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

Supporting Information

2D van der Waals heterostructures of graphitic BCN as direct Z-scheme photocatalysts for overall water splitting: the role of polar π–conjugated moieties

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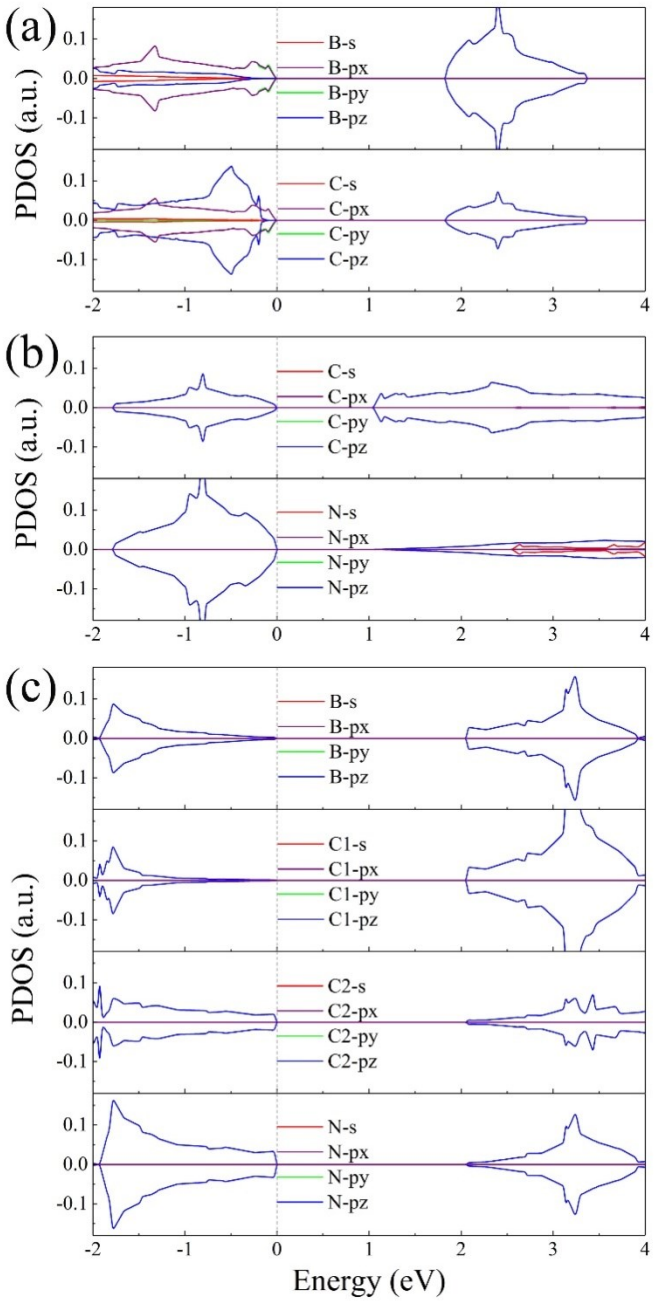

Figure S1 Partial density of states (PDOS) of (a) BC_3, (b) C_3N and (c) BC_6N monolayers.

