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

Novel C_4P_2 Monolayers: Forming Z-scheme Heterojunction and Janus Structure for High-efficiency Metal-free Photocatalytic Water Splitting

Jiahe Lin[a*] and Bofeng Zhang[b*]

[a]*School of Science, Jimei University, Xiamen, 361021, China*

[b]*Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China*

ABSTRACT

Metal-free two-dimensional (2D) semiconductors have garnered significant attention in the realm of photocatalytic water splitting, primarily owing to their inherent clean, stable, and efficient photoresponsive properties. Motivated by it, we have proposed two types of stable C_4P_2 monolayers with indirect band gaps, mediocre carrier mobility and excellent optical absorption in visible-light and ultraviolet regions. Although the too-low work function of monolayer α-C_4P_2 and the too-high work function of monolayer β-C_4P_2 make them only suitable for single-side redox reaction in photocatalytic water splitting, the creation of an α-C_4P_2/β-C_4P_2 Z-scheme heterojunction, combined with the Janus monolayer γ-C_4P_2 that integrates features of both α and β structures, effectively addresses this limitation, fulfilling the prerequisites for comprehensive photocatalytic water splitting. Furthermore, the calculations indicate that the α-C_4P_2/β-C_4P_2 Z-scheme heterojunction and Janus monolayer γ-C_4P_2 not only demonstrate improved carrier mobility and optical absorption but also feature internal electric fields that effectively enhance driving energy and photo-induced charge separation. Notably, Janus monolayer γ-C_4P_2 achieves a high electron mobility of ~10^5 cm^2/Vs and an impressive solar-to-hydrogen conversion efficiency of 25.62%.

* Corresponding author: Jiahe Lin and Bofeng Zhang, E-mail: linjiahe@jmu.edu.cn and zhangbofeng@stu.xmu.edu.cn.

Eq. (1):

$$E_{coh} = \frac{E_{tot} - 4E_{atom}(C) - 2E_{atom}(P)}{6} \quad (1)$$

Where E_{tot} is the total energy of monolayer α-C_4P_2 and β-C_4P_2, and the $E_{atom}(C)$ and $E_{atom}(P)$ are the energy of free C and P atoms, respectively.

Eq. (2)

$$\mu = \frac{\hbar^3 e C_{2D}}{k_B T m^* m_d E_l^2} \quad (2)$$

where C_{2D} is the effective elastic modulus obtained from $C_{2D} = 2\left[\partial^2 E / \partial(\Delta a / a_0)^2\right] / S_0$, in which the a_0 is the lattice constant without strain, the Δa presents the deformation of a_0, the S_0 is the total area of structures without strain, and the E is the total energy of these monolayers with the strain along specific direction. The T is set as 300 K to represent room temperature. The m^* is effective mass along specific direction, and the m_d is average effective mass defined as $m_d = \sqrt{m_X^* m_Y^*}$. The E_l is the deformation potential constant defined by $E_l = \partial E_{edge} / \partial(\Delta a / a_0)$, where E_{edge} is the change of the CBM and VBM with the strain along specific direction.

Eq. (3-5):

$$A(\omega) = 1 - e^{-\alpha(\omega) \cdot \Delta z} \quad (3)$$

$$\alpha(\omega) = \frac{\omega \varepsilon_2}{cn} \quad (4)$$

$$n = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}} \quad (5)$$

Where $A(\omega)$ presents the optical absorbance, $\alpha(\omega)$ presents the absorption coefficient, ΔZ presents the primitive-cell size in the direction of vacuum layer, n presents the index of refraction, ε_1 and ε_2 respectively present the real and imaginary parts of their dielectric function, ω presents the incident light frequency, c presents the speed of light in vacuum.

Eq. (6-7):

$$E_{QPG} = (E_{OP} + 0.4)/0.79 \quad (6)$$

$$E_B = E_{QPG} - E_{OP} \quad (7)$$

Where the E_{OP}, E_{QPG} and E_B are optical gaps, quasi particle bandgaps and exciton binding energy, respectively.

Eq. (8-12):

The optical absorption efficiency (η_{abc}):

$$\eta_{abc} = \frac{\int_{E_g}^{\infty} p(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)} \quad (8)$$

Where the E_g is the band gap, and $P(\hbar\omega)$ is the AM 1.5G solar energy flux as functional of the photon energy $\hbar\omega$.

The efficiency of carrier utilization (η_{cu}) :

$$\eta_{cu} = \frac{\Delta G \int_{E}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)} \quad (9)$$

Where the ΔG is 1.23 eV describing the potential difference of water splitting, and E is the photon energy actually used for water splitting, which is defined as:

$$E = \begin{cases} E_g \ (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2) \ (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2) \ (\chi(H_2) \geq 0.2, \chi(H_2) < 0.6) \\ E_g + 0.8 - \chi(H_2) - \chi(O_2) \ (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases} \quad (10)$$

Where the $\chi(H_2)$ and $\chi(O_2)$ are the overpotential for hydrogen evolution reaction and the overpotential for oxygen evolution reaction, respectively.

