Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Data

Strain-induced Dirac cone-like electronic structures and semiconductor-semimetal transition in graphdiyne

Hui-Juan Cui[1], Xian-Lei Sheng[2], Qing-Bo Yan[3], Qing-Rong Zheng[1], and Gang Su[1*]

[1]*School of Physics, University of Chinese Academy of Sciences, P. O. Box 4588, Beijing 100049, China*

[2]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P. O. Box 4588, Beijing 100190, China*

[3]*College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, P. O. Box 4588, Beijing 100049, China*

1. Tight-binding model for graphdiyne under biaxial strain and no strain

For convenience of characterizing the hopping matrix, we label each carbon atom by a number as in Fig. S1.

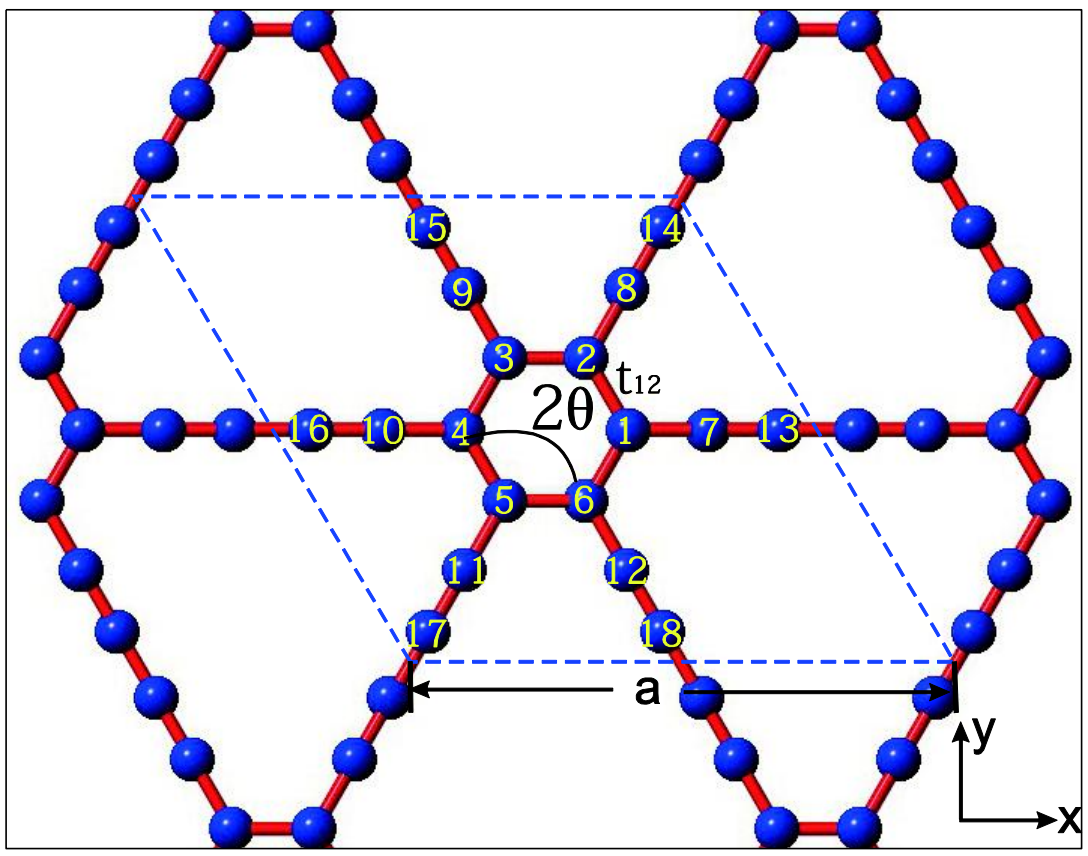

Fig. S1. Schematic structure of graphdiyne, and the label of carbon atoms in a unit cell (the parallelogram) for the hopping matrix of Hamiltonian. $t_{i,j}$ is defined as the hopping amplitude between site i and site j labeled by numbers (from 1 to 18).

