

**Supplementary information for enhanced stability of two-dimensional halide
perovskites under an electric field for photocatalytic H₂ splitting**

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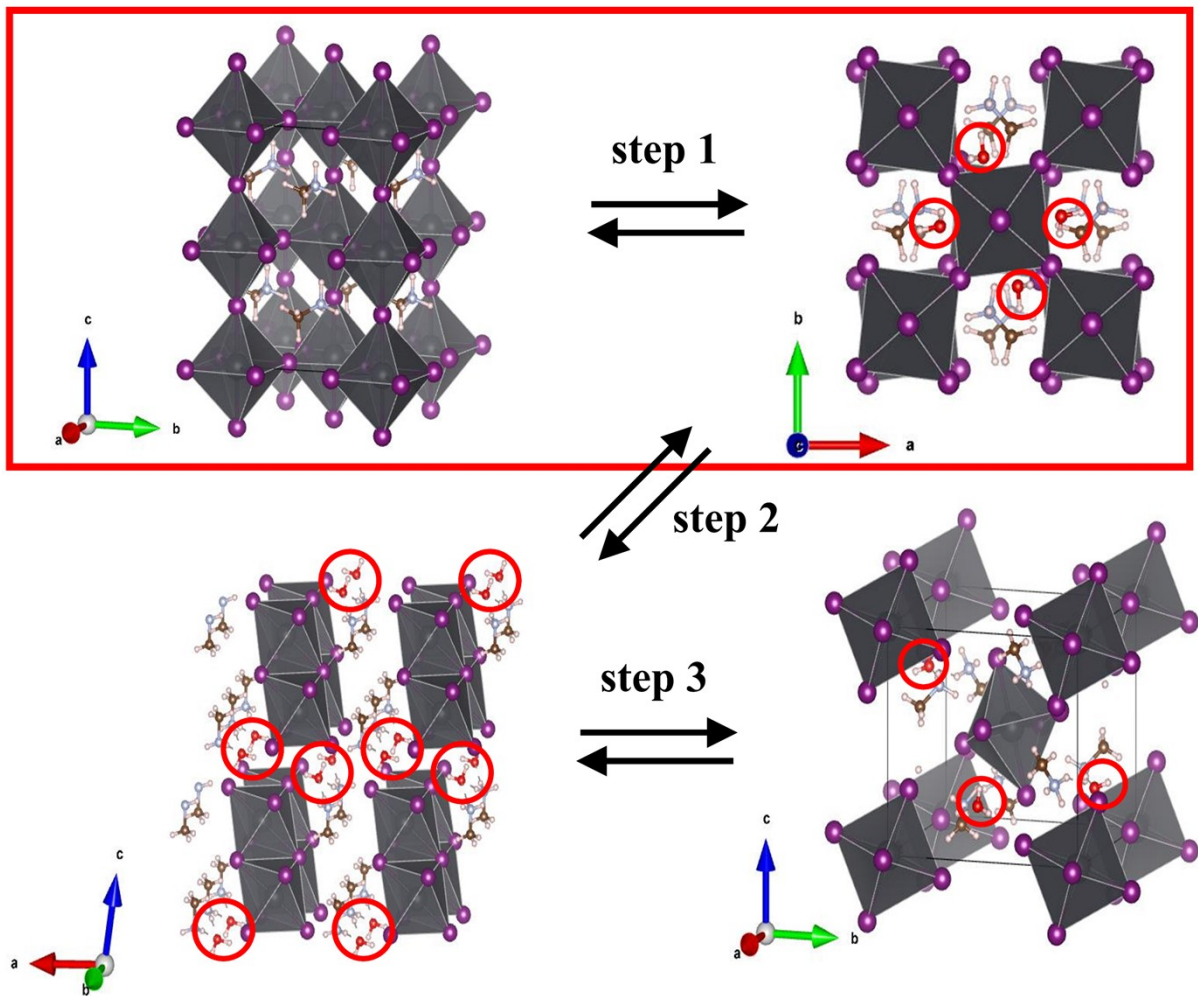


Fig. S1. Degradation mechanism for the octahedron structure of 3D halide perovskite under humid condition. The positions of H_2O molecules in each structure are highlighted as a red circle.

