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

Supplementary material

The regulating effect of boron doping and its concentration on the photocatalytic overall water splitting of polarized g-C_3N_5 material

Xianghong Niu[1]*, Xuemei Zhang[1], Anqi Shi[2], Dazhong Sun[1], Dingbang Chen[1], Lu Zhang[1], Jialin Huang[1], Liqing Liu[1], Bing Wang[3]*, Xiuyun Zhang[4]*

[1]School of Science, Nanjing University of Posts and Telecommunications, Nanjing, 210023, China

[2]State Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China

[3]Institute for Computational Materials Science, Joint Center for Theoretical Physics (JCTP), School of Physics and Electronics, Henan University, Kaifeng, 475004, China

[4]College of Physics Science and Technology, Yangzhou University, Yangzhou 225002, China

* E-mail: xhniu@njupt.edu.cn; wb@henu.edu.cn; xyzhang@yzu.edu.cn

Calculation details:

The calculation of optical properties

The photo-absorption coefficient $I(\omega)$ is calculated by the following equations:

$$I(\omega) = \frac{\sqrt{2}\omega}{c}\left[\sqrt{\left(\varepsilon^{'}(\omega)\right)^2 + \left(\varepsilon^{''}(\omega)\right)^2} - \varepsilon^{'}(\omega)\right]^{1/2} \quad (1)$$

where c is the speed of light, $\varepsilon^{'}(\omega)$ and $\varepsilon^{''}(\omega)$ are the real part and imaginary part of the dielectric function ε, respectively. The imaginary part of dielectric function $\varepsilon^{''}(\omega)$ is a Cartesian tensor which is composed by the element $\varepsilon_{\alpha\beta}^{''}(\omega)$:

$$\varepsilon_{\alpha\beta}^{''}(\omega) = \frac{4\pi^2 e^2}{\Omega}\lim_{q\to 0}\frac{1}{q^2}\sum_{C,V,k} 2w_k\delta(\varepsilon_{Ck} - \varepsilon_{Vk} - \omega) \times \left\langle u_{Ck+e_\alpha q}|u_{Vk}\right\rangle\left\langle u_{Ck+e_\beta q}|u_{Vk}\right\rangle^* \quad (2)$$

where Ω is the volume of the pristine cell, q is the electron momentum operator, C and V are the indices of conduction and valence bands, respectively. k is the Bloch wave vector, w_k is the weight of the k point, e_α is the unit vector in Cartesian coordinates. u_{Ck}, u_{Vk}, and ε_{Ck}, ε_{Vk} are the wavefunction and corresponding eigenvalue at the k point, respectively.

Photocatalytic water-splitting reaction

For HER, the reaction path is:

$$H^+ + e^- + * \rightleftharpoons *H \quad (1)$$

in which the $*$ and $*H$ represent the clean slab and the slab adsorbed a hydrogen atom, respectively.

The respective change of Gibbs free energy ΔG in the reaction path of HER is calculated by:

$$\Delta G = G_{*H} - G_* - G_{(H^+ + e^-)} \quad (2)$$

in which the G_{*H}, G_*, and G_H are the Gibbs free energies of $*H$, $*$, and $(H^+ + e^-)$, respectively. The $G_{(H^+ + e^-)}$ is calculated by:

$$G_{(H^+ + e^-)} = G_{H_2}/2 \quad (3)$$

in which the $G_{H_2}/2$ represents the Gibbs free energy of H_2.

For all the cases, the Gibbs free energy G is calculated by:

$$G = E + ZPE - TS \quad (4)$$

in which the E is the total energy of species obtained from calculations, ZPE is the zero point energy and S is the entropy at 298 K in the calculated systems.

