Supporting Information

Extended Layer-by-Layer Madelung Potential Analysis on Layered Oxyhalides Photocatalysts and Other Layered Systems

Daichi Kato,[a] Ryu Abe, [*,a,b] and Hiroshi Kageyama [*,a,b]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate school of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[b] CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

Table of Contents

1. Supporting Figures and Tables

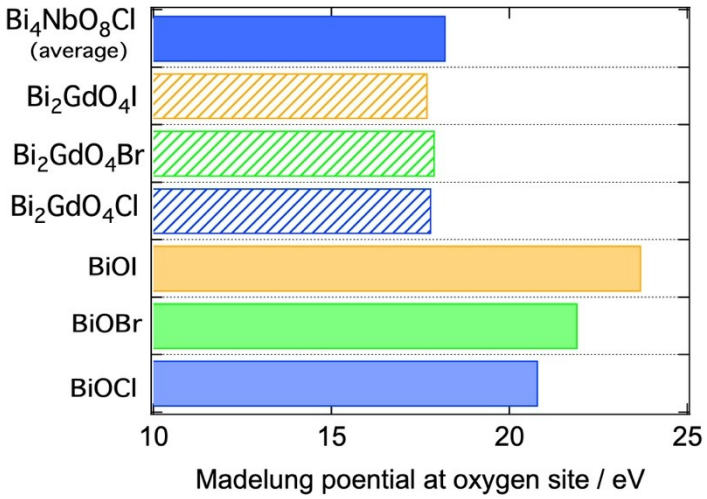

Figure S1. Madelung potential at the oxygen site of the fluorite-type layer in Bi_4NbO_8Cl, BiOX and Bi_2GdO_4X calculated by the Fourier method implemented in VESTA program.[34] The data shown here are reproduced from the previous report.[15] For Bi_4NbO_8Cl, the average value of four oxygen sites in the Bi_2O_2 slab is given (see Figure S2).

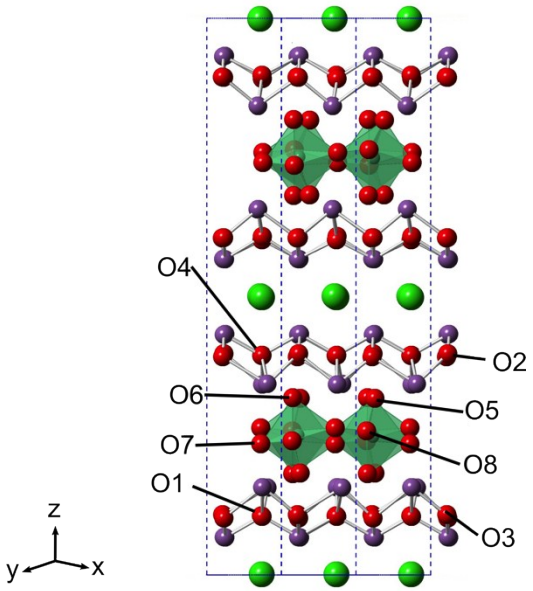

Figure S2. Crystal structure of Bi_4NbO_8Cl.

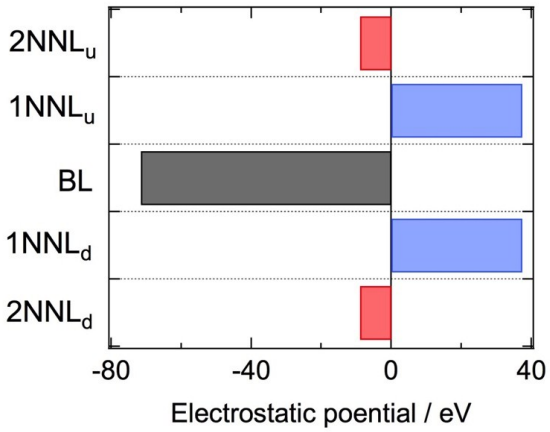

Figure S3. Electrostatic potential at the oxygen site in BiOCl from each sublayer, calculated using the sphere model. The data shown here are reproduced from the previous report.[15]