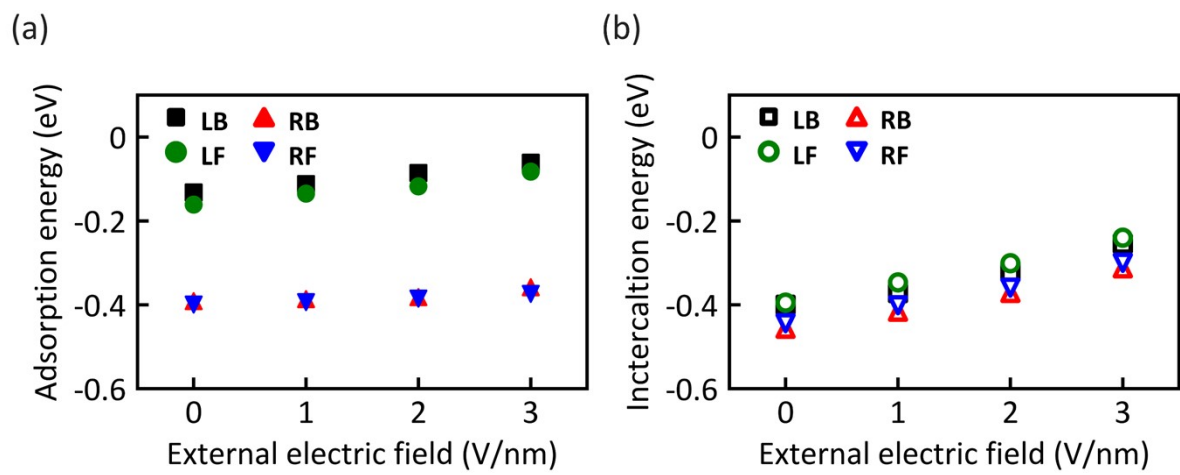


Fig. S2. The (a) adsorption and (b) intercalation energy of all positions depending on the external electric field (\vec{E}_{ext}).

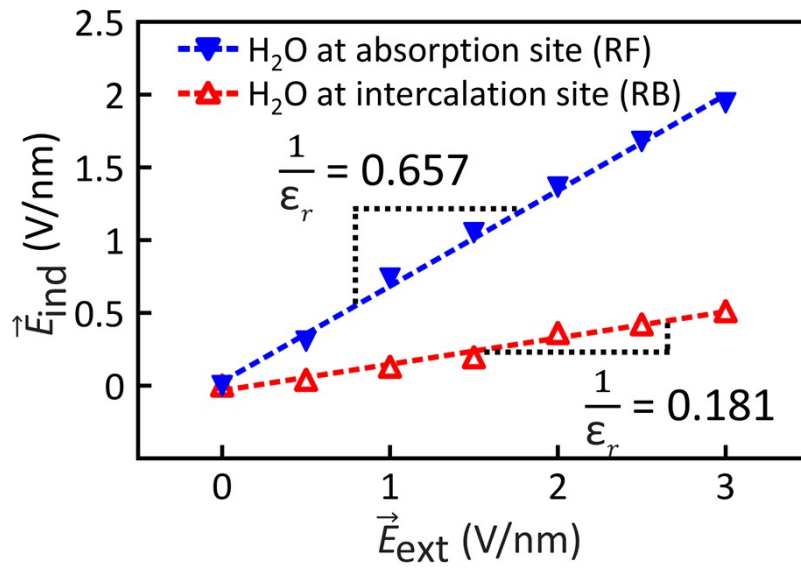


Fig. S3. The induced local electric field (\vec{E}_{ind}) at the position of adsorbed (or intercalated) H₂O molecule in the BMPI structure. Relative permittivity (ϵ_r) is the reciprocal of the slope of the linear fitting between \vec{E}_{ind} and \vec{E}_{ext} .

