ACS APPLIED ELECTRONIC MATERIALS

Functional Carbon and Silicon Monolayers in Biphenylene Network

Taylan Gorkan, Şafak Çallıoğlu, Salih Demirci, Ethem Aktürk,* and Salim Ciraci*

ABSTRACT: We investigated the effects of vacancy, void, substitutional impurity, isolated adsorption of selected adatoms, and their patterned coverage on the physical and chemical properties of metallic carbon and silicon monolayers in a biphenylene network. These monolayers can acquire diverse electronic and magnetic properties to become more functional depending on the repeating symmetry, size of the point defects, and on the type of adsorbed adatoms. While a carbon monovacancy attains a local magnetic moment, its void can display closed edge states with interesting physical effects. Adsorbed light-transition or rare-earth metal atoms attribute magnetism to these monolayers. The opening of a gap in the metallic density of states, which depends on the pattern and



density of adsorbed hydrogen, oxygen, and carbon adatoms, can be used as the band gap engineering of these two-dimensional materials. The energy barriers against the passage of oxygen atoms through the centers of hexagon and octagon rings are investigated, and the coating of the active surfaces with carbon monolayers is exploited as a means of protection against oxidation. We showed that the repulsive forces exerting even at distant separations between two parallel, hydrogenated carbon monolayers in a biphenylene network can lead to the superlow friction features in their sliding motion. All these results obtained from the calculations using the density functional theory herald critical applications.

KEYWORDS: carbon and silicon monolayers in biphenylene network, functionalization, adatom coverage, mono- and divacancy formation, void formation, chemisorption of selected atoms, hydrogenation, oxidation, carbonation, superlow friction, coating of active surfaces, band gap engineering

INTRODUCTION

Further to graphene, the synthesis of another two-dimensional (2D) allotrope of carbon in a biphenylene network has been achieved.^{1,2} This allotrope, a nanosized but nonhexagonal, atomically thin layer of carbon consists of adjacent octagon-(o), hexagon-(h), and square-(s) rings, which is briefly specified as an ohs structure in the text. It is a semiconductor for narrow quasi-one-dimensional (1D) nanoribbons but is a metal for wide nanoribbons and 2D monolayers. Similar structures for carbon³⁻⁹ and BN¹⁰ have been proposed/ predicted or treated theoretically. Motivated by the recent, experimental work by Fan et al.,² we performed an extensive theoretical study¹¹ not only on carbon in ohs structure but also on ohs monolayers of group IV elements (Si, Ge) and group IV-IV (SiC, GeC, SnC), III-V (BN, BP, BAs, BSb, AlN, AlP, GaN, InN), and II-VI (ZnSe) compounds and their multilayers as well as three-dimensional (3D) periodic ohs crystals. We investigated their dynamical and thermal stabilities and their mechanical and electronic properties. Our study,¹¹ which predicted many interesting features of these ohs structures, unveiled a new class of 2D materials as the counterpart of the same elements or compounds in the honeycomb network.¹²⁻¹⁶ In contrast to the free-standing, semimetallic, 2D graphene,¹⁷ and silicene and germanene¹²⁻¹⁶ monolayers showing massless Fermion behavior, C, Si, and Ge ohs monolayers are found to be good metals. It has been shown that the 2D ohs monolayers can form also quasi-1D nanotubes and nanoribbons⁶ with diverse edge geometries.¹¹ Furthermore, when some of these monolayers are stacked, stable bilayers, multilayers, and stable 3D layered structures like graphite can form under the weak van der Waals interaction. Conversely, in specific bilayers and multilayers like Si, Ge ohs and compounds like GaN ohs, strong vertical bonds are constructed between layers forming a network of connected octagon and square rings in the side view. More importantly, 3D layered C ohs, which is an analogue of semimetallic graphite in a honeycomb network, was also found to be a good metal with high state density at its Fermi level to constitute a new, 3D metallic allotrope of carbon.

 Received:
 April 11, 2022

 Accepted:
 May 23, 2022

 Published:
 June 7, 2022





In the past, monitoring electronic, magnetic, and optical properties of 2D materials like graphene, to make them functional for a given purpose, has been extensively exploited theoretically and experimentally. For example, point defects, like vacancy and divacancy in either isolated or patterned forms in the monolayer,¹⁸⁻²² were shown to lead to serious local modifications in the electronic structure of graphene.^{23–26} It was shown that semimetallic graphene can acquire different electronic states upon the coverage of selected atoms. Upon hydrogenation, 27-31 oxidation, 32-36 fluorination, or chlorination, 37-39 semimetallic graphene becomes a semiconductor. Not only electronic structures of 2D monolayers but also their mechanical, optical, and magnetic properties are modified to obtain new functional properties.^{40–48} As an example, the inplane stiffness and Poisson's ratio of graphene decrease when hydrogenated from both sides to form graphane.⁴⁰ Each hydrogen vacancy created in graphane attributes a magnetic moment.⁴⁹ While the solar absorbance of graphene is enhanced with glycine coating,⁴² upon the coverage by specific adatoms and molecules graphene-based nanostructures can change to be a high capacity hydrogen storage medium.⁴³⁻⁴⁵ Recently, it has been shown that silicene covered by Gd atoms changed to a 2D ferromagnetic material;^{50,51} this magnetic state by itself underwent a change like ferrimagnetic, antiferromagnetic depending on the thickness.

In this study, we explored how the properties of C ohs and Si ohs monolayers can be modified locally through the formation of point defects, such as vacancy, divacancy, voids, substitution, and chemisorption of individual atoms. We also investigated the changes of the electronic and magnetic states upon the decorating/coating of their surfaces by selected adatoms. To this end, we considered the formation of individual vacancy, divacancy, patterned hole (antidot), and substitution of foreign atoms and investigated the resulting equilibrium atomic structure together with associated formation energies and local changes in the electronic structure. The adsorption of individual adatoms, such as H, O, C, Si, F, Ti, and Gd, were examined to find the equilibrium binding site and related binding energy. Furthermore, we considered the decoration and full coverage (or coating) of C ohs and Si ohs by H, O, and C and explored novel functionalities thereof with possible applications as a proof of concept. Earlier studies showed that the adatoms considered in this study can form strong bonds with graphene and silicene and modify their physical properties significantly depending on their decoration. In particular, Gd-coated graphene and silicene have gained importance recently because of their 2D magnetism. We believe that the interaction of these adatoms with 2D metallic ohs monolayers can lead to interesting physical effects.

