Supplementary Materials

Tables

Table S1 The variation of structural parameters. Δa and Δc are variation of lattice constants; Δd_i is bond length variation, $\Delta \alpha_j$ is bond angle variation, and E_{for} is the formation energy of the doping system. *Dist* is the distance between impurity level and VBM.

D/BiOX	Δa/Å	Δc/Å	Δd_1/Å	Δd_2/Å	Δd_3/Å	Δd_4/Å	$\Delta \alpha_1$/°	$\Delta \alpha_2$/°	E_{for}/eV	*Dist*/ Å
Ag/BiOF	0.061	0.002	-0.274	-0.275	-0.281	-0.276	45.079	44.992	-8.12	1.391
Ag/BiOCl	-0.015	0.44	-0.253	-0.285	-0.265	-0.274	40.427	40.122	-8.06	0.953
Ag/BiOBr	-0.016	0.771	-0.278	-0.275	-0.276	-0.276	40.275	40.275	-8.07	0.717
Ag/BiOI	-0.013	0.289	0.197	0.198	0.182	0.197	-7.190	-7.711	-8.06	0.006
Pd/BiOF	0.060	-0.008	-0.296	-0.309	-0.304	-0.300	44.778	44.838	-5.95	2.606
Pd/BiOCl	-0.002	-0.016	-0.296	-0.296	-0.295	-0.295	50.832	50.822	-5.95	2.259
Pd/BiOBr	-0.012	0.361	-0.298	-0.299	-0.298	-0.299	47.197	47.241	-5.95	2.097
Pd/BiOI	-0.012	0.283	-0.030	-0.299	-0.301	-0.302	45.424	47.406	-5.96	0.065

The constant *a* of Ag-doped BiOX (X = Cl, Br, and I, except F) is slightly reduced while the constant *c* of the four BiOX compounds increases, compared to the undoped BiOX structures. The bond length *d* deceases and band angle α increases after Ag was doped into BiOX (X = F, Cl, and Br), which is opposite over the Ag-doped BiOI model. Similar changes were observed on the Ag-doped BiOCl and BiOBr models. For Pd-doped BiOX, the trend of *a* variation is consistent with Ag-doped models but the *c* is less than pure BiOF and BiOCl. Pd-BiOX (X = F, Cl, and Br) models are similar to the Ag-doped BiOX models in term of the bond length variation. Both the Pd and Ag doped BiOI samples show opposite trends. The positive bond angle variations of Pd-doped BiOI are tremendous compared to Ag-doped BiOI.

Table S2 The net charge and bond population for pure and Ag-doped BiOX based on Mulliken charge analysis. The locations of O*i*-Bi,Oi-D are showed in Figure 1c.

BiOX	net charge/e				population/e							
	Bi	O	X	D	O_1-Bi	O1-D	O2-Bi	O2-D	O3-Bi	O3-D	O4-Bi	O4-D
BiOF	1.62	-0.93	-0.7		0.12		0.12		0.12		0.12	
Ag/BiOF		-0.89	-0.65	0.65		0.28		0.28		0.28		0.28
Pd/BiOF		-0.75	-0.65	0.21		0.32		0.32		0.32		0.32
BiOCl	1.47	-0.92	-0.54		0.12		0.12		0.12		0.12	
Ag/BiOCl		-0.79	-0.49	0.62		0.28		0.28		0.28		0.28
Pd/BiOCl		-0.76	-0.35	0.29	0.29	0.29		0.29		0.29		0.29
BiOBr	1.31	-0.90	-0.40				0.12		0.12		0.12	
Ag/BiOBr		-0.78	-0.45	0.58	0.22	0.22		0.22		0.22		0.22
Pd/BiOBr		-0.75	-0.40	0.19		0.32		0.32	0.32	0.32		0.32