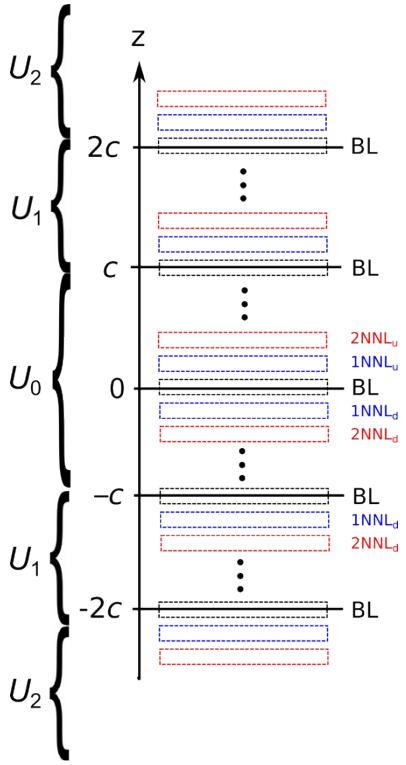

Figure S4. The unit for calculation, U_m, defined as a set of sublayers with the z coordinate of $(m-1)c \leq |z| < mc$ (where m = 1, 2, 3 ...).

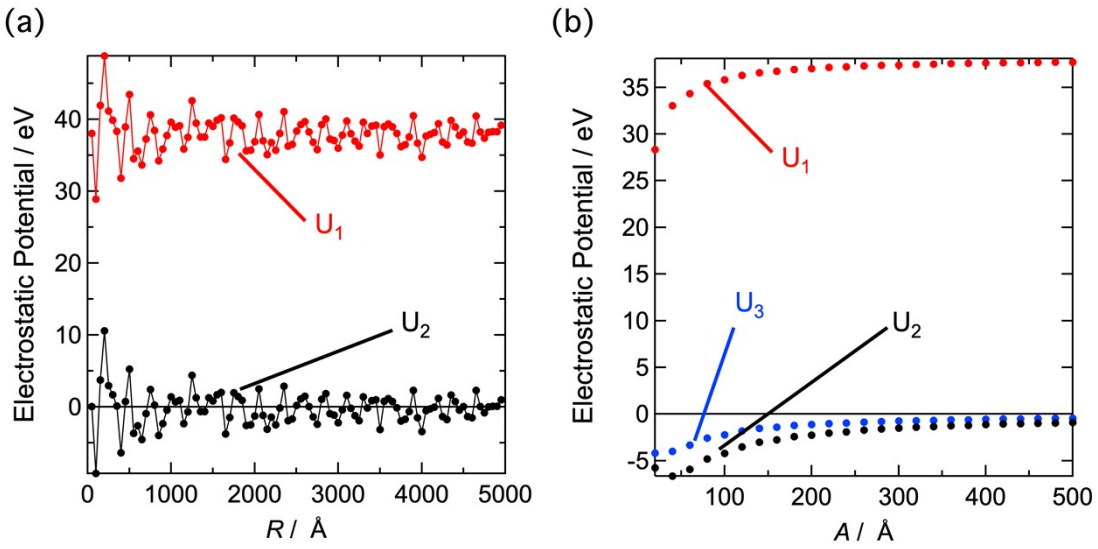

Figure S5. Electrostatic potential at oxygen site of BiOCl from U_m (m = 1, 2 for cylinder model and m = 1, 2, 3 for square-prism model) as a function of R and A.

