Supplementary Material for g-ZnO/Si_9C_{15}: A S-scheme Heterojunction with High Carrier Mobility for Photo-electro Catalysis Water Splitting

Yang Shen [1,*], Zhihao Yuan [1], Zhen Cui [2,*], Deming Ma [1], Pei Yuan [1], Fengjiao Cheng [3], Kunqi Yang [1], Yanbo Dong [1] and Enling Li [1,*]

[1] School of Science, Xi'an University of Technology, Xi'an 710054, China;

[2] School of Automation and Information Engineering, Xi'an University of Technology, Xi'an 710048, China

[3] School of Electrical Engineering, Xi'an University of Technology, Xi'an 710054, China

* Correspondence: shenyang@xaut.edu.cn; zcui@xaut.edu.cn; lienling@xaut.edu.cn

Part A: The calculation mothed of carrier mobility

The carrier mobility is calculated as follows:

$$\mu=\frac{e\hbar^3 C_{2D}}{k_B T m_e^* m_d (E_1^i)^2} \quad (1)$$

where e, $\hbar$, k_B, T, m_e*, and m_d are electron charge, simplify Planck constant, Boltzmann constant, temperature, the direction of Zigzag and Armchair orientation effective quality, and average effective quality. Further, m_d is determined by the following formula: $m_d = \sqrt{m_x^* m_y^*}$. The E_1^i is the potential deformation constant of electrons and holes in the direction of transmission in the CBM or VBM, the calculation formula is: $E_1^i = \Delta E_i / (\Delta l / l_0)$, where ΔE_i (i for CBM or VBM) is the energy change of CBM or VBM under external strain, and $\triangle l$ is the deformation of l_0 with strain. The calculation equation for the elastic modulus (C_{2D}) of the two-dimensional material is as follows:

$C_{2D}=\left[\partial^2 E/\partial l^2\right]$, where E, l, and S_0 are the total strain energy, applied strain, and Lattice area of the two-dimensional system at equilibrium, respectively.

Part B: The calculation method of the Solar to hydrogen (STH) efficiency and corrected STH efficiency

The STH efficiency is:

$$\eta_{\mathrm{STH}} = \eta_{\mathrm{abs}} \times \eta_{\mathrm{cu}} \tag{2}$$

where η_{abs} and η_{cu} are the efficiency of light absorption and carrier utilization, respectively.

The η_{abs} is calculated by:

$$\eta_{\mathrm{abs}} = \frac{\int_{E_g}^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)}{\int_{0}^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)} \tag{3}$$

where $P(\hbar\omega)$ is the AM 1.5G standard solar spectrum at the photon energy $\hbar\omega$, and E_g represents the bandgap of the g-ZnO/Si_9C_{15} heterojunction.

The η_{cu} is determined as:

$$\eta_{\mathrm{cu}} = \frac{\Delta G\int_{E_{\min}}^{\infty} \frac{P(\mathrm{h}\omega)}{\mathrm{h}\omega}\,\mathrm{d}(\mathrm{h}\omega)}{\int_{E_g}^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)} \tag{4}$$

where ΔG equals to 1.23 eV for water splitting. The $E_{\min}$ is the energy of photons, which can be determined by:

$$E_{\min} = \begin{cases} E_g, \ , \ , & \left(\chi(\mathrm{H_2}) \geq 0.2 \quad \chi(\mathrm{O_2}) \geq 0.6\right) \\ E_g + 0.2 - \chi(\mathrm{H_2}), \ , \ , & \left(\chi(\mathrm{H_2}) < 0.2 \quad \chi(\mathrm{O_2}) \geq 0.6\right) \\ E_g + 0.6 - \chi(\mathrm{O_2}), \ , \ , & \left(\chi(\mathrm{H_2}) \geq 0.2 \quad \chi(\mathrm{O_2}) < 0.6\right) \\ E_g + 0.8 - \chi(\mathrm{H_2}) - \chi(\mathrm{O_2}), & \left(\chi(\mathrm{H_2}) < 0.2 \quad \chi(\mathrm{O_2}) < 0.6\right). \end{cases} \tag{5}$$

where the $\chi(H_2)$ and $\chi(O_2)$ are the potential provided (shown in Fig. 4 (b)) by photo-generated carriers that can drive the hydrogen evolution reduction (HER, vs. NHE) and oxygen evolution reactions (OER, vs. NHE), respectively. Considering the effect of polarity of the g-ZnO/Si_9C_{15} heterojunction on the electron-hole separation, the corrected STH efficiency is:

$$\eta'_{\mathrm{STH}} = \eta_{\mathrm{STH}} \times \frac{\int_0^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)}{\int_0^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega) + \Delta\Phi\int_{E_{\min}}^{\infty} \frac{P(\mathrm{h}\omega)}{\mathrm{h}\omega}\,\mathrm{d}(\mathrm{h}\omega)} \tag{6}$$

where $\Delta\Phi$ the difference of vacuum level between such surfaces of the g-ZnO/Si_9C_{15} heterojunction.

