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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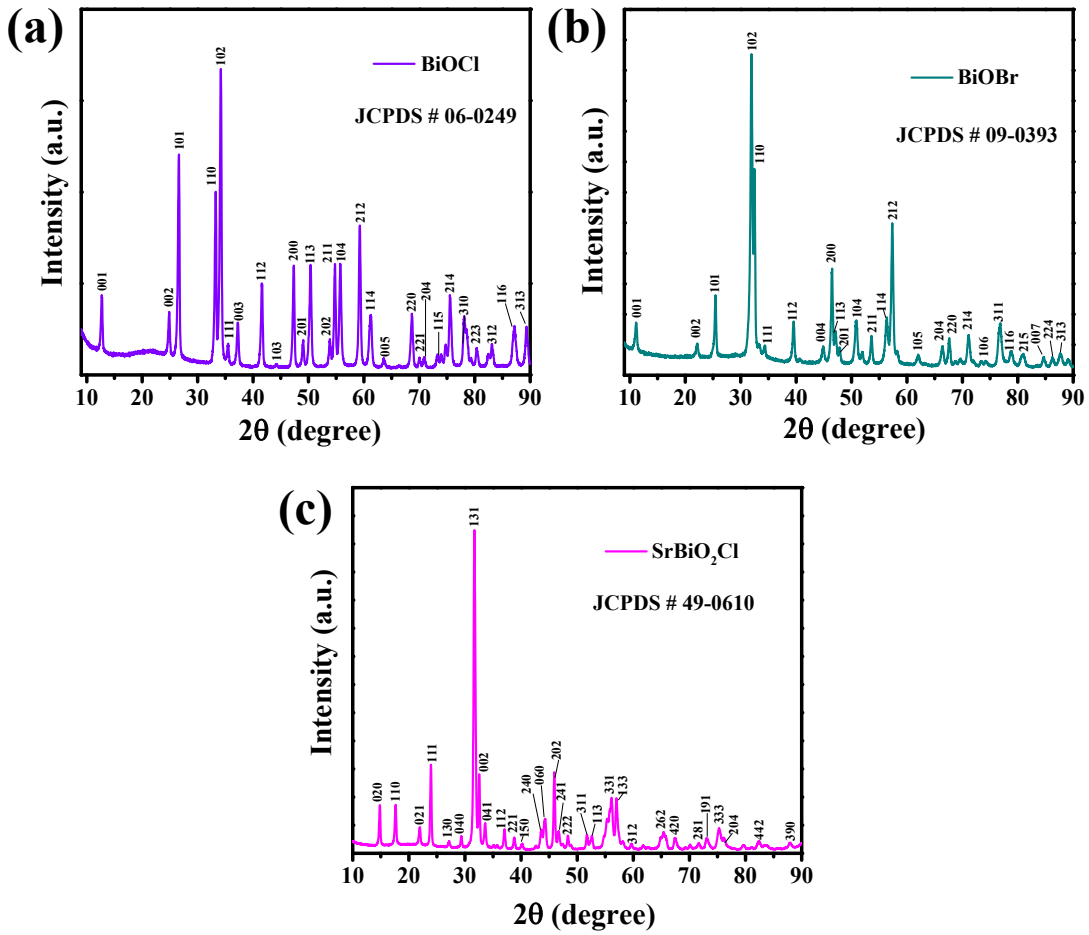

Fig. S1. P-XRD data of synthesized Sillén phases, (a) BiOCl, (b) BiOBr, and (c) $SrBiO_2Cl$.

