Supplementary Materials

Improving Quantum Capacitance of Graphene-Based Supercapacitors by the Doping and Co-doping: A First Principles Calculations

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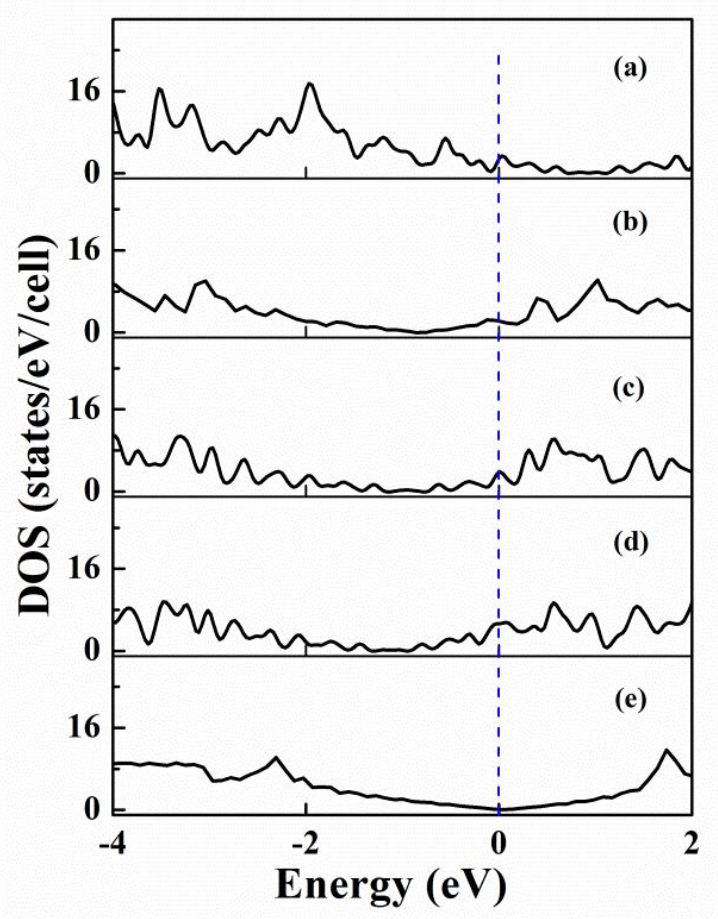

Figure S1. (a)-(e) Density of states (DOS) of quanternary B(N, P, S)-doped graphene, and pristine graphene, corresponding to Figure 1(a) with doping concentrations of 3.1%. Note that the total DOS are the sum of spin-up and spin-down bands.