The reaction path of OER follows the classical four-electron step:

First step: $H_2O(l) + * \rightleftharpoons *OH + H^+ + e^-$ (5)

Second step: $*OH \rightleftharpoons *O + H^+ + e^-$ (6)

Third step: $*O + H_2O(l) \rightleftharpoons *OOH + H^+ + e^-$ (7)

Fourth step: $*OOH \rightleftharpoons * + O_2(g) + H^+ + e^-$ (8)

The respective ΔG in the reaction path of OER is calculated by:

$H_2O(l) + * \rightleftharpoons *OH + H^+ + e^-$:

$$\Delta G1 = G_{*OH} + G_{(H^+ + e^-)} - G_* - G_{H_2O(l)} \quad (9)$$

$*OH \rightleftharpoons *O + H^+ + e^-$:

$$\Delta G2 = G_{*O} + G_{(H^+ + e^-)} - G_{*OH} \quad (10)$$

$*O + H_2O(l) \rightleftharpoons *OOH + H^+ + e^-$:

$$\Delta G3 = G_{*OOH} + G_{(H^+ + e^-)} - G_{*O} - G_{H_2O(l)} \quad (11)$$

$*OOH \rightleftharpoons * + O_2(g) + H^+ + e^-$:

$$\Delta G4 = G_{*} + G_{(H^{+} + e^{-})} + G_{O_2(g)} - G_{*OOH} \quad (12)$$

in which the G_{*OH}, G_{*O}, and G_{*OOH} represent the Gibbs free energies of respective related intermediates residing on the catalysts. The $G_{H_2O(l)}$ and $G_{O_2(g)}$ represent the Gibbs free energies of H_2O and O_2, respectively.

The overpotential (η) reflects the reaction kinetics as a sign of the energy barrier or activation energy in the OER reaction, which can be clearly combined with the performance of the photocatalysts. The η which treated as judging the catalytic performance of OER can be obtained by using the subsequent equations:

$$\eta = [max(\Delta G1, \Delta G2, \Delta G3, \Delta G4) - 1.23]/e \quad (13)$$

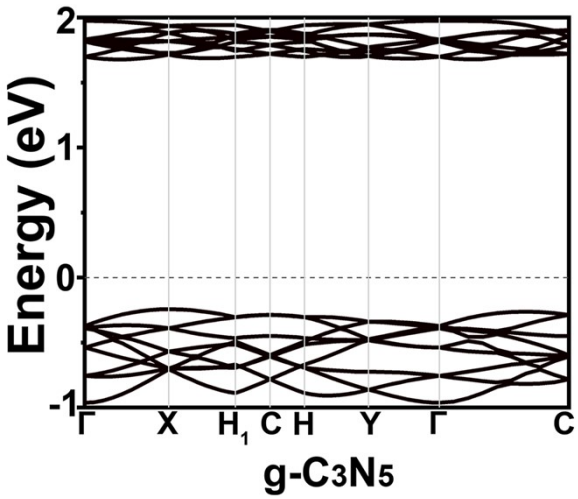

Figure S1 The band structure of the pristine g-C_3N_5 calculated by GGA-PBE. The label is the pristine structure corresponding to Fig. 1.