Figures

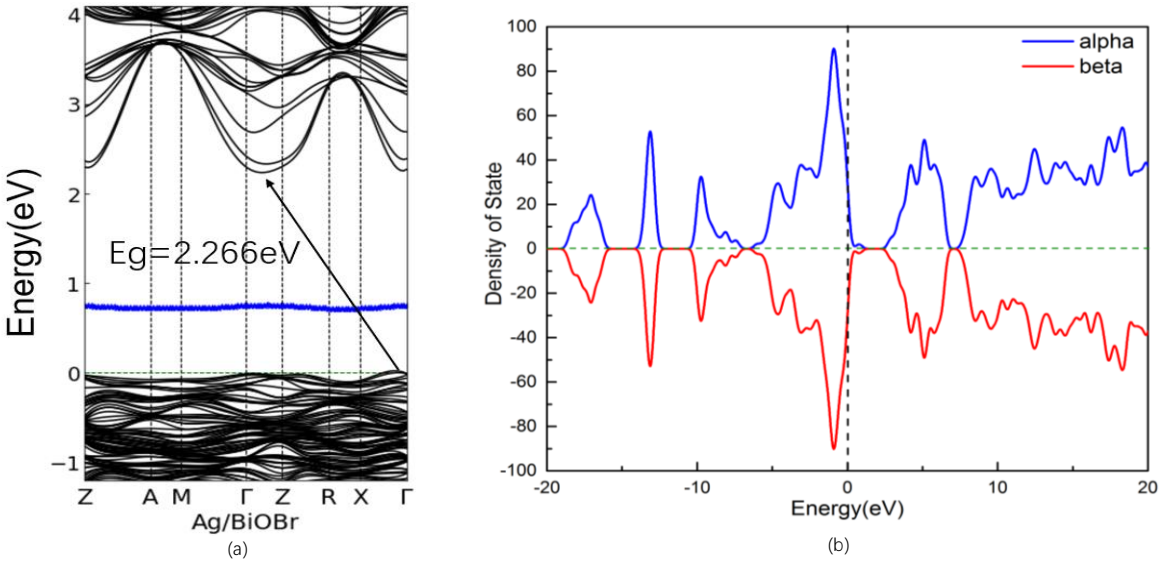

Figure S1 The tested graphs of Ag-doped BiOBr model considering spin and 3x3x2 k points. The fermi energy is set at the zero point. The (a) is the band structure and the gap is 2.29eV and the distance is 0.913eV similar to later results. The (b) is the figure of density of state of the model and the plots alpha and beta spin are symmetry about x axis.