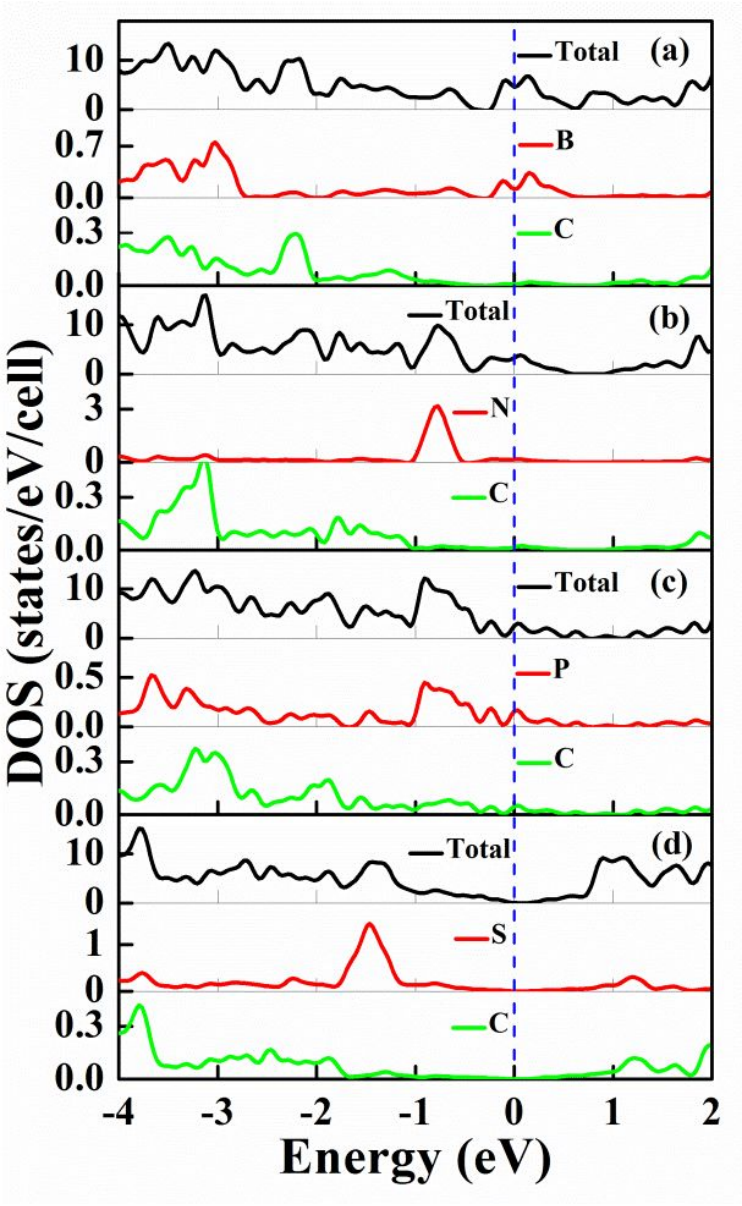

Figure S2. (a)-(d) Density of states (DOS) and local density of states (LDOS) of B, N, P and S of defected graphene model in Figure 1(b) with doping concentrations of 3.1%. Note that the total DOS and LDOS are the sum of spin-up and spin-down bands.

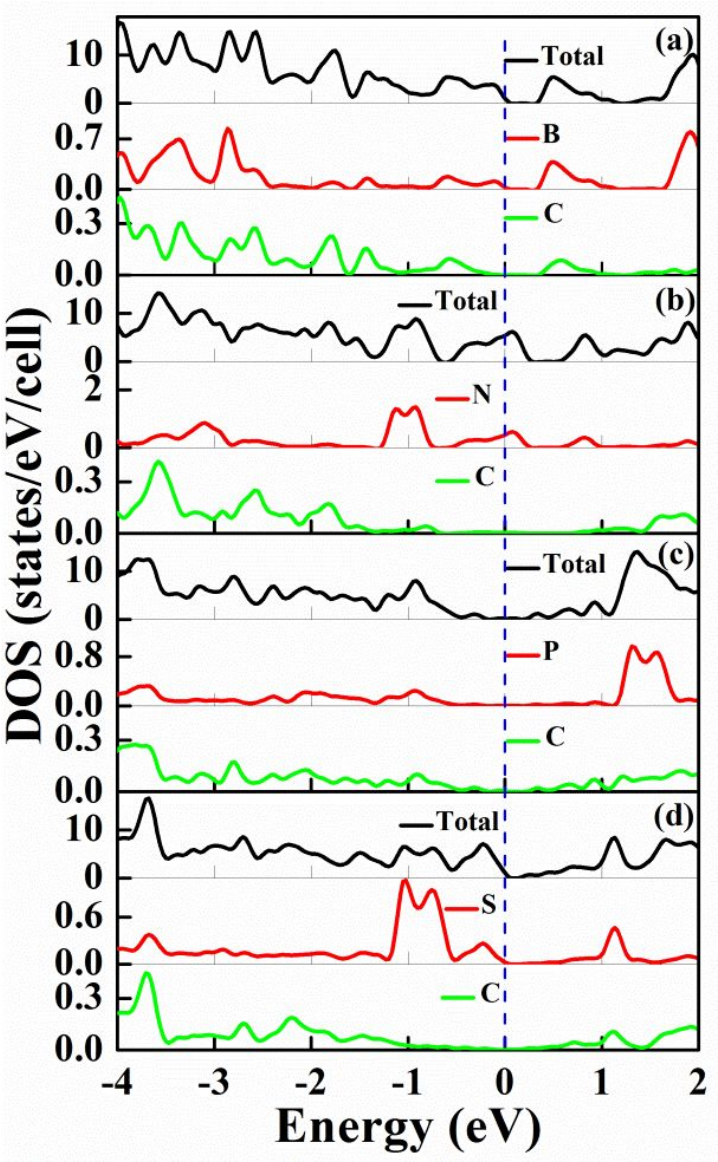

Figure S3. (a)-(d) Density of states (DOS) and local density of states (LDOS) of B, N, P and S of defected graphene model in Figure 1(c) with doping concentrations of 6.2%. Note that the total DOS and LDOS are the sum of spin-up and spin-down bands.