Part C: The calculation method of the power conversion efficiency (PCE)

The PCE (η_{PCE}) of the g-ZnO/Si_9C_{15} heterojunction is calculated as follws:

$$\eta_{\mathrm{PCE}} = \frac{\beta_{\mathrm{FF}} J_{\mathrm{SC}} V_{\mathrm{OC}}}{P_{\mathrm{Solar}}} = \frac{0.65\left(E_{\mathrm{g}} - E_{\mathrm{CBO}} - 0.3\right)\int_{E_{\mathrm{g}}}^{\infty} \frac{P(\mathrm{h}\omega)}{\mathrm{h}\omega}\,\mathrm{d}(\mathrm{h}\omega)}{\int_0^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)} \tag{7}$$

where the β_{FF} is the fill factor (0.65). The J_{SC} is short circuit current: $E_{\mathrm{g}} - E_{\mathrm{CBO}} - 0.3$, where E_{g} and E_{CBO} is donor bandgap and CB offset, respectively. The V_{OC} is the open circuit voltage: $\int_{E_{\mathrm{g}}}^{\infty} \frac{P(\mathrm{h}\omega)}{\mathrm{h}\omega}\,\mathrm{d}(\mathrm{h}\omega)$, where $P(\hbar\omega)$ is the AM 1.5G solar flux at the photon energy $\hbar\omega$. The P_{solar} is the total incident solar power per unit area: $\int_0^{\infty} P(\mathrm{h}\omega)\,\mathrm{d}(\mathrm{h}\omega)$.

Part D: The Hydrogen evolution reaction (HER) process and the calculation method of reaction Gibbs free energy

The HER process consists of the following steps:

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

$$*H + (H^+ + e^-) \rightarrow H_2 + *$$

where * indicates free site of absorbability on heterojunction surface. *H represents H atom absorbed on the surfaces the g-ZnO/Si_9C_{15} heterojunction. Under standard conditions (pH= 0, P= 1 bar, T= 298.15 K), the Gibbs free energy of $H^+ + e^-$ corresponds to that of a half of H_2 molecule at NHE. Reaction Gibbs free energy (G) is calculated as follows:

$$G = \Delta E + \Delta \mathrm{ZPE} - T\Delta S + \Delta G_{\mathrm{U}} \tag{8}$$

where ΔE, ΔZPE, and TS represent adsorption energy, difference of zero-point energy, and difference of entropy (under the T = 298.15 K), respectively. The $\Delta G_{\mathrm{U}} = -eU$ is the influence of voltage on energy, where e is the elementary charge, and U is the potential measured against the NHE. The repair of entropy and zero-point energy is obtained by vibration frequency calculation. The zero-point energy can be determined by the sum of all vibration modes and calculated as follows:

$$\mathrm{ZPE} = 1/2 \sum_{i}^{k} h\nu_i \tag{9}$$

where h and ν_i represent the Planck constant and the frequency corresponding to the i-th vibration mode, and k is the number of vibration modes. The TS values is calculated as follow:

$$TS = k_{\mathrm{B}}T\left[\sum_{i}^{k} \ln\left(\frac{1}{1-e^{-h\nu_i/k_BT}}\right) + \sum_{i}^{k} \frac{h\nu_i}{k_BT}\left(\frac{1}{e^{h\nu_i/k_BT}-1}\right) + 1\right] \tag{10}$$

where k_{B} represents the Boltzmann constant. Ideally, when the theoretically applied voltage U = 0 V, the HER can be spontaneously driven without additional power. The η^{HER} depends on the increment ($\Delta G_{*\mathrm{H}}$) of the Gibbs free energy in the reaction, and the

η^{HER} is calculated as follows:

$$G^{\mathrm{HER}} = \{\Delta G_{*\mathrm{H}}\}$$

$$\eta^{\mathrm{HER}} = G^{\mathrm{HER}} / e \tag{11}$$

Part E: The adsorption sites of H atom adsorbed on the Si9C15 interface and the g-ZnO interface

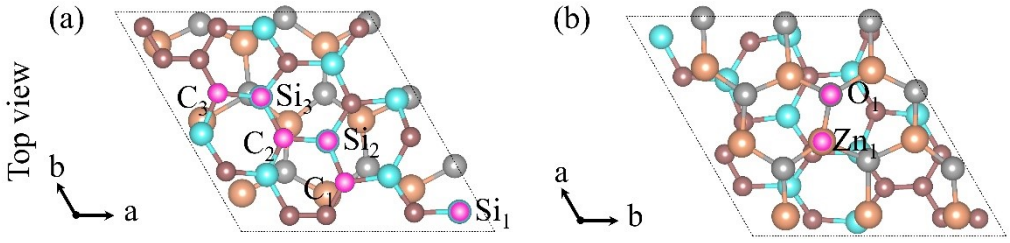

Fig. S. 1 The crystal structure and adsorption site of H atom adsorbed on (a) Si_9C_{15} interface and (b) g-ZnO interface of the g-ZnO/ Si_9C_{15} heterojunction, respectively. The orange, gray, blue, brown, peach balls represent Zn, O, Si, C, H atoms, respectively. The purple sphere represents the adsorption site.