Supplementary note 1. Binding energy decomposition and the field dependency

The binding energy (E^{bind}) means the energy of BMPI with adsorbed (or intercalated) H_2O referenced to the energies of pristine BMPI and free H_2O . It is defined as $E^{\text{bind}} = E_{\text{RP}+\text{H}_2\text{O}} - (E_{\text{RP}} + E_{\text{H}_2\text{O}})$, where $E_{\text{RP}+\text{H}_2\text{O}}$, E_{RP} , and $E_{\text{H}_2\text{O}}$ are the DFT total energies of the BMPI with adsorbed (or intercalated) H_2O , the pristine BMPI, and the free H_2O molecule in the vacuum, respectively. The adsorption (or intercalation) energy could be decomposed into two components, $E^{\text{bind}} = E^{\text{inter}} + E^{\text{dist}}$, where E^{inter} , and E^{dist} are the interaction and distortion energies, respectively.

The first term, E^{inter} is defined as $E^{\text{inter}} = E_{\text{RP}+\text{H}_2\text{O}} - (E_{\text{RP}}^* + E_{\text{H}_2\text{O}}^*)$. Here, E_{RP}^* and $E_{\text{H}_2\text{O}}^*$ are DFT total energies of the distorted BMPI and H_2O structures upon adsorption (or intercalation), respectively, in which their atomic structures are captured from the relaxed atomic structure of BMPI with H_2O molecule. The second term, E^{dist} is the structural distortion energy of BMPI (E^{dist}) upon adsorption (or intercalation) which is defined as $E^{\text{dist}} = E_{\text{RP}}^{\text{dist}} + E_{\text{H}_2\text{O}}^{\text{dist}} = (E_{\text{RP}}^* - E_{\text{RP}}) + (E_{\text{H}_2\text{O}}^* - E_{\text{H}_2\text{O}})$. The interaction energy between BMPI and adsorbed (or intercalated) H_2O molecule (BMPI- H_2O interaction energy) includes the hydrogen bond and van der Waals interactions, and the dipole interaction of H_2O . E^{dist} includes the distortion energy of BMPI and H_2O at the adsorption (or intercalation). The change of the distortion energy with the external field is negligibly small (Fig. S4), while E^{dist} is significant ($E_{\text{int}}^{\text{dist}} = 0.77$ and $E_{\text{ad}}^{\text{dist}} = 0.3$ eV) (Fig. S4). In other words, the change of binding energy with the electric field is mostly attributed to the change in the interaction energy.