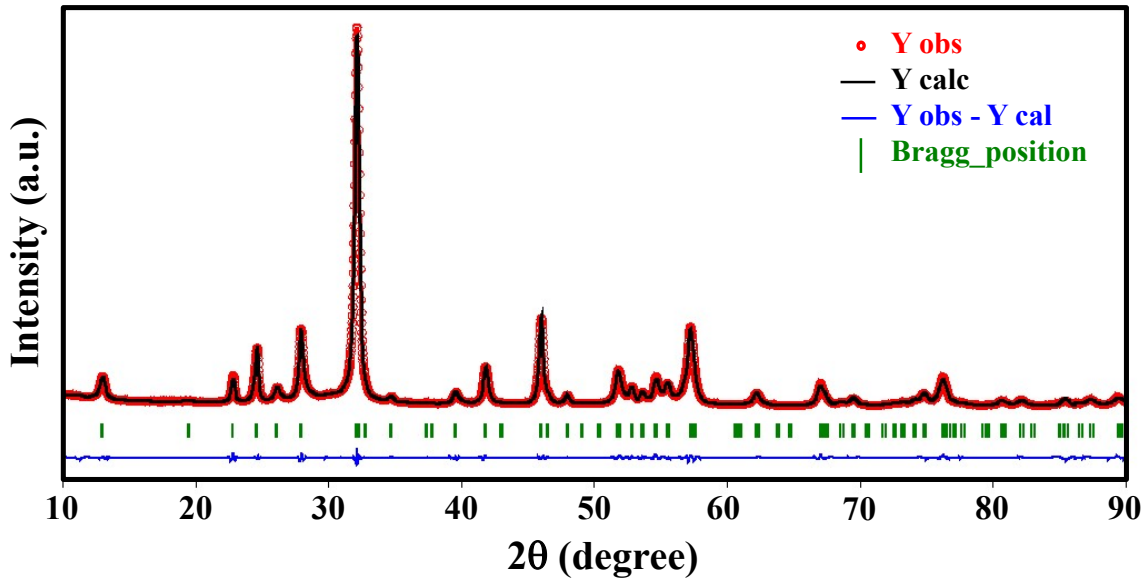

Figure S2. Rietveld Refinement profile of $SrBi_3O_4Cl_3$ (SBOCl).

Table S1. Rietveld Refined Lattice Parameters, Reliability Factors, Positional (*x*, *y*, *z*) and Occupancy Parameters for $SrBi_3O_4Cl_3$

Atom	**Wyckoff site**	***x***	***y***	***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
O1	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 $SrBi_3O_4Cl_2Br$

Atom	**Wyckoff site**	***x***	***y***	***z***	$\mathbf{f_{occ}}$
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
Cl2	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
O1	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 $\chi^2 = 4.44$.

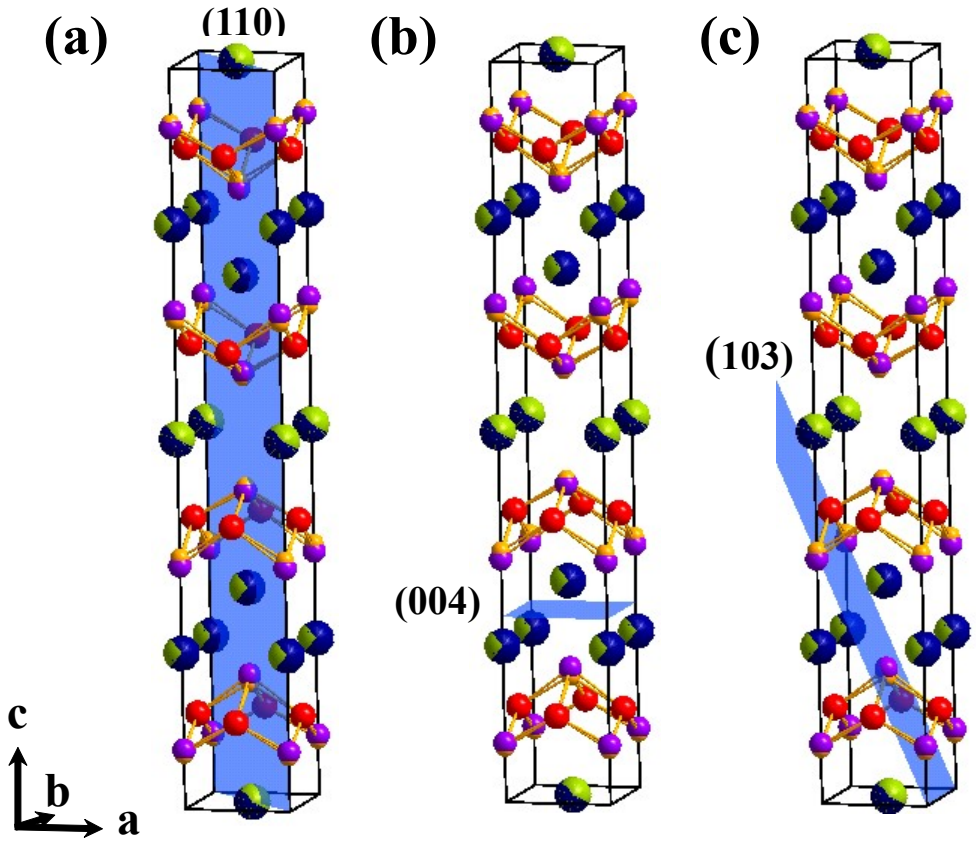

Figure S3. Different lattice planes of $SrBi_3O_4Cl_2Br$ crystal structure.

