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

How Size, Edge Shape, Functional Group and Embeddedness Influence Electronic Structure and Partial Optical Properties of Graphene Nanoribbons

Jin Feng,[a] Xinlong Mao,[a] Hongxia Zhu,[b] Mengdi Cui,[a] Zhe yang,[a] Yuchen Ma,[c] Dapeng Zhang,[a]* Siwei Bi[a]*

a. School of Chemistry and Chemical Engineering, Qufu Normal University, P. R. China

b. School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Science)

c. School of Chemistry and Chemical Engineering, Shandong University

*Corresponding author: Dapeng Zhang; Siwei Bi.

E-mail: zdp1014636837@hotmail.com; siweibi@126.com

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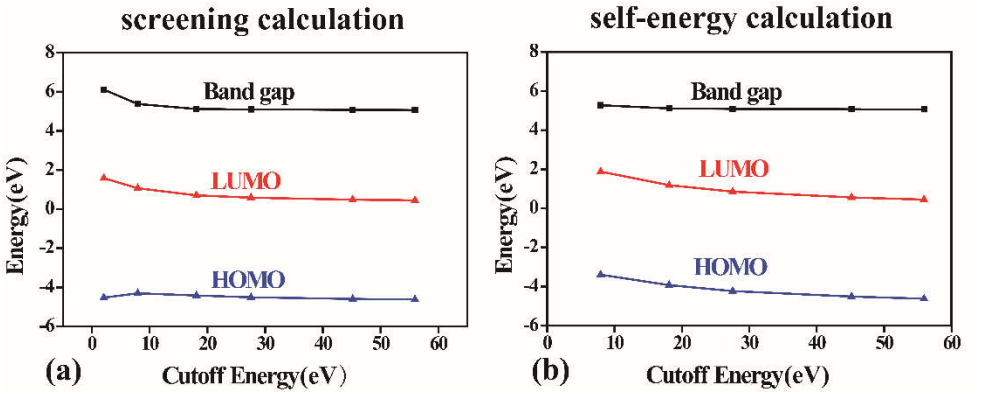


Figure S1 Calculated GW HOMO, LUMO and band gap energies of AGNR-NH_2 with the number of graphene rings 8 versus cutoff energy of unoccupied orbitals in the screening calculation(a) and self-energy calculation (b). The cutoff energy is relative to the CBM energy.

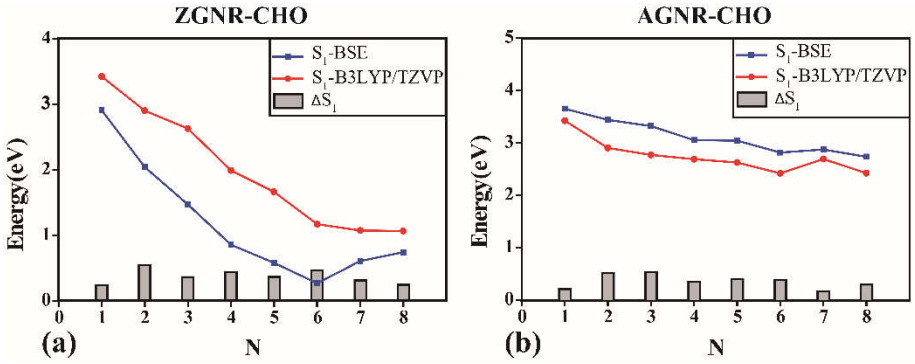
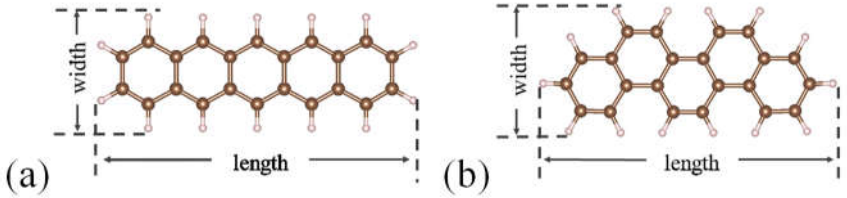