Highlights of our results obtained from first-principles density functional theory (DFT) calculations can be summarized as follows: (i) While an isolated monovacancy in C ohs acquires a local magnetic moment, that in Si ohs is nonmagnetic. (ii) Isocoric substitutional atoms in C ohs can be constructed, which can yield n- or p-type localized impurity levels in the band gap of its semiconductor state constructed by its hydrogenation. (iii) Adsorption of selected adatoms can give rise to resonance states in the spectrum, which can be localized only when adatom–adatom distances decrease at relatively higher coverage/concentration. (iv) When adsorbed, Ti and Gd atoms can attribute local magnetic moments to these metallic layers. (v) An energy band gap can open in the metallic state density, and local magnetic moments can be acquired depending on the value and symmetry of the coverage of H adatoms adsorbed to C ohs. (vi) It is found that the coating of active surfaces by C ohs constitutes a weaker barrier to their oxidation as compared to that of graphene due to octagon rings having relatively larger holes. (vii) The calculated interaction force between two parallel, fully hydrogenated C ohs monolayers is repulsive for a wide range of the separation of those monolayers. This situation can be exploited for superlow friction in the sliding motion of these monolayers.

METHOD

Calculations based on the DFT were performed using VASP⁵² packages. Projector-augmented wave potentials⁵³ and the exchange-correlation potential within the generalized gradient approximation with the Perdew, Burke, and Ernzerhof (PBE) functional⁵⁴ were used. Electronic wave functions were expanded by plane-wave basis sets up to the electron kinetic energy cutoff of 520 eV. The dipole correction and the van der Waals correction within the method of Grimme (DFT-D3)^{55,56} were taken into account. The effect of the dipole correction on the results is found to be minute. Brillouin zone (BZ) integration was performed with a Γ -centered k-point grid in all the electronic calculations. Ionic relaxation was realized by a conjugate gradient algorithm. All atoms in the supercell were relaxed until the energy difference between the successive steps was less than 10^{-5} eV and the force on each atom was less than 10^{-2} eV/Å. In addition, maximum pressure on the lattice was lowered to 0.1 kbar. A dense k-mesh like 12×14 was used for the primitive cells based on a convergence analysis; the k-mesh was rescaled according to the size and symmetry of the supercells used in each calculation. Also, the Heyd-Scuseria-Ernzerhorf (HSE06) hybrid functionals method⁵⁷ was applied to obtain corrected band gap values. An HSE06 functional is constructed by mixing 25% of the Fock exchange with 75% of the PBE exchange and 100% of the PBE correlation. Small magnetic moments of some functional surfaces are confirmed by performing calculations using a local basis set.58

To account for the on-site Coulomb interaction⁵⁹ in a Gd adatom including 4f orbitals,^{60–62} calculations were performed by including a Hubbard U correction to PBE, with interaction parameters of U = 6.7 eV and J = 0.7 eV.⁵¹

Earlier, the stability of all ohs structures in a different dimensionality was assured by the dynamical and thermal stability analyses.¹¹ The adsorption of a single adatom on an extended C ohs or Si ohs is not expected to lead to a structural instability of these monolayers, except local deformations. Here we tested the stability of C ohs and Si ohs, which are fully covered by adatoms. In addition, the stability of the functional surfaces constructed on a Si ohs monolayer in a relatively smaller supercell is tested in consideration of the possibility that the weak $\pi - \pi$ interaction due to long Si–Si bonds might make defected or adatom-covered functional Si ohs structures prone to the instability. Hence, the structural stability of all the functional surfaces reported here are assured based on extensive stability tests. The dynamical stability analysis was performed by using the density functional perturbation theory (DFPT), to calculate phonon spectra.⁶³ The structures having vibration modes with frequencies $\omega^2 > 0$ for all *k* in the first BZ are considered to be stable. The thermal stability of the same systems is tested by ab initio molecular dynamics (AIMD) calculations at finite temperature. The time step between ionic



Figure 1. Atomic structures, calculated energy band structures, and state densities. (a) (left) Primitive unit cell of C ohs monolayer (shaded) in planar geometry with top and side views of the atomic structure. Two different atomic sites A and B are shown. Together with the A and B sites, the D, E, and H sites indicate possible adsorption sites for the chemisorption of adatoms. (middle) Map of electron localization function of C ohs monolayer. (right) Energy-band structure of C ohs with the corresponding total and orbital projected DOS. Zero of the energy is set to E_F shown by a dotted line. (b) Same for Si ohs monolayer, which is buckled.

iterations was taken to be 2 fs. After every 50 steps, the velocities were rescaled to match the desired temperature. The net charge on selected adatoms was calculated by a Bader analysis.⁶⁴ All the structures were visualized in the VESTA code.⁶⁵ In order to resolve the electronic structure originating defects or adatoms, we used a small Gaussian broadening with a smearing energy of 0.05 eV.

BARE C OHS AND SI OHS MONOLAYERS

We start with a brief outline about the atomic and electronic structure of C ohs and Si ohs monolayers as background information to be used in forthcoming sections. For further details, one can refer to ref 11. In both monolavers, each atom is threefold-coordinated to allow sp² hybridization of atomic orbitals like their counterparts in a honeycomb network. However, since the bond angles in the ohs monolayers deviate from $2\pi/3$, sp² hybridization becomes deformed to result in different orbital combinations at different atomic sites and different bond lengths. This situation gives rise to two different atomic sites, namely, A-site (carbon atoms situated at the corners shared by two adjacent octagons and one hexagon) and B-site (carbon atoms situated at the corner shared by an adjacent octagon, hexagon, and square), which are distinguished in the C ohs monolayer (see Figure 1a). Accordingly, the interaction of C atoms with foreign atoms and point defect formation in a C ohs monolayer becomes rather site-specific. Moreover, three different rings, namely, octagons, hexagons, and squares, constitute also different regions of charge density and crystal potential in the monolayer; the landscape of the potential near their centers is also different. In this respect, ohs

structures display differences from those in hexagonal counterparts. While C ohs monolayer is planar, the Si ohs structure is buckled and has A and B sites with more complex orbital character. In Figure 1, the atomic structure, energy band structure, total and orbital projected densities of states (DOS) of C ohs and Si ohs monolayers are presented.