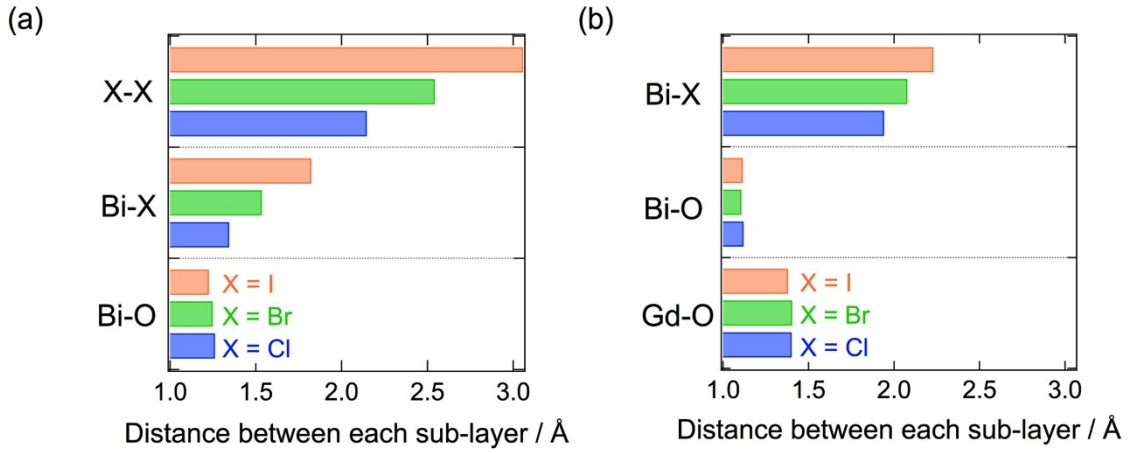

Figure S6. Distance between each sublayer for (a) BiOX (X = Cl, Br, I) and (b) Bi_2GdO_4X (X = Cl, Br, I). Blue, green and orange bars indicate Cl-, Br- and I- containing compounds.

Table S1. Crystal structure of non-distorted hypothetical lattice of Bi_4NbO_8Cl with the *P*4/*mmm* space group.

	x	*y*	*z*
Bi1	0	0	0.3122
Bi2	0.5	0.5	0.1332
Nb	0.5	0.5	0.5
O1	0.5	0.5	0.3625
O2	0.5	0	0.2086
O3	0	0.5	0.5
Cl	0	0	0

* Lattice constants are a = 3.8669 Å and c = 14.41 Å

Table S2. Crystal structure of non-distorted *hypothetical* lattice of Bi_2WO_6 with the *I*4/*mmm* space group.*

	x	*y*	z
Bi1	0.5	0.5	0.1697
Bi2	0.5	0.5	–0.1753
W	0	0	0
O1	0	0.5	0
O2	0	0	0.1065
O3	0	0	–0.1112
O4	0	0.5	0.25

* Optimized cell parameters are a = 3.8503 Å and c = 16.4324 Å

Table S3. Crystal structure of non-distorted *hypothetical* Bi_4NbO_8Cl with the *P*4/*mmm* space group after the structural optimization using DFT calculation*

	x	*y*	*z*
Bi1	0	0	0.3154
Bi2	0.5	0.5	0.1375
Nb	0.5	0.5	0.5
O1	0.5	0.5	0.358
O2	0.5	0	0.2135
O3	0	0.5	0.5
Cl	0	0	0

* Optimized cell parameters are a = 3.8289 Å and c = 16.2653 Å

Table S4. Reported lattice parameters of BiOX and Bi_2GdO_4X

	a / Å	c / Å	Δc / Δa
BiOCl [19]	3.89	7.35	
BiOBr [20]	3.92	8.11	25.3
BiOI [21]	4.00	9.15	16.4
Bi_2GdO_4Cl [18]	3.88	8.92	
Bi_2GdO_4Br [18]	3.90	9.17	12.5
Bi_2GdO_4I [18]	3.93	9.58	13.2

2. Quantitative evaluation of electrostatic potential from sublayers in BiOCl

Here, we discuss the reason why electrostatic potential created from each sublayer is proportional to the lateral size and formal charge of sublayer. Let us discuss using cylinder model since cylinder model is easier to deal with than square-prism model for this purpose and shows the same behavior with the square-prism model in terms of electrostatic potential from each sublayer (Figure S7).

