

**Table S1.** The calculated lattice parameters constants  $a$  (Å) of BiOX ( $X = \text{Cl}, \text{Br}, \text{I}, \text{Cl}_{0.5}\text{Br}_{0.5}, \text{Br}_{0.5}\text{I}_{0.5}, \text{Cl}_{0.5}\text{I}_{0.5}$ ) monolayer.

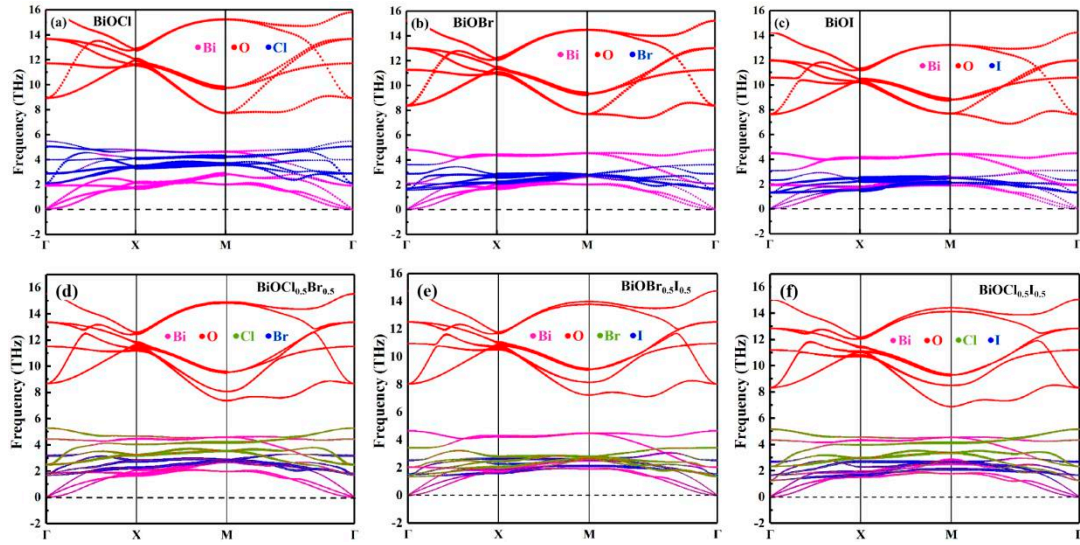
System	BiOCl	BiOCl <sub>0.5</sub> Br <sub>0.5</sub>	BiOBr	BiOCl <sub>0.5</sub> I <sub>0.5</sub>	BiOBr <sub>0.5</sub> I <sub>0.5</sub>	BiOI
$a$ (Å)	3.876	3.900	3.926	3.945	3.970	4.015
Ref. <sup>39</sup> (Cal.)	3.889		3.930			4.014
Ref. <sup>23</sup> (Cal.)	-		-			4.020
Ref. <sup>40</sup> (Exp.)	3.890		3.916			3.985

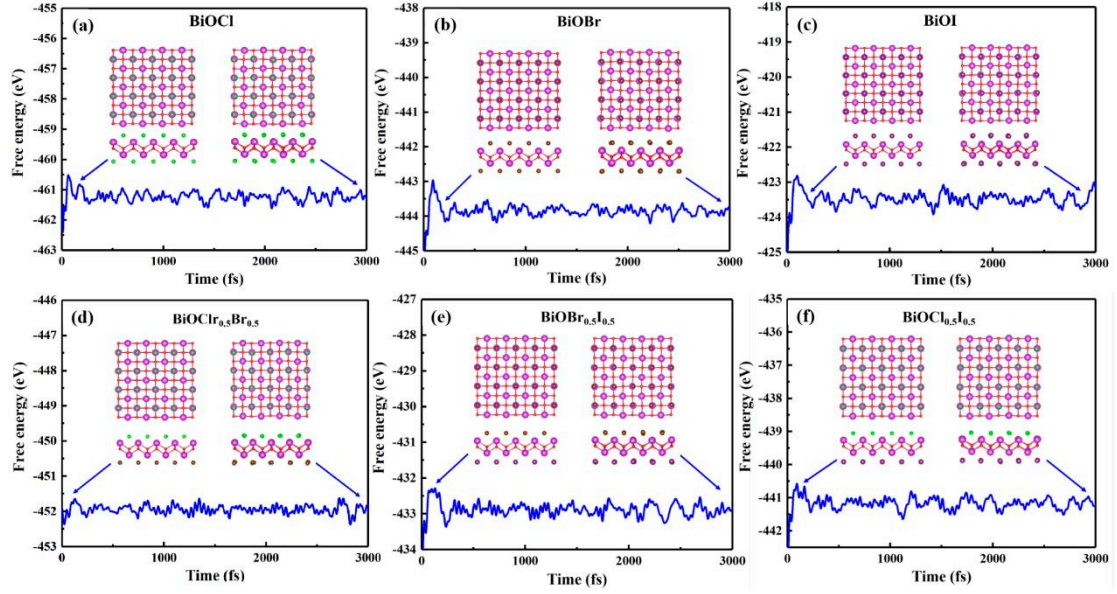
**Table S2.** The calculated HSE06-based band gaps of BiOX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) monolayer.