The Hamiltonian can be written as in Wannier representation

$$\hat{H} = \sum_{\vec{r},\vec{\delta}} \hat{\psi}^{\dagger}_{\vec{r}} T_{\vec{\delta}} \hat{\psi}_{\vec{r}+\vec{\delta}} \tag{1}$$

where $\hat{\psi} = (\hat{c}_{\vec{r},1}, \hat{c}_{\vec{r},2}, \hat{c}_{\vec{r},3}, \hat{c}_{\vec{r},4} \cdots \hat{c}_{\vec{r},17}, \hat{c}_{\vec{r},18})$, and $\delta = \{\vec{e}_x, \vec{e}_y, -\vec{e}_x, -\vec{e}_y, 0\}$. After making Fourier transform, we have

$$\hat{H} = \hat{\psi}^{\dagger}_{\vec{k}} \mathrm{H}_{\vec{k}} \hat{\psi}_{\vec{k}} \tag{2}$$

with

$$H_{\vec{k}} = \sum_{\vec{\delta}} T_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}} = \begin{pmatrix}
0 & t_1 & 0 & 0 & 0 & t_1 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_1 & 0 & t_1 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & t_1 & 0 & t_1 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & t_1 & 0 & t_1 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & t_1 & 0 & t_1 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_1 & 0 & 0 & 0 & t_1 & 0 & 0 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 \\
0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 \\
0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 \\
0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 \\
0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 \\
0 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 \\
0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{ik_x} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{i(k_x\cos\theta + k_y\sin\theta)} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{i(-k_x\cos\theta + k_y\sin\theta)} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & t_4 e^{-ik_x} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & t_4 e^{i(-k_x\cos\theta - k_y\sin\theta)} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & t_4 e^{i(k_x\cos\theta - k_y\sin\theta)} & 0 & 0 & 0
\end{pmatrix}$$

where k_x and k_y are the x and y components of momentum of π electrons, and the lattice spacing a_0=1 is taken. For the unstrained graphdiyne, there are four independent hopping amplitudes t_1, t_2, t_3, t_4, and the corresponding values are listed in Table 1. Because of its C_{6v} symmetry, we have $t_{1,2} = t_{2,3} = t_{3,4} = t_{4,5} = t_{5,6} = t_{6,1} = t_1$; $t_{1,7} = t_{2,8} = t_{3,9} = t_{4,10} = t_{5,11} = t_{6,12} = t_2$; $t_{7,13} = t_{8,14} = t_{9,15} = t_{10,16} = t_{11,17} = t_{12,18} = t_3$; $t_{13.16} = t_{14,17} = t_{15,18} = t_{16,13} = t_{17,14} = t_{18,15} = t_4$, respectively.

For the case under biaxial strains, the Hamiltonian is the same as that for the unstrained case due to the same symmetry.

Table S1. The values of t and θ for different strains

strain	$t_1\ (eV)$	$t_2\ (eV)$	$t_3\ (eV)$	$t_4\ (eV)$	θ°
no strain	-3.4655	-3.5371	-4.0475	-3.6752	60
biaxial (5%)	-3.2675	-3.2360	-3.8162	-3.3662	60
biaxial (9%)	-3.0694	-2.9159	-3.5850	-3.0692	60
biaxial (15%)	-2.6734	-2.2156	-3.1224	-2.3492	60

For graphene, there is only one independent parameter $t = -2.7(eV)$.

2. Tight-binding model for graphdiyne under uniaxial strain

For the uniaxial strain (armchair and zigzag direction), there are eight independent t_{ij} due to the broken symmetry of graphdiyne, $t_{1,2} = t_{1,6} = t_{3,4} = t_{4,5} = t_1$; $t_{2,3} = t_{5,6} = t_1'$; $t_{1,7} = t_{10,4} = t_2$; $t_{8,2} = t_{3,9} = t_{5,11} = t_{6,12} = t_2'$; $t_{7,13} = t_{10,16} = t_3$; $t_{8,14} = t_{9,15} = t_{11,17} = t_{12,18} = t_3'$; $t_{13,16} = t_{16,13} = t_4$; $t_{14,17} = t_{15,18} = t_{17,14} = t_{18,15} = t_4'$. The Hamiltonian matrix has the form of

$$H_{\vec{k}}' = \begin{pmatrix}
0 & t_1 & 0 & 0 & 0 & t_1 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_1 & 0 & t_1' & 0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & t_1' & 0 & t_1 & 0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & t_1 & 0 & t_1 & 0 & 0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & t_1 & 0 & t_1' & 0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_1 & 0 & 0 & 0 & t_1' & 0 & 0 & 0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 \\
t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 \\
0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & 0 & 0 \\
0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & 0 \\
0 & 0 & 0 & t_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 \\
0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 \\
0 & 0 & 0 & 0 & 0 & t_2' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' \\
0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{2ik_x\cos\theta} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{i(k_x\cos\theta+k_y\sin\theta)} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_4 e^{i(-k_x\cos\theta+k_y\sin\theta)} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3 & 0 & 0 & t_4 e^{-2ik_x\cos\theta} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & t_4 e^{i(-k_x\cos\theta-k_y\sin\theta)} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & t_3' & 0 & 0 & t_4 e^{i(k_x\cos\theta-k_y\sin\theta)} & 0 & 0 & 0
\end{pmatrix}$$

