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# Electronic properties of a graphene/periodic porous graphene heterostructure

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ABSTRACT

Recently, two-dimensional van der Waals materials such as graphene and hexagonal boron nitride have attracted interest as research topics. The two-dimensional material of polyphenylene superhoneycomb network (PSN) is similarly interesting because it is a type of periodic porous graphene. In this paper, we report a first-principles study of the geometric and electronic properties of vertical heterostructures comprising graphene and PSN. AA, AA′, and AB stacking configurations of a graphene sheet on a PSN sheet produce band gaps of 63, 16, and 3 meV, respectively. We also determine the relationships between the band gap and the interlayer distance between the graphene and PSN sheets. Finally, we present computationally simulated scanning tunneling microscopy images, which indicate the local electronic structures of the surfaces of the graphene and PSN sides.

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## 1. Introduction

Graphene has attracted great interest because it possesses unique characteristics such as high electrical conductivity and outstanding mechanical properties [1–8]. The discovery of graphene has significantly increased research on various two-dimensional (2D) materials such as hexagonal boron nitride and transition-metal dichalcogenides, and the field of 2D materials is expanding to investigate heterostructures containing multiple 2D materials. Recently, several van der Waals heterostructures were prepared experimentally. These heterostructured materials were found to have unique properties, and several new phenomena have been observed within them [9–14]. Consequently, the need for theoretical research to discover and understand the properties of experimentally observed and theoretically simulated heterostructures has increased.

In 2009, Bieri et al. succeeded in synthesizing a polyphenylene superhoneycomb network (PSN), a periodic porous graphene sheet with a periodicity of 1 nm or less [15]. An attractive property of porous graphene is its angstrom-scale periodicity. Regular, uniform, and porous structures are necessary to increase the performance and expand the applicability of porous carbon materials, including porous graphene. In addition, theoretical investigations have predicted that PSN can be used in hydrogen storage or refinement, and that it has a semiconductor-like band gap [16,17].

In the present study, the structural and electronic characteristics of vertical graphene/PSN (Gr/PSN) heterostructures, in which one layer of PSN and one layer of graphene are held together by van der Waals interaction, were investigated using ab initio calculations. Like vertical graphene/hexagonal boron nitride heterostructures [18–20], the vertical Gr/PSN heterostructures also exhibit asymmetry in interlayer potential because PSN is a type of periodic porous graphene sheet. Such interlayer potential asymmetry causes band gap opening in graphene, which may improve the room-temperature pinch-off characteristics of graphene-based field effect transistors [21]. In particular, we focus on the changes in the electronic structure of graphene caused by interactions with PSN. We consider three different stacking configurations for a heterostructure consisting of a graphene sheet and a PSN: AB, AA, and AA′. Regarding the band gap size, we find that a band gap in graphene is induced by stacking with a PSN layer that is free of significant atomic deformation or extrinsic defects. In addition, we obtain computationally simulated scanning tunneling microscopy (STM) images of the Gr/PSN heterostructures. The images show the changes in the electronic structure of a PSN (graphene) layer caused by that of a graphene (PSN) layer on each surface, as well as the pore shapes exhibited on each side of the heterostructure for the three stacking configurations.

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## 2. Computational details

Using density functional theory (DFT) [22], the geometric and electronic characteristics of a PSN monolayer and Gr/PSN heterostructures were studied. We used plane-wave basis sets and the projector augmented wave (PAW) pseudopotential implemented in the Vienna Ab Initio Simulation Package (VASP) [23,24]. The cut-off electron kinetic energy was set to 500 eV. The exchange-correlation energy was modeled using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) functional [25]. Because GGA functionals do not describe van der Waals interactions well, a separate correction was necessary for systems where van der Waals interactions were dominant. In this study, we used the Tkatchenko–Scheffler (TS) method [26] as a correction scheme. In order to confirm that the TS method is sufficient to describe the van der Waals heterostructures, we considered four additional van der Waals correction methods: DFT-D2 [27], DFT-D3 [28], DFT-D3 with the Becke–Johnson damping function [DFT-D3 (BJ)] [29], and optB86b-vdW [30,31] for comparison. In addition, we used Γ-centered $10 \times 10 \times 1$ and $30 \times 30 \times 1$ $k$ point grids for the relaxation and electronic structure calculations, respectively, suitable for the hexagonal symmetry of the system. Lattice-constant optimization was performed using the third-order Birch–Murnaghan equation of state [32,33]. Using the Tersoff–Hamann method [34], STM images were obtained from the integrated partial charge densities in a given energy window.

## 3. Results and discussion

We optimized the structure of one PSN layer and obtained the minimum energy geometry and its corresponding electronic structure. As shown in Fig. 1(a), the length of one side of a rhombus-shaped primitive cell is 7.51 Å. This length, which is equal to the distance between pores in the PSN, was determined experimentally as approximately 7.4 Å [15]. In Fig. 1(a), $C_\alpha$ represents a carbon atom bonded to one hydrogen and two carbon atoms, and $C_\beta$ denotes a carbon atom bonded to three neighboring carbon atoms. Our first-principles calculations reveal that the $C_\alpha$–$C_\beta$ bond length is 1.40 Å, and that the $C_\alpha$–H bond length is 1.09 Å. Meanwhile, the $C_\beta$–$C_\beta$ bond length is 1.49 Å. Fig. 1(b) shows the electronic structure of one layer of the PSN structure. Interestingly, this structure has a band gap of 2.40 eV at the $K$-point, which is in agreement with the literature [16,17].

