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

Supplementary Information

Biphenylene Monolayer: A Novel Nonbenzenoid Carbon allotrope with Potential Applications as Anode Materials for High-performance Sodium Ion Batteries

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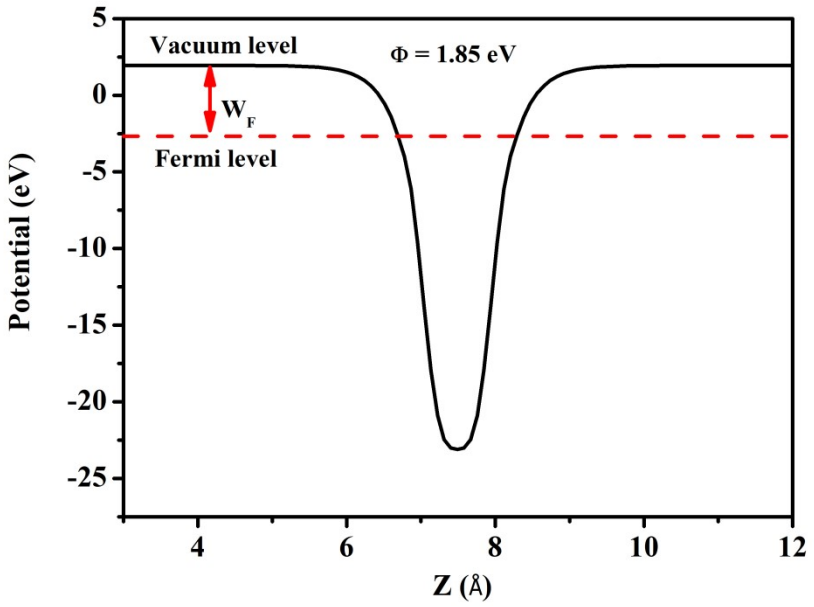


Fig. S1 The electrostatic potential along the z-direction.

The work function (W_F) of two-dimensional biphenylene was calculated via the following expression:

$$W_F = \Phi - E_F$$

where Φ is the electrostatic energy in the vacuum away from the surface, E_F is the Fermi energy.

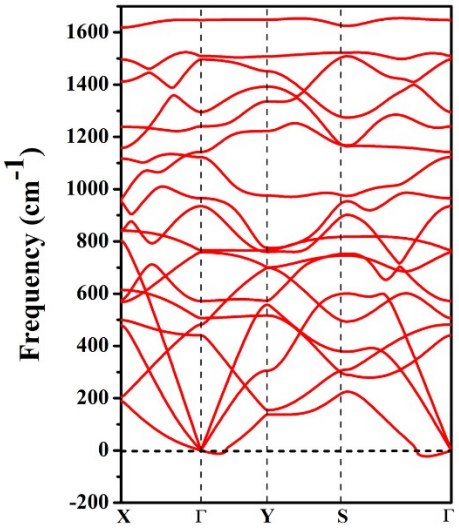


Fig. S2 The calculated phonon spectra of the 2D biphenylene monolayers. The small "U-shape" negative values near gamma point is a signature of the flexural acoustic mode but not instability, and is a common phenomenon in first-principles calculations of 2D materials.[Ref.S1]

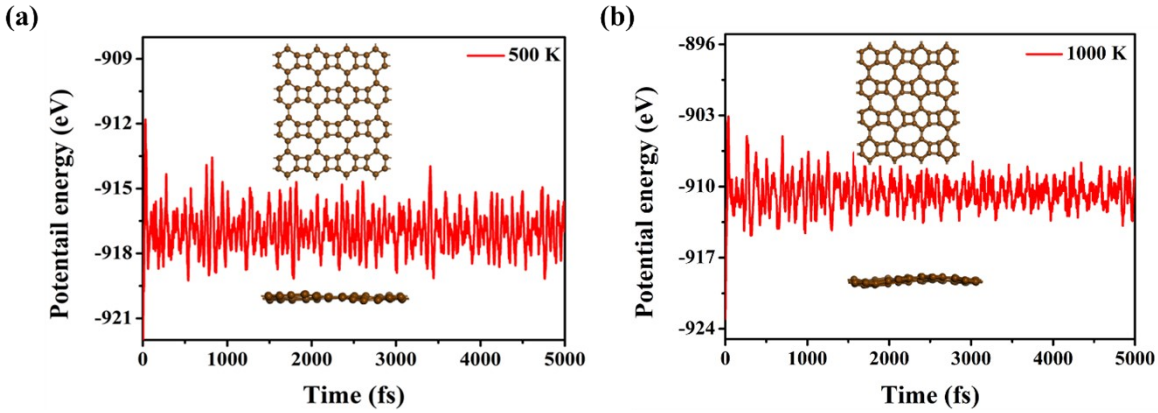


Fig. S3 Variation in potential energy at 500 (a) and 1000 K (b), and the insect is the final structure of biphenylene during 5 ps' FPMD simulation. C atoms are represented by brown balls.

