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Insights into the mechanism of enhanced visible-light photocatalytic activity of black phosphorus/$BiVO_4$ heterostructure: a first-principles study

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1. The optimized geometry of black phosphorus/$BiVO_4$ heterostructure are shown in Figure S1. Considering four representational high-symmetric stacking patterns: (1) the underlayer of the phosphorene layer directly aligns with and above the top sites of the top O atom of $BiVO_4$(001) surface, denoted in the P1 structure (Figure S1 a-b). (2) the upper layer of the phosphorene layer aligns with the top O atom of $BiVO_4$(001) surface, denoted the P2 structure(Figure S1 b). (3) the middle-point of the top P-P bond of the phosphorene layer aligns with the top O atom of $BiVO_4$(001) surface, denoted the P3 structure (Figure S1 c). (4) the middle-point of the bottom of P-P bond of the phosphorene layer aligns with and above the hollow sites the top O atom of $BiVO_4$(001) surface, denoted in the P4 structure (Figure S1 d)

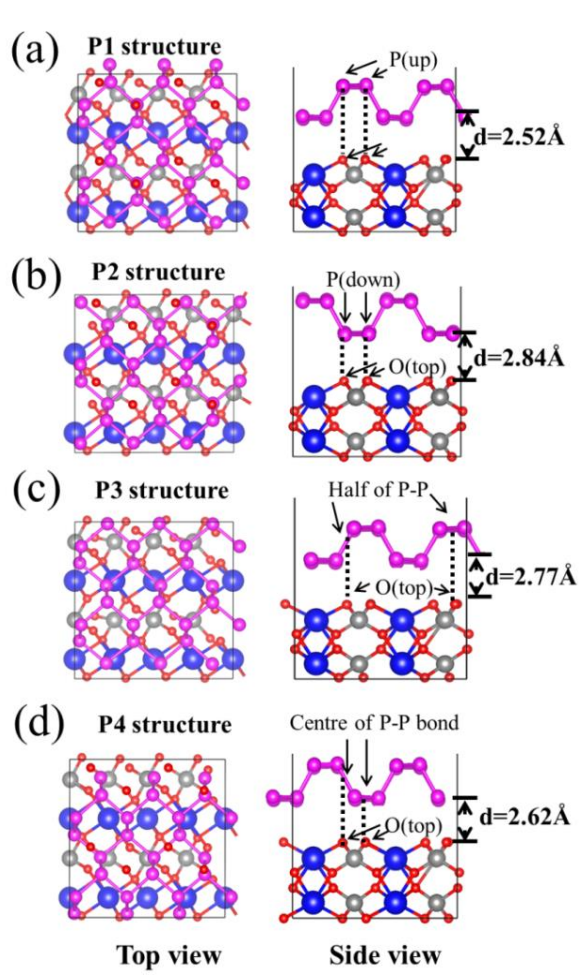

Figure S1: (a) The optimized geometry of black phosphorus/$BiVO_4$ heterostructure for P1(a), P2(b), P3(c), P4(d) structure, respectively.

2、Relative total energy of the four representational high-symmetric stacking patterns. The P4 structure demonstrates the lowest energy, which indicate that the P4 structure is most energetically favorable.

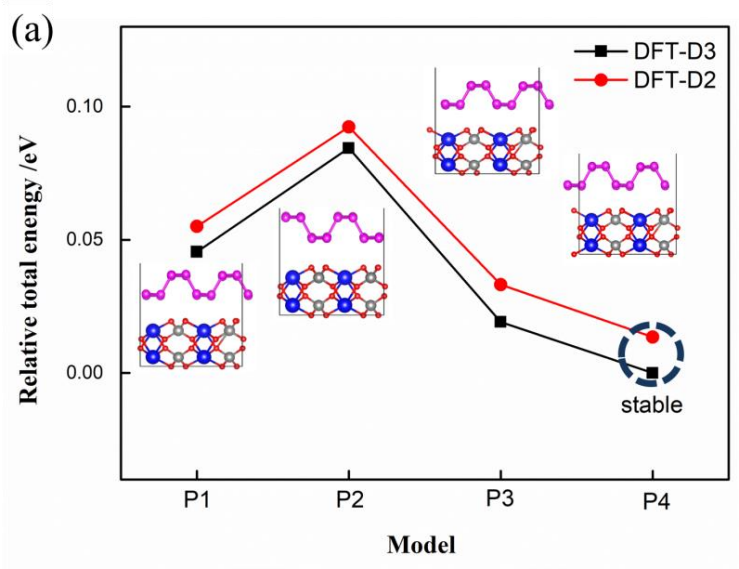

Figure S2: Relative total energy of the four representational high-symmetric stacking patterns calculated by DFT-D3 and DFT-D2 method, respectively.

Table 1. Band gaps of the referred materials.

Method	BP mono	BP bulk	$BiVO_4$ bulk	$BiVO_4$(001)	BP/$BiVO_4$	Source
photoluminescence (optical gap, eV)	2.0	0.35				Buscema[4]
	2.0-2.1	0.33				Gomez[6]
	1.45					Wang[7]
			2.4			Song[8]
			2.4	2.54		Xi[9]
electrical (mobility gap, eV)	0.98	0.30				Das[5]
Computation (band gap, eV)	2.0	0.3				Tran[1]
	1.94	0.43				Liang[2]
	1.51	0.36				Qiao[12]
	1.01	0.31				Liu[3]
	1.07	0.43				Gomez[6]
			2.16			Walsh[10]
			2.09/2.41(HSE)			Wadnerkar[11]
Computation (band gap, eV)	0.98	0.15	2.05	2.52	0.76	this work
	1.51	0.50	2.60	2.96	0.89	

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