Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information Text

Polaron Formation in Two-Dimensional Bismuth Oxyhalides BiOX (X = Cl, Br, I)

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1. Computation details

Phonon frequencies and electron-phonon coupling matrix elements were calculated using density functional perturbation theory (DFPT). For the ground-state electronic structure and lattice dynamics calculations of monolayer bismuth oxyhalides BiOX (X = Cl, Br, I), sampling was performed using a 12×12×1 k-point mesh and a 6×6×1 q-point mesh, respectively. The electronic bands, phonon spectra, and electron-phonon coupling matrix elements were then interpolated onto dense grids via Wannier interpolation. To minimize the influence of periodic image interactions, the monolayer structure was retained in the calculations, with the lattice parameter along the c-direction expanded by a factor of four.[1] The optimized lattice parameters are in good agreement with experimental values: BiOCl (calculated: a=b=3.89 Å, c=29.97 Å, experimental: a=b=3.89 Å, c=7.37 Å), BiOBr (calculated: a=b=3.94 Å, c=33.57 Å; experimental: a=b=3.92 Å, c=8.10 Å), and BiOI (calculated: a=b=4.03 Å, c=38.41 Å; experimental: a=b=4.00 Å, c=9.14 Å).[2, 3]

To achieve maximally localized Wannier functions, six lowest conduction bands and six highest valence bands were selected for analyzing electron and hole polarons, respectively. The valence bands of bismuth oxyhalides BiOX, (X = Cl, Br, I) are predominantly composed of X np (n=3, 4, 5) orbitals, while the conduction bands are dominated by Bi 6p orbitals.[4, 5]Based on this electronic structure, the formation energies of electron and hole polarons were investigated primarily through Bi 6p and X np (n=3, 4, 5) orbitals.

2. The equation of polaron formation energy

In the EPW code, the polaron problem can be transformed into the solution of coupled nonlinear equations related to polaron energy, wave function, and atomic displacements.[6, 7] The basic principle of this method is that the DFT formation energy of a polaron can be expressed as a functional of the polaron wavefunction $\psi(r)$ and the self-interaction of atomic displacements $\Delta\tau_{\kappa\alpha p}$.

$$\Delta E_f = \int dr\psi^*(r)\hat{\mathrm{H}}_{KS}^{0}\psi(r) + \sum_{\kappa\alpha p}\int dr\frac{\partial V_{KS}^{0}}{\partial\tau_{\kappa\alpha p}}|\psi(r)|^2\Delta\tau_{\kappa\alpha p} + \frac{1}{2}\sum_{\kappa\alpha p}C_{\kappa\alpha p} \quad (1)$$

where $\hat{\mathrm{H}}_{KS}^{0}$ and $C_{\kappa\alpha p,\kappa'\alpha'p'}^{0}$ are the Kohn-Sham Hamiltonian and the interatomic force constant matrix in the ground-state structure without the polaron, respectively.[8] The ground-state wavefunction $\psi(r)$ and atomic displacements $\Delta\tau_{\kappa\alpha p}$ for polaron formation can be obtained by minimizing the total DFT energy functional after adding an extra electron to the crystal. This is equivalent to solving the following set of coupled equations:[9]

$$\hat{\mathrm{H}}_{KS}^{0}\psi(r) + \sum_{\kappa\alpha p}\frac{\partial V_{KS}^{0}(r)}{\partial\tau_{\kappa\alpha p}}\Delta\tau_{\kappa\alpha p}\psi(r) = \varepsilon\psi(r) \quad (2)$$

$$\Delta\tau_{\kappa\alpha p} = -\sum_{\kappa'\alpha'p'}(C^0)^{-1}_{\kappa\alpha p,k'\alpha'p'}\int dr\frac{\partial V_{KS(r)}^{0}}{\partial\tau_{\kappa'\alpha'p'}}|\psi(r)|^2 \quad (3)$$

where V_{KS}^{0} is the Kohn-Sham potential in the ground-state structure without the polaron, and ε is the quasiparticle excitation energy of the polaron.[10] To circumvent large-scale supercell calculations, EPW reformulates equations (2) and (3) into forms that rely solely on the Kohn-Sham states, phonons, and electron-phonon matrix elements obtained from calculations using the primitive cell of the crystal. To this end, the wavefunction is expanded in the basis of the Kohn-Sham states:

$$\psi(r) = \frac{1}{\sqrt{N_{uc}}}\sum_{nk}A_{nk}\psi_{nk} \quad (4)$$

The atomic displacements are expanded in the basis of lattice vibrational eigenmodes:

$$\Delta\tau_{\kappa\alpha p} = -\frac{2}{N_{uc}}\sum_{qv} B_{qv}^{*}\sqrt{\frac{\hbar}{2M_{\kappa}\omega_{qv}}}e_{\kappa\alpha,v}(q)e^{iq\cdot R_p} \quad (5)$$

where $N_{uc} = N_1 \times N_2 \times N_3$ represents the total number of primitive cells contained within the supercell. where M_{κ} is the mass of atom κ, and R_p is the lattice vector of unit cell p. Based on these definitions, Equations (2) and (3) transform into a set of nonlinear equations concerning the polaron coefficients A_{nk} and B_{qv}.