Notably, because of the deformation of sp^2 hybridized orbitals, bands mainly derived from p_z orbitals cross the Fermi level at different k-points of the Brillouin zone and give rise to a significant state density at the Fermi level. On the one hand, this situation attributes a good metallicity to both C ohs and Si ohs monolayers. Here, the metallic charge is expected to screen the local disturbances in the crystal potential. On the other hand, if the defects and adatom coverage are extended, the coupling between them can open a band gap between valence and conduction bands.

POINT DEFECTS

We first investigate the selected point defects in C and Si ohs monolayers. These are the formation of vacancy, divacancy, antidot and some substitutional atom (impurity) defects. We examine the local structural deformations together with the energies involved in their formation and their effects on the electronic energy spectrum and the magnetic state. As vacancy, we consider only the single vacancy formed at either the A or B site; we consider divacancy as being formed at adjacent A and B sites together and void or antidot. In order to mimic an isolated point defect and hence to hinder defect—defect interactions within the periodic boundary conditions, we use supercell geometry. Isolated vacancies in C ohs monolayer are



Figure 2. Optimized atomic structures (left) and the associated TDOS and LDOS at nearest host atoms (specified by numerals) surrounding the missing atom(s) (right) calculated for various point defects (single vacancy and divacancy) formed in C ohs monolayer. The calculated magnetic moments of the atoms surrounding the missing atom of a single vacancy (in Bohr magneton, μ_B) are indicated. The zero of energy is set at the Fermi level. (a) Single vacancy formed at the A site. (b) Single vacancy formed at the B site. (c) Divacancy formed at A and B sites together. (d) A void or antidot surrounded by 16 host C atoms with closed edge states constructing sharp peaks in LDOS.

examined using its (4×5) supercell comprising 120 host atoms and allowing the minimum separation between two point defects of ~18 Å. Relatively larger lattice constants of Si ohs monolayer allow us to use a relatively smaller (3×4) supercell. The final equilibrium atomic structure of these point defects was attained first by removing a host atom at a specific site(s) of a bare monolayer and then by optimizing the atomic structure to attain minimum total energy and lattice pressure.

The calculation of the formation energy of a vacancy (without entropy contribution) began with a known expression,⁶⁶ and it is cast in a simple form, since the size of the supercell is as large as ~ 18 Å \times 18 Å, and the maximum pressure on the lattice was lowered to 0.1 kbar. Accordingly, the effect of the relaxation of the large repeating volume on the energy is negligible, and the supercell has a minimum in the Born-Oppenheimer surface. This form, which has been commonly used in various theoretical studies $^{66-70}$ in terms of energies obtained in first-principles calculations, can be expressed as $E_{Vf} = E_T[VS] - (N - n)E_T[BS]/N$. Here, N and n stand for the total number of atoms in the bare supercell without vacancy and the number of missing atoms in the defected supercell, respectively. $E_{\rm T}[{\rm VS}]$ and $E_{\rm T}[{\rm BS}]$ stand for the total energies of the supercell with and without vacancy, respectively. In this expression, $E_{\rm Vf}$ is given with reference to the host atom in a perfect monolayer. Positive values of $E_{\rm Vf}$ indicate that energy is needed to create an isolated vacancy. The formation energy of a vacancy determines the concentration of this defect at a given temperature according to the Arrhenius relation. The effect of any isolated point defect or vacancy on the electronic energy structure was clarified by the total density of states (TDOS) and the local density of states (LDOS) at the host atoms surrounding the defect.

In Figure 2, the optimized structures of a supercell of C ohs comprising a single vacancy defect at A and B sites and also a divacancy are shown. The state density around the defect is shown by the density of states projected to the atoms (indicated by numerals) surrounding the missing atoms. Local changes of the optimized atomic structure of C ohs monolayer upon the formation of a single vacancy at the A-site can be

seen in Figure 2a. A hexagon ring between two squares changed to a pentagon ring, and two adjacent octagon rings joined and formed an irregular ring surrounded by 13 carbon atoms. This structural change accompanied by a big hole in the monolayer took place at the expense of $E_{\rm Vf}$ = 6.45 eV per vacancy. As for the vacancy formed at the B site, an adjacent square ring, two adjacent hexagon rings, and one adjacent octagon ring have changed to one pentagon ring, one hexagon ring, and a large hole surrounded by nine carbon atoms in Figure 2b. The formation energy is calculated to be $E_{\rm Vf} = 5.12$ eV. This indicates that the B-site vacancy concentration is higher than that of the A-site vacancy. Notably, vacancies formed at the A site and B site acquired a permanent magnetic moment of $\mu = 1.0 \ \mu_{\rm B}$ per cell due to an unpaired spin. The spin-polarized density of states projected on the host atoms surrounding the missing host atom (LDOS) indicate changes in the electronic structure caused by the formation of a vacancy. Because of the twofold coordination of specific C atoms around the A- and B-site vacancy, sharp peaks of state density of opposite spin polarization occur above and below the Fermi level. These are, actually, resonance states occurring at specific energies of the spectrum. Calculated magnetic moments of these specific C atoms have the highest value on twofold coordinated ones as seen in Figure 2a,b. In the case of a divacancy constructed by removing C atoms at the adjacent A and B sites, one hexagon ring, one square ring, and two octagon rings changed to one trigonal ring and one large ring surrounded by 10 C atoms.