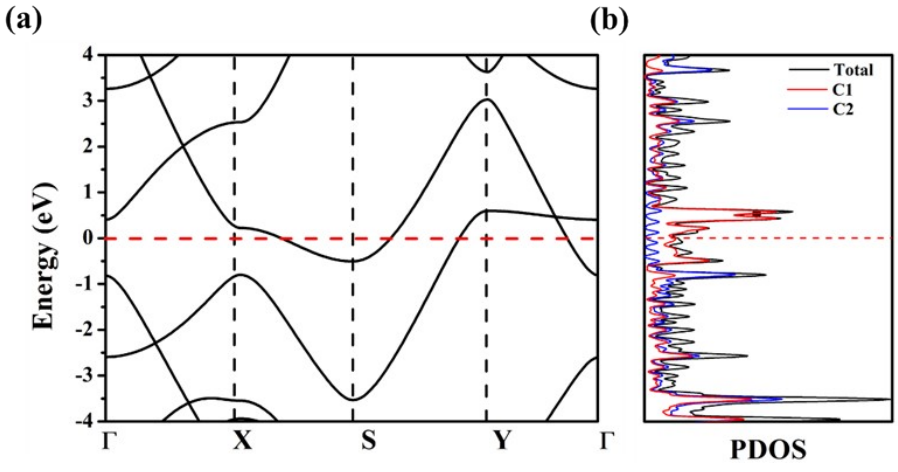


Fig. S4 The band structure (a) and the partial density of states (b) of the biphenylene monolayer. The Fermi energy is set to 0 eV as indicated by the red horizontal dashed lines.

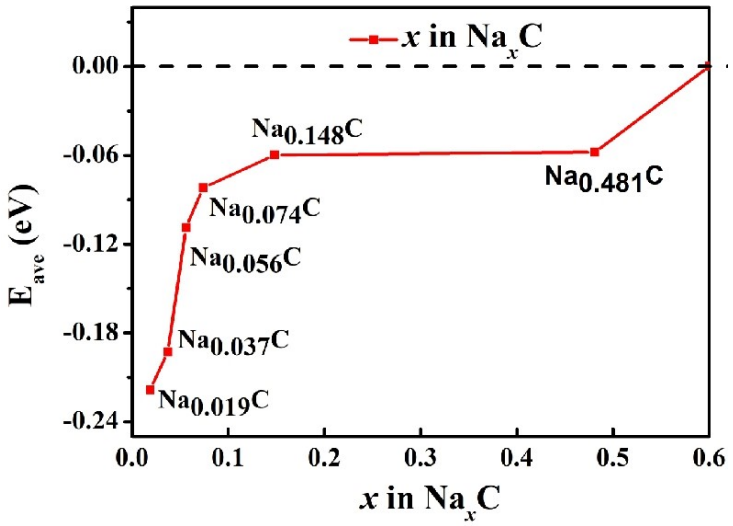
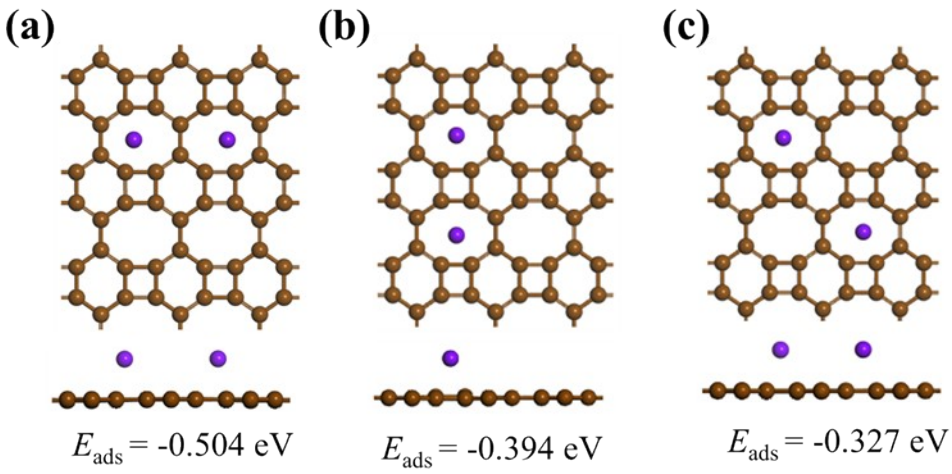


