## Modulation of electronic and mechanical properties of phagraphene via hydrogenation and fluorination

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## Section S1. Calculations of $E_{\rm b}$ and $E_{\rm f}$

The binding energy  $E_b$  and formation energy  $E_f$  are employed to characterize the stability of system and provided by:<sup>1</sup>

$$E_{\rm b} = \left[ E_{\rm H-PHA/F-PHA} - (E_{\rm PHA} + nE_{\rm H/F}) \right] / n \tag{1}$$
$$E_{\rm f} = \left[ E_{\rm H-PHA/F-PHA} - (E_{\rm PHA} + nE_{\rm H_2/F_2} / 2) \right] / n \tag{2}$$

where  $E_{\text{H-PHA/F-PHA}}$  and  $E_{\text{PHA}}$  represent the total energies of hydrogenated/fluorinated phagraphene and pristine phagraphene, respectively.  $E_{\text{H/F}}$  and  $E_{\text{H}_2/\text{F}_2}$  are the total energies of a free H/F atom and a H<sub>2</sub>/F<sub>2</sub> molecule, and *n* denotes the number of adsorbed H/F atoms. In Equation (1), the smaller  $E_{\text{b}}$  means the stronger covalent bond. In Equation (2), the negative (positive) value of  $E_{\text{f}}$  indicates that the process is exothermic (endothermic). The system is stable with a negative value of  $E_{\text{f}}$ , whereas it is metastable or unstable with a positive value of  $E_{\text{f}}$ . The smaller  $E_{\text{f}}$  means the higher stability.

## Section S2. Calculations of elastic constants

The nonlinear elastic constants were evaluated by performing a least-squares fitting to the 2nd P-K stress-strain data.<sup>2</sup> For 2D sheets, by employing the standard Voigt notation (i.e., 1-xx, 2-yy, and 6-xy), the energy of elastic strain per unit area is given by:<sup>3</sup>

$$U(\varepsilon) = \frac{1}{2}C_{11}\varepsilon_{xx}^{2} + \frac{1}{2}C_{22}\varepsilon_{yy}^{2} + C_{12}\varepsilon_{xx}\varepsilon_{yy} + 2C_{66}\varepsilon_{xy}^{2}$$
(3)

where  $C_{ij}$  (i,j = 1, 2, or 6) is component of the elastic modulus tensor. The elastic constants are obtained by fitting the elastic strain energy curves under uniaxial or equal-biaxial strain.

		H-PHA	F-PHA
$d_{ ext{C-H/F}}\left( ext{\AA} ight)$	C1-H/F	1.110	1.374
	C2-H/F	1.109	1.371
	C3-H/F	1.106	1.381
	C4-H/F	1.105	1.378
	C5-H/F	1.111	1.383
	C6-H/F	1.107	1.385

Table S1. Bond distance  $d_{C-H/F}$  of fully H-PHA and F-PHA.



Figure S1. Fluctuations of T and  $E_t$  for fully H-PHA (a) and fully F-PHA (b) at 300 K. Inserts are

the final structures at the setting temperature.



Figure S2. Four configurations of 60% hydrogenated phagraphene. Upside and underside are

viewed from different angles.



Figure S3. Band structures and total DOS of 60% hydrogenated phagraphene from PBE functional. (a)-(d) correspond to the configurations in Figure S2(a)-(d), respectively.



Figure S4. Band structures and DOS of fully H-PHA (a) and fully F-PHA (b) from PBE functional.



Figure S5. Four configurations of fully hydrogenated phagraphene. Upside and underside are

viewed from different angles.



Figure S6. Band structures and total DOS of four fully hydrogenated phagraphene from PBE functional. (a)-(d) correspond to the configurations in Figure S5(a)-(d), respectively.



Figure S7. The stress-strain curves of fully H-PHA (a) and fully F-PHA (b) from PBE functional.

The red arrows indicate the fracture strains.



Figure S8. The band structures of fully H-PHA from HSE06 functional with tensile strains 0.05

(a), 0.07 (b), 0.10 (c), 0.13 (d), 0.15 (e), and 0.17 (f), respectively.



Figure S9. The band structures of fully F-PHA from HSE06 functional with strains 0.03 (a), 0.05 (b), 0.07 (c), 0.10 (d), and 0.13 (e), respectively.



Figure S10. The 3D (a) and 2D (b) charge density distributions of phagraphene. The yellow isosurface represents the charge density of 0.25 electron•Å<sup>-3</sup>.

- 1. D. Yi, L. Yang, S. Xie and A. Saxena, *RSC Adv.*, 2015, **5**, 20617-20622.
- 2. X. Wei, B. Fragneaud, C. A. Marianetti and J. W. Kysar, *Phys. Rev. B*, 2009, 80.
- S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe and P. Jena, *Proc. Natl. Acad. Sci.*,2015, 112, 2372-2377.