$$\frac{2}{N_{uc}}\sum_{qmv} B_{qv}g_{mnv}^{*}(k,q)A_{mk+q} = (\varepsilon_{nk} - \varepsilon)A_{nk} \quad (6)$$

$$B_{qv} = \frac{1}{N_{uc}}\sum_{mnk} A_{mk+q}^{*}\frac{g_{mnv}(k,q)}{\hbar\omega_{qv}}A_{nk} \quad (7)$$

These relations are referred to as the ab initio polaron equations. Where ε_{nk} is the Kohn-Sham eigenvalue, ω_{qv} is the phonon frequency, and $g_{mnv}(K,q)$ is the electron-phonon matrix element.[11, 12] The polaron formation energy in Equation (1) can be expressed in terms of the polaron coefficients A_{nk} and B_{qv} as:[9]

$$\Delta E_f = \frac{1}{N_{uc}}\sum_{nk} |A_{nk}|^2(\varepsilon_{nk} - \varepsilon_{CBM}) - \frac{1}{N_{uc}}\sum_{qv} |B_{qv}|^2 h\omega_{qv} \quad (8)$$

where ε_{CBM} is the Kohn-Sham eigenvalue of the conduction band minimum, and ħ is the reduced Planck constant. This expression applies to electron polarons. For hole polarons, ε_{CBM} is replaced by the eigenvalue of the valence band maximum, and the sign of the first term on the right-hand side of Eq. (8) is reversed. Equations (4), (5), and (8) give the real-space wave function of the polaron, the associated atomic displacements, and its formation energy, respectively.

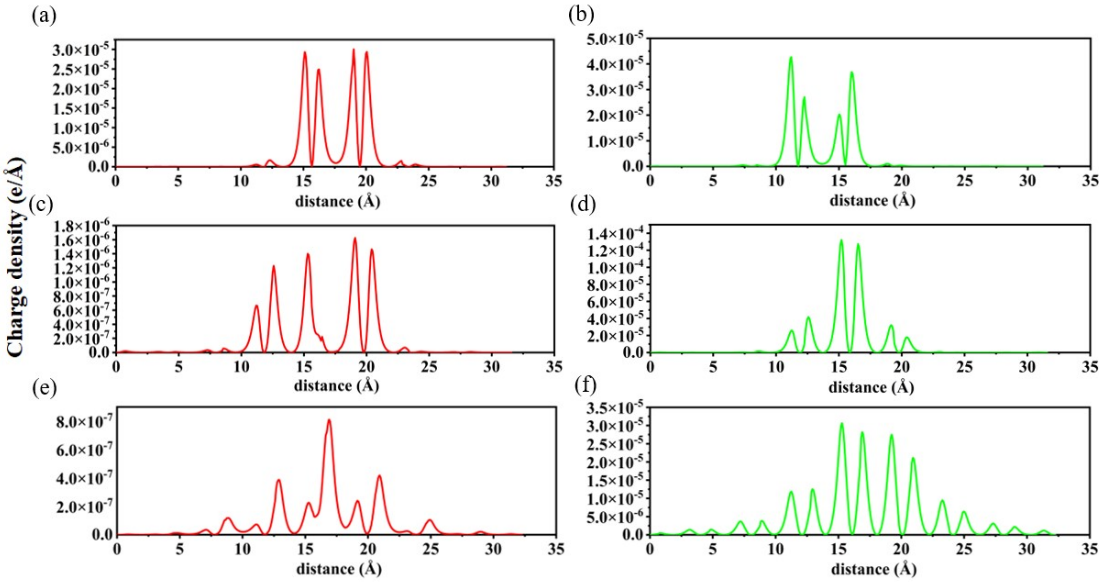

Figure S1. Charge density plots of hole polarons in BiOX (X = Cl, Br, I). The red and green curves in the figures represent the polaron distributions along the [100] and [010] directions, respectively. Figure (a), (c), and (e) show the spatial distribution of polarons along the [100] direction for BiOCl, BiOBr, and BiOI, with spatial extents of approximately 7.5 Å, 12 Å, and 20 Å, respectively. Figure (b), (d), and (f) present the polaron spatial distributions along the [010] direction for BiOCl, BiOBr, and BiOI, corresponding to spatial extents of about 7.5 Å, 12 Å, and 30 Å.

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