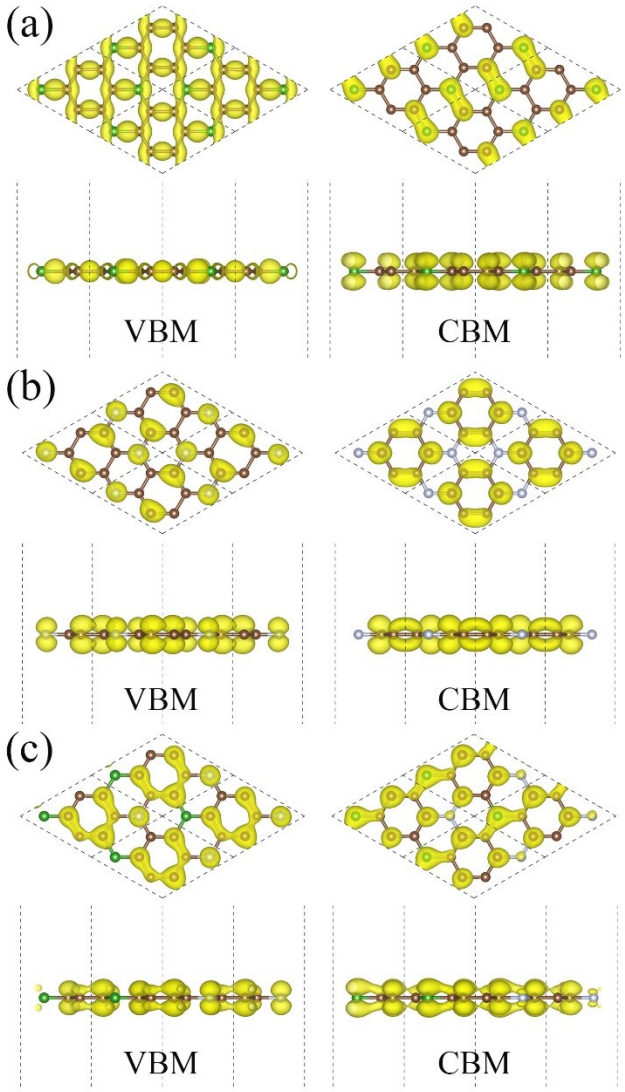

Figure S2 Band decomposed charge density of (a) BC_3, (b) C_3N and (c) BC_6N monolayers, and the isosurface value is 0.008 e Å^{-3}.

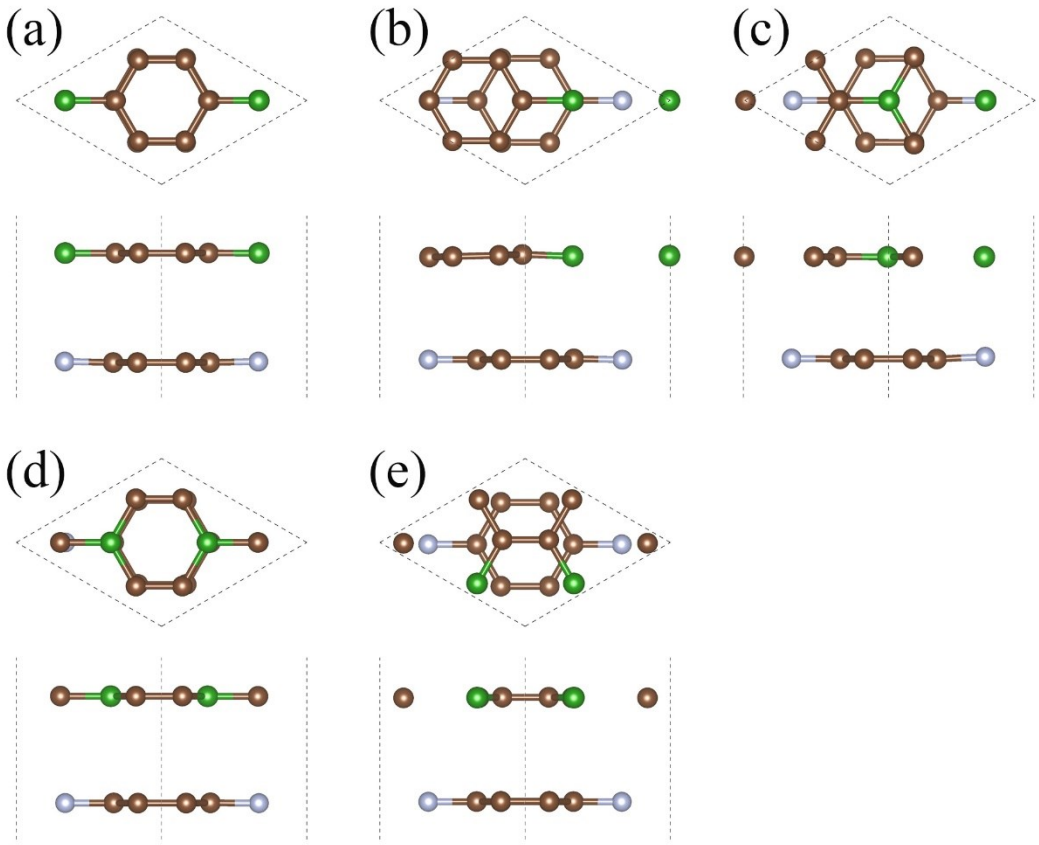

Figure S3 Top view of five stacking configurations for BC_3 on C_3N in our investigation. (a) AA, (b) AB, (c) AC, (d) AD and (e) AE. Green, brown and grey balls denote B, C and N atoms, respectively.