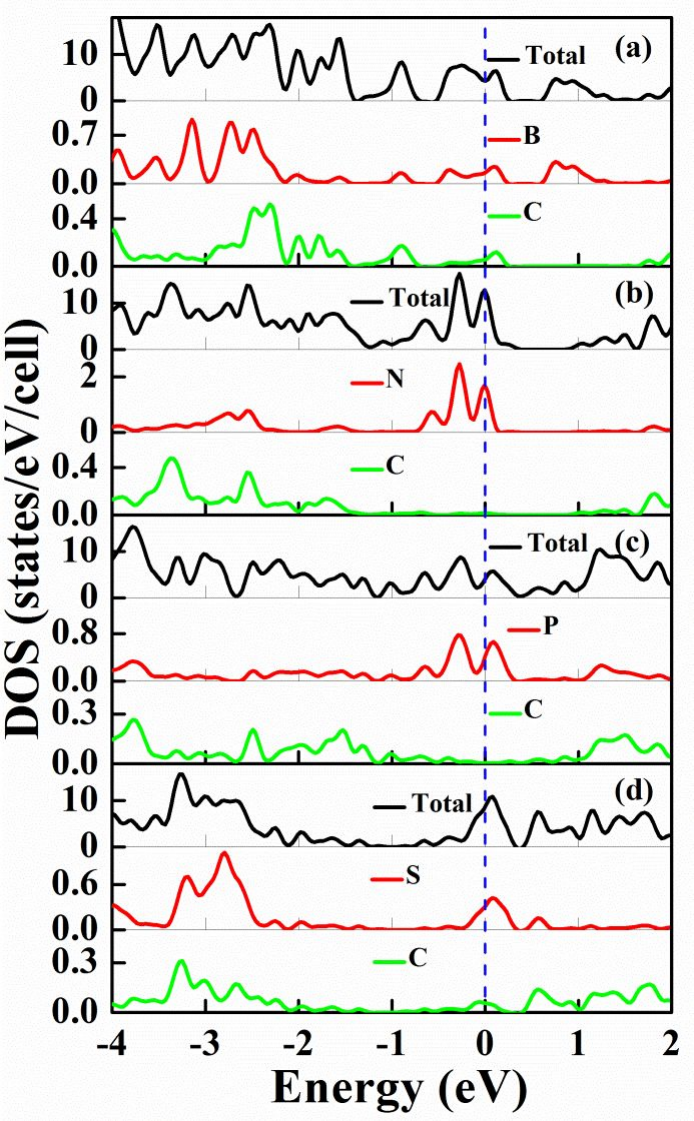

Figure S4. (a)-(d) Density of states (DOS) and local density of states (LDOS) of B, N, P and S of defected graphene model in Figure 1(d) with doping concentrations of 9.4%. Note that the total DOS and LDOS are the sum of spin-up and spin-down band.