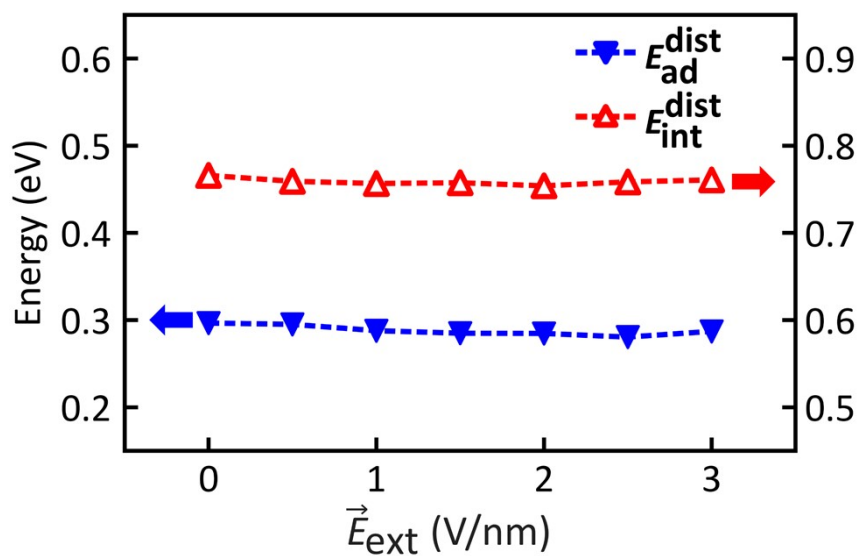


Fig. S4. The change in the distortion energy of BMPI for the adsorption (or intercalation) of H₂O molecule ($E_{\text{ad(int)}}^{\text{dist}}$) with the external electric field. E^{dist} is defined as $E^{\text{dist}} = (E_{\text{RP}}^* - E_{\text{RP}}) + (E_{\text{H}_2\text{O}}^* - E_{\text{H}_2\text{O}})$, where E_{RP}^* and $E_{\text{H}_2\text{O}}^*$ are DFT total energies of the BMPI-only and H₂O-only structures, respectively, in which their atomic structures are captured from the relaxed atomic structure of BMPI with H₂O molecule.