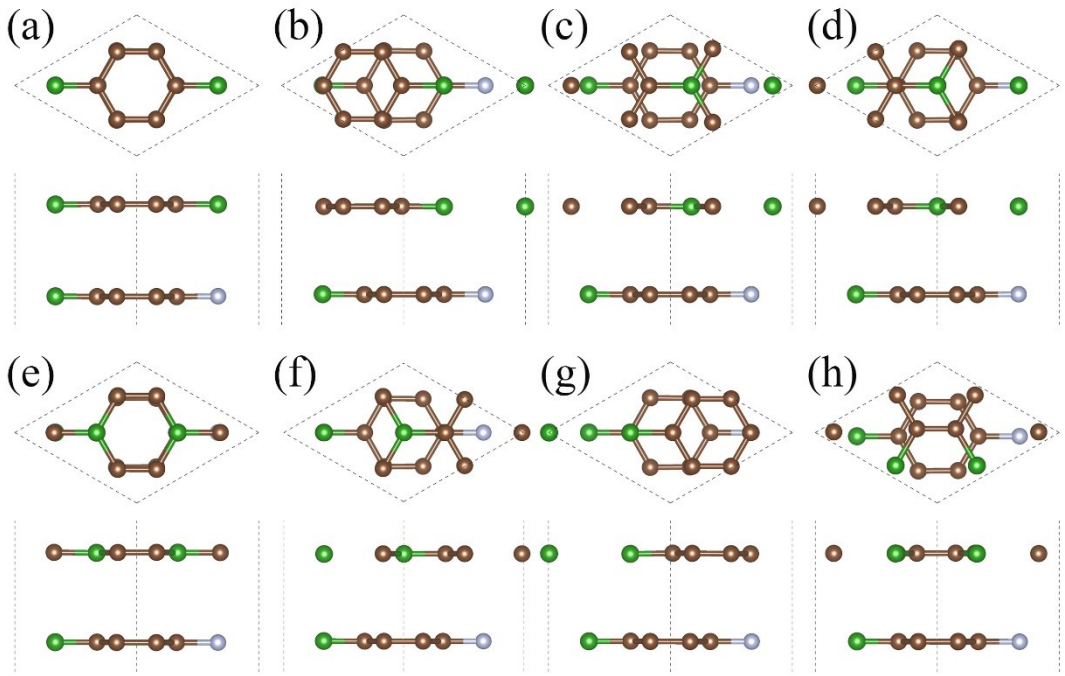

Figure S4 Top view of eight stacking configurations for BC_3 on BC_6N in our investigation. (a) AA, (b) AB, (c) AC, (d) AD, (e) AE, (f) AF, (g) AG and (h) AH. Green, brown and grey balls denote B, C and N atoms, respectively.

