₄Cl₃

Atom	Wyckoff site	x	У	Z	f _{occ}
Bi2	4e	0	0	0.3432	0.528
Sr2	4e	0	0	0.3287	0.472
Bi1	4e	0	0	0.0717	0.972
Sr1	4e	0	0	0.0800	0.028
Cl2	4e	0	0	0.2100	1.000
Cl1	2b	0	0	0.5000	1.000
01	8g	0	0.5	0.1114	1.000

Space group: *I*4/*mmm*; *a* = *b* = 3.9481(1) Å and *c* = 27.3516(9) Å; Reliability factors: R_{Bragg} = 1.07 %, R_f = 2.29 %, R_p = 5.13 %, R_{wp} = 5.45 %, and χ^2 = 6.42.

Table S2. Rietveld Refined Lattice Parameters, Reliability Factors, Positional (x, y, z) and Occupancy Parameters for SrBi₃O₄Cl₂Br

Atom	Wyckoff site	x	У	Z	f _{occ}
Bi2	4e	0	0	0.3393(2)	0.528
Sr2	4e	0	0	0.3286(6)	0.472
Bi1	4e	0	0	0.0742(1)	0.972
Sr1	4e	0	0	0.0800	0.028
CI2	4e	0	0	0.2108(5)	0.850
Br2	4e	0	0	0.2108(5)	0.150
Cl1	2b	0	0	0.5000	0.300
Br1	2b	0	0	0.5000	0.700
01	8g	0	0.5	0.1178(1)	1.000

Space group: *I*4/*mmm*; *a* = *b* = 3.9520(1) Å and *c* = 27.3775(9) Å; Reliability factors: $R_{Bragg} = 1.03$ %, $R_f = 1.17$ %, $R_p = 4.12$ %, $R_{wp} = 4.53$ %, and $\chi^2 = 4.44$.



Figure S3. Different lattice planes of $SrBi_3O_4Cl_2Br$ crystal structure.

(a)	Bi	Element	Avg. At. %	Cal At %	(c)	Element	Avg. At. %	Cal At %
(••)		Sr	13.47	14.28	(0)	Sr	13.74	14 28
Ē			13.47	14.20		51	13.74	14.20
6-		Bi	49.21	42.86	6-	Bi	48.36	42.86
35/eV		Cl	37.31	42.86	ss/eV	Cl	37.90	42.86
4-	p				4-			
21	ST				2-1-2-1			
- 0 §	B	dania da a seconda a	Bi Bi	8 8 5 8 5	8	Bi	Bi Bi	8 8 5 8 5
•	2	4 6	8 10	12 14 16	0-1	iii 4 6	8 10	12 14 16
						0:		
(b)	Bi	Element	Avg. At. %	Cal. At. %	(d)	Element	Avg. At. %	Cal. At. %
(b)	Bi	Element Sr	Avg. At. % 13.11	Cal. At. % 14.28	(d)	Element Sr	Avg. At. % 12.93	Cal. At. % 14.28
(b)	Bi	Element Sr Bi	Avg. At. % 13.11 48.39	Cal. At. % 14.28 42.86	(d)	Element Sr Bi	Avg. At. % 12.93 49.12	Cal. At. % 14.28 42.86
(b)	B1	Element Sr Bi Cl	Avg. At. % 13.11 48.39 25.27	Cal. At. % 14.28 42.86 28.57	(d)	Element Sr Bi Cl	Avg. At. % 12.93 49.12 24.36	Cal. At. % 14.28 42.86 28.57
(b)	E	Element Sr Bi Cl Br	Avg. At. % 13.11 48.39 25.27 13.23	Cal. At. % 14.28 42.86 28.57 14.28	(d)	Element Sr Bi Cl Br	Avg. At. % 12.93 49.12 24.36 13.59	Cal. At. % 14.28 42.86 28.57 14.28
(b)	8 8 8	Element Sr Bi Cl Br	Avg. At. % 13.11 48.39 25.27 13.23	Cal. At. % 14.28 42.86 28.57 14.28	(d)	Element Sr Bi Cl Br	Avg. At. % 12.93 49.12 24.36 13.59	Cal. At. % 14.28 42.86 28.57 14.28

Figure S4. EDX spectra of (a) SBOCI, (b) SBOCIBr, (c) SBOCI-NS and (d) SBOCIBr-NS.



Figure S5. BET adsorption-desorption isotherms of SBOCI, SBOCIBr, SBOCI-NS and SBOCIBr-NS.



Figure S6. (a) UV-Vis DRS and (b) corresponding Tauc plot of precursor Sillén compounds.



Figure S7. (a) UV-Vis DRS and (b) corresponding Tauc plot of X1X2 Sillén compounds.



Figure S8. Mott-Schottky plots of (a) BiOCl, (b) BiOBr, (c) SrBiO₂Cl, (d) SBOCl, (e) SBOCl-NS, (f) SBOClBr and (g) SBOClBr-NS.

S. No.	Compound	VBM (V)	CBM (V)	Band Gap (eV)
1	BiOCI	2.82	- 0.66	3.48
2	BiOBr	2.41	- 0.49	2.90
3	SrBiO ₂ Cl	3.00	- 0.63	3.63
4	SBOCI	2.18	- 0.44	2.62
5	SBOCI-NS	2.09	- 0.54	2.63
6	SBOCIBr	2.09	- 0.55	2.64
7	SBOCIBr-NS	1.62	- 1.01	2.63

 Table S3. VBM, CBM and Band Gap Values of X1, X2 and X1X2 Sillén Compounds

Table S4. VBM and CBM Values of SBOCIBr and SBOCIBr-NS calculated from UPS Data

S. No.	Compound	VBM (eV)	CBM (eV)
1	SBOCIBr	- 6.59	- 3.95
2	SBOCIBr-NS	- 6.12	- 3.49



Figure S9. EIS data with equivalent circuit diagram of SBOCI, SBOCI-NS, SBOCIBr and SBOCIBr-NS.

S. No.	Compound name	R _{ct} (Ω)
1.	SBOCI	77.2
2.	SBOCIBr	81.0
3.	SBOCI-NS	67.2
4.	SBOCIBr-NS	78.0

Table S5. Equivalent Circuit Fitting Parameter (R_{ct}) of EIS Data



Figure S10. Post-photocatalytic characterization of SBOCIBr-NS, (a) P-XRD data and (b) FE-SEM image with elemental composition.



Figure S11. XPS spectra of (a) Bi 4f and (b) Br 3d for SBOCIBr-NS.

Table S6. Br/Bi XPS Peak Area Ratios for SBOCIBr-NS Before and After Photocatalytic Reaction,

along with the Reaction in Dark Condition

Compound	Before	After Irradiation	Dark
SBOCIBr-NS	1.00	0.97	0.96