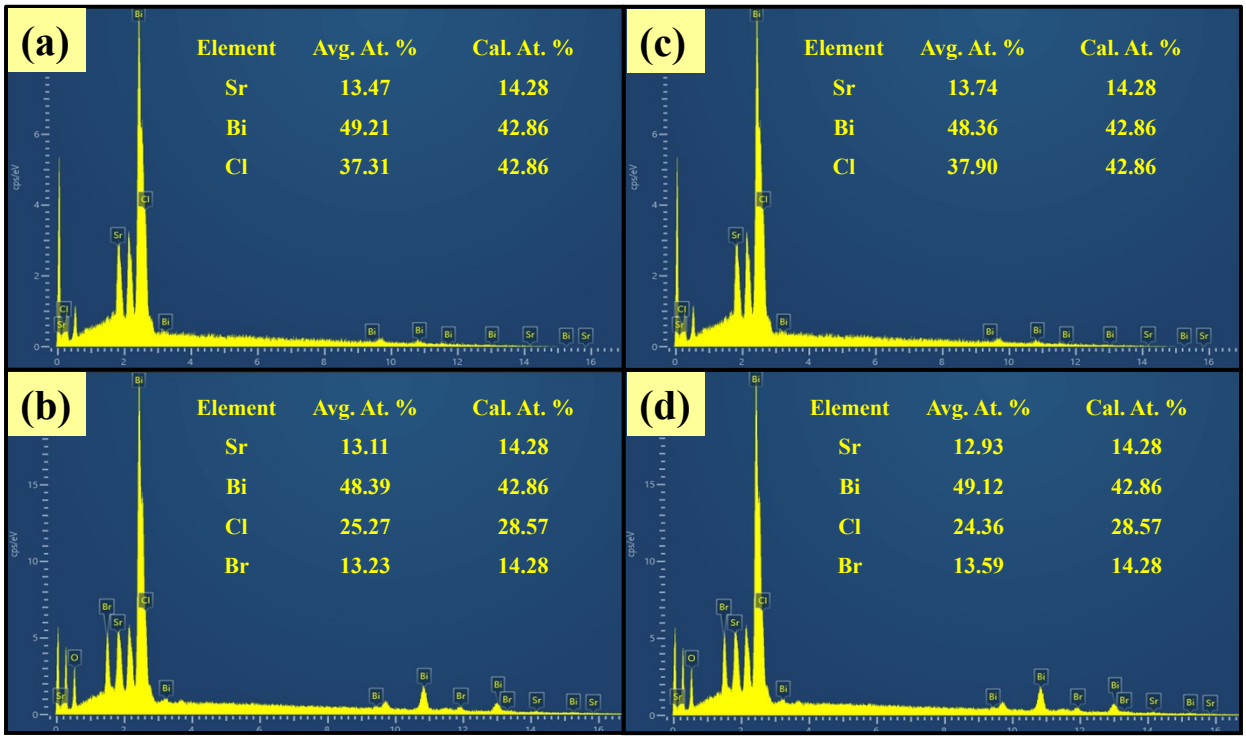

Figure S4. EDX spectra of (a) SBOCl, (b) SBOClBr, (c) SBOCl-NS and (d) SBOClBr-NS.