Table S2. The fitting values of t for different cases

strain	$t_1(eV)$	$t_1'(eV)$	$t_2(eV)$	$t_2'(eV)$	$t_3(eV)$	$t_3'(eV)$	$t_4(eV)$	$t_4'(eV)$	θ°
Armchair (5%)	-3.20	-3.11	-3.20	-3.37	-3.73	-3.81	-3.36	-3.52	58.13
Armchair (9%)	-3.02	-2.94	-2.49	-3.16	-3.27	-3.58	-2.69	-3.30	56.69
Armchair(15%)	-2.62	-2.49	-1.76	-2.76	-2.98	-3.12	-2.08	-2.88	54.54
Zigzag (5%)	-3.11	-3.19	-3.34	-2.89	-3.72	-3.64	-3.45	-3.30	62.87
Zigzag (9%)	-2.83	-2.99	-3.47	-2.87	-3.49	-3.70	-3.12	-2.85	62.90
Zigzag (15%)	-2.27	-1.98	-3.53	-2.47	-3.34	-3.53	-3.53	-2.30	64.42
Zigzag (19%)	-2.06	-3.66	-3.21	-2.25	-3.11	-3.27	-3.29	-1.91	65.79

3. The electron density change of the valence band maximum

The electron density change at the valence band maximum for different cases is shown in Fig. S2.

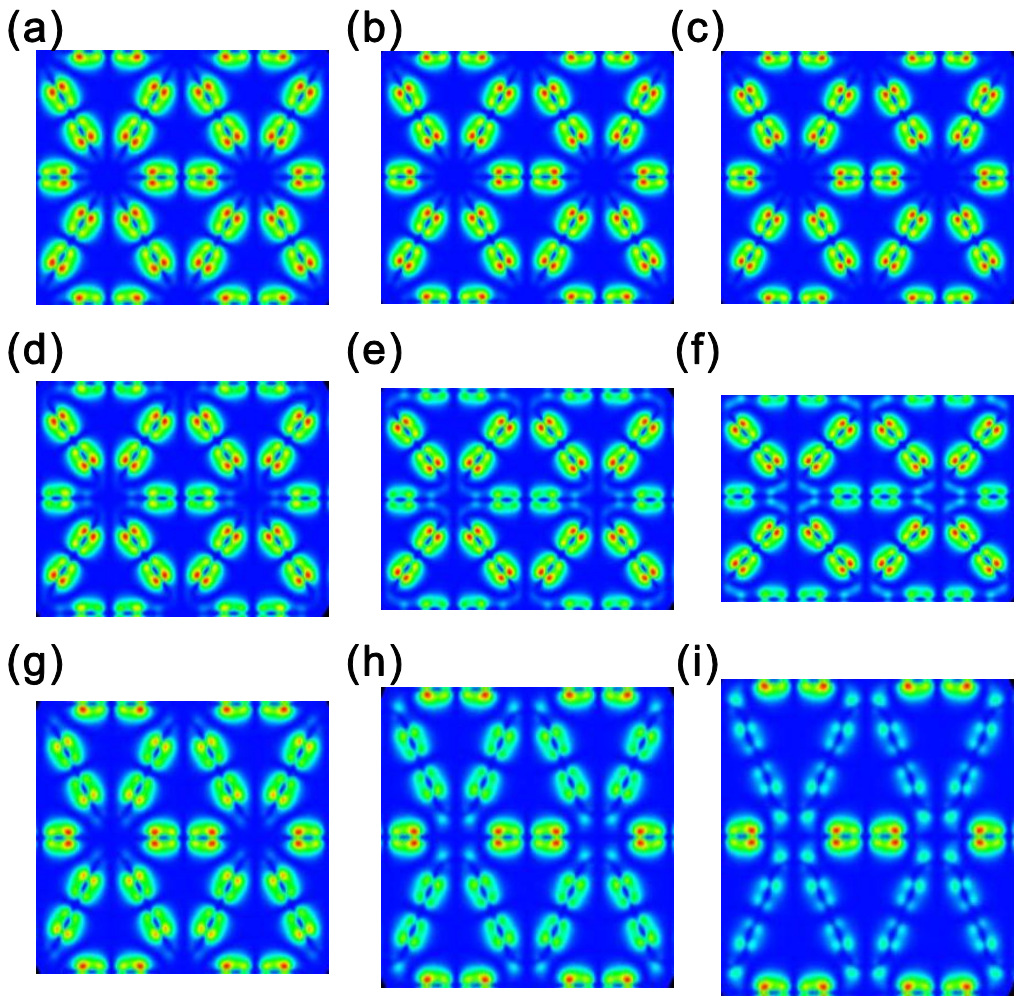

Fig. S2. The distribution of electron density of the valence band maximum under (a) no strain, biaxial strains of (b) 9% and (c) 15%, uniaxial tensile strains along the armchair direction with the strain of (d) 5%, (e) 9% and (f) 15%, and along the zigzag direction with the strain of (g) 5%, (h) 15% and (i) 19%.