Divacancy is nonmagnetic and has formation energy of 5.64 eV; it is smaller than that of monovacancy formed at the A site but larger than that at the B site. Under small and comparable entropy effects and at low temperature, their concentrations normally follow the same order of the formation energies calculated above. This is an interesting and unusual situation that occurs due to the rebondings originated from nonuniform C–C bonding in the C ohs structure. The effects of this nonmagnetic divacancy on the electronic energy structure are shown in Figure 2c. The contribution of atoms surrounding the removed, two carbon atoms are rather uniform. We note that divacancies formed in adjacent A and A sites or B and B



Figure 3. Atomic structures (top) and the LDOS, at nearest host atoms surrounding the defect (bottom) calculated for various point defects formed in Si ohs monolayer. (a) Vacancy formed at the A site. (b) Vacancy formed at the B site. (c) Divacancy formed at A and B sites together.

sites can lead to different defect structures but are left out of the scope of the present study.

While the metallicity of C ohs monolayer is maintained in a system including a single (noninteracting) vacancy, a mesh of vacancy defect allowing some coupling between adjacent defects is expected to lead to diverse electronic and magnetic states. At this point, we investigated a void or simple antidot surrounded by 16 C atoms described in Figure 2d. Such a void can be considered also as a patterned defect with some defectdefect interaction owing to its relatively large size in the $(4 \times$ 5) supercell. One sees that the state density at $E_{\rm F}$ is decreased, but the states derived from C atoms surrounding the void have given rise to a sharp peak below -2 eV and above +3 eV. Some of the states contributing to these peaks are identified to be edge states of the antidot. The charge density isosurfaces demonstrate that these edge states have given electronic charge localized on the C atoms forming the edge of the void as shown in Figure 2d. We attribute importance to these closed edge states because they bear upon various physical effects. First of all, edge-state electrons are expected to construct persistent currents under the magnetic field applied perpendicular to the monolayer. Second, the Aharonov-Bohm effect related to these closed edge states can be of fundamental interest.

In addition to the vacancy defects, we also studied the doping of C ohs monolayer by the substitution of a single B and N atom at either the A or B site. Substitutional defects (or impurities) are known to be important for semiconducting host crystals, since there are n- or p-type localized states of impurities, which may occur at the band gap edges and, hence, may extend the applications of host crystal in electronics. Although C ohs monolayer being a good metal will not allow the occurrence of localized impurity states, localized gap states can occur when C ohs is hydrogenated to open a band gap. The formation energy in the substitution of C ohs by atoms like B and N can be calculated with reference to the energies of the substituting and substituted host atoms in their stable structures (molecules) using the expression^{71,72} $E_{\rm Sf} = E_{\rm T}[\rm SD] - E_{\rm T}[\rm BS] - E_{\rm T}[\rm SA] + E_{\rm T}[\rm HA]$. Here, $E_{\rm T}[\rm SD]$, $E_{\rm T}[\rm BS]$,

 $E_{\rm T}$ [SA], and $E_{\rm T}$ [HA], are, respectively, the total energies of the supercell including one substituting atom, the bare supercell, the substituting atom in its stable structure, and the C host atom in its C ohs monolayer. We note that the last two energies, namely, $E_{\rm T}$ [SA] and $E_{\rm T}$ [HA], include their cohesion (binding) energies in addition to their free atom energies, and all were calculated in comparable cells using the same calculation parameters. $E_{\rm Sf} > 0$ indicates that the formation of a substitutional atom defect requires energy. The calculated formation energies are relatively small, since these atoms are adjacent to the host atom in the periodic table; hence, they are isochoric. The formation energies $E_{\rm Sf}$ are 0.79 and 0.33 eV for a B atom substituting a C atom at A and B sites are 1.02 and 0.54 eV.

The vacancy defects in Si ohs monolayer differ from those in C ohs monolayer since the defect formed in a small supercell causes squeezing of the structure resulting in a decrease of 2D lattice constants. However, the extended squeezing would be minute for an isolated vacancy. Hence, the calculation of vacancies in the (3×4) supercell of Si ohs monolayer was performed only by the optimization of atomic positions in the supercell. Accordingly, the $E_{\rm Vf}$ of the vacancy at the A and B sites of Si ohs is found to be 1.70 and 1.98 eV, respectively. The formation energy of divacancy formed by removing Si atoms situated at adjacent A and B sites is calculated to be 2.29 eV. In Figure 3, we show the optimized atomic structures of vacancy and divacancy, which are reminiscent of those created in C ohs in Figure 2.

Cumulative LDOS at the atoms surrounding the removed host atom in Figure 3 shows that the prime effects of vacancies on the electronic structure appear at ~ 1 eV below and above the Fermi level as resonance states. For divacancy, the resonance states become dispersed with a maximum density at -2 eV. However, the contribution of states associated with vacancy and divacancy at the Fermi level is negligible. This may imply the opening of a band gap in Si ohs at a high concentration of these point defects. The vacancy and divacancy created in Si ohs here are nonmagnetic.



Figure 4. Optimized atomic structures (top and side views) of adatoms adsorbed to C ohs corresponding to the equilibrium binding geometries (maximum binding energy) and their TDOS and LDOS calculated at the adatom and nearest host atoms. The zero of energy is set to the Fermi level. (a) H atom. (b) O atom. (c) C atom. (d) Si atom. (e) Gd atom. (f) Ti Atom.

Earlier, Rahaman et al.⁶ tested the stability of C ohs monolayer against the formation of various point defects including the specific vacancies and the divacancy discussed above. On the basis of structure optimizations performed using a similar method and AIMD calculations at T = 300 K, they concluded that the optimized local structure of point defects and the rest of the C ohs monolayer around the defect remain robust. The optimized atomic structures corresponding to the ones treated in this study are in agreement. We note that our objectives here are to calculate the formation energies of these defects and to reveal how they modify the electronic structure of the bare C ohs monolayer for purposes of functionalization. Additionally, the present study shows that similar isolated point defects formed in a stable Si ohs monolayer can have differences from those in C ohs.