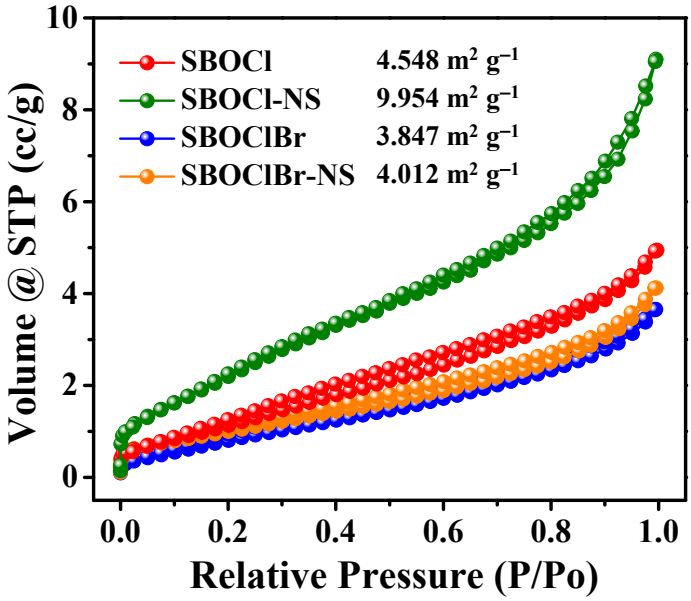

Figure S5. BET adsorption–desorption isotherms of SBOCl, SBOClBr, SBOCl-NS and SBOClBr-NS.

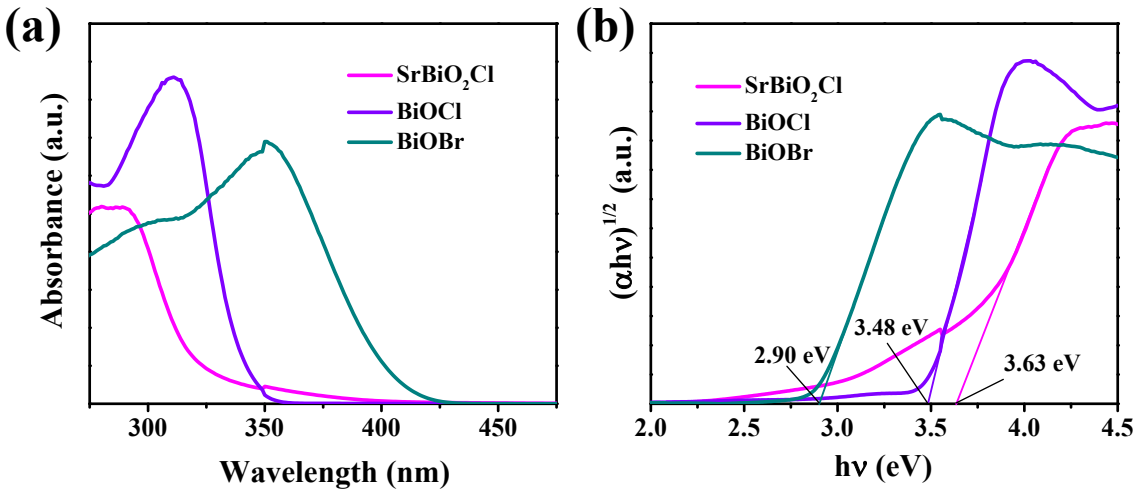

Figure S6. (a) UV-Vis DRS and (b) corresponding Tauc plot of precursor Sillén compounds.

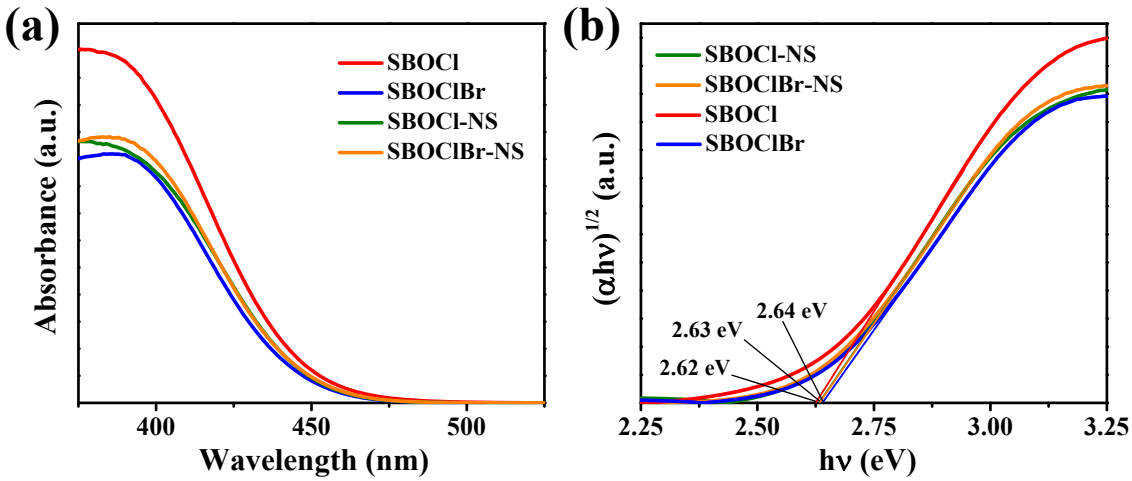

Figure S7. (a) UV-Vis DRS and (b) corresponding Tauc plot of X1X2 Sillén compounds.

