Supporting Information

Crystal-Phase Engineering of ZrS_2/γ-BC_6N Heterostructures for Enhanced Type-II Photocatalytic Water Splitting

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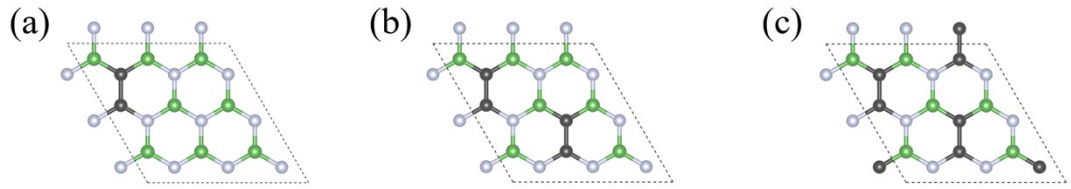

Fig.S1. (a-c) are top-down views of the single-layer structures h-BC_xN (x = 2, 4, 6) respectively.

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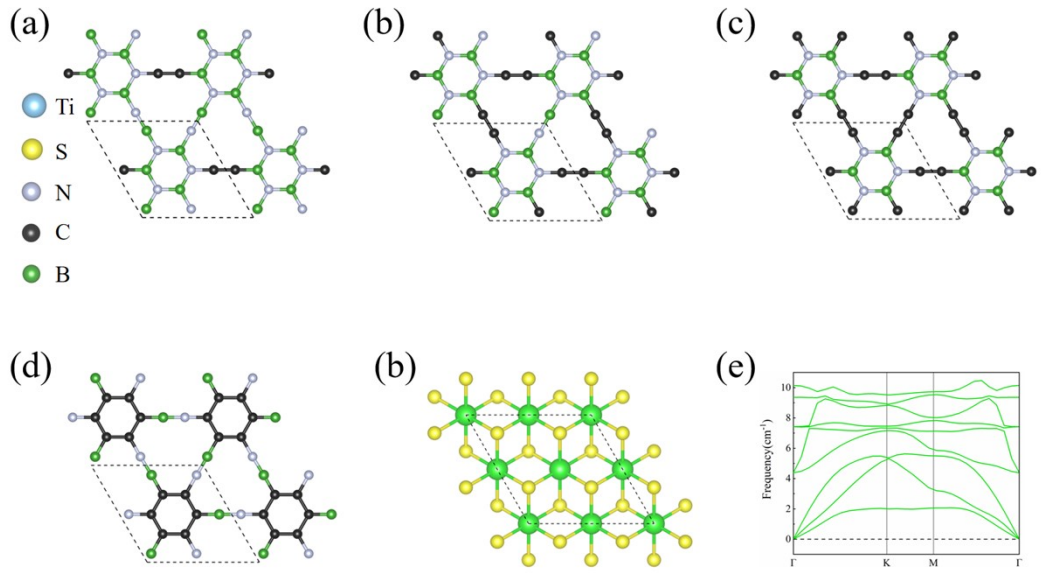

Fig.S2. (a–d) are top-down views of γ-BC_xN monolayer structures (x = 2, 4, 6), respectively. (e) and (f) are top-down views of the ZrS_2 monolayer structure and the corresponding high-symmetry *K*-path ($\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$) phonon dispersion relations, respectively.