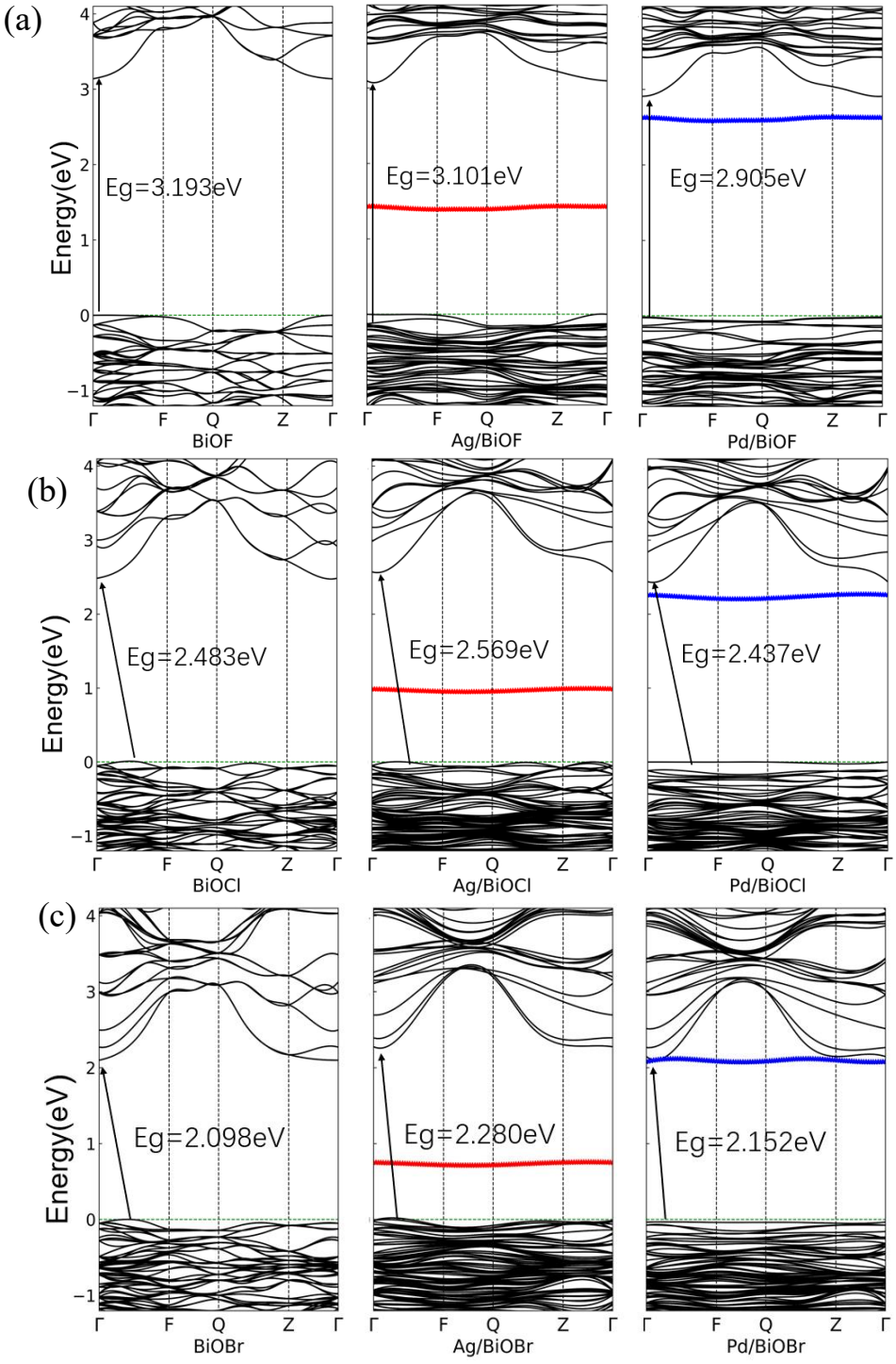

Figure S2 The band structures of pure and D-doped BiOX (D = Ag, Pd; X = F, Cl, Br, I). The Fermi level E-E_f is set at valence band maximum, that is zero point.