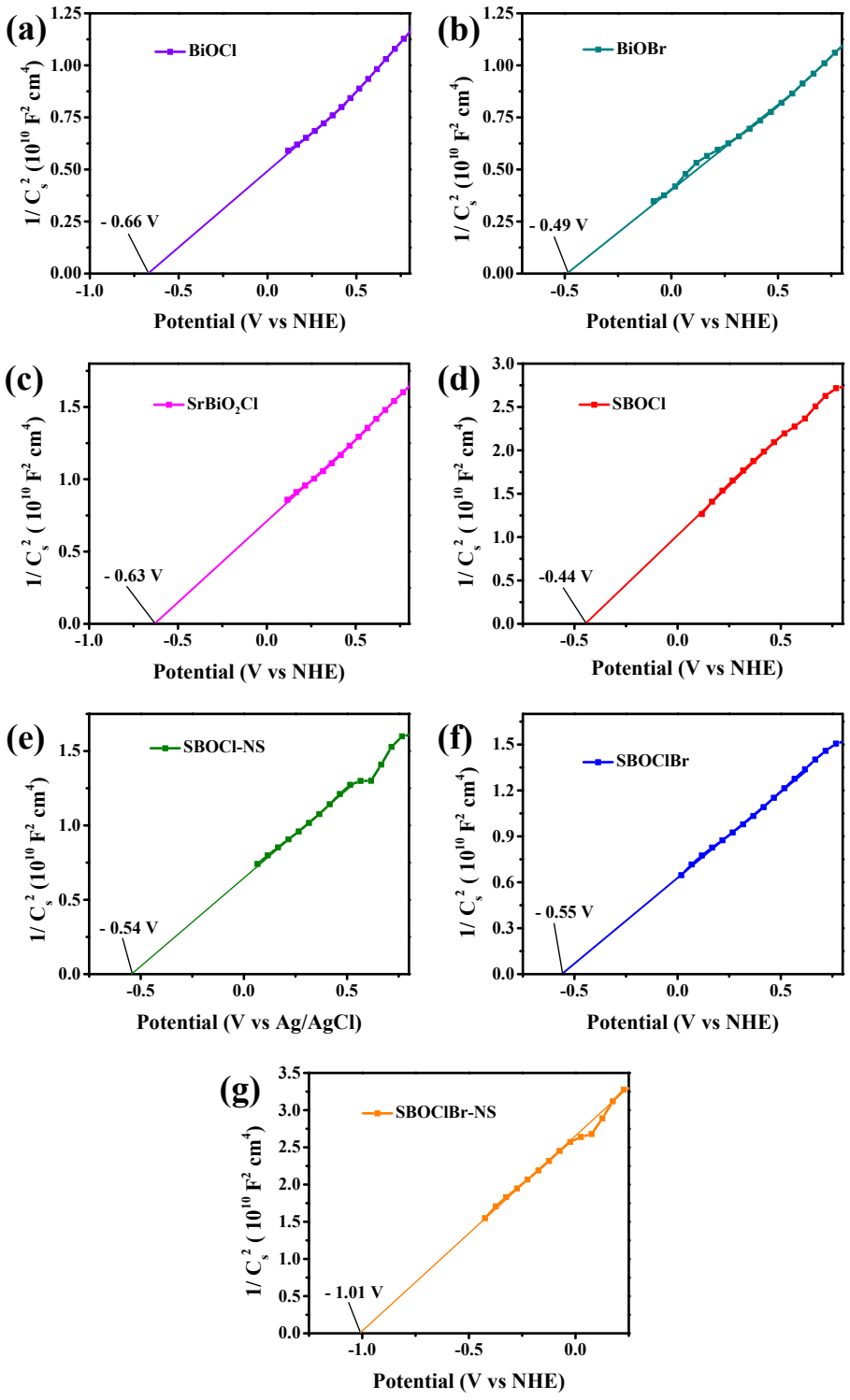

Figure S8. Mott-Schottky plots of (a) BiOCl, (b) BiOBr, (c) $SrBiO_2Cl$, (d) SBOCl, (e) SBOCl-NS, (f) SBOClBr and (g) SBOClBr-NS.