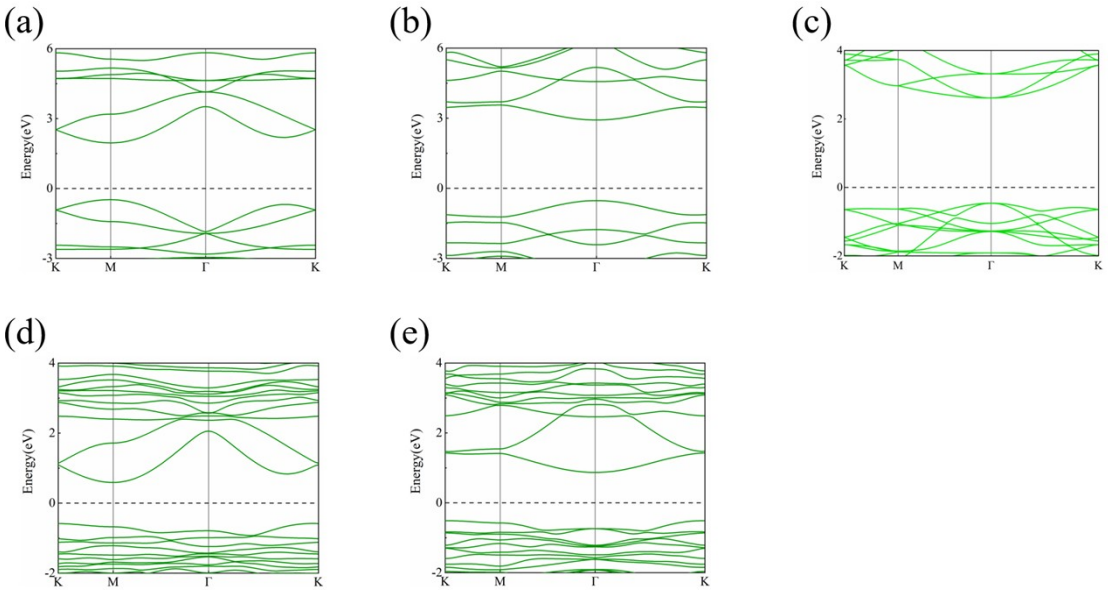

Fig.S3. (a-e) represent the band structures of γ-BC_6N, h-BC_4N, and monolayer ZrS_2; and the heterostructures ZrS_2/γ-BC_6N and ZrS_2/h-BC_4N, respectively, as calculated by the PBE method.