CHEMISORPTION OF INDIVIDUAL ATOMS

To functionalize graphene^{27-39,73-75} and silicene,⁷⁶⁻⁷⁹ the chemisorption of adatoms to these monolayers has been treated experimentally and theoretically in the past. These monolayers have uniform structures consisting of planar and buckled hexagons. However, because of deformed sp² hybridization, adsorptions of adatoms to C ohs and Si ohs monolayers are expected to be rather different and can reveal crucial inputs for the functionalization of these metallic monolayers through decoration and coating. When decorated with selected atoms, it is anticipated that C ohs and Si ohs monolayers can acquire rather unique properties for different applications. Here, we first investigate the chemisorption of selected individual atoms like H, O, C, Si, F, Ti, and Gd to C ohs and Si ohs monolayers. To this end, we use the supercell geometry as described in the previous section to mimic isolated adsorbed adatoms. This way, the adatom-adatom interactions are minimized. We used the (4×5) supercell for C ohs and the (2×2) supercell for Si ohs. Since Si ohs

monolayer is an open structure as compared to C ohs and, hence, is buckled, we tested the possible effects of the size of the supercell on the calculated atomic and electronic structure due to the single adatom adsorption. Our results obtained using the (2×3) supercell did not differ from those obtained using the (2×2) supercell.

The binding energy of an adatom is a critical value in the chemisorption and is calculated by the expression $E_{\rm b} = E_{\rm T}[{\rm BS}]$ + $E_{\rm T}[A] - E_{\rm T}[AS]$ in terms of the total energies of the bare supercell $E_{\rm T}[{\rm BS}]$, free adatom $E_{\rm T}[{\rm A}]$, and of single adatom adsorbed to supercell $E_{\rm T}[AS]$. Note that, according to this definition, $E_{\rm b} > 0$ indicates that the adatom can be bound to the substrate, or stated differently, the adsorption process is preferred. The equilibrium geometry and hence the strongest binding energy of an adatom is determined by placing the adatom above the various possible adsorption sites of these monolayers and subsequently by optimizing the atomic structure to attain minimum total energy and minimum lattice pressure. Possible sites of adsorption are A and B sites and also H (above the center of hexagon), D (above the center of square), and E (above the center of octagon) sites and bridge sites above either A-A or B-B bonds. These sites are described in Figure 1a. It is noted, however, that, in some cases, the equilibrium binding occurred at a location different from what the structure optimization using conjugate gradient started initially. Hence, our search for the equilibrium site is not limited to the above possible adsorption cites. Carrying optimization calculations for all these sites, the one that attains the lowest total energy (or highest binding energy) is set as the equilibrium site for a given adatom on the substrate in hand. In Figure 4, we show the calculated equilibrium atomic structures of the selected adatoms adsorbed to C ohs monolayers and their relevant state densities. The equilibrium binding energy calculated by PBE+(DFT-D3), $E_{\rm b}$, and the bond length

Table 1. Equilibrium Binding Energies E_b (in eV) of Various Adatoms Adsorbed to C ohs and Si ohs Monolayers Calculated Using PBE+(DFT-D3) and Their Distances to Nearest Host Atom d (in Å)^{*a*}

pubs.acs.org/acsaelm

		Н	0	С	Si	F	Gd	Ti
C ohs	$E_{\rm b}$ (eV/atom)	2.38	3.41	4.12	3.17	2.03	2.83 (7.86)	4.08 (0.95)
	d (Å)	1.11	1.28	1.28	1.80	2.29	2.25	1.68
Si ohs	$E_{\rm b}~({\rm eV/atom})$	2.81	6.98	8.14	5.09	5.65	5.48 (7.13)	5.17 (0.87)
	d (Å)	1.50	1.71	1.84	2.38	1.64	2.86	2.56
<i>a</i> ₇ 1						_		

^aLocal magnetic moments (in Bohr magneton, $\mu_{
m B}$ per supercell) of adatoms attaining a magnetic state are indicated in parentheses.

corresponding to nearest adatom-host atom distance d are listed in Table 1.

A single H atom is adsorbed to the B site of the (4×5) supercell of C ohs with $E_{\rm b}$ = 2.38 eV contributing to the band states below ca. -1.0 eV but mainly at -2.0 eV (see Figure 4a). The host carbon atom underneath is pulled up to make an sp³-like hybridization. As one can infer from the chemisorption of a single H atom to graphene, the adsorbed H atom becomes positively charged by donating electrons to carbon atoms. A Bader analysis⁶⁴ results in an effective charge of ca. +0.1 e on H adatom. The equilibrium position of O is found at the B-B bridge site with a binding energy of $E_{\rm b}$ = 3.41 eV and contributes to the band states mainly near -2.0 eV. According to the Bader analysis,⁶⁴ adsorbed O has an effective charge of ca. -0.8 e. A single C adatom having four valence electrons is bound above the D site by forming four bonds with underlying four C host atoms at the corners of the square ring. Si adatom being a group IV element like the host C atom is also adsorbed at the D site with a major contribution to the density of states at -3.3 eV. The binding energy $E_{\rm b} = 3.17$ eV. The fluorine adatom is adsorbed to C ohs monolayer with $E_{\rm b} = 2.03$ eV. Its major contribution to valence band states occurs at -3.0 eV.