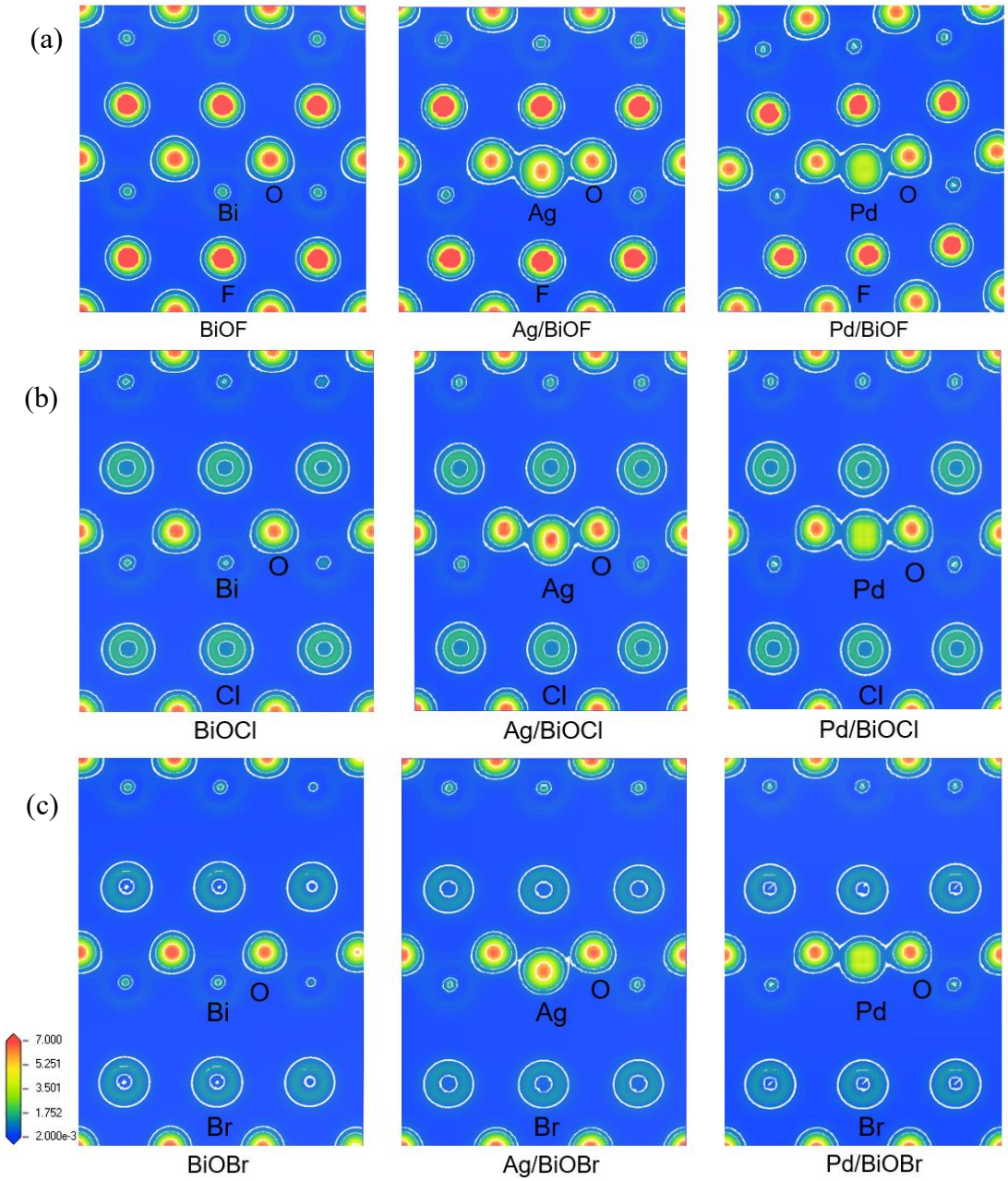

Figure S3 The charge density of pure and doped BiOX (101) （X=F, Cl, Br）

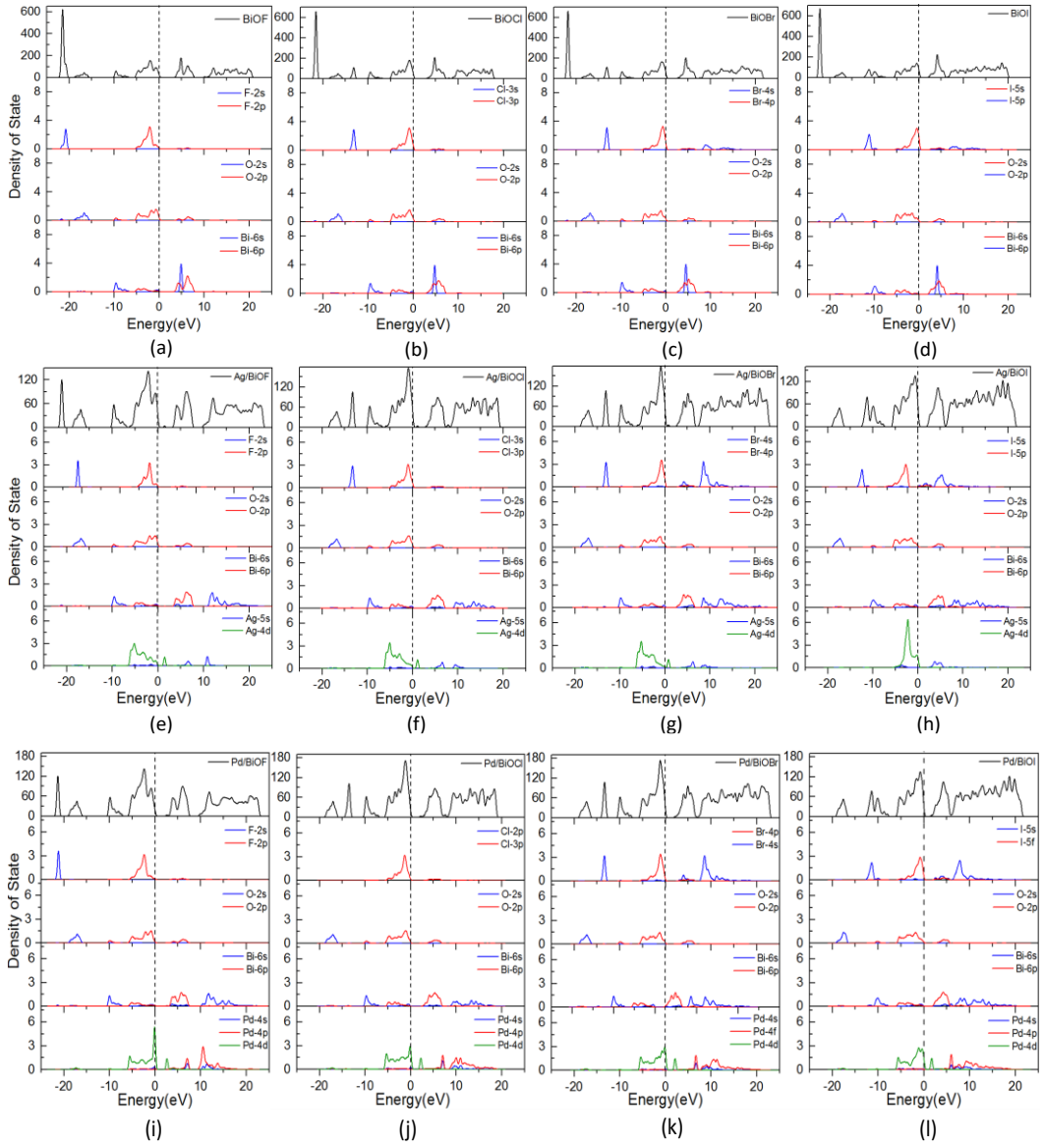

Figure S4 The total and partial density of state of pure and D-doped BiOX (X = F, Cl, Br, I). The Fermi energy is set at 0 point.

The total and partial density of states (DOS) of the pure and D-doped BiOX were calculated and plotted in Figure S4 (a)-(i) within the range of -25 to 25 eV and local enlarged diagrams (m)-(t). The Fermi energy level is set as 0 eV located at VBM. The DOS peaks of the pure BiOF, between the -22.2 to -20.1 eV are mainly dominated by the F-2s state and secondarily by the O-2s state. The other models are similar. The up-shifting of X-ns band occurs with the increase of halogen atomic numbers. In all the BiOX models, the X-np (n = 2, 3, 4) and O-2p states plus with small amounts of Bi-6s state contribute to the energy bands in the vicinity of VBM. The CBM is made of the Bi-6s, Bi-6p and O-

2p states. From the analysis above, the orbital hybridization occurs among the X-np, O-2p states and small quantity of Bi-6s state in the vicinity of the VBM, and another occurs between Bi-6s, Bi-6p and O-2p states near the CBM. In particular, the DOS peaks of O-2p states in the conduction band are larger than X- np states. This indicates that between Bi atoms and O atoms there are certain portion of covalent bond, which is consistent with previous analysis. The X-ns state shifts up with the increase of X atomic numbers. This illustrates the reason of the reduced band gap is due to along with the growing atomic numbers.