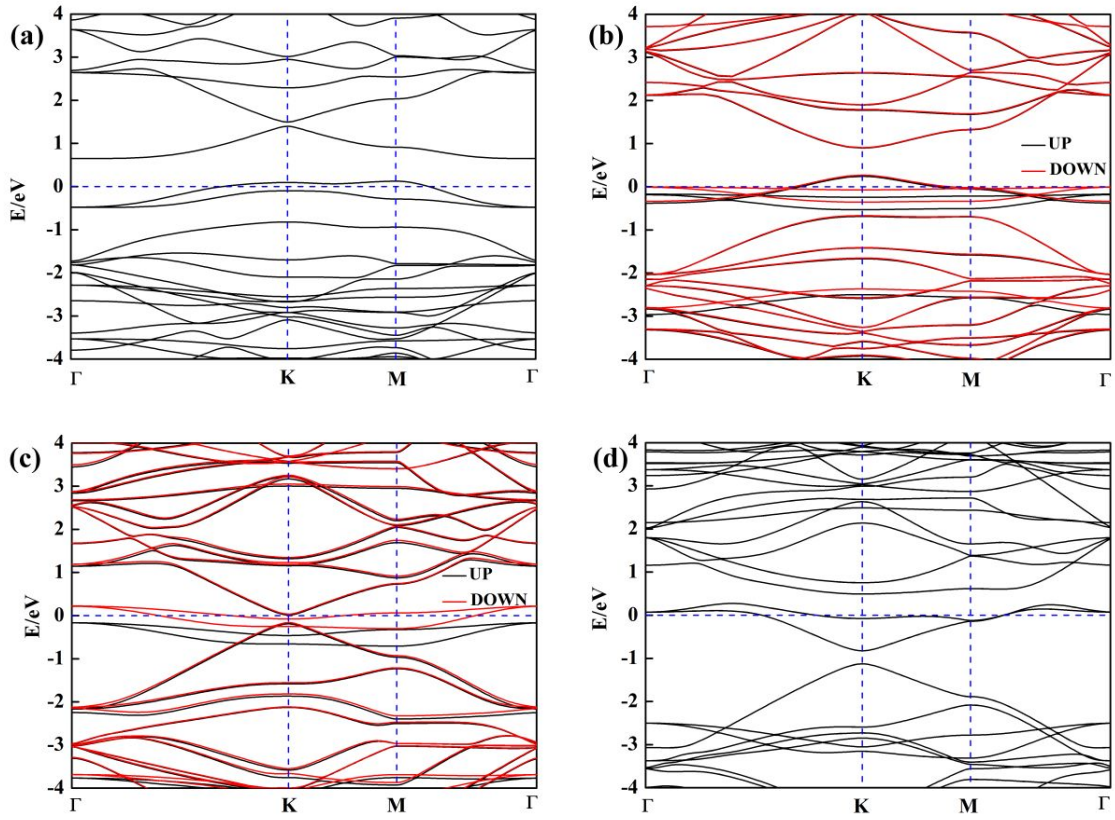

Figure S5. (a)-(d) The spin-up and spin-down band structures of B, N, P and S doping graphene model in Figure 1(d) with doping concentrations of 9.4%.

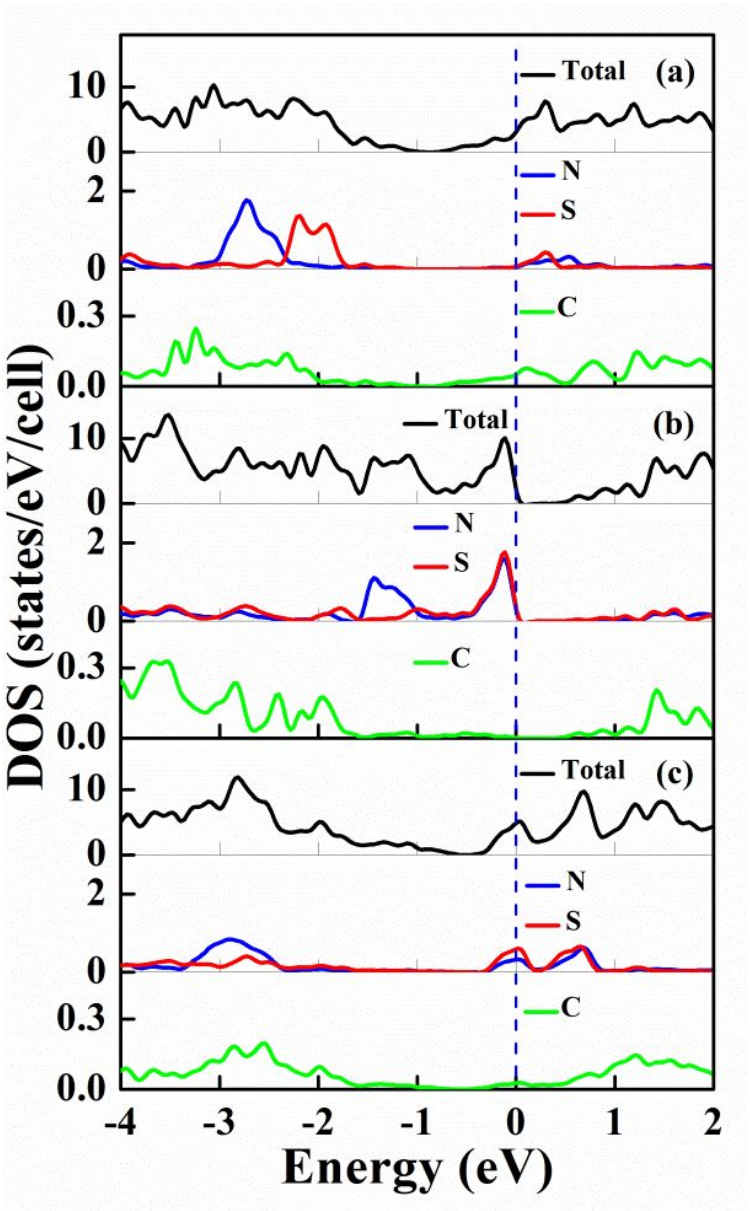

Figure S6. Density of states (DOS) and local density of states (LDOS) of defected graphene model in Figure 1(e)-(g) with N/S co-doping including (a) NSS, (b) NNS, (c) NS.

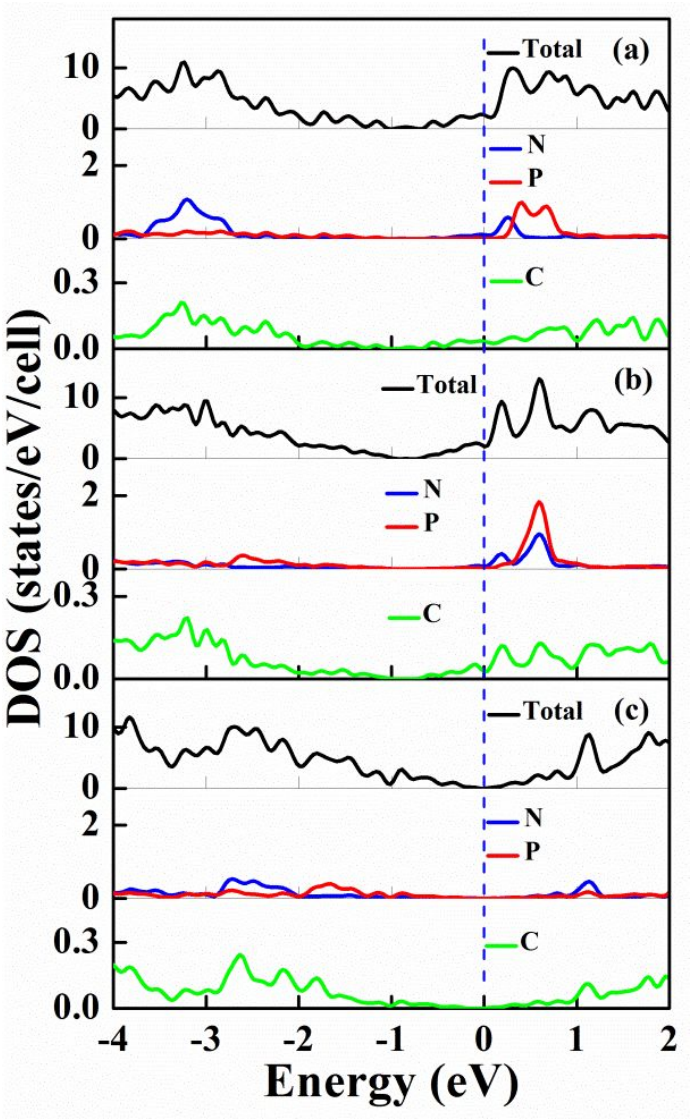

Figure S7. Density of states (DOS) and local density of states (LDOS) of defected graphene models in Figure 1(e)-(g) with N/P co-doping including (a) NPP, (b) NNP, (c) NP.

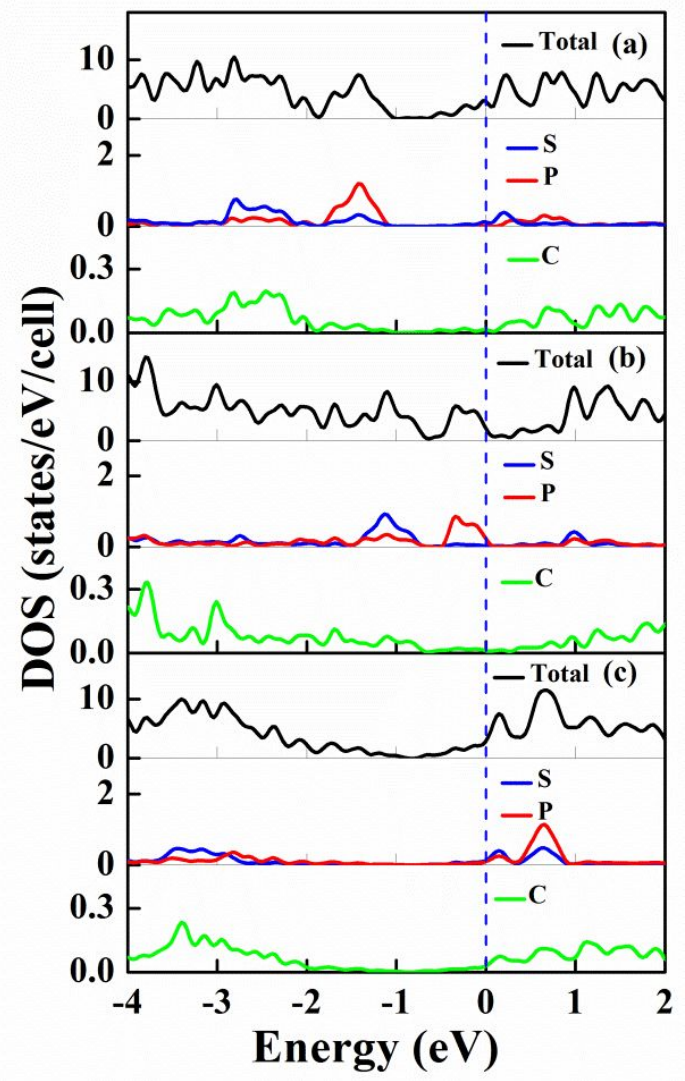

Figure S8. Density of states (DOS) and local density of states (LDOS) of defected graphene models in Figure 1(e)-(g) with P/S co-doping including (a) PSS, (b) PPS, (c) PS.

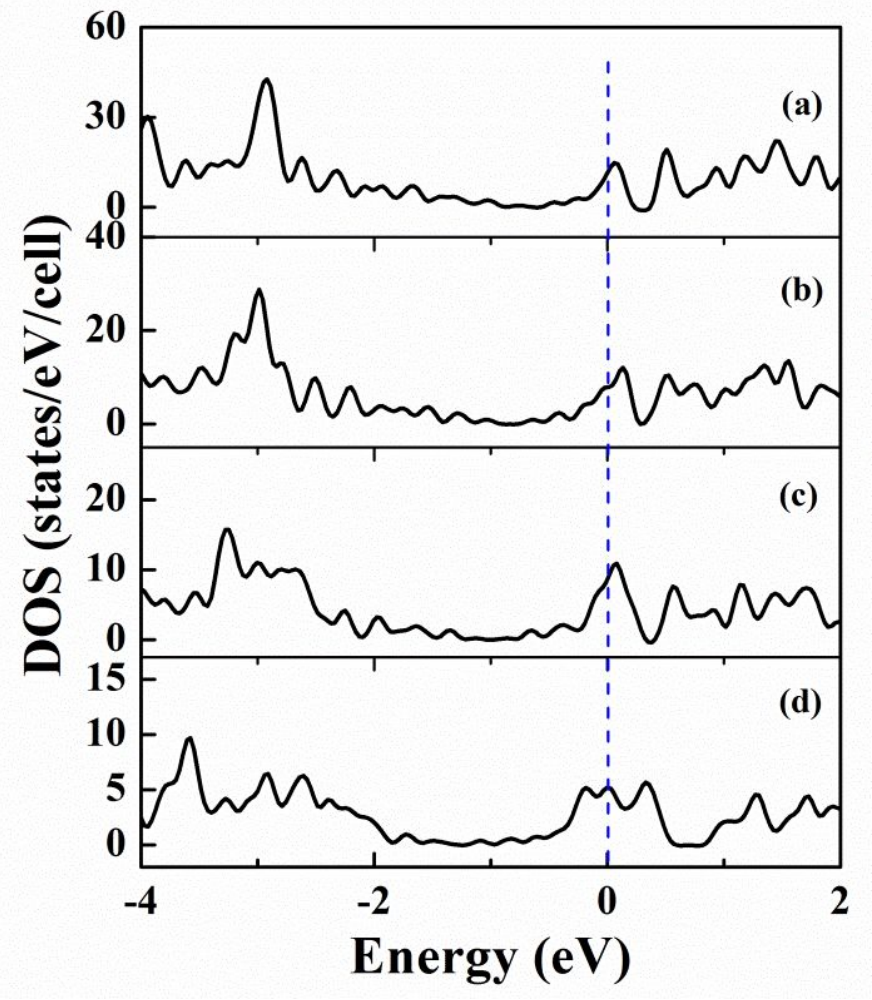

Figure S9. Density of states (DOS) of defected graphene model in Figure 1(d) with different triple S-doping concentrations including (a) 4.2%, (b) 6%, (c) 9.4%, and (d) 16.7%.