After the structural optimization of one PSN layer, the minimum-force structure of the commensurate Gr/PSN heterostructure was obtained by considering van der Waals interactions. As seen in Fig. 2(a), we considered three types of stacking structures: AB, AA, and AA′. In AB stacking, the PSN layer is positioned on top of the graphene layer but shifted, and a carbon atom in the graphene layer sits at the center of each PSN hexagon. In AA stacking, the C atoms in the graphene and PSN layers are perfectly superimposed. In AA′ stacking, the AA-stacked PSN layer is shifted by half a hexagon length relative to the graphene layer. The lattice constant ($a$), interlayer distance ($d$), and interlayer binding energy ($E_{int}$) were determined preferentially. The interlayer binding energy is defined by the following equation:

$$E_{int} = E[\mathrm{Gr} + \mathrm{PSN}] - E[\mathrm{Gr}] - E[\mathrm{PSN}]. \tag{1}$$

Here $E[\mathrm{Gr} + \mathrm{PSN}]$ is the total energy of the Gr/PSN heterostructure. $E[\mathrm{Gr}]$ and $E[\mathrm{PSN}]$ are the total energies of the graphene and PSN sheets, respectively. The results are shown in Fig. 2(b) and Table 1. In calculating the interlayer binding energies, the TS and optB86b-vdW methods tend to yield larger binding energies than the other correction methods do. All methods retain the order of stabilities such that AB (AA) stacking is the most (least) stable.

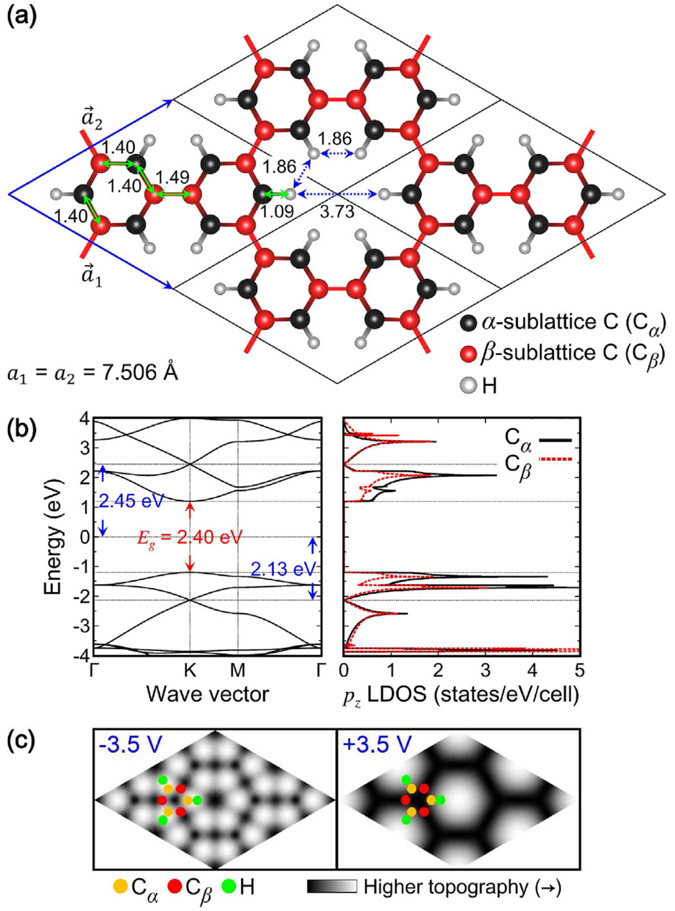

**Fig. 1.** Atomic and electronic structure of PSN monolayer, calculated by TS method. (a) Optimized atomic geometry by a $2 \times 2$ supercell to indicate the structure of the pore at the center of the figure. The atom pairs $C_\alpha$ (black) and $C_\beta$ (red) belong to different sublattices inside each hexagonal carbon ring. The numbers show the distance between atoms (Å). (b) Band structure (left) and $p_z$ orbital-projected local density of states (right) for six $C_\alpha$ atoms and six $C_\beta$ atoms. The Dirac points are shown at 2.45 and −2.13 eV at the $K$-point. (c) Simulated STM images in the constant-current mode at the bias voltages of −3.5 (left) and 3.5 V (right). The Fermi energies corresponding to the zero-energy level are all set to the center between the conduction-band minimum and the valence-band maximum at the $K$-point in the band structure. (A colour version of this figure can be viewed online.)

In comparing the interlayer binding energies of the three types of stacking structures, the AB structure is found to be the most stable. The AA structure is 3.3 meV/atom higher in binding energy per atom than the AB structure, and the AA′ structure is 0.6 meV/atom higher in energy per atom than the AB. Therefore, AB, AA′, and AA are more stable in this order, which is also the order of stabilities in two-layer graphene [35]. The bond lengths between the atoms in PSN differ from those of pure PSN, since the periodicity of PSN is matched to that of graphene in this study. The $C_\alpha$–$C_\beta$ bond length inside the hexagonal carbon ring is 1.39 Å, the $C_\beta$–$C_\beta$ bond length connecting two hexagonal carbon rings is 1.47 Å, the $C_\alpha$–H bond length is 1.08 Å, and the bond length between two carbons in the graphene is 1.43 Å, throughout all stacking configurations. When compared to the structure containing only PSN, the $C_\alpha$–$C_\beta$ and the $C_\alpha$–H bond lengths are all decreased by 0.01 Å, while compared to the structure of only graphene, the bond length between two carbons is increased by 0.01 Å. The distance between graphene and PSN is 3.36 Å; this is closest to the value observed in AB. The interlayer distances in AA and AA′ are 3.41 and 3.39 Å, respectively.

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