Fig. S5 The average energy per Na (E_{ave}) in Na_xC with respect to biphenylene monolayer and Na bulk bcc metal.



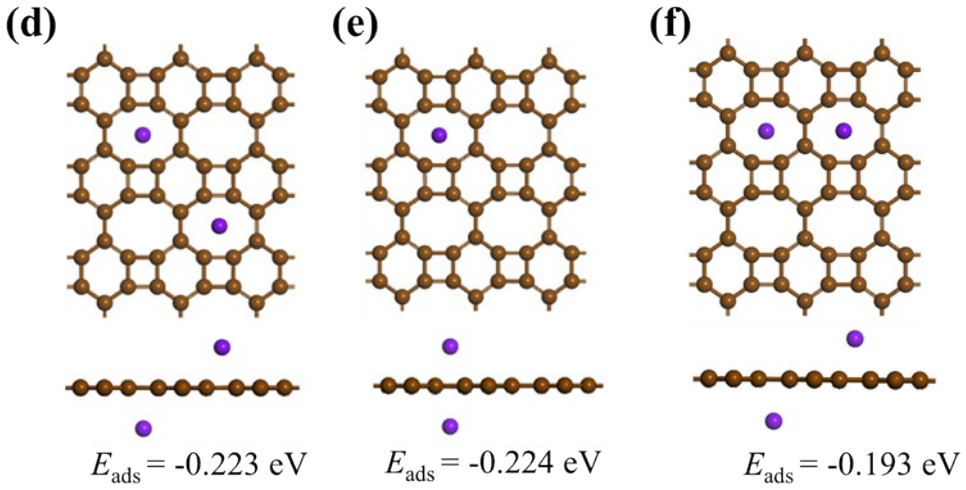


Fig. S6 The optimized configurations and the corresponding average adsorption energies of Na for $Na_{0.056}C$. The brown and purple balls represent carbon and sodium, respectively.

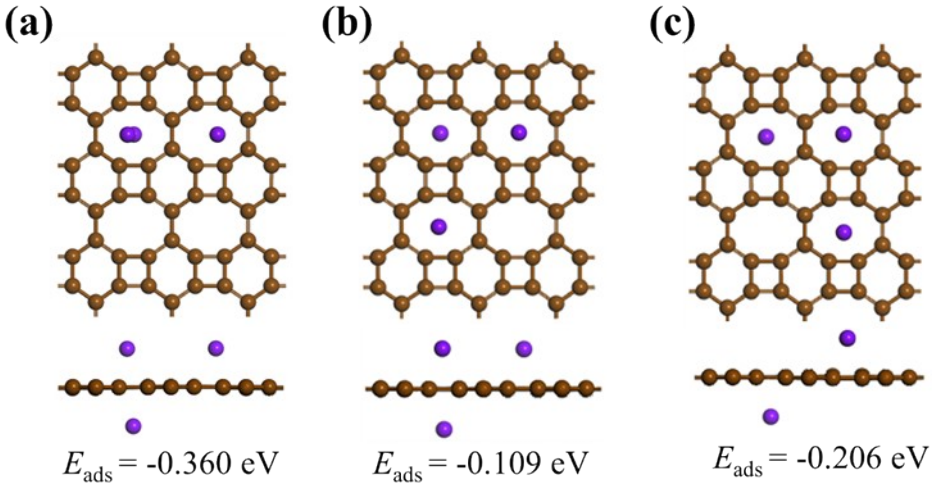


Fig. S7 The optimized configurations and the corresponding average adsorption energies of Na for $Na_{0.074}C$. The brown and purple balls represent carbon and sodium, respectively.

