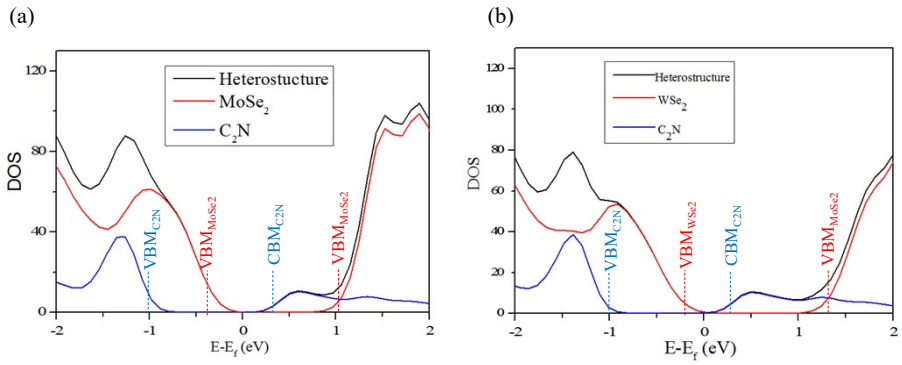


***Figure S1**: Project density of states of (a) $C_2N/MoSe_2$ and (b) $C_2N/WSe_2$ heterostructures, respectively, at equilibrium geometry.*

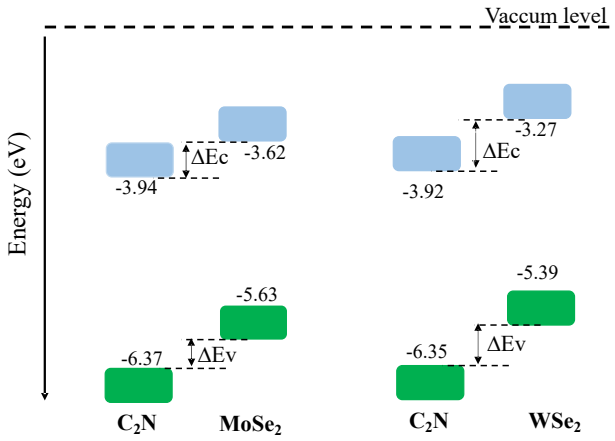


***Figure S2** : Band alignments of heterostructures at interactive configurations at HSE06 level.*

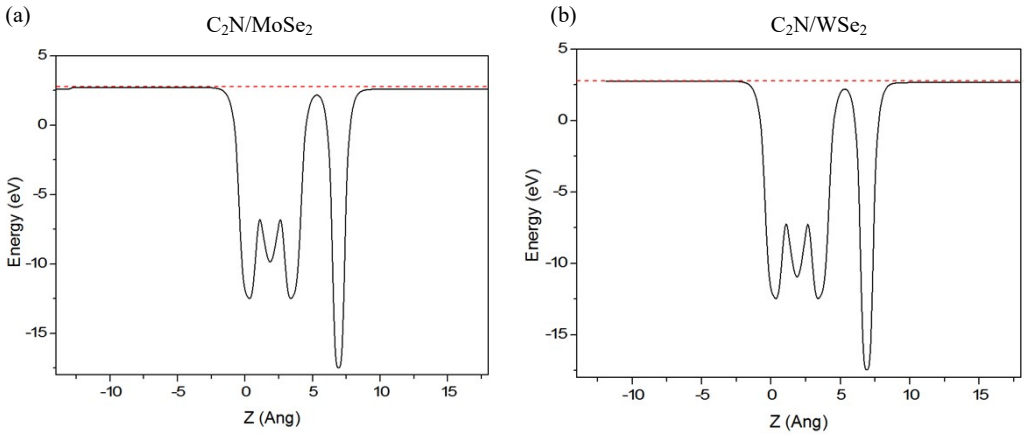


**Figure S3**: *Figure S1: Plane-averaged electrostatic potential along the normal direction of (a) $C_2N/MoSe_2$ and (b) $C_2N/WSe_2$ heterostructures, respectively, at equilibrium geometry.*

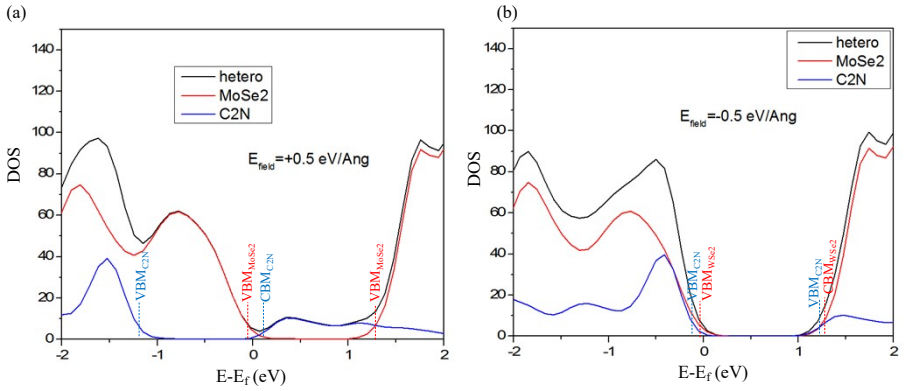


**Figure S4**: *Figure S1: Representative Project density of states of $C_2N/MoSe_2$ heterostructure, at different applied electric field ($E_{field}$ = -0.5 and +0.5 V/Ang )*

**Gibbs free energy**

The $\Delta G_{\mathrm{H}*}$ is estimated by using the following equation (1) [1]:

$$\Delta G_{\mathrm{H}*} = \Delta E_{\mathrm{H}} + \Delta E_{ZPE} - T\Delta S_{\mathrm{H}} \quad (1)$$

where $\Delta E_{\mathrm{H}}$ is the differential hydrogen adsorption energy, which is defined as:

$$\Delta E_{\mathrm{H}} = E(\mathrm{C_2N} + \mathrm{H}) - E(\mathrm{C_2N}) - \mathrm{E}(\mathrm{H_2})/2 \quad (2)$$

where $E(\mathrm{C_2N} + \mathrm{H}) - E(\mathrm{C_2N})$ are total energies of the C2N monolayer (or heterostructures) with and without hydrogen adsorption. $T$ denotes room temperature and $\Delta S_{\mathrm{H}}$ is considered as half of the entropy of $H_2$ in the gas phase under standard conditions. $\Delta E_{ZPE}$ denotes zero-point energy difference between adsorbed hydrogen and gas-phase hydrogen. $\Delta E_{ZPE} - T\Delta S_{\mathrm{H}}$ is about 0.24 eV.

[1] Shao, Y.; Shi, X.; Pan, H. Electronic, Magnetic, and Catalytic Properties of Thermodynamically Stable Two-Dimensional Transition-Metal Phosphides. *Chem. Mater.* **2017**, *29*, 8892–8900.