System	BiOCl	BiOBr	BiOI
Band gap (eV)	3.745	3.354	2.278
Ref. <sup>39</sup> (Cal.)	3.79	3.41	2.3
Ref. <sup>23</sup> (Cal.)	-	-	2.28

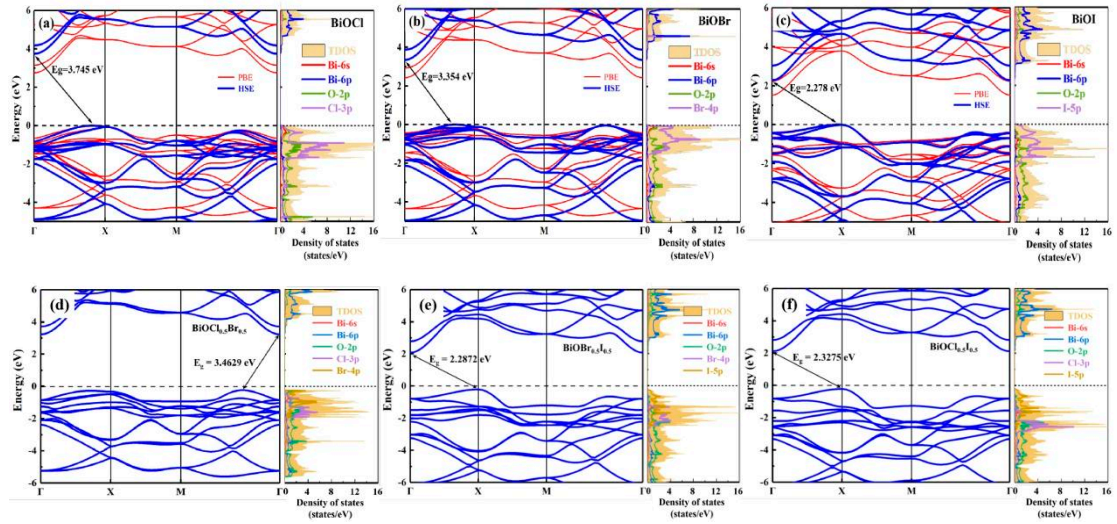
**Table S3.** The variation of calculated static dielectric constant  $\epsilon(0)$  and static refractive index  $n(0)$  of BiOX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) with the layer numbers.

System	BiOCl		BiOBr		BiOI	
	$\epsilon(0)$	$n(0)$	$\epsilon(0)$	$n(0)$	$\epsilon(0)$	$n(0)$
1 Layer	1.70	1.30	1.83	1.35	2.15	1.47
2 Layers	2.23	1.49	2.41	1.55	3.08	1.75
3 Layers	2.49	1.58	2.78	1.67	3.42	1.85
4 Layers	2.81	1.68	3.17	1.78	3.98	1.99
5 Layers	2.93	1.71	3.28	1.81	4.26	2.06
Bulk	4.41	2.10	4.96	2.23	6.22	2.49