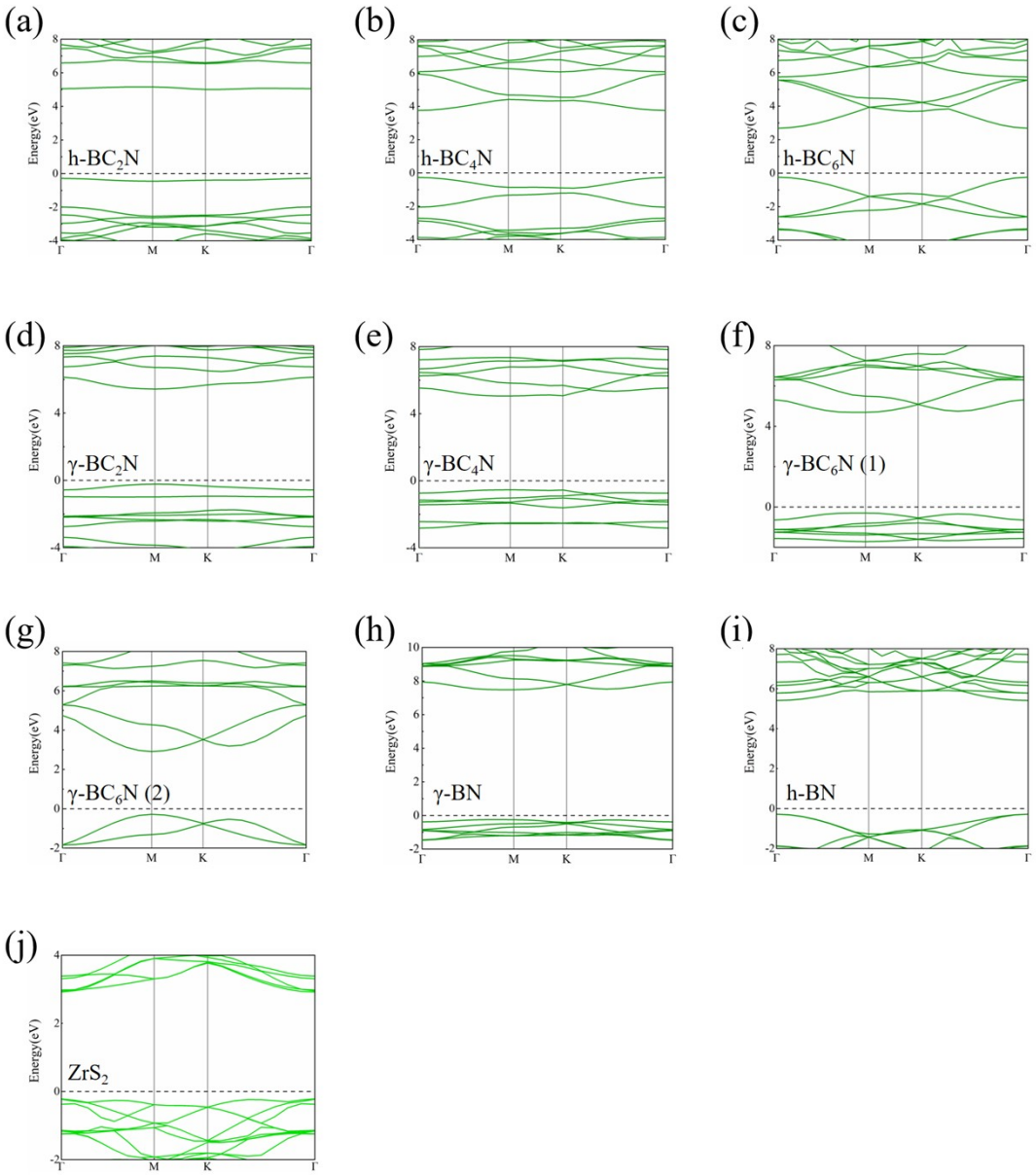

Fig.S4. (a-j) represent the band structure diagrams for each monolayer under the HSE06 method.

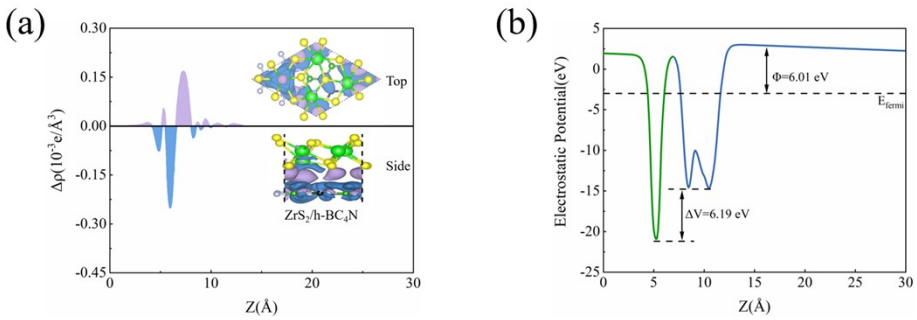

Fig.S5. (a) Charge density distribution map of the ZrS_2/h-BC_4N heterostructures (blue and purple in the inset denote charge accumulation and loss respectively). (b) Electrostatic potential distribution map of the ZrS_2/h-BC_4N heterostructures.

Table S1. The energy of CBM and VBM (E_{CBM} and E_{VBM}), the overpotentials of HER and OER ($\chi(H_2)$ and $\chi(O_2)$), the calculated E_g ($E_{g\text{-}HSE06}$) of HSE06, and the energy conversion efficiency η_{STH} of STH at the band-edge position of the different heterostructures under different strains

	Water splitting edges		$\chi(H_2)$	$\chi(O_2)$	$E_{g\text{-}HSE06}$	η_{STH}
	E_{CBM}(eV)	E_{VBM}(eV)	(eV)	(eV)	(eV)	(%)
$ZrS_2/\gamma\text{-}BC_6N$	-4.23	-5.64	1.62	0.33	2.3	15.54
$ZrS_2/\gamma\text{-}BN$	-3.92	-5.60	2.2	2.05	3.11	5.04
$ZrS_2/h\text{-}BC_4N$	-3.94	-5.69	0.71	0.86	3.06	5.8
$ZrS_2/h\text{-}BN$	-4.08	-5.79	0.5	0.51	3.55	1.15

Table S2. Band gaps(E_g), CBO, power conversion efficiency (PCE) and absorption confficient of different heterostructures.

	E_g	CBO	PCE	Absorption Coefficient
$ZrS_2/\gamma\text{-}BC_6N$	2.3	0.2	10.5%	4.10×10^5 cm^{-1}
$ZrS_2/\gamma\text{-}BN$	3.06	0.33	4.78%	1.80×10^5 cm^{-1}
$ZrS_2/h\text{-}BC_4N$	3.55	0.3	2.45%	2.80×10^5 cm^{-1}
$ZrS_2/h\text{-}BN$	2.77	0.27	10.37%	1.73×10^5 cm^{-1}

Table S3. Defect formation energy

	Energy(eV)
$\gamma\text{-}BC_2N$	-1.34250782
$\gamma\text{-}BC_4N$	-4.01080547
$\gamma\text{-}BC_6N$	-9.46246252