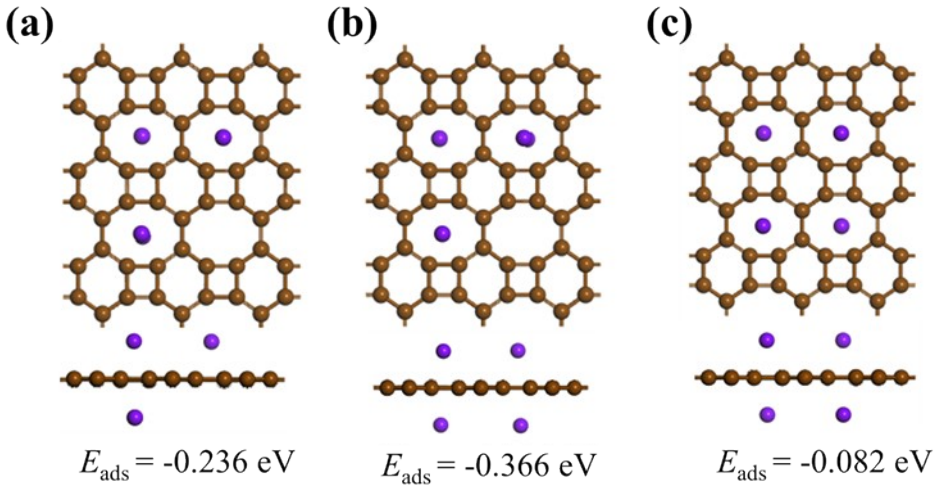


Fig. S8 The optimized configurations and the corresponding average adsorption energies of Na for $Na_{0.074}C$. The brown and purple balls represent carbon and sodium, respectively.

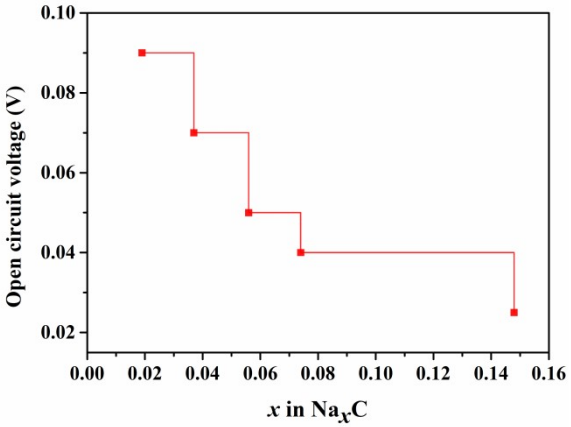


Fig. S9 The open circuit voltage profile as a function of Na concentration.

The OCV can be evaluated from the following common half-cell reaction of the charge/discharge process:

$$C + xNa^{n+} + xne^{-} \leftrightarrow Na_xC \quad \text{(S1)}$$

when the volume and entropy effects during the sodiation process were neglected, the OCV can be derived from the average adsorption energy (E_{ave}) as:

$$\mathrm{OCV} = -E_{\mathrm{ave}}/xne \tag{S2a}$$

$$E_{\mathrm{ave}} = (E_{\mathrm{C}} - E_{\mathrm{Na}x\mathrm{C}} - xE_{\mathrm{Na\text{-}bulk}})/x \tag{S2b}$$

where E_{C}, $E_{\mathrm{Na}x\mathrm{C}}$, and $E_{\mathrm{Na\text{-}bulk}}$ are the energy of pristine biphenylene monolayer, the total energy of Na adsorbed biphenylene monolayer, and the energy per Na atom in the sodium *bcc* bulk, respectively, n is the number of valence electron (n = 1 for Na), x is the chemical content of sodium atoms.

Table S1. The calculated lattice constant (*a*, *b*, in Å), lattice change of biphenylene monolayer without and with adsorbed Na atoms.

	a (Å)	*b* (Å)	Lattice variation (%)	
C	11.298	13.557		
$Na_{0.019}C$	11.311	13.566	0.12	0.07
$Na_{0.037}C$	11.318	13.566	0.18	0.07
$Na_{0.056}C$	11.326	13.566	0.25	0.07
$Na_{0.074}C$	11.331	13.566	0.29	0.07
$Na_{0.148}C$	11.357	13.566	0.52	0.07
$Na_{0.481}C$	11.440	13.579	1.26	0.16

Reference:

[Ref.S1] (a) H. Yin, G. Zheng, Y. Wang and B. Yao, *Phys. Chem. Chem. Phys*., 2018, **20**, 19177−19187; (b) V. Zólyomi, N. D. Drummond and V. I. Fal'ko, *Phys. Rev. B*, 2014, **89**, 205416.