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

S. No.	Compound	VBM (V)	CBM (V)	Band Gap (eV)
1	BiOCl	2.82	– 0.66	3.48
2	BiOBr	2.41	– 0.49	2.90
3	$SrBiO_2Cl$	3.00	– 0.63	3.63
4	SBOCl	2.18	– 0.44	2.62
5	SBOCl-NS	2.09	– 0.54	2.63
6	SBOClBr	2.09	– 0.55	2.64
7	SBOClBr-NS	1.62	– 1.01	2.63

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

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

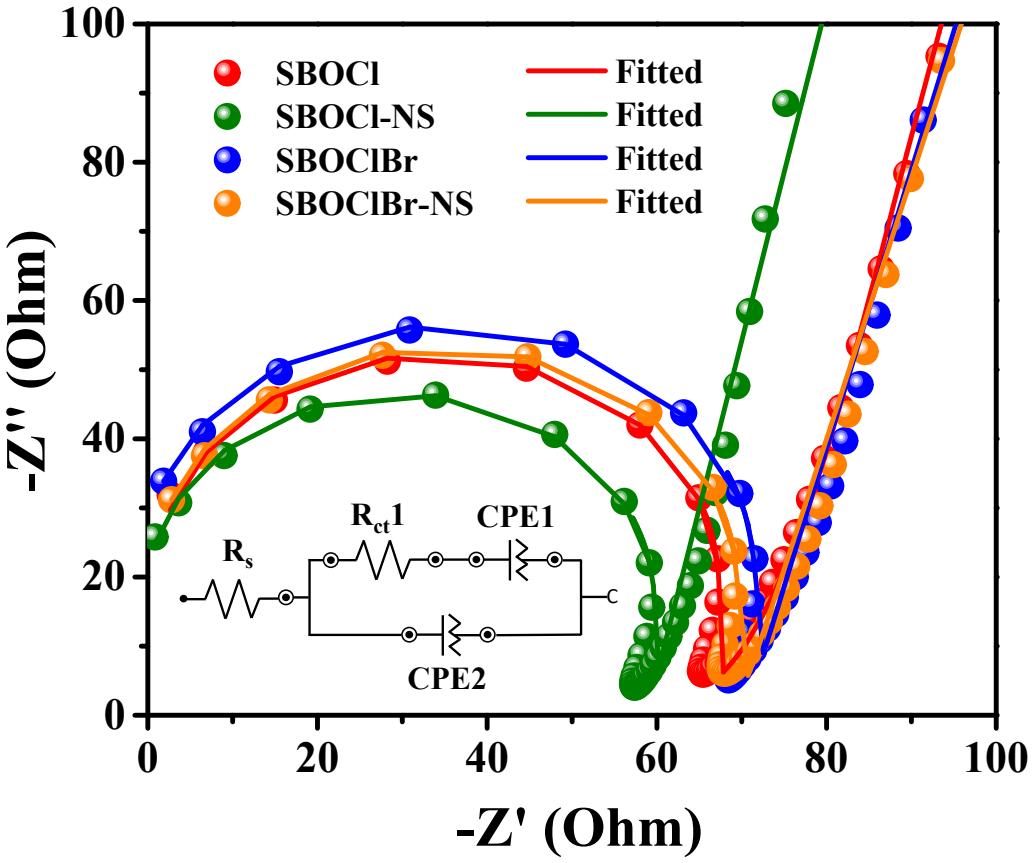

Figure S9. EIS data with equivalent circuit diagram of SBOCl, SBOCl-NS, SBOClBr and SBOClBr-NS.