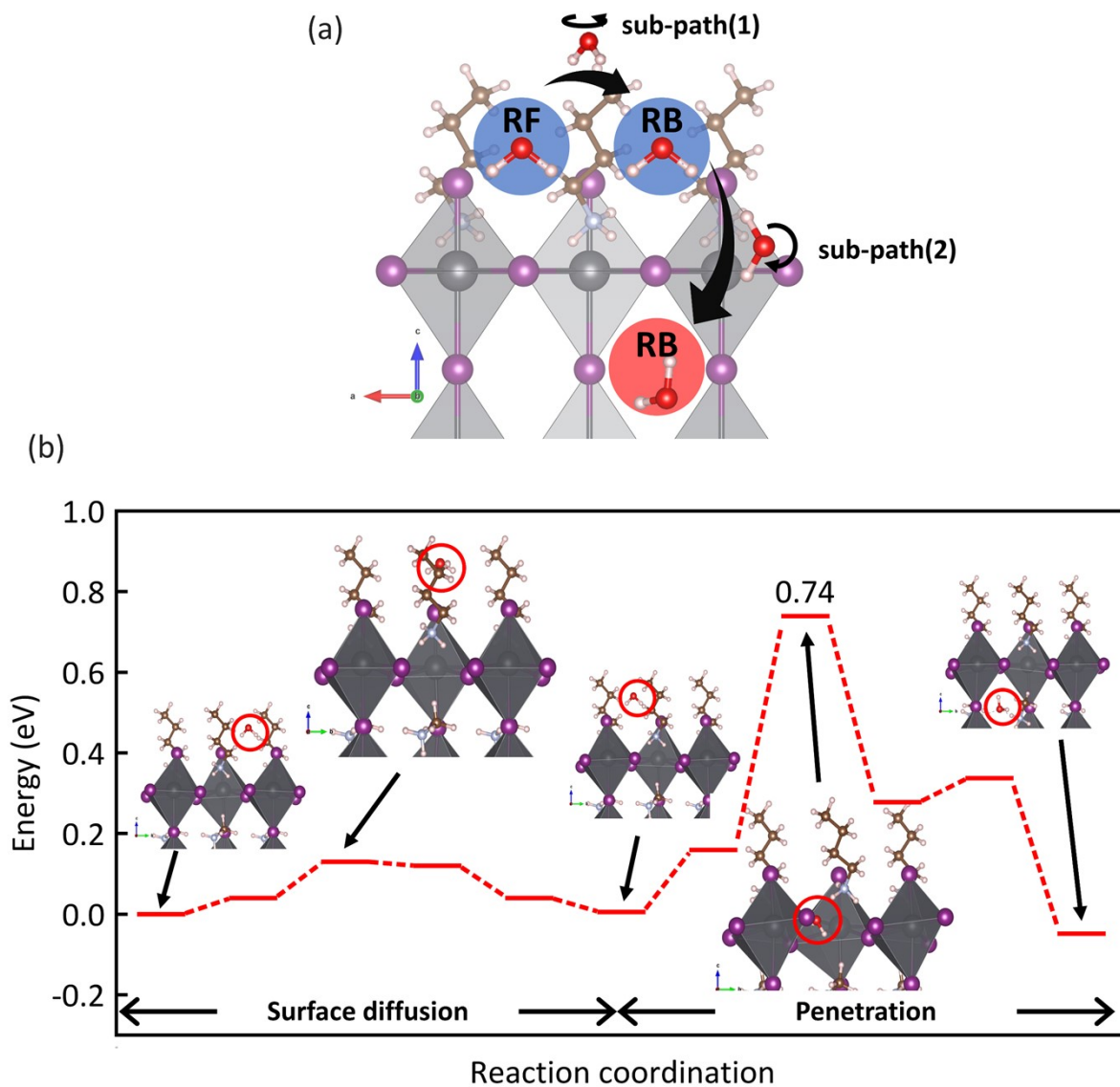


Fig. S5. (a) A schematic figure for the migration path of H₂O from the surface RF site to the intercalated RB site through the surface RB site. **(b)** The energy and the atomic structure of the selected transition states during the migration path. The DFT total energy of the initial state is set to zero.

Supplementary note 2. A vacuum level and work function near the surface under the external electric field

The vacuum level of a surface is calculated by the planner-averaged local potential, V_z , i.e., $V_z(z, \vec{E}_{\text{ext}}) = \int_{\text{cell}} V_{\text{H}}(x, y, z, \vec{E}_{\text{ext}}) dx dy / \int_{\text{cell}} dx dy$, where $V_{\text{H}}(x, y, z, \vec{E}_{\text{ext}})$ is the Hartree potential of the BMPI at the position (x, y, z) calculated with \vec{E}_{ext} , and the integration is done over the calculated unit cell. The vacuum level of the upper layer was defined as the local maximum value near the upper layer surface. While the vacuum level of the lower layer was defined the potential at the point where the magnitude of the planner averaged local electric field, $E_z = -dV_z(z, \vec{E}_{\text{ext}})/dz$, starts changing rapidly from the applied external electric field.

A work function, ϕ , near the upper or lower layer were calculated as $\phi = E_{\text{vacuum}} - \mu$, where ϕ is the work function, E_{vacuum} is the potential energy of vacuum near the surface of the upper or lower layer (Fig. S6) and μ is the chemical potential. Fig. S6 (c) shows the work functions of upper and lower layers as functions of \vec{E}_{ext} . The work functions near the upper and lower layers are 5.01 and 3.8 eV, respectively, under 0 V/nm. The work function of the upper layer linearly decreases as \vec{E}_{ext} increases, $\phi^{\text{upper}} = 5.01, 4.60, 4.30, \text{ and } 3.9$ eV for $\vec{E}_{\text{ext}} = 0, 1, 2, \text{ and } 3$ V/nm, respectively. In contrast, the work function of the lower layer linearly decreases as \vec{E}_{ext} increases, $\phi^{\text{lower}} = 3.80, 4.30, 4.90, 5.30$ eV for $\vec{E}_{\text{ext}} = 0, 1, 2, \text{ and } 3$ V/nm, respectively (Fig. S6 (c)-(g)).