The adsorption of specific adatoms like Gd and Ti is of interest, since they can attribute magnetic properties through their incomplete 3d and 4f shells, respectively, when adsorbed to C ohs monolayers (see Figure 4e,f). Note that 2D magnetism has been a field of current interest owing to possible spintronics applications. Recent studies showed that silicene monolayer acquired a ferromagnetic ground state at finite temperature upon Gd adatom coverage.^{50,51} Here, Gd is adsorbed to the A-A bridge site with $E_b = 2.89$ eV and acquires a magnetic moment per unit cell of 7.86 $\mu_{\rm B}$ constructed mainly from 4f orbitals of a Gd atom. If the size of the supercell allows a significant adatom-adatom interaction, the magnetic moments of these magnetic adatoms can be aligned to construct a ferro- or antiferromagnetic order depending on their exchange interaction. The transition temperatures of these magnetic ground states can be determined by carrying out Monte Carlo calculations.⁵¹ A Ti adatom adsorbed to the H site with a binding energy $E_{\rm b}$ of 4.08 eV attains a total magnetic moment of ~1.0 $\mu_{\rm B}$ per unit cell. Earlier, light transition-metal atoms, Sc, Ti, and V, adsorbed to graphene were known for their high capacity H₂ molecule storage.⁴³⁻⁴⁵ A Ti adatom adsorbed also to the same site on C ohs monolayer is expected to form the same kind of weak bonds with each hydrogen molecule around it to hold as many as four of them. Although Ti coverage of C ohs monolayer is beyond the scope of the present study, the clustering or dimer formation of Ti atoms adsorbed nearest hexagons does not occur here, since equilibrium H sites are wide apart.43-45

In Figure 5 the charge density isosurfaces of one H or O adatom absorbed to the (4×5) supercell of C ohs monolayer are presented. In contrast to the finite charge density at the



Article

Figure 5. Top and side views of charge density isosurfaces of single H and O adatoms adsorbed to C ohs at the equilibrium binding sites. (a) H and (b) O adatoms.

center of the square ring, holes are seen at the center of octagon and hexagon rings. A relatively larger hole at the center of octagon may enhance the diffusion of atoms and molecules through the monolayer. The charge distribution around the adatoms is in compliance with the Bader analysis discussed above. Charging of H or O adatom covered surfaces of C ohs monolayer attributes critical functionalities to ohs monolayers as discussed in the forthcoming sections.

Single adatoms (H, O, C, Si, F, Ti, and Gd) adsorbed to Si ohs monolayer display significant differences from those on C ohs due to longer Si–Si bonds and hence weaker π -bonds. Si ohs being a metal, the adsorption of an isolated adatom can have also little effect on the state density, and its metallicity is normally maintained. However, the supercell size of (2 × 2) used for Si ohs monolayer may not be sufficiently large to mimic the isolated adsorption for C and O adatoms; strong back bonds with specific adatoms may open a narrow band gap between conduction and valence bands.

A hydrogen adatom is adsorbed to the B site of a (2×2) supercell of Si ohs with a binding energy of 2.81 eV as described in Figure 6a. Upon chemisorption of H adatom, the host Si atom underneath is pulled up, but the metallic state is not altered. For the same supercell, the equilibrium adsorption site of O occurs above the A site by forming bridge bonds with two Si atoms of different square rings with a binding energy of 6.98 eV. This structure, however, opens a band gap of 0.4 eV in the metallic state density of Si ohs. Upon Heyd-Scuseria-Ernzerhorf (HSE) correction, the band gap rises to 0.56 eV. This result is important and indicates that two bands crossing just above the Fermi level are split and open a band gap upon the formation of strong O-Si bonds with three host Si atoms underneath. The majority of the contribution of the adsorbed O adatom and its bonds with nearest host atoms to the electronic structure occurs near -4 eV. The above results concerning H and O chemisorption did not change when these



Figure 6. Optimized atomic structures (top and side views) of single adatoms adsorbed to the (2×2) supercell of Si ohs corresponding to the equilibrium binding geometries (maximum binding energy) and their TDOS and LDOS calculated at the adatom and the nearest host atoms forming bonds with it. Atoms labeled with chemical symbol. (a) H. (b) O. (c) C. (d) Si. (e) F. (f) Gd. (g) Ti.

adatoms adsorbed to the (2×3) supercell of Si ohs. Because of a strong C-Si interaction, a C adatom on Si ohs leads to a massive deformation on the atomic structure, as described in Figure 6c, constructing a tetrahedron-like configuration with four C–Si bonds with their angles ranging from 81° to 121°. In a (2×2) supercell strong interatomic interactions including vdW forces can modify the atomic structure and lattice parameters significantly. Accordingly, the binding energy of an optimized structure is already high and 7.90 eV and increases to 8.14 eV by the inclusion of a vdW interaction. In the end, an indirect band gap of 0.14 eV is opened. Apparently, the adsorption O and C treated using (2×2) supercells are low coverage, patterned decorations rather than an isolated chemisorption. They can give rise to stable structures assured by AIMD at T = 1000 K, which may be modified significantly from original bare ohs monolayers and can be used to tune their band gap.

When adsorbed at the A site, the Si adatom pushes the host Si atom underneath and eventually forms a dumbbell-like structure, which also occurred in silicene monolayer. The dumbbell-like atomic structure continued to exist at T = 1000K. Because of this reconstruction of atoms, the bands around $E_{\rm F}$ are modified, but the system continued to be a metal. Fluorine F, having higher electronegativity relative to Si, is adsorbed at the B site with $E_b = 5.65$ eV forming flat bands at ca. -5.5 eV. Even if the bands near the Fermi level are modified, they continue to maintain the system in a metallic state. The atomic structure around F adatom remains stable even at T = 1000 K.

The Gd atom adsorbed near a H site in the supercell acquires a total magnetic moment of $\mu = 7.13 \ \mu_{\rm B}$ per unit cell as depicted in Figure 6f. However, these magnetic moments prefer to have an antiferromagnetic order, since it is 7 meV more favorable energetically as compared to the ferromagnetic order despite a small Gd-Gd coupling. On the one hand, this situation is in contrast with the ferromagnetic order, where one Gd atom is adsorbed to each H site of silicene monolayer.⁵¹ On the other hand, the equilibrium binding energy of Gd to Si ohs is stronger than that Gd atom adsorbing at the H site of silicene. This can be due to deformed sp² hybridization in Si ohs, which can construct stronger bonds with the adsorbed Gd atom.⁵¹ The equilibrium site for the adsorbed Ti adatom on the (2×2) supercell of Si ohs is deduced between the H site and B-B bridge site, as shown in Figure 6g. The binding is rather strong, and $E_{\rm b}$ = 5.17 eV. After the adsorption of Ti



Figure 7. Variation of the optimized energy as a function of the distance from the monolayer calculated for O atoms passing from the top to the bottom side through the center of hexagon (dark blue curve) and octagon (light green curve) on a straight path (indicated by red dots). The heights of the energy barriers are indicated by arrows. (a) C ohs monolayer. (b) Si ohs monolayer.

adatom, the (2×2) supercell acquires a total magnetic moment of $\mu = 0.87 \ \mu_{\rm B}$ per unitcell.