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

S. No.	Compound name	R_{ct} (Ω)
1.	SBOCl	77.2
2.	SBOClBr	81.0
3.	SBOCl-NS	67.2
4.	SBOClBr-NS	78.0

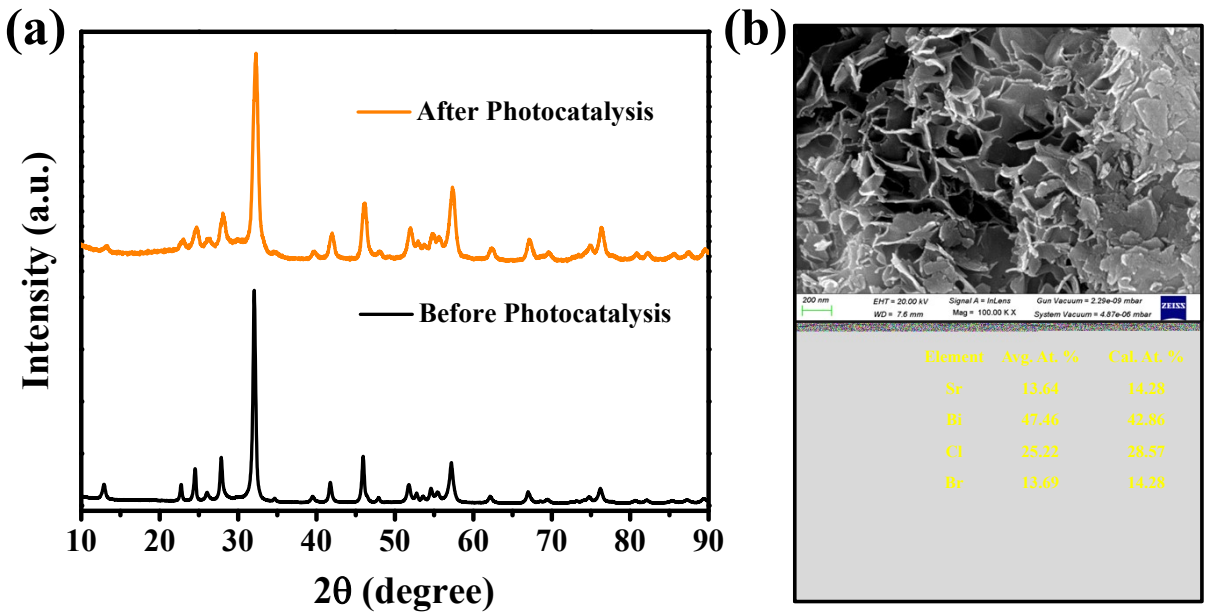

Figure S10. Post-photocatalytic characterization of SBOClBr-NS, (a) P-XRD data and (b) FE-SEM image with elemental composition.

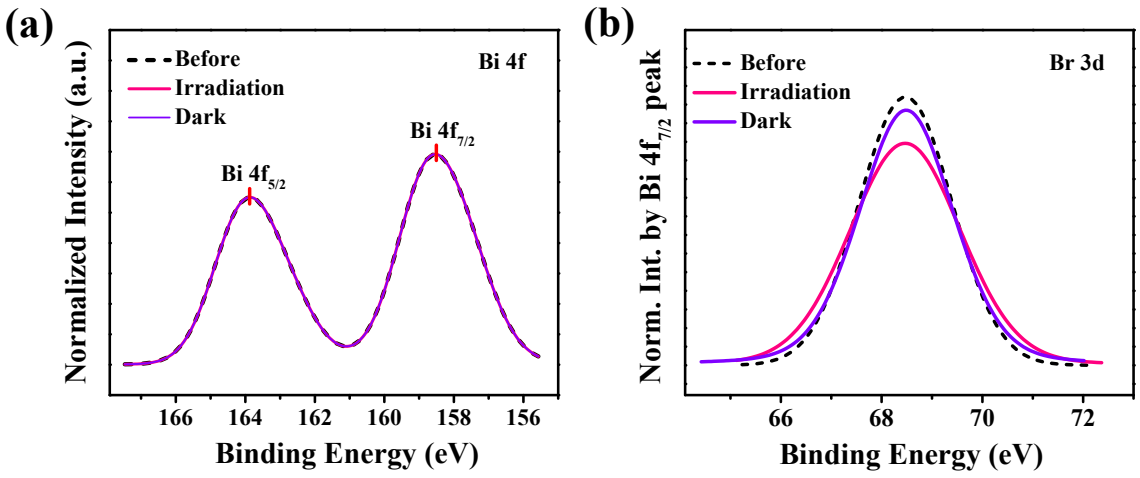

Figure S11. XPS spectra of (a) Bi 4f and (b) Br 3d for SBOClBr-NS.

Table S6. Br/Bi XPS Peak Area Ratios for SBOClBr-NS Before and After Photocatalytic Reaction, along with the Reaction in Dark Condition

Compound	**Before**	**After Irradiation**	**Dark**
SBOClBr-NS	1.00	0.97	0.96