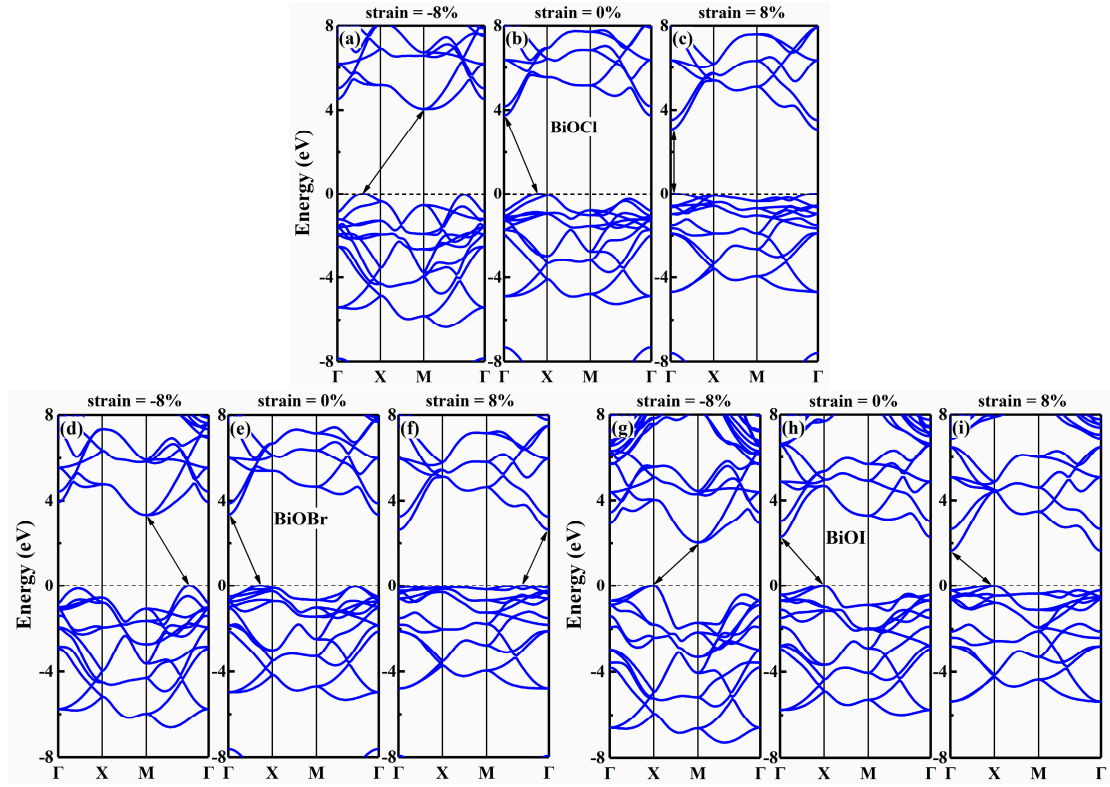
**Figure S1.** (a-f) The phonon spectra of the BiOX ( $X = \text{Cl}, \text{Br}, \text{I}, \text{Cl}_{0.5}\text{Br}_{0.5}, \text{Br}_{0.5}\text{I}_{0.5}, \text{Cl}_{0.5}\text{I}_{0.5}$ ) monolayer.  $\Gamma$ -X-M- $\Gamma$  are the high symmetric points.



**Figure S2.** (a–f) The free energy variation in the AIMD simulation at constant temperature (300K) of the BiOX ( $X = \text{Cl}, \text{Br}, \text{I}, \text{Cl}_{0.5}\text{Br}_{0.5}, \text{Br}_{0.5}\text{I}_{0.5}, \text{Cl}_{0.5}\text{I}_{0.5}$ ) monolayer.



**Figure S3.** Left panels of (a–f): the band structures of the BiOX ( $X = \text{Cl}, \text{Br}, \text{I}, \text{Cl}_{0.5}\text{Br}_{0.5}, \text{Br}_{0.5}\text{I}_{0.5}, \text{Cl}_{0.5}\text{I}_{0.5}$ ) monolayers along the high-symmetry lines  $\Gamma$ – $X$ – $M$ – $\Gamma$ ; Right panels of (a–f): the total and projected DOS of the BiOX ( $X = \text{Cl}, \text{Br}, \text{I}, \text{Cl}_{0.5}\text{Br}_{0.5}, \text{Br}_{0.5}\text{I}_{0.5}, \text{Cl}_{0.5}\text{I}_{0.5}$ ) monolayer.



**Figure S4.** Band structures of (a)(b)(c) BiOCl, (d)(e)(f) BiOBr, and (g)(h)(i) BiOI monolayers under biaxial strain at -8%, 0% and 8%.