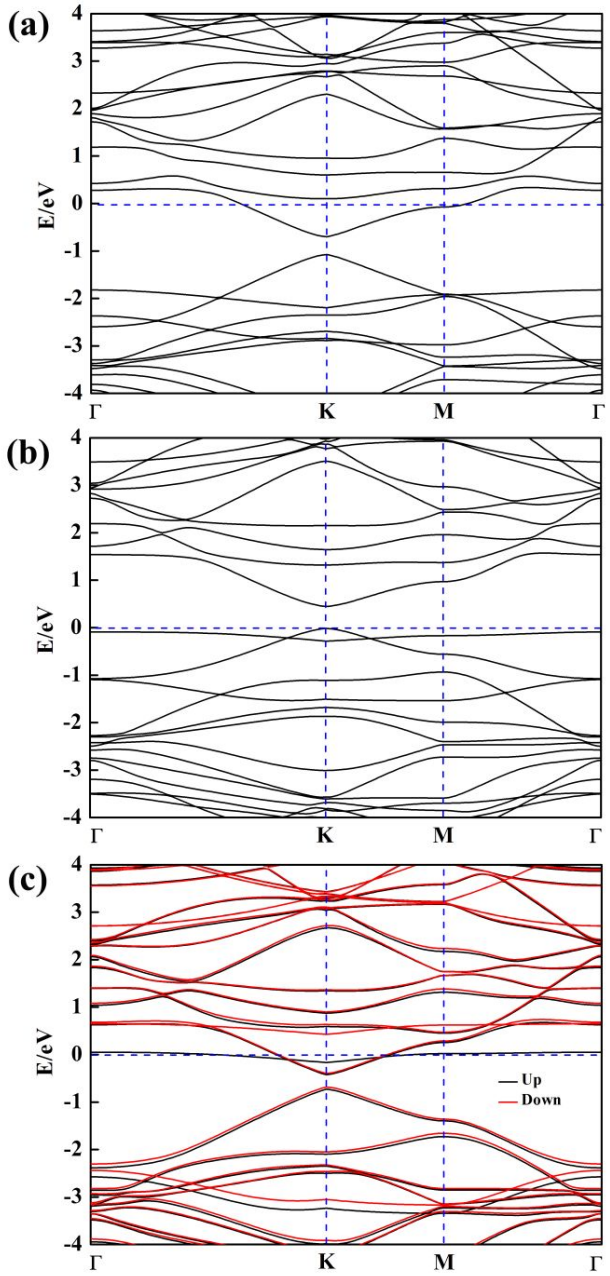

Figure S10. The spin-up and spin-down band structures of defected graphene model in Figure 1(e)-(g) with N/S co-doping including (a) NSS, (b) SNN, (c) NS.

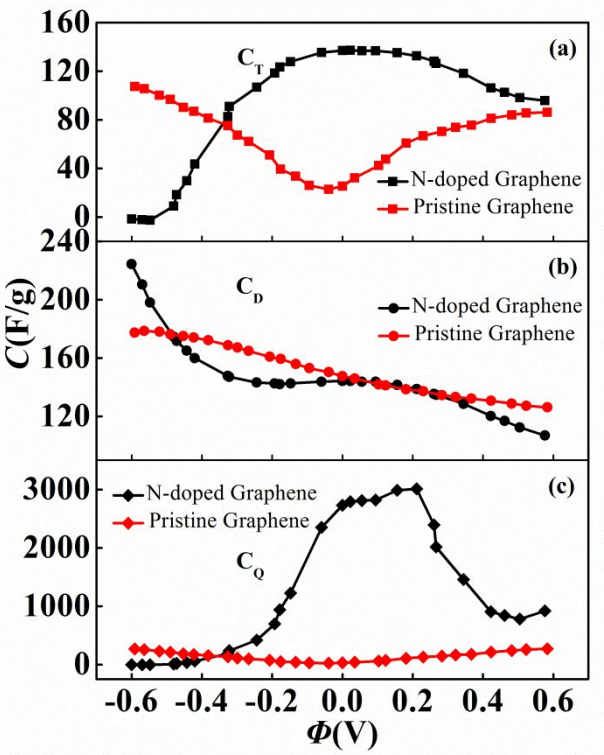

Figure S11. (a)Total interfacial capacitance(C_T), (b)Electric double-layer capacitance (C_D), and (c) quantum capacitance (C_Q) of nitrogen-doped and pristine graphene. The C_D capacitance is obtained from classical MD simulation for the 1 M NaCl aqueous electrolyte[23].

The formation energies of doped graphene for the four ways of doping in Figure 1are calculated by the formulas,

$$\Delta E_{q-N(B,P,S)}(x) = E_{df-\mathrm{G}}(x) - (n-1)\mu_C - \mu_{N(B,P,S)} \quad (1)$$

$$\Delta E_{1-N(B,P,S)}(x) = E_{df-\mathrm{G}}(x) - (n-1)\mu_C - \mu_{N(B,P,S)} \quad (2)$$

$$\Delta E_{2-N(B,P,S)}(x) = E_{df\text{-}\mathrm{G}}(x) - (n-2)\mu_C - 2\mu_{N(B,P,S)} \quad (3)$$

$$\Delta E_{3-N(B,P,S)}(x) = E_{df\text{-}\mathrm{G}}(x) - (n-3)\mu_C - 3\mu_{N(B,P,S)} \quad (4)$$

where $\Delta E_{q\text{-}N(B,P,S)}(x)$, $\Delta E_{3\text{-}N(B,P,S)}(x)$, $\Delta E_{2\text{-}N(B,P,S)}(x)$, and $\Delta E_{1\text{-}N(B,P,S)}(x)$ were the formation energies of quanternary-N (B, P and S) doping, single pyridine-B(N, P and S) doping, double pyridine-B(N, P and S) doping and triple pyridine-B(N, P and S) doping in Figure1(a)-(d), respectively. $E_{df\text{-}\mathrm{G}}(x)$ was the total energy of defect graphene with n atoms for seven types of doping graphene including the co-doping ways in Figure 1(e)-(g). μ_C, μ_N, μ_B, μ_P and μ_S represented the total energies per atom of pristine graphene, N_2 molecules, B_{12}, P_4 and S_8, respectively. N_2 molecules, bulk B_{12}, bulk P_4 and bulk S_8 are chosen to be as the reference states because they are the low-energy ground states of S, P, B and N, respectively. All the results were obtained with the supercells P(4 × 4) in Figure 1.

Table S1. Calculated parameters for B, N, P and S doping graphene with the models (a-g) in Figure 1, including X-X(C) bond distance, C-X-C bond angle, formation energy ΔE_f, charges located on adatom (ρ^B) and C atom obtained with Bader charge analysis.

System	Dopants (X)	*d(C-X)* Å	*d(X-X)* Å	*C-X-C* (deg)	ΔE_f (eV)	ρ^B charge (e)	Average of C charge(e)	$(C_Q)_{max}$ (μF/cm^2)
Model-a	B	1.48	-	120.01	1.25	+1.89	-0.06	55.1
	N	1.41	-	120.01	0.89	-1.26	+0.04	58.5
	P	1.61	-	120.01	3.74	+2.47	-0.08	90.3
	S	1.62	-	120.01	4.34	+0.19	-0.006	81.2
Model-b	B	1.52	-	110.51	6.53	+1.52	-0.05	58.2
	N	1.33	-	122.05	5.31	-1.16	+0.04	32.8
	P	1.85	-	88.91	3.62	+1.93	-0.06	26.4
	S	1.63	-	108.93	6.04	+0.58	-0.02	12.8
Model-c	B	1.49	2.27	114.92	5.29	+1.49	-0.11	49.6
	N	1.35	2.64	121.71	4.95	-1.19	+0.08	54.5
	P	1.69	1.92	105.83	5.69	+1.51	-0.11	9.2

	S	1.66	2.11	105.08	4.06	+0.55	-0.04	62.9
Model-d	B	1.52	2.16	111.36	4.66	+1.35	-0.14	70.9
	N	1.34	2.54	122.15	3.73	-1.19	+0.13	118.4
	P	1.67	2.11	107.58	7.77	+1.36	-0.15	75.3
	S	1.64	2.21	110.17	3.71	+0.51	-0.05	93.5
Model-e NNS	S	1.68	2.28(S-N)	102.41	1.79	+2.94	+0.09	83.3
	N	1.34	2.68(N-N)	123.91		-2.75		
	N	1.34				-2.75		
Model-f NSS	N	1.35	2.37(N-S)	123.19	2.57	-2.71	-0.04	67.1
	S	1.63	2.21(S-S)	108.63		+1.83		
	S	1.66				+1.94		
Model-g NS	S	1.88	2.13(S-N)	94.52	3.13	+0.49	+0.07	44.9
	N	1.35		122.77		-2.55		
	-	-		-		-		
Model-e NNP	N	1.37	2.59(N-N)	117.89	2.93	-2.83	+0.023	75.4
	N	1.44		117.89		-2.81		
	P	1.80	1.89(N-P)	92.91		+4.99		
Model-f NPP	N	1.36	2.38(N-P)	120.83	4.81	-2.65	-0.14	90.9
	P	1.69	1.96(P-P)	108.72		+3.23		
	P	1.67				+3.31		
Model-g NP	N	1.38	1.99(N-P)	119.38	2.45	-2.78	-0.076	8.1
	P	1.83		93.05		+4.99		
	-	-		-		-		
Model-e PPS	P	1.66	2.13(P-P)	107.60	6.06	+2.82	-0.29	53.1
	P	1.66		107.60		+2.80		
	S	1.66	2.11(P-S)	105.48		+2.56		
Model-f PSS	P	1.65	2.16(P-S)	109.06	4.72	+3.01	-0.31	62.6
	S	1.65	2.15(S-S)	107.78		+2.80		
	S	1.65		107.78		+2.85		
Model-g PS	P	1.79	2.07(P-S)	97.34	4.78	+4.99	-0.22	63.3
	S	1.62		113.99		+1.26		
	-	-		-		-		