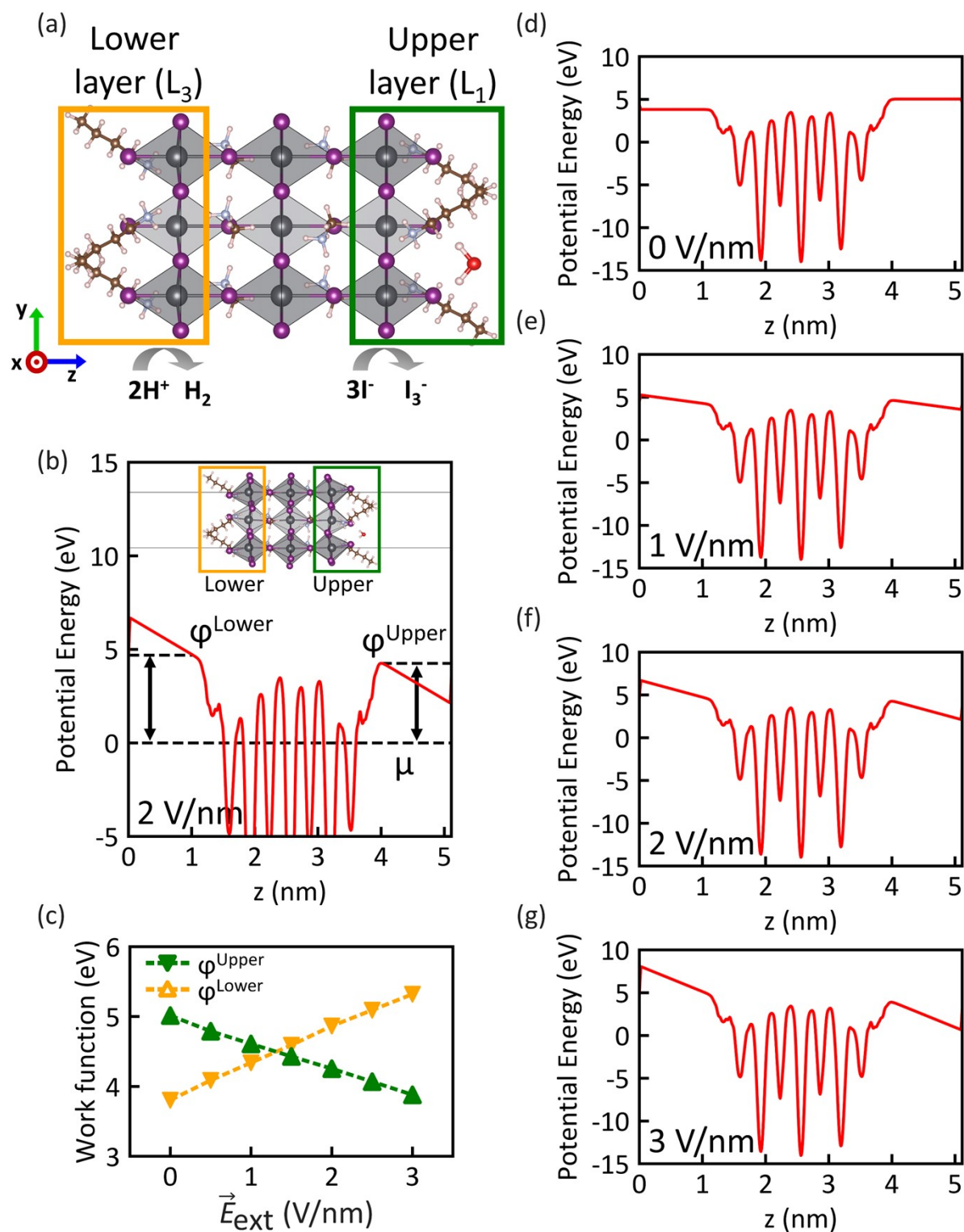


Fig. S6. (a) A schematic for the upper and lower layer of BMPI. (b) A schematic figure for determining an effective work function (φ) at each layer (L_1 and L_2). (c) The effective work function of each layer depending on the \vec{E}_{ext} . In (c) μ is the chemical potential. Planner averaged local potential of BMPI with H_2O absorbed on the surface RF site under (d) 0 V/nm , (e) 1 V/nm , (f) 2 V/nm , and (g) 3 V/nm \vec{E}_{ext} .