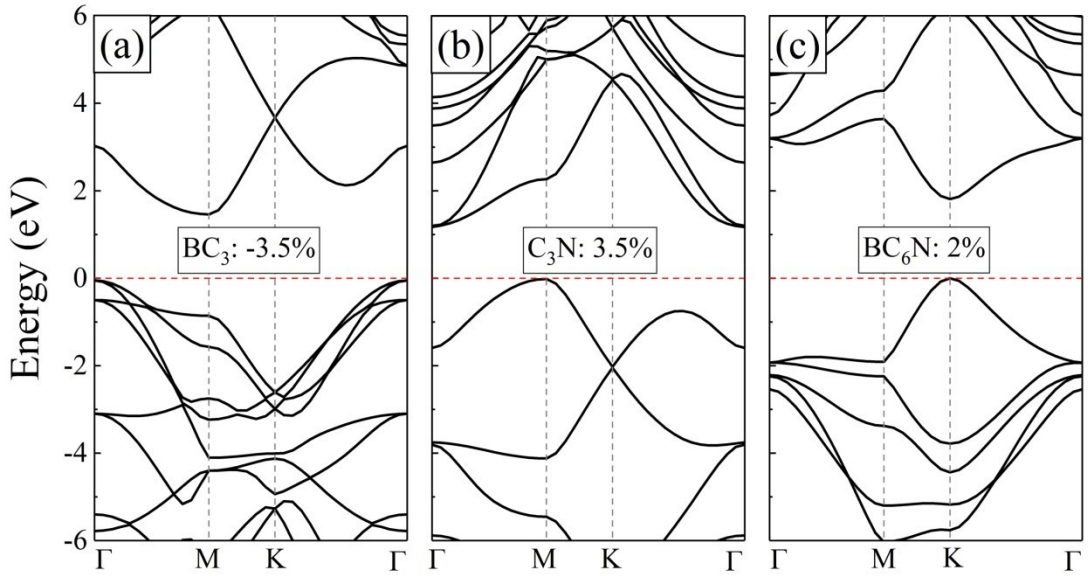

Figure S5 Electronic band structures of monolayer (a) BC_3 under the compressive strain of -3.5%, (b) C_3N under the tensile strain of 3.5%, and (c) BC_6N under the tensile strain of 2%.

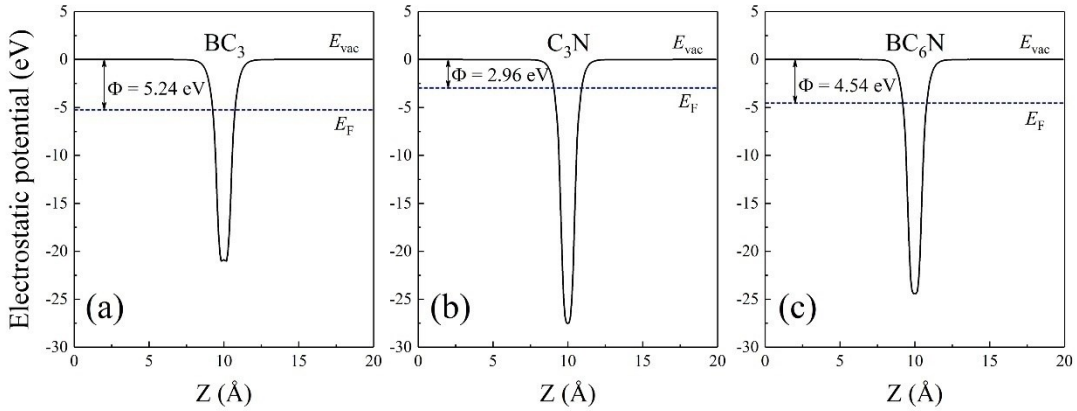

Figure S6 Electrostatic potentials of (a) BC_3, (b) C_3N and (c) BC_6N monolayers. The vacuum level is set to zero.

Table S1 Calculated interlayer spacing (d) and binding energy (E_b) of five stacking configurations for BC_3/C_3N heterostructures in our investigation.

Stacking Pattern	d (Å)	E_b (meV/atom)
AA	3.266	-29.36
AB	3.096	-36.99
AC	3.046	-39.33
AD	3.194	-32.55
AE	3.108	-36.14

Table S2 Calculated interlayer spacing (d) and binding energy (E_b) of eight stacking configurations for BC_3/BC_6N heterostructures in our investigation.

Stacking Pattern	d (Å)	E_b (meV/atom)
AA	3.323	-24.09
AB	3.171	-28.34
AC	3.176	-27.91
AD	3.182	-27.37
AE	3.239	-27.13
AF	3.204	-27.33
AG	3.166	-28.99
AH	3.178	-28.68

The adsorption energies of hydrogen and oxygen intermediates in the HER and OER on BC_3/C_3N and BC_3/BC_6N heterostructures are calculated using the following equations:

$$\Delta E_{H^*} = E_{monolayer+H} - E_{monolayer} - 1/2\ E(H_2)) \quad (1)$$

$$\Delta E_{O^*} = E_{monolayer+O} - E_{monolayer} - (E(H_2O) - E(H_2)) \quad (2)$$

$$\Delta E_{OH^*} = E_{monolayer+OH} - E_{monolayer} - (E(H_2O) - 1/2\ E(H_2)) \quad (3)$$

$$\Delta E_{OOH^*} = E_{monolayer+OOH} - E_{monolayer} - (2E(H_2O) - 3/2\ E(H_2)) \quad (4)$$

where $E_{monolayer+H}$, $E_{monolayer+O}$, $E_{monolayer+OH}$ and $E_{monolayer+OOH}$ are the total energies of BCN monolayers with the adsorption of H, O, OH and OOH on the active site (*), respectively. $E(H_2O)$ and $E(H_2)$ are the total energies of H_2O and H_2 molecules in free gas phases.