We now address an interesting issue of whether C ohs monolayer can prevent active surfaces from oxidation (or corrosion) like its counterpart graphene.^{80,81} On the one hand, as an atomically thin, metallic layer, C ohs would be an excellent coating material to protect surfaces from oxidation. On the other hand, one may contemplate that the hole at the center of the octagon being relatively larger than the hole at the center of the hexagon (see Figure 5) may weaken this capacity of C ohs. In this study, we present a simple analysis to explore the capacity of C ohs in protecting surfaces from oxidation. For the sake of comparison, we did the same analysis also for Si ohs monolayer. To this end, we calculated the energy barrier posed to oxygen atoms as they are passing through the holes at the centers of hexagons and octagons. This barrier is an obstacle that oxygen atoms must overcome as they are diffusing through C ohs and Si ohs monolayers to arrive at the active surface underneath. We considered that a single O atom starts from a height above the H(E) site and goes to an equivalent point below the monolayer following a straight path. For each fixed position of O atom on this path we performed the total energy calculations by relaxing the position of all host atoms. Our results in Figure 7 summarize our analysis. The energy barrier against the passage of O atom is rather high through the hexagons of C ohs (21.4 eV), even higher than that through the hexagons of graphene calculated earlier to be 10.12 eV.⁸¹ As found in graphene, the actual barrier energy can be smaller than the calculated barrier through a straight path, since the diffusing O atom can follow a minimum energy path. Thus we expect that the energy barrier on the minimum-energy path passing through the hexagon of C ohs is still higher than that found for graphene. Unfortunately, the passage of an O atom from the atmosphere through the hexagon is not the only available path. In fact, the passage through the octagon provides with a more open hole exerting even a smaller barrier. This barrier energy following a straight path is calculated to be 5.8 eV, close to one-fourth of that through the hexagon. Hence, the energy barrier can even be smaller, when an O atom follows a minimum energy path. In this respect, the capacity of C ohs monolayer in protecting the active surfaces from oxidation is relatively lower as compared to graphene. As for Si ohs monolayer with relatively longer bonds and larger holes, it poses only a small barrier of 0.4 eV through the hexagon but no barrier at all for the diffusion through the octagon.

COVERAGE/COATING OF C OHS AND SI OHS

High and full coverages of C ohs and Si ohs monolayers by the selected adatoms like H, O, C, and F on a single side or both sides lead to hydrogenation, oxidation, carbonation, and fluoridation, which are of particular interest. In the end, their physical and chemical properties can undergo dramatic changes. For example, while both monolayers are good 2D metals, they may undergo a metal—insulator transition and have an energy band gap varying with the coverage. In fact, as shown in the foregoing section, even at the low coverage of Si ohs monolayer, like one single O atom adsorbed to each (2×2) supercell, the metallic state has changed to a semiconductor. Moreover, the width of a band gap can change with coverage pattern allowing a kind of band engineering in the 2D materials.

In the past, hydrogen coverage of graphene has been a focus of interest. Because of relatively smaller C-C bond lengths and uniformity of C sites in graphene, hydrogenation has been achieved by saturating alternating C atoms by H adatoms from different sites. In this fully hydrogenated graphene, named as graphane, sp² hybridized bonding is modified to sp³-like bonding accompanied by the buckling of alternating carbon atoms. The situation is, however, different in C ohs due to its deformed sp² hybridization leading to diverse bond lengths and bond angles.¹¹ For the same reason, C atoms exhibit inequivalent chemical activities. In view of the results obtained from the adsorption of a single H adatom to the (4×5) supercell of C ohs, we first examined the hydrogenation of C ohs from a single side, which would easily be achieved for C ohs grown on a substrate. However, on the one hand, we found that the full hydrogenation (each C atom saturated by one H adatom) cannot be achieved on a single side; it is unfavorable energetically. On the other hand, a patterned coverage of H adatom at low concentration can be achieved on a single side, and the electronic and magnetic states are modified. As an example, calculations performed using PBE, HSE, 57 and a local basis⁵⁸ resulted in a nonmagnetic state, if single hydrogen is adsorbed to (1×1) , (2×1) , (2×3) , (3×3) , and (4×5) cells. However, the adsorption of a single H atom to (1×2) , (2×2) , (3×2) leads to a magnetic state with the magnetic moment $\mu \approx 0.9 \ \mu_{\rm B}$. We believe that the alternation of the magnetic state with the symmetry/size of the repeating cell (or pattern) is beyond the numerical error. It is interesting to note that HSE calculations on the (1×2) supercell of C ohs with one single H adatom adsorbed predict an integer magnetic moment μ of 1.0 $\mu_{\rm B}$ rendering a ferromagnetic semiconductor.

In addition to these diverse magnetic states, the electronic state can also undergo striking changes depending on the patterned coverage. For example, in the half coverage, where the host C atoms at one side are saturated alternatingly by H adatoms, the metallic C ohs monolayer undergoes a metal insulator transition and changes to a ferromagnetic semiconductor. This result demonstrates that one can construct 2D materials with unusual properties from the metallic C ohs via a patterned adsorption of adatoms.