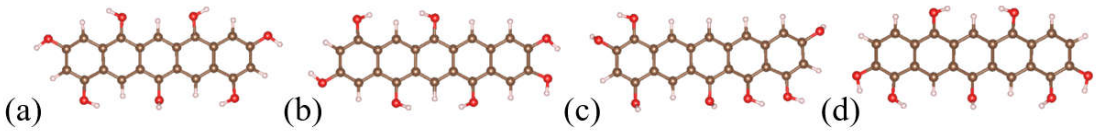
Figure S2 The first excited state S_1 obtained by BSE method and TDDFT at the B3LYP/TZVP level, and △S is the energy difference between the two methods.



(c)

ZGNRs	Width (Å)	Length (Å)	AGNRs	Width (Å)	Length (Å)
3Z-COOH	9.28	13.64	**3A-COOH**	10.28	9.33
3Z-CHO	7.34	11.69	**3A-CHO**	8.33	9.71
3Z-NH2	8.14	9.12	**3A-NH2**	6.93	11.48
3Z-OH	7.22	11.21	**3A-OH**	7.15	9.25
ZGNR-H (N=1)	4.97	4.31	**AGNR-H (N=1)**	5.55	4.31
ZGNR-H (N=2)	4.97	6.74	**AGNR-H (N=2)**	5.55	6.74
ZGNR-H (N=3)	4.97	9.20	**AGNR-H (N=3)**	5.55	9.27
ZGNR-H (N=4)	4.97	11.65	**AGNR-H (N=4)**	5.55	11.48
ZGNR-H (N=5)	4.97	14.11	**AGNR-H (N=5)**	5.55	13.59
ZGNR-H (N=6)	4.97	16.56	**AGNR-H (N=6)**	5.55	15.78
ZGNR-H (N=7)	4.97	19.01	**AGNR-H (N=7)**	5.55	17.90
ZGNR-H (N=8)	4.97	21.47	**AGNR-H (N=8)**	5.55	20.08

Figure S3 (a) and (b) are the structures for ZGNR and AGNR. (c) is the width and length for GNRs.



(e)

Energy	S1 (eV)	T1 (eV)	T2 (eV)	VBM (GW)	CBM (GW)	dipole moment (electrons x Angstroem)
a	1.78	0.64	1.75	-5.31	-0.62	0.000032
b	1.74	0.59	1.78	-5.09	-0.50	0.106091
c	1.79	0.64	1.79	-5.06	-0.52	0.379262
d	1.69	0.59	1.72	-5.14	-0.55	0.000004

Figure S4 (a) is an axisymmetric structure for 5-ZGNR-OH as shown in Fig. 1. (d) is another axisymmetric 5-ZGNR-OH. (b) and (c) are two asymmetric structures for 5-ZGNR-OH. The excited states are obtained from TDDFT method, while the orbital energy from GW method.

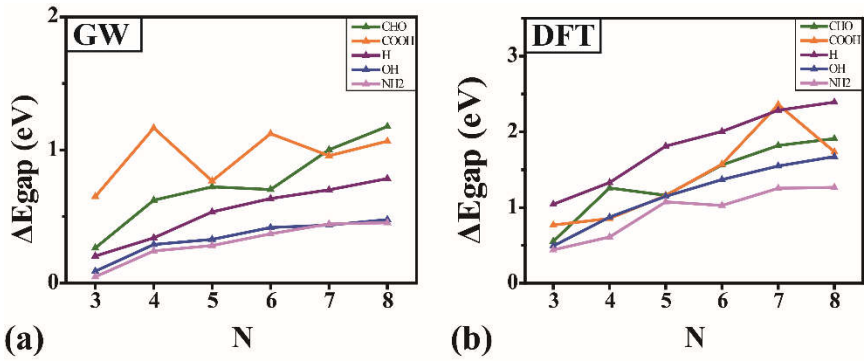


Figure S5 The difference of band energy between AGNRs and ZGNRs in GW method (a) and DFT method (b).