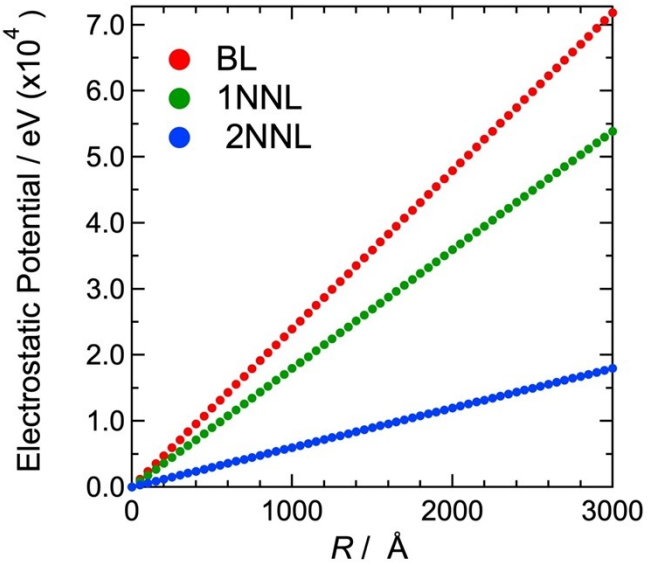

Figure S7. The absolute value of electrostatic potential from BL, 1NNL and 2NNL in BiOCl calculated with the cylinder model as a function of R.

Due to the tetragonal symmetry of BiOCl, ions in each sublayer form the square network (Figure S8). If the radius of the circle, R, is sufficiently large, the point charges arranged at a regular interval can be treated as a uniformly distributed charge with the charge density of n/a^2, where a is the lattice constant (3.887 Å) and n is the number of ions in the sublayer within the unit cell. The electrostatic potential, ΔE, generated by this uniform charge in a narrow region between two circles with the radius of R and $R + \Delta R$ (grey region in Figure S9) is given by

$$\Delta E = \frac{Z}{4\pi\varepsilon_0 R} \times (\pi(R + \Delta R)^2 - \pi R^2) \times \frac{n}{a^2}$$

where Z is the valence of the constituent ions and ε_0 is the vacuum permittivity. The gradient $\Delta E/\Delta R$ is given by

$$\frac{\Delta E}{\Delta R} = \frac{Z}{4\pi\varepsilon_0} \times (2\pi - \pi\frac{\Delta R}{R}) \times \frac{n}{a^2}$$

Since ΔR is much smaller than R, the $\Delta R/R$ term can be ignored. As a result, the gradient becomes independent of R. This is consistent with a linear relationship, and $\Delta E/\Delta R$ can

simply be determined by the formal charge of each sublayer ($Z \times n$). The formal charge is 4 for BL ($[O_2]^{4-}$), 3 for 1NNL ($[Bi]^{3+}$) and 1 for 2NNL ($[Cl]^{-}$), so the values of $\Delta E/\Delta R$ calculated from the above equation are 23.96 for BL, 17.97 for 1NNL and 5.99 for 2NNL, which are equal to the slope obtained from the linear fit of Figure S7.

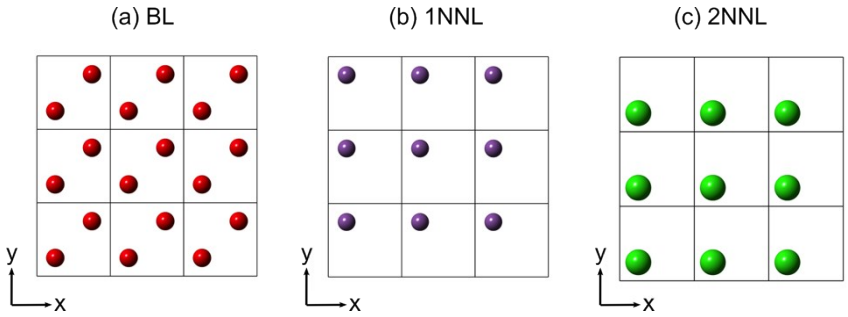

Figure S8. Atomic arrangement in each sub-layer for BiOCl: (a) BL, (b) 1NNL and (c) 2NNL. Red, purple and yellow-green balls are oxygen, bismuth and chlorine ions, respectively. The square represents a tetragonal unit cell (a = 3.887 Å).

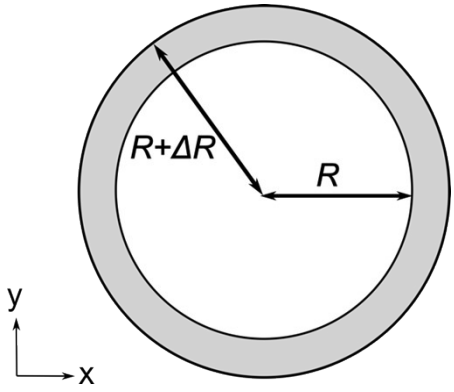

Figure S9. The schematic illustration of the calculation region for ΔE.