Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Band Alignment Control in Blue Phosphorus/C_2N Van Der Waals Heterojunction by Electric Field

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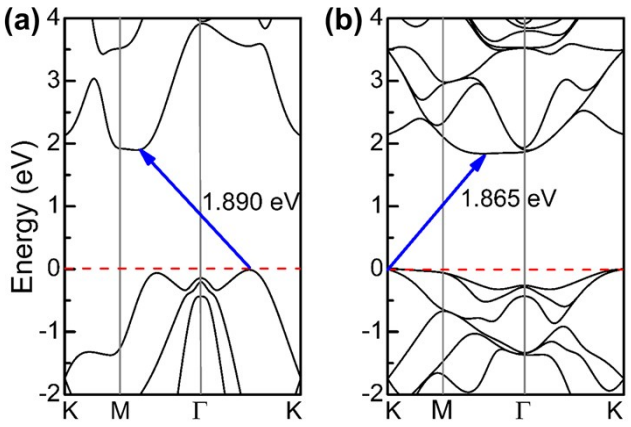

Fig. S1 The calculated band structures of (a) a unit cell of monolayer BlueP, with (b) a 2×2 supercell of monolayer BlueP by PBE functional.

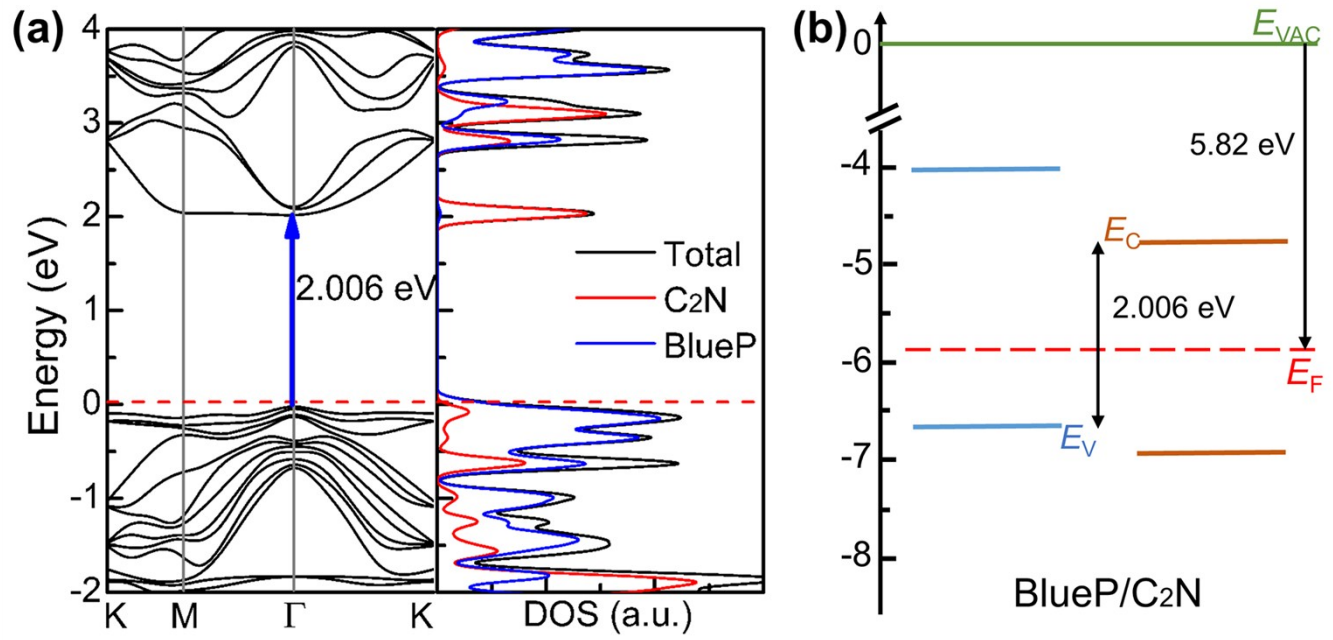

Fig. S2 The calculated (a) band structure and DOS, along with (b) band alignment of BlueP/C_2N heterojunction by HSE06 functional.

Our results demonstrate that the direct band gap at the Γ point for the BlueP/C_2N heterojunction obtained by HSE06 is 2.006 eV, as shown in Fig. S2(a), which is larger about 0.5 eV than that of PBE one. One can see from the DOS that the CBM is dominated by C_2N monolayer and the VBM is mainly determined by BlueP monolayer, coincide with the results at PBE level. It shows from Fig. S2b that a type-II heterojunction can be realized between C_2N and BlueP monolayers, thus the favorable spatial separation of photogenerated electrons and holes can be expected.

The carrier effective mass can be calculated by the following equation:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{h^2}\frac{\partial^2 E}{\partial k_i \partial k_j}, i, j = x, y, z \quad (1)$$

From the Equation, we can obtain the effective mass of the electron (or hole) by the second derivative of the top of the valence band (or the bottom of conduction band) for the wave vector. Although m^* is a second-order tensor with nine components, it can be taken as a scalar. Three directions (*x, y, z*) are calculated when we calculate energy band.

$$\frac{1}{m^*} = \frac{1}{h^2}\frac{\partial^2 E(k)}{\partial k^2} \quad (2)$$

where k is the wave vector, $\hbar$ is the reduced Planck constant, and $E(k)$ is the dispersion relation.

Before exploring the effective mass in heterojunction, the effective masses of C_2N monolayer are calculated to be $m^*_e = 0.45m_0$, $m^*_h = 5.1m_0$ (m_0 is the free-electron mass). The electron effective mass and hole effective mass of BlueP monolayer are $m^*_e = 0.11m_0$, $m^*_h = 0.63m_0$, respectively. The m^*_h of the C_2N monolayer is much larger than the m^*_e of C_2N, indicating much lower hole mobility in the C_2N monolayer, coincide with other results.[28] For BlueP, the m^*_h is also higher than m^*_e, which agree well with previous reports.[34] In the heterojunction, holes have much higher mobilities than those of any of single layers because $m^*_h = 0.41m_0$, while the electron mobility is moderate with $m^*_e = 0.61m_0$.