4. The hole density change of the conduction band minimum

The hole density change at the conduction band minimum for different cases is shown in Fig. S3

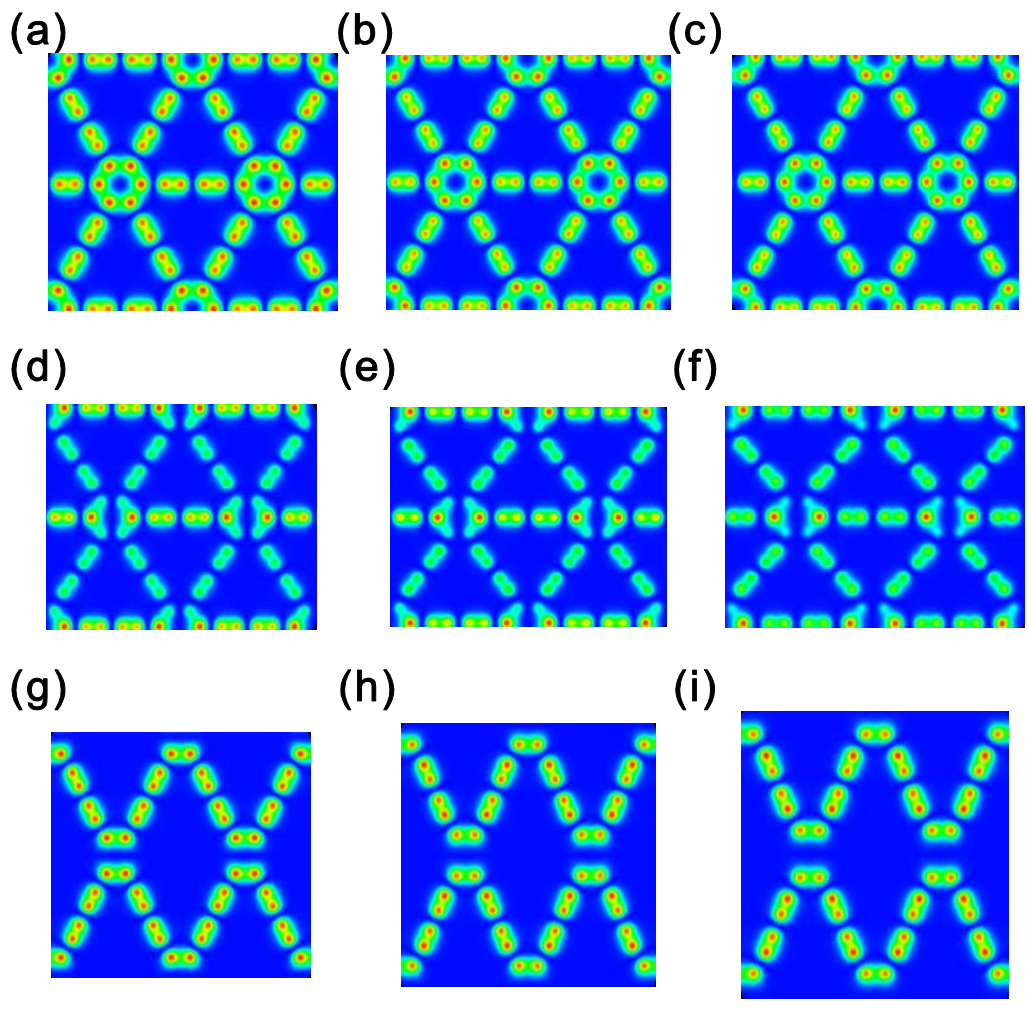

Fig. S3. The distribution of hole density of the conduction band minimum under (a) no strain, biaxial strains of (b) 9% and (c) 15%, uniaxial tensile strains along the armchair direction with the strain of (d) 5%, (e) 9% and (f) 15%, and along the zigzag direction with the strain of (g) 5%, (h) 15% and (i) 19%.