Table S3 Adsorption sites and energies ΔE of H* in the HER on BC_3/C_3N and BC_3/BC_6N heterostructures, according to Equation (1).

	Site	ΔE (eV)
C_3N in BC_3/C_3N	N	2.14
	C	0.53
BC_6N in BC_3/BC_6N	N	1.73
	C1(-B)	1.02
	C2(-N)	0.98
	B	1.36

Table S4 Adsorption sites and energies ΔE of O*, OH* and OOH* in the OER on BC_3/C_3N and BC_3/BC_6N heterostructures, according to Equations (2), (3) and (4).

	Intermediates	Site	ΔE (eV)
BC_3 in BC_3/C_3N	O*	B-C Bridge	0.21
	OH*	B	0.19
	OOH*	B	0.57
BC_3 in BC_3/BC_6N	O*	B-C Bridge	0.75
	OH*	B	0.71
		C	1.64
	OOH*	B	0.87

Table S5 Effective masses m^*, elastic modulus C_{2D}, deformation potentials E_d and mobilities μ for electrons (e) and holes (h) along the x and y directions of monolayer BC_3, C_3N, and BC_6N and bilayer BC_3/C_3N and BC_3/BC_6N heterostructures.

Materials (direction)	m^*/m_0		C_{2D} (N m^{-1})	E_d (eV)		μ (cm^{2}V^{-1}s^{-1})	
	e	h		e	h	e	h
BC_3 (x)	0.169	0.764	267.099	3.763	5.514	7083.18	786.17
BC_3 (y)	0.457	0.699	266.982	3.742	5.228	1518.07	465.21
C_3N (x)	0.618	0.148	371.635	5.078	8.321	1426.95	2452.46
C_3N (y)	0.683	0.353	371.570	4.807	4.814	1197.74	2090.79
BC_6N (x)	0.212	0.195	318.425	4.264	3.521	8735.55	13928.16
BC_6N (y)	0.184	0.177	318.361	4.721	3.400	9248.62	18536.67
BC_3/C_3N (x)	0.170	0.170	610.996	4.732	5.564	20299.69	14682.66
BC_3/C_3N (y)	0.452	0.400	610.906	3.890	5.341	4516.23	2707.13
BC_3/BC_6N (x)	0.167	0.225	568.357	3.835	6.042	25733.34	7674.79
BC_3/BC_6N (y)	0.472	0.190	573.550	3.764	5.493	6157.73	7182.72

Table S6 Mobilities for electrons (*e*) and holes (*h*) along the *x* and *y* directions of monolayer BC_3, C_3N, and BC_6N, under the compressive or tensile strains, comparable to the values in heterostructures (in units of $cm^2V^{-1}s^{-1}$).

Monolayer	Strain	*e*		*h*	
		x	*y*	*x*	*y*
BC_3	0	7083.18	1518.07	786.17	465.21
	-3.5%	8170.40	1832.74	810.55	600.87
C_3N	0	1426.95	1197.74	2452.46	2090.79
	3.5%	1181.86	1089.67	2058.58	1810.84
BC_6N	0	8735.55	9248.62	13928.16	18536.67
	2%	7912.19	8398.43	12444.62	16801.67

Table S7 Mobilities for electrons (*e*) and holes (*h*) along the *x* and *y* directions of component electrodes of BC_3/C_3N and BC_3/BC_6N heterostructures, participating in the HER and OER (in units of $cm^2V^{-1}s^{-1}$).

Heterostructure	Component electrode	*e*		*h*	
		x	*y*	*x*	*y*
BC_3/C_3N	BC_3	-	-	769.99	695.43
	C_3N	657.11	718.07	-	-
BC_3/BC_6N	BC_3	-	-	1179.53	1528.11
	BC_6N	7839.32	11176.18	-	-