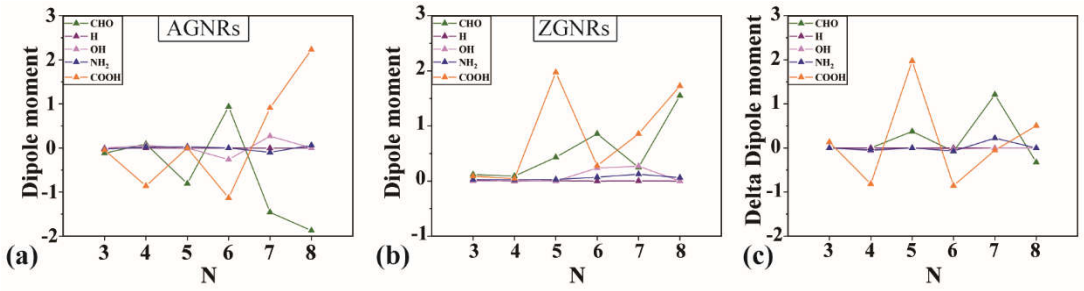


Figure S6 The dipole moment for AGNRs (a) and ZGNRs (b), and the delta dipole moment between them(c), where the unit is electrons x Angstroem.

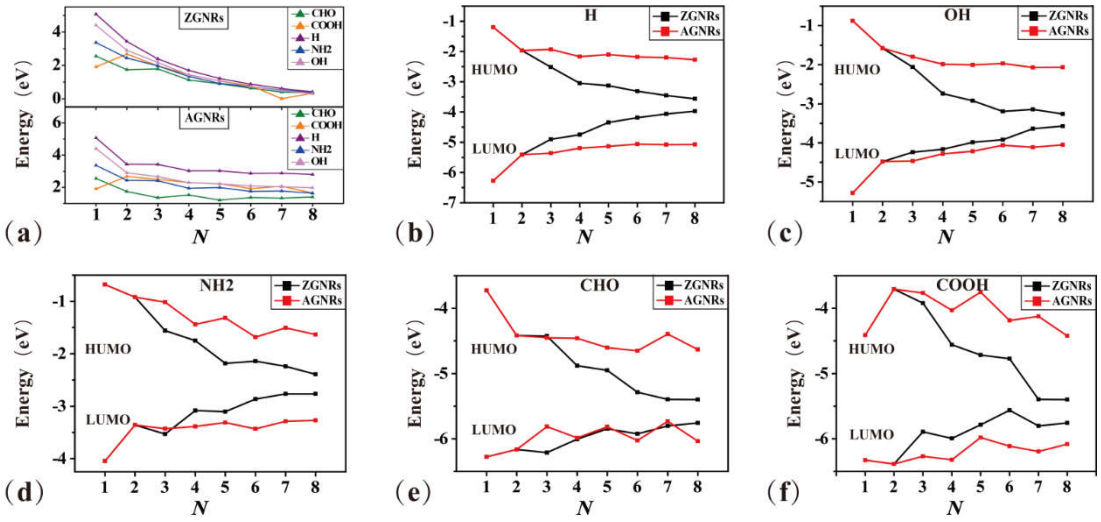


Figure S7 (a) is the band gap for ZGNRs and AGNRs, whose structures are shown in Figure 1, with N from 1 to 8. (b), (c), (d), (e) and (f) are the energies of HOMO and LUMO for GNRs, where the R presents H, OH, NH_2, CHO and COOH, respectively. All data are obtained by DFT method. The vacuum energies (E_v) of all GNRs are set to 0.

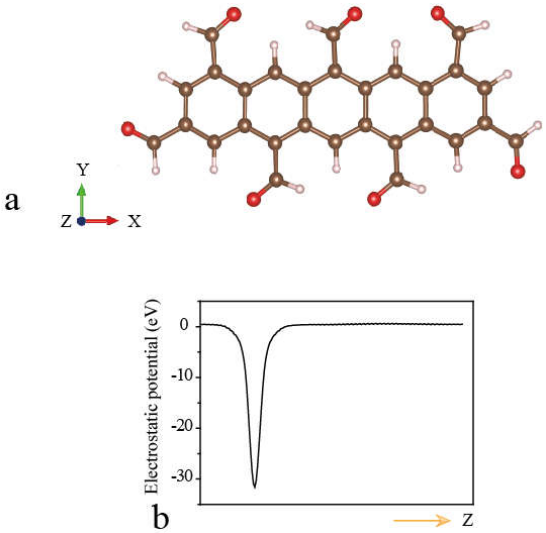
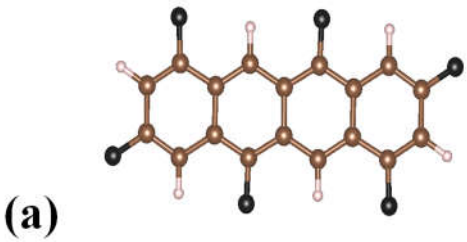
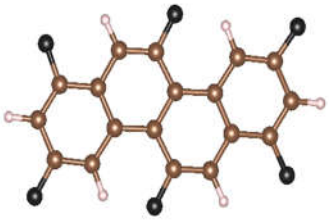


Figure S8 (a) Structure, (b) electrostatic potential and (c) orbital energies of CN-H-dot with n=4.

As shown in Fig. S8a, the planar CN-dot is placed on the XY plane and the direction of the vacuum layer is Z. The electrostatic potential in Fig. S8b changes with Z, and the highest steady electrostatic potential is set to be vacuum energy level. When the energies of orbitals are adjusted with respect to the vacuum energy level (set to zero), energy levels in DFT for different CN-dots become comparable.



(a)



(b)

(c)

Number of charge	CHO	COOH	NH_2	OH
ZGNRs	-0.5388	-0.3208	2.2109	2.7600
AGNRs	-0.5004	-0.2240	2.1139	2.5848

Figure S9 The structures for ZGNRs (a) and AGNRs (b) with N=4, where the C atom, H atom and R are shown in brown, pink and black. The number of charge for the C atoms in brown in (a) and (b) is shown in (c) while R are CHO, COOH, H, NH_2 and OH.

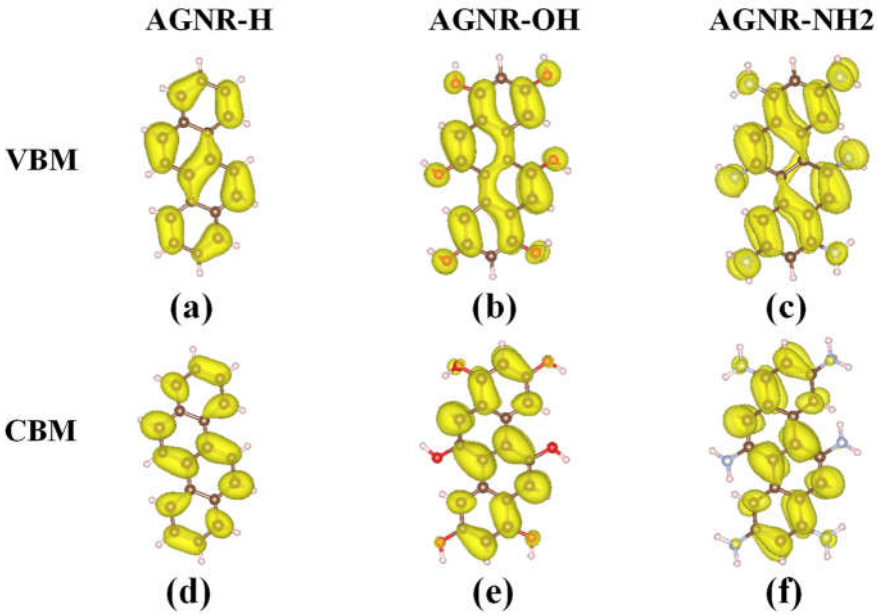


Figure S10 The orbital distributions for AGNR-H, AGNR-OH and AGNR-NH_2.

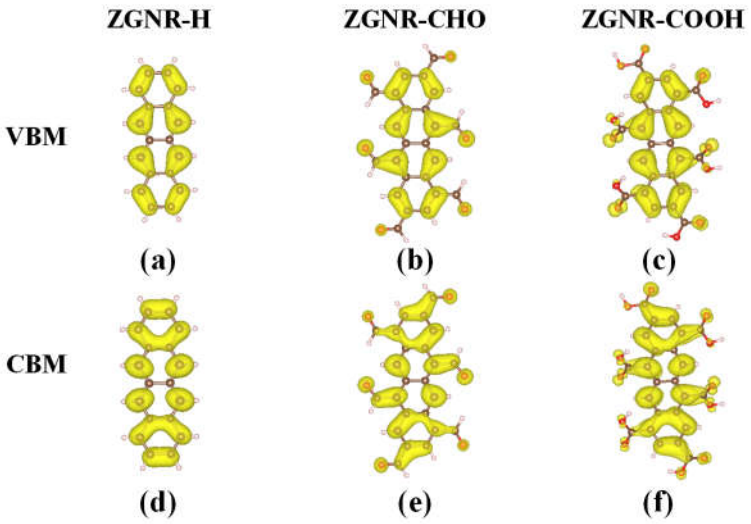


Figure S11 The orbital distributions for ZGNR-H, ZGNR-CHO and ZGNR-COOH.

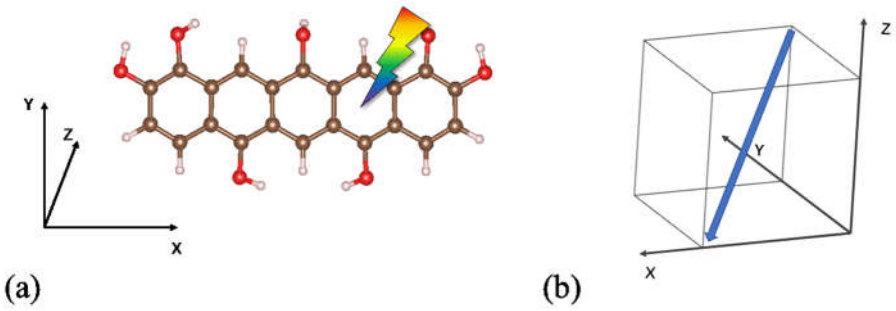


Figure S12 (a) The structure of GNR in the x, y plane. (b) The bule line indicates the direction of incident light.

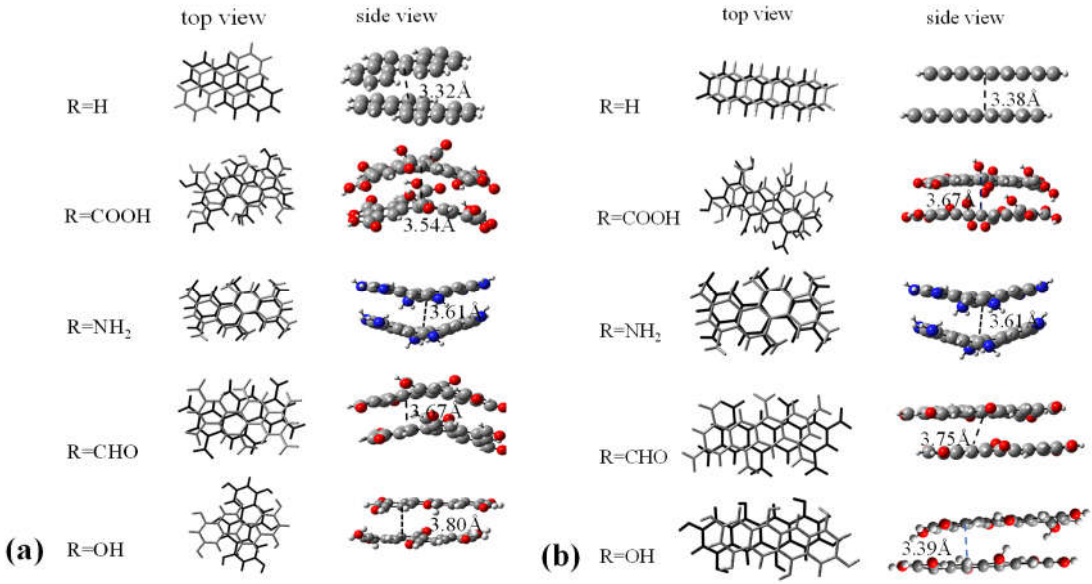


Figure S13 The structures for AGNRs dimer (a) and ZGNRs dimer (b) with N=4.

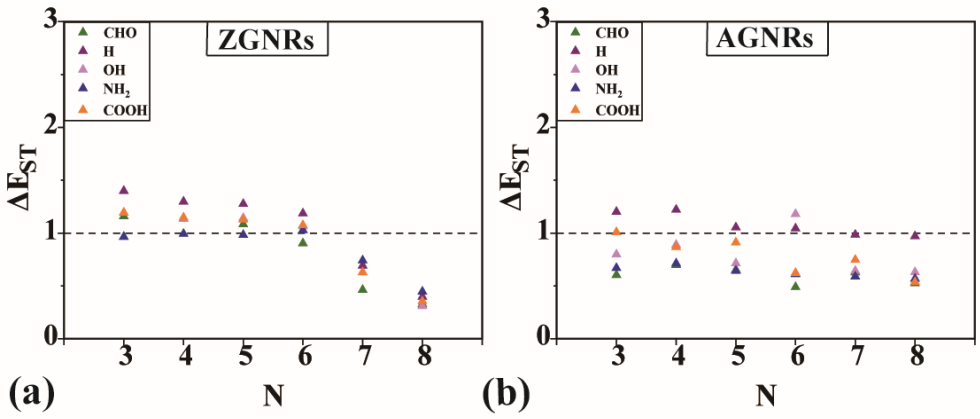


Figure S14 The energy difference between S_1 and T_1 ($\triangle E_{ST}$).

ZGNRs	OH			CHO			COOH			NH2			H		
N	S1	T2	T1	S1	T2	T1	S1	T2	T1	S1	T2	T1	S1	T2	T1
1	5.13	4.53	3.80	3.42	2.43	2.91	4.50	4.01	3.27	4.77	4.29	3.72	5.37	4.68	3.75
2	3.83	3.55	2.67	2.90	2.55	2.04	3.61	3.27	2.38	3.34	3.21	2.36	4.41	3.98	2.77
3	3.02	3.03	1.83	2.63	2.46	1.47	2.81	2.76	1.61	2.74	2.68	1.78	3.26	3.32	1.86
4	2.19	2.30	1.05	1.99	1.89	0.86	2.19	2.17	1.05	2.08	2.21	1.09	2.50	2.54	1.20
5	1.78	1.75	0.64	1.66	1.54	0.58	1.76	1.73	0.64	1.59	1.58	0.60	1.96	1.94	0.68
6	1.37	1.32	0.30	1.17	1.24	0.27	1.45	1.33	0.37	1.35	1.31	0.33	1.56	1.46	0.38
7	1.20	1.22	0.57	1.07	1.06	0.61	1.17	1.11	0.54	1.16	1.09	0.42	1.38	1.34	0.69
8	1.07	1.16	0.76	1.07	1.01	0.74	1.07	1.03	0.72	1.07	0.99	0.62	1.27	1.25	0.87

Table S1 The values of S_1, T_1 and T_2 for ZGNRs by TDDFT.

AGNRs	OH			CHO			COOH			NH2			H		
N	S1	T2	T1	S1	T2	T1	S1	T2	T1	S1	T2	T1	S1	T2	T1
1	5.13	4.53	3.80	3.42	2.43	2.91	4.50	4.01	3.27	4.77	4.29	3.72	5.37	4.68	3.75
2	3.83	3.55	2.67	2.90	2.55	2.04	3.61	3.27	2.38	3.34	3.21	2.36	4.41	3.98	2.77
3	3.42	2.79	2.62	2.77	2.59	2.17	3.39	2.93	2.39	3.18	2.58	2.51	3.99	3.49	2.79
4	3.11	2.92	2.23	2.69	2.43	1.99	3.08	2.68	2.21	2.69	2.47	1.98	3.78	3.24	2.56
5	2.96	2.48	2.24	2.63	2.27	1.97	3.05	2.57	2.14	2.73	2.29	2.09	3.60	2.97	2.55
6	3.31	2.58	2.13	2.42	2.20	1.93	2.72	2.43	2.10	2.47	2.24	1.85	3.52	2.86	2.48
7	2.78	2.38	2.14	2.69	2.20	2.06	2.85	2.36	2.11	2.48	2.18	1.90	3.45	2.75	2.46
8	2.72	2.39	2.09	2.42	2.13	1.90	2.47	2.26	1.93	2.32	2.02	1.76	3.41	2.69	2.44

Table S2 The values of S_1, T_1 and T_2 for AGNRs by TDDFT.

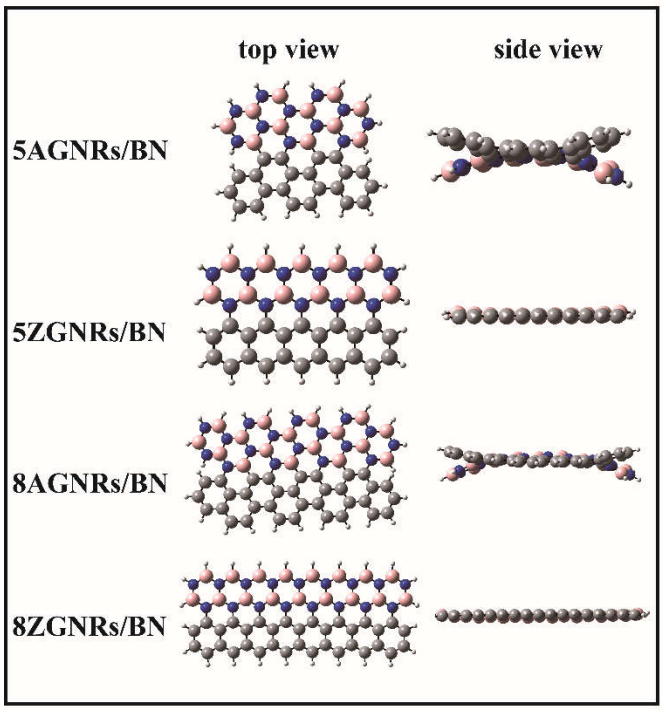


Figure S15 The structures for GNRs-H/BN with N=5 and N=8.

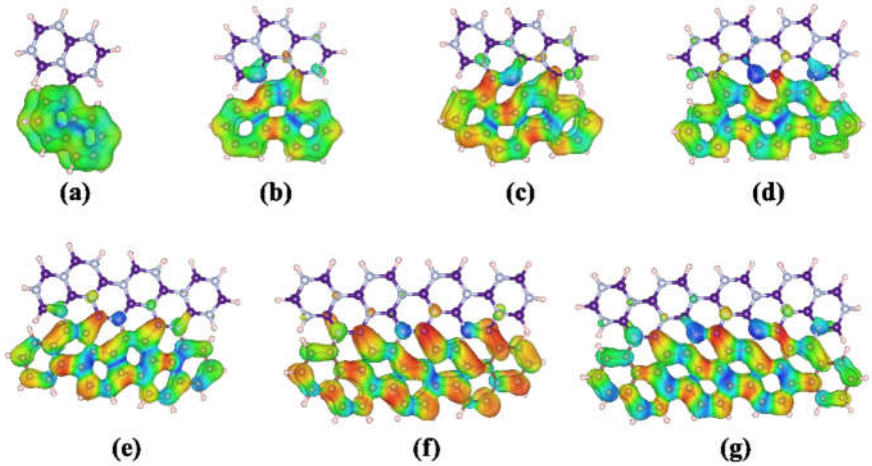


Figure S16 The electron (blue) and hole (red) distributions for AGNRs/BN.

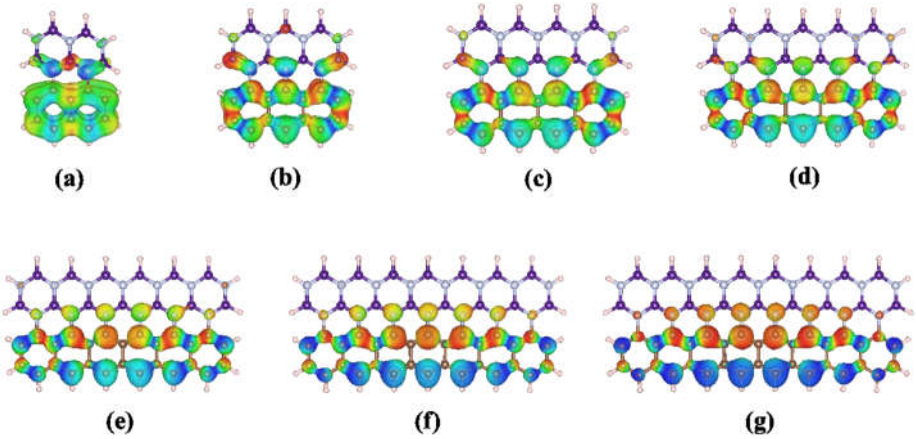


Figure S17 The electron (blue) and hole (red) distributions for ZGNRs/BN-N.

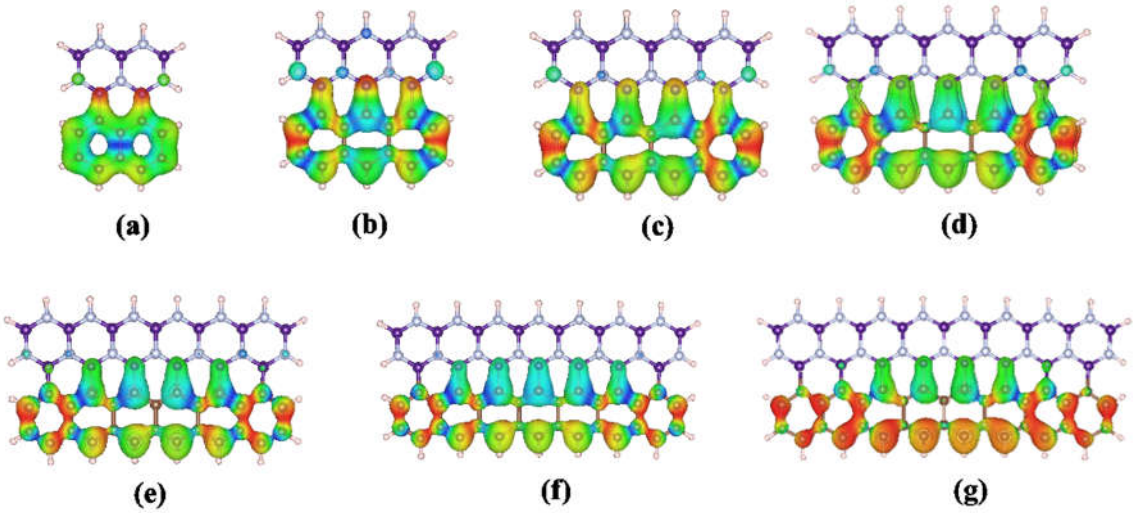


Figure S18 The electron (blue) and hole (red) distributions for ZGNRs/BN-C.