After this discussion of patterned coverage or decoration of ohs monolayers, we now return to their full coverage. A recent theoretical study found that specific full hydrogenation of C ohs is a ground state and has the formation energy only ca. $-12 \text{ meV/atom smaller than that of graphane like hydrogenation.}^{82}$ We believe that, experimentally, this ground state of H coverage may be difficult to realize due to the uncertainties of incoming H atoms to select well-determined sites on C ohs. Here, as a proof of concept, we consider graphane-like full coverage, where C atoms are saturated alternatingly from the top side and bottom side as shown in Figure 8a. Upon this coverage of H, carbon atoms raised and



Figure 8. Full coverage of C ohs monolayer by H and O atoms. Atomic configuration of coverage with top and side views, energy band structure, and the TDOS together with LDOS at adatom. (a) CH ohs. H adatoms are shown by gray balls saturating host C atoms alternatingly from the top and bottom. (b) C ohs monolayer covered by O atoms. O atoms are represented by red balls forming bridge bonds with B–B bonds of the square ring alternatingly from the top and bottom. Zero of energy is set to the top of the valence band.

lowered to have a buckling of 0.42 Å to construct sp³-type bonding. The average binding energy is calculated to be $\overline{E}_b =$ 2.75 eV. By performing ab initio phonon and AIMD calculations at high temperature, we assured this H-covered C ohs has a dynamical and thermal stability. It is a wide band gap semiconductor with an indirect band gap of 3.82 eV calculated by PBE. The flat bands with energy between -2 and -4 eV are derived from C-H bonds. We expect that the width of the band gap can further increase in HSE calculations. We specify this hydrogenated monolayer as CH ohs.

At this point, we will address an important issue related to the hydrogenated CH ohs monolayer. Earlier, it was shown

that the friction constant between two slidings, diamond-like carbon-coated surfaces in relative motion was lowered dramatically upon the hydrogenation of the surfaces leading to a superlow friction.⁸³ In view of the progress made on the atomic-scale friction,^{84,85} we propose a system of superlow friction consisting of two parallel CH ohs monolayers as described in Figure 9a. Normally, an interaction or adhesion force F_i acts, when the spacing between nearest H atoms in different surfaces of these hydrogenated monolayers is small. Here, the variation of the interaction energy E_i between these surfaces, with the spacing z and the force $F_i = -\partial E_i / \partial z$ thereof, is calculated from first principles and is presented in Figure 9b,c, respectively. The force acting between the hydrogenated surfaces starts to become repulsive already for z < 1.9 Å, where E_i has a minimum value. Surprisingly, this spacing is almost 3 times the bond distance of a H₂ molecule. The excess positive charge on H atoms of both surfaces, which occurred due to electron donation to host C atoms, is responsible for this repulsive force range, which starts even at a large separation. The repulsive force acting from a large z prevents the asperities or bonds of sliding surfaces from going into each other. Even under a perpendicular loading force F_{N} , hydrogenated surfaces are kept apart from each other, so that the elastic deformation of C-H molecules through bending is reduced. Accordingly, the elastic energy stored in the stick phase of the stick-slip motion⁸⁶ will excite a limited number of phonon modes in the slip phase. On the one hand, at the end, the friction between sliding surfaces can be reduced by coating with CH ohs monolayers. On the other hand, in the sliding motion of a bare and flat metal surface under the normal loading force, z is small, and hence atoms (or bonds) at each surface undergo large displacements from their equilibrium positions in the course of slip, and a large amount of mechanical energy is converted to elastic energy. When released suddenly in the course of slip, the large amount of phonon density is excited, and hence the mechanical energy is dissipated in the sliding friction leading to a high friction constant. Most recently, the band gap engineering through the decoration of C ohs by H atoms was investigated.⁸⁷ Zhang et al. predicted that the thermal transport of C ohs is suppressed significantly upon the full coverage of H due to enhanced phonon scattering rate.⁸⁸ A modification of magnetic and electronic properties of C ohs through hydrogen coverage and decoration can lead to future applications as discussed in the forthcoming section.

Oxidation of C ohs through oxygen adatoms forming bridge bonds on B–B bonds of the square ring alternatingly from the top and bottom as shown in Figure 8b is another critical coverage we took into consideration in this study. Once C ohs is covered by O adatoms, a direct band gap of 2.76 eV is opened in the metallic state density of bare C ohs; the bands with low dispersion at the edge of conduction and valence bands carry a significant contribution of O adatoms. Most recently, on the basis of DFT calculations Liu et al. showed that C ohs is a metal-free candidate for facilitating the electrochemical oxygen reduction reaction for fuel-cell technologies.⁸⁹

Carbonation of C ohs monolayer can be achieved by adsorbing C adatoms above the center of each square ring (D site), which was demonstrated to be an equilibrium position for the chemisorption of an individual C adatom in the foregoing section. The stability of this carbonation is ensured by the phonon calculations as well as AIMD simulations at T =1000 K. The major effect of the carbonation is the opening of a



Figure 9. (a) Two parallel CH ohs monolayers. Carbon and hydrogen atoms are shown by large orange and small gray balls, respectively. The distance between H atoms in opposite surfaces is z. (b) The calculated interaction energy E_i , between these monolayers as a function of z. At z = 1.9 Å, E_i attains its minimum value. (c) The calculated interaction (or adhesion) force F_i . For z < 1.9 Å, F_i becomes repulsive.

very small direct band gap of 40 meV in the metallic state density. Fluorine atoms can provide full coverage of C ohs by adsorbing to the host carbon atoms at the top site alternatingly from the top and bottom side. The full coverage of C ohs with F is assured to be stable. Upon fluorination, the metallic C ohs monolayer changes to a semiconductor with an indirect band gap of 3.07 eV.

Because of its relatively longer Si–Si bonds, Si ohs can be hydrogenated fully by saturating each Si atom by one H adatom from a single side as well as from both sides, like graphane. However, the latter described in Figure 10a is 443 meV more favorable energetically relative to the single-side coverage. The calculated average binding energy \overline{E}_b is 2.88 eV. An indirect band gap of 2.30 eV is opened in the metallic state density of bare Si ohs. Flat bands between -2 and -3 eV are derived from Si–H bands. Hence, upon the hydrogenation of Si ohs, the metallic monolayer changes to a semiconductor with a wide band gap and becomes further stabilized. This state of fully hydrogenated Si ohs keeps the promises of various applications as pointed out above for C ohs.

In the full coverage of Si ohs, O adatoms form A–A and B– B bridge bonds from top and bottom. This coverage geometry has been arrived at by attaