Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Efficient Charge Separation and Visible-Light Response of Two-Dimensional Janus Group-III Monochalcogenide multilayers

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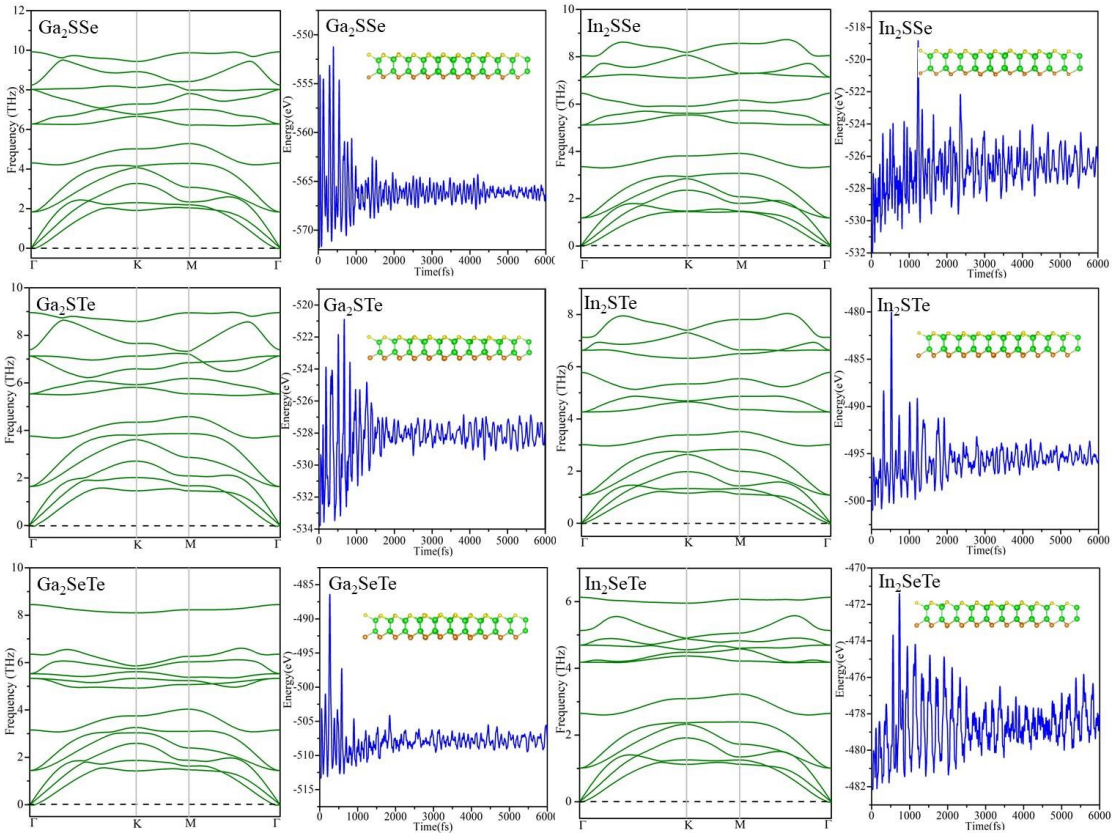

Fig. S1 Phonon dispersion curves (left panels) and variation of total energy against the time in AIMD simulations (right panels) for Janus M_2XY monolayers. The temperature is set to 300 K. The insets show snapshots of atomic structures at the end of AIMD simulations.

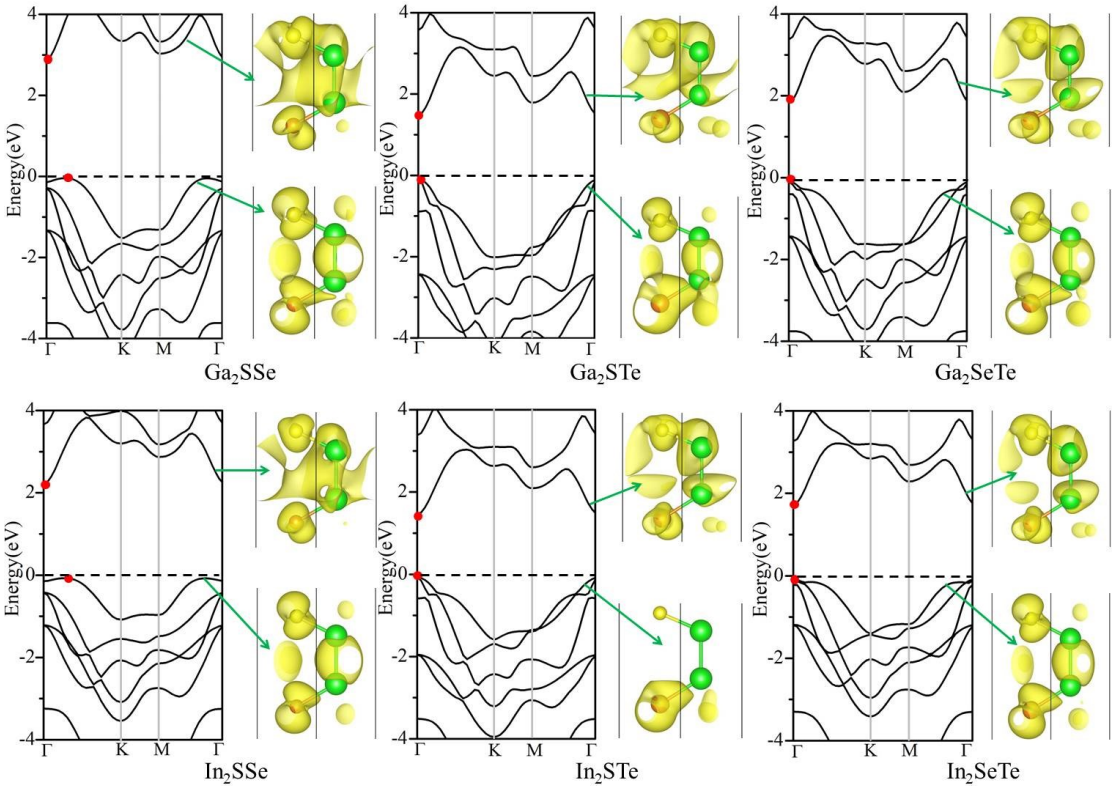

Fig. S2 The band structures (Left panels) and partial charge density of CB and VB (right panels) of Janus M_2XY monolayers according to the HSE06 functional. Fermi level is indicated by a dashed line. The VBM and CBM are shown with red points. The isosurface value is 0.003 e/bohr^3.

The different stacking and stability for Janus multilayer

Here, we consider three different stacking configurations in the vertical direction with five possible high-symmetry stacking orders in the in-plane direction for each stacking configuration. The stability of the multilayer can be evaluated by binding energy E_b according to the following equation:

$$E_b = (E_n - nE_{monolayer})/S$$

where E_n is the total energy of Janus M_2XY multilayer (n is the number of the layers) with a different stacking pattern and $E_{monolayer}$ is the total energy of isolated Janus M_2XY monolayer, while S is the transverse area of multilayer. The calculated binding energy (E_b), and ground-state stacking order for bilayer are listed in Table S1. The disparity in the magnitude of their corresponding binding energy and ground-state stacking order for different stacking pattern are found. The negative binding energies indicate that Janus M_2XY bilayers are energetically favorable and can be easily formed by an exothermic reaction. However, the ground-state stacking order is different for Janus M_2XY bilayer with different system, except the X-Y-X-Y stacking configurations, whose ground-state structure are all H4 stacking order, as listed in Table S1. As for trilayer, quadlayer and pentalayer, the geometry structure and calculated binding energy (E_b) are shown in Fig. S3. It is obviously that the multilayer structure becomes more and more energetic stability with increasing the number of layer.

Table S1. The calculated binding energy E_b (meV/Å^2) and the ground-state stacking order for each bilayer system.

bilayer system	X-Y-X-Y		Y-X-X-Y		X-Y-Y-X	
	E_b	stacking	E_b	stacking	E_b	stacking
Ga_2SSe	-19.67	H4	-18.79	H4	-20.81	H2
Ga_2STe	-20.56	H4	-18.56	H4	-24.26	H3
Ga_2SeTe	-21.09	H4	-20.03	H4	-22.83	H3
In_2SSe	-20.17	H4	-19.56	H2	-20.94	H4
In_2STe	-21.18	H4	-20.19	H3	-23.45	H3
In_2SeTe	-21.48	H4	-20.88	H4	-22.15	H2

Table S2. The calculated interlayer distance d (Å) for Janus M_2XY multilayer. d_1, d_2, d_3, and d_4 are labeled in Fig. S7(a).

multilayer		Ga_2SSe	Ga_2STe	Ga_2SeTe	In_2SSe	In_2STe	In_2SeTe
trilayer	d_1	3.063	3.145	3.165	2.860	2.920	2.938
	d_2	3.073	3.113	3.127	2.825	2.879	2.900
quadlayer	d_1	3.098	3.138	3.158	2.847	2.899	2.912
	d_2	3.070	3,128	3.146	2.862	2.905	2.920
	d_3	3.071	3.139	3.158	2.849	2.890	2.910
pentalayer	d_1	3.103	3.131	3.148	2.837	2.895	2.914
	d_2	3.079	3.119	3.134	2.848	2.902	2.917
	d_3	3.059	3.123	3.137	2.853	2.903	2.920
	d_4	3.062	3.131	3.148	2.837	2.890	2.910

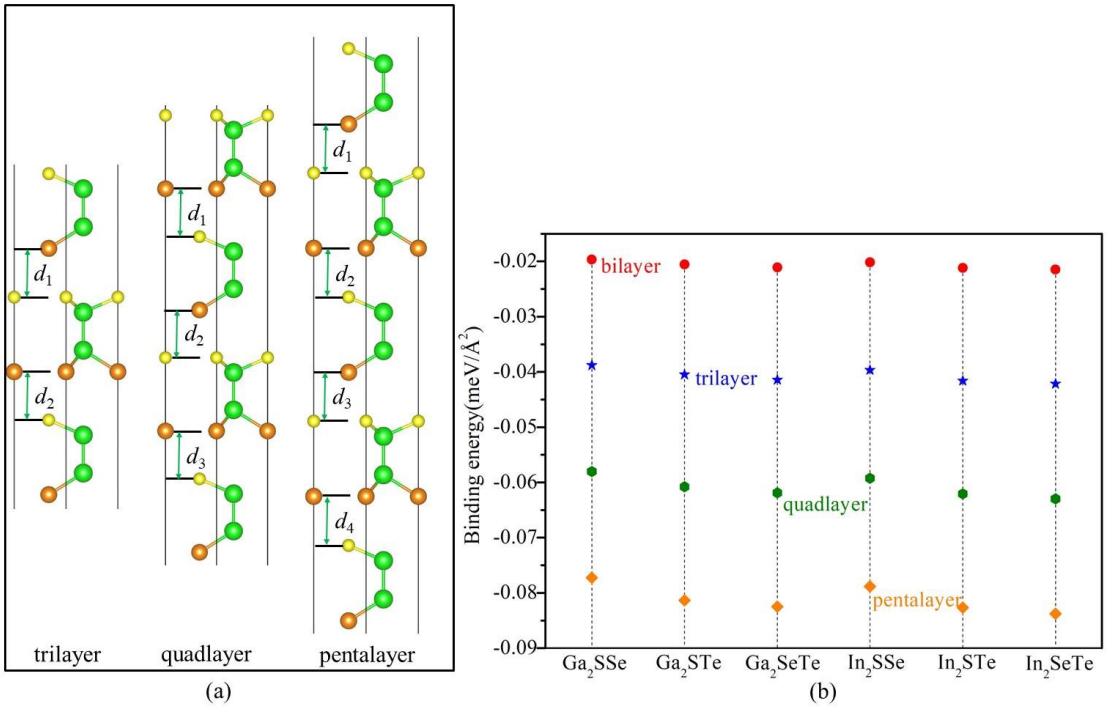

Fig. S3 (a) Side views and (b) the binding energies of Janus M_2XY multilayer. The interlayer distance d is marked in the figure and the values are listed in Table S2.

Due to the larger time consuming, only the bilayers of phonon dispersion curves in X-Y-X-Y stacking configuration are calculated with 4×4×1 supercell and 3×3×1 *k* points, as shown in Fig. S4. All the phonon modes of bilayer structures are similar to the case of monolayers and are all positive, indicating that they are dynamical stability. At the same time, we perform the ab initial dynamics simulation at 300 K with the simulation time lasts for 6 ps for all the multilayer structures. The snapshots of atomic structures at the time of 6 ps are shown in Fig. S5. It is clearly seen that there are not significant distortions for them, confirming their thermal stability.

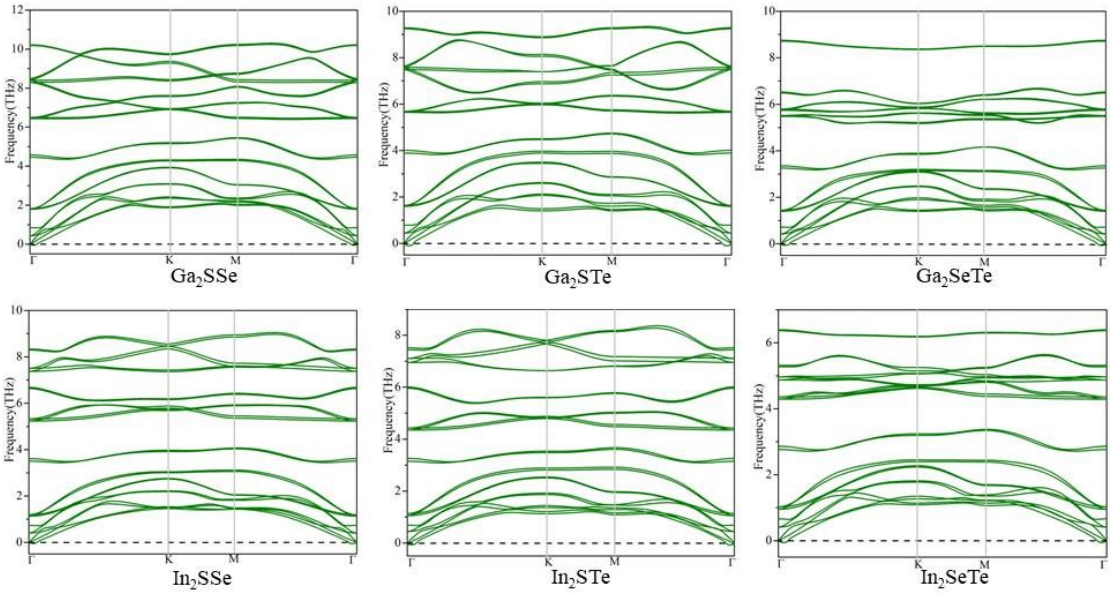

Fig. S4 Phonon dispersion curves for Janus M_2XY bilayers, respectively.

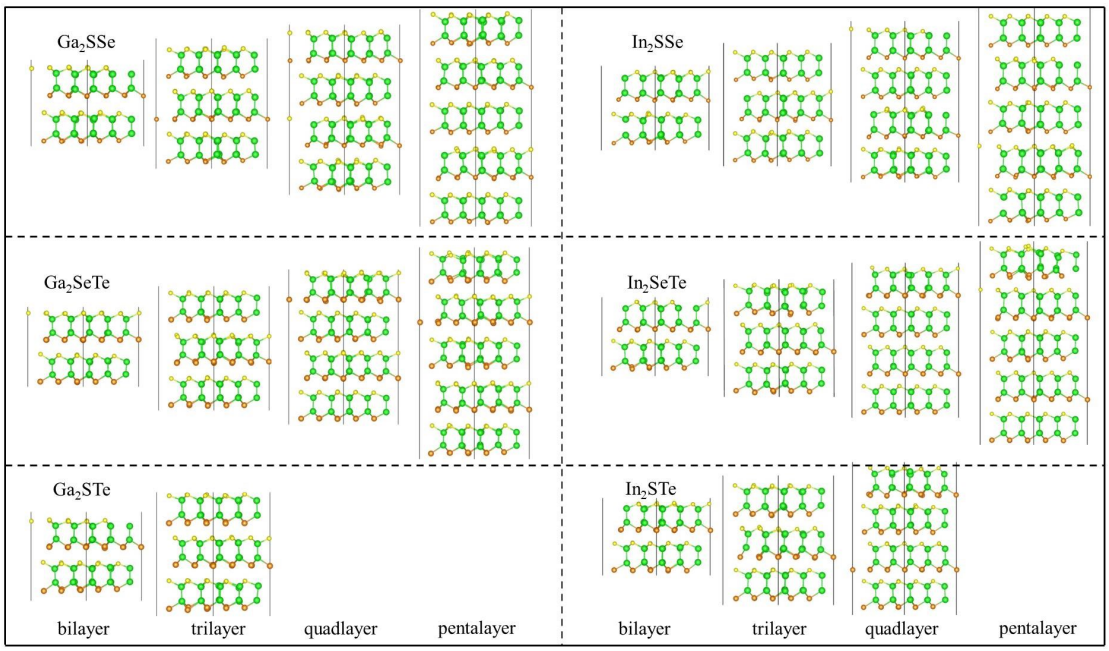

Fig. S5 The snapshot of atomic structures for Janus multilayers after first-principles molecular dynamics simulation, respectively.

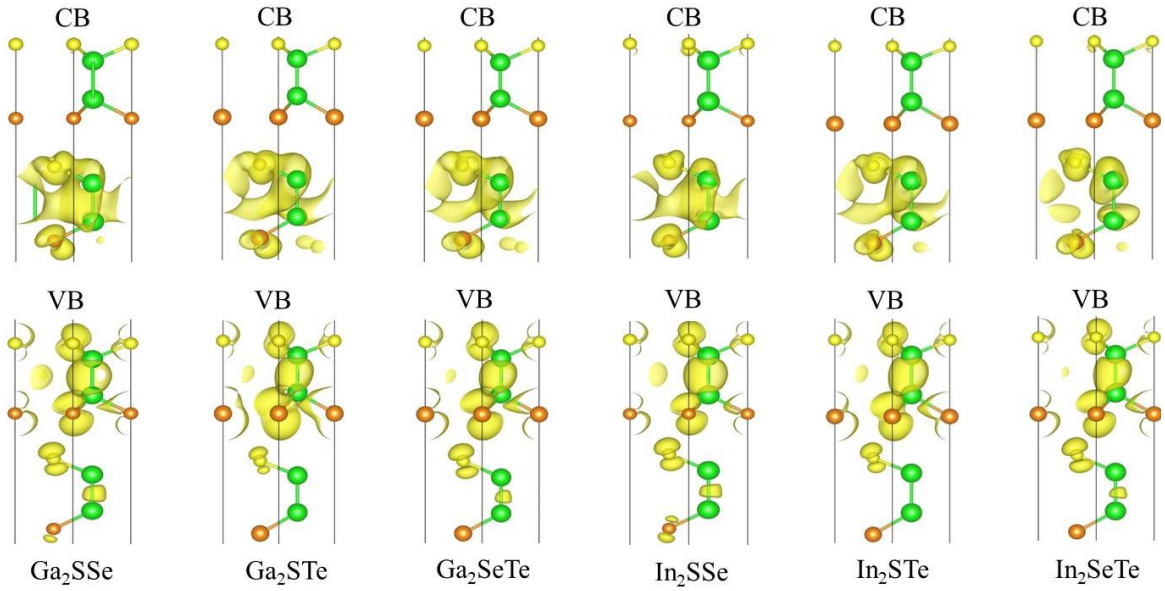

Fig. S6 The partial charge density of CB and VB of Janus M_2XY bilayers in X-Y-X-Y stacking configuration according to the HSE06 functional. The isosurface value is 0.003 e/bohr^3.

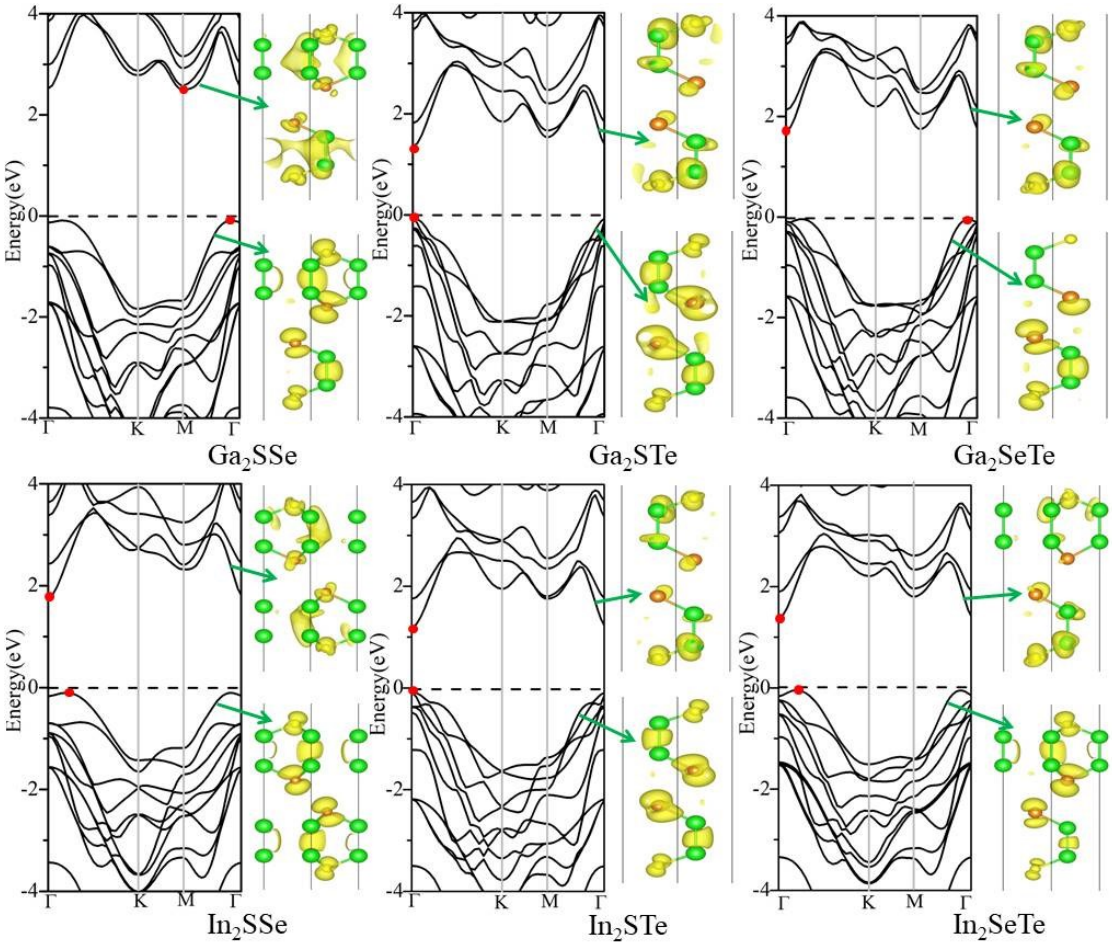

Fig. S7 The band structures (Left panels) and partial charge density of CB and VB (right panels) of Janus M_2XY bilayers in X-Y-Y-X stacking configuration according to the HSE06 functional. The Fermi level is indicated by a dashed line. The VBM and CBM are shown with red points. The isosurface value is 0.003 e/bohr^3.

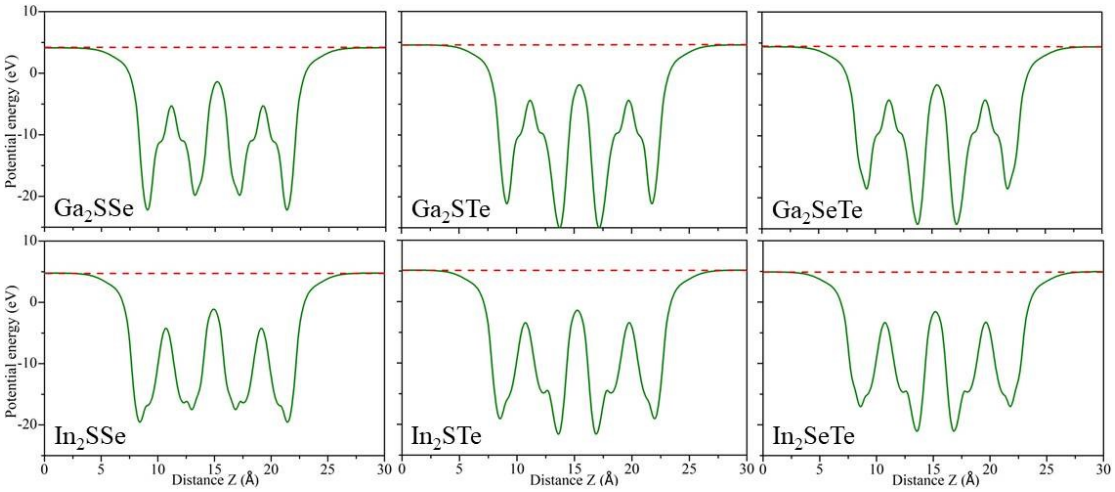

Fig. S8 Planar average electrostatic potential energy of the Janus M_2XY bilayer in X-Y-Y-X stacking configuration.

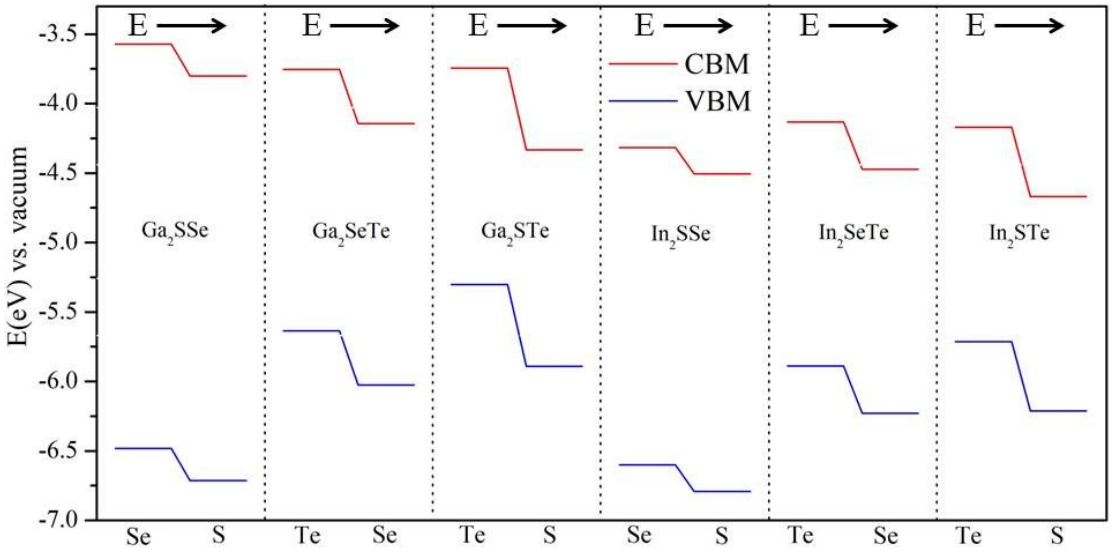

Fig. S9 Band alignments of Janus M_2XY monolayers where the vacuum level is set to 0 eV. E denotes the internal electric field.

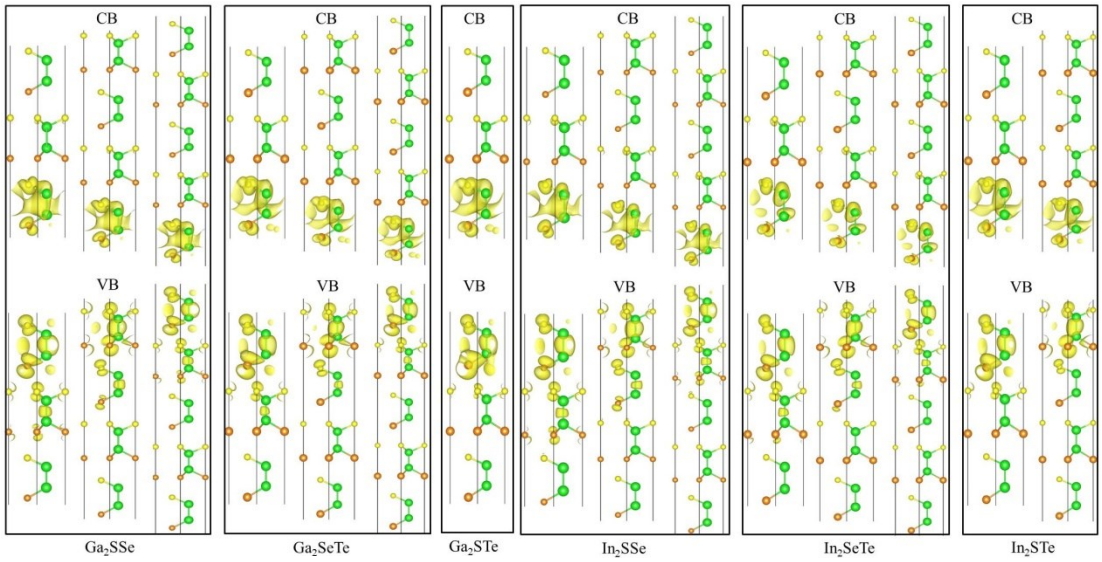

Fig. S10 The partial charge density of conduction band (Top) and valence band (Bottom) for Janus M_2XY multilayer in X-Y-X-Y stacking configuration. The isosurface value is 0.003 e/ bohr^3.

Free energy difference (ΔG)

Free energy difference (ΔG) for water redox reactions is evaluated based on the spin-polarized calculation, according to the following equation

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + \Delta G_U$$

where ΔE is the absorption energy of the intermediates. ΔZPE and ΔS are the differences of zero point energy and entropy between the adsorbed intermediates and the gas phase. T is the temperature (298.15K in our work). ΔG_{pH} and ΔG_U are the free energy correction, which depends on the pH value and applied electrode potential U, respectively. They can be calculated by:

$$\Delta G_{pH} = -k_B T \ln(10) \cdot \mathrm{pH} \approx -0.059\mathrm{eV} \cdot \mathrm{pH}$$
$$\Delta G_U = -eU$$

Hydrogen Evolution Reaction (HER)

HER mechanism involves two-electron pathways, satisfying the following two elementary steps:

$$* + \mathrm{H^+} + \mathrm{e^-} \rightarrow *\mathrm{H}$$
$$*\mathrm{H} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2} + *$$

Oxygen Evolution Reaction (OER)

OER mechanism involves four-electron oxidation pathways, which can be demonstrated by

$$*+H_2O \rightarrow *OH+H^+ + e^-$$

$$*OH \rightarrow *O + H^+ + e^-$$

$$*O+H_2O \rightarrow *OOH+H^+ + e^-$$

$$*OOH \rightarrow * + O_2 + H^+ + e^-$$

where $*$ represents the active site, *OH, *O, *OOH and *H represent the adsorbed intermediates.