The solar-to-hydrogen (STH) efficiency (η_{sth}):

$$\eta_{sth} = \eta_{abc} \times \eta_{cu} \quad (11)$$

The corrected STH efficiency (η_{sth}') with considering the effect of internal electric fields:

$$\eta_{sth}^{'} = \eta_{sth} \times \frac{\int_0^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega)d(\hbar\omega) + \Delta\phi \int_{E_g}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}$$

(12)

Where the $\Delta\phi$ is the electrostatic potential differences between the top and bottom sublayers in monolayer γ-C_4P_2.

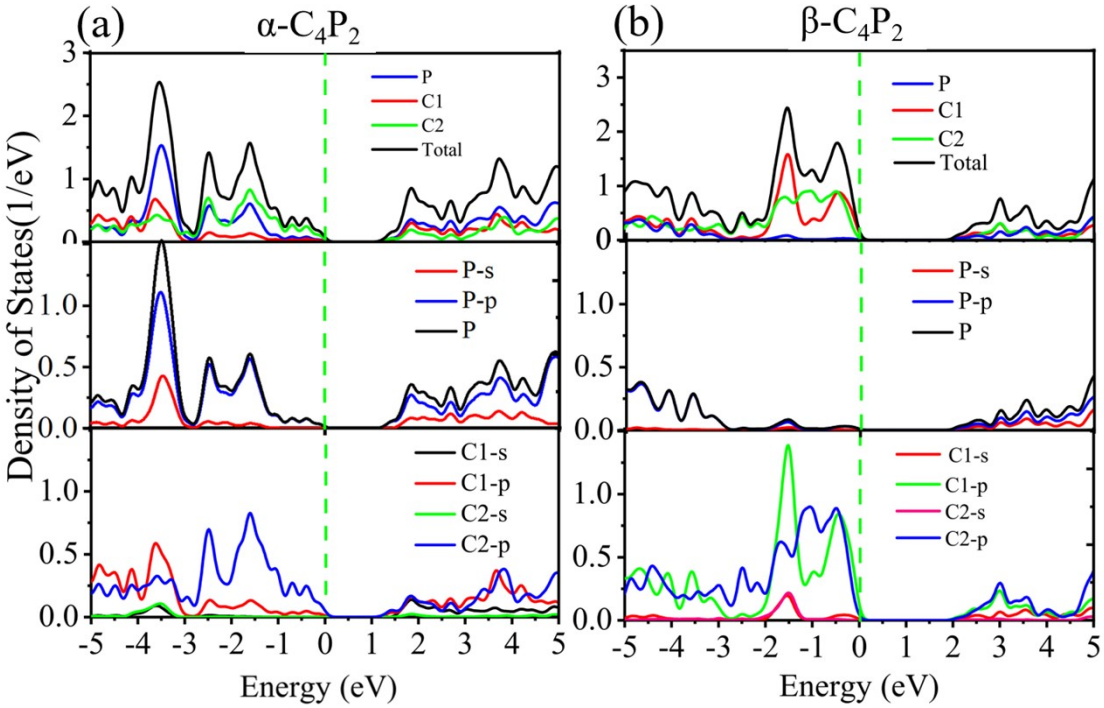

Fig. S1. (a) and (b) are the PDOS of monolayer α-C_4P_2 and β-C_4P_2, respectively.

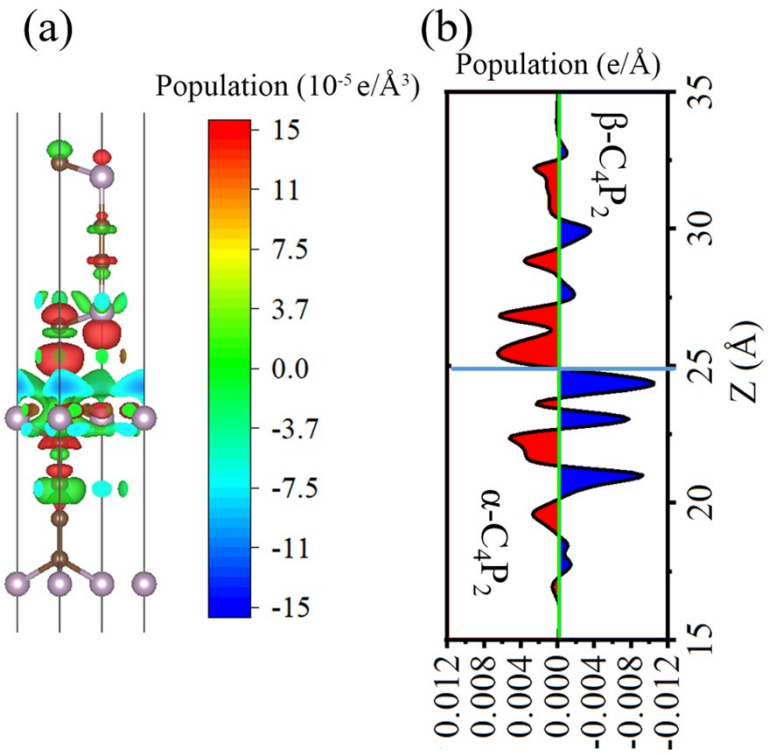

Fig. S2. (a) is the charge density difference of α-C_4P_2/β-C_4P_2 heterojunction. (b) is the plane-integrated electron density difference along the vertical direction for the α-C_4P_2/β-C_4P_2 heterojunction.