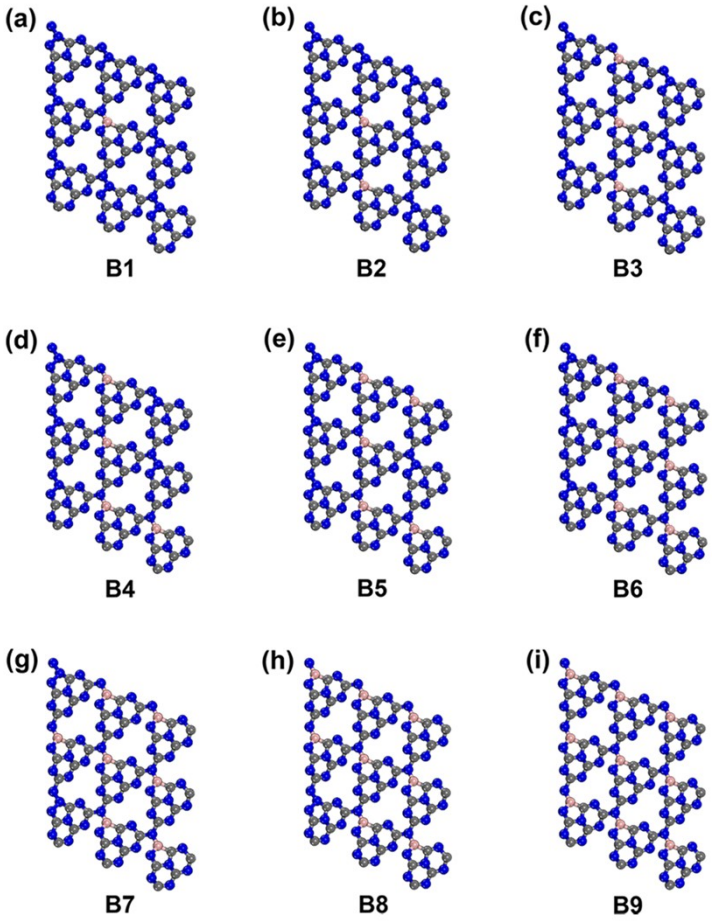

Figure S2 The optimized structures of boron-doped g-C_3N_5. The boron atoms replace nitrogen atoms of pristine g-C_3N_5. The pink, blue, and gray balls represent the boron, nitrogen, and carbon atoms, respectively. The labels are the replaced structures corresponding to Fig. 3.

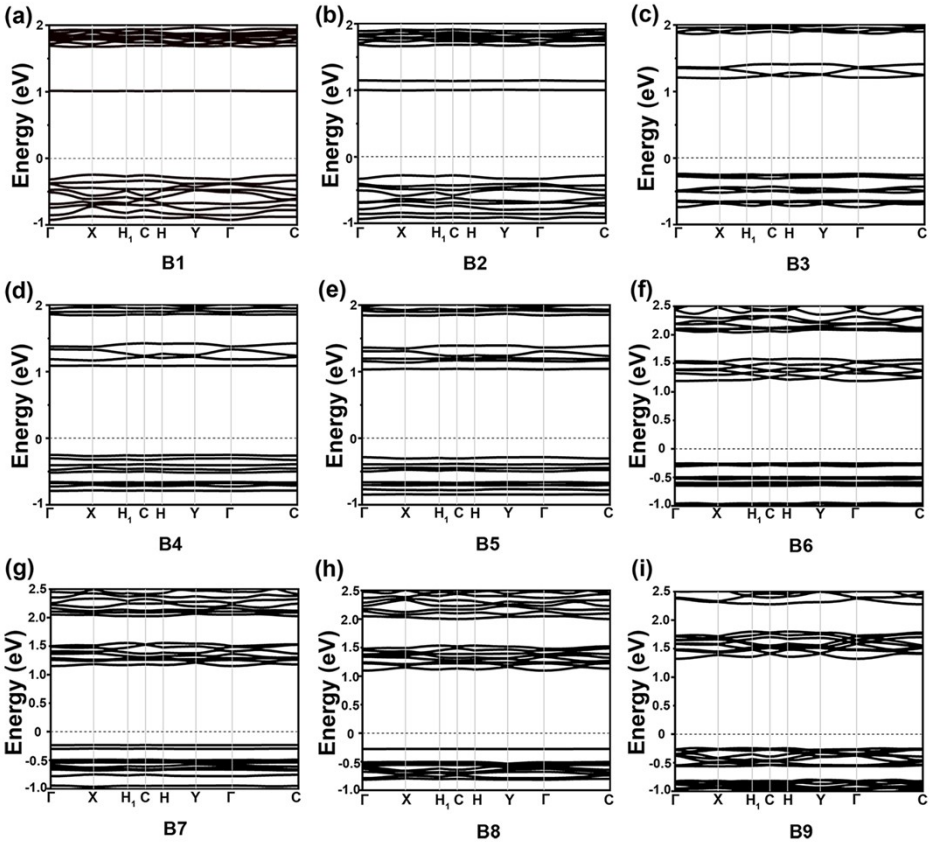

Figure S3 The band structures of boron-doped g-C_3N_5 calculated by GGA-PBE. The boron atoms replace nitrogen atoms of pristine g-C_3N_5. The labels are the replaced structures corresponding to Fig. 3.

Table S1. The effective masses(m^*/m_e) of electrons and holes for all undoped and B-doped g-C_3N_5.

carrier type	g-C_3N_5	B1	B2	B3	B4	B5	B6	B7	B8	B9
e	1.38	1.83	1.88	1.63	2.66	2.89	1.20	4.15	3.26	2.10
h	1.32	1.97	2.83	5.60	6.11	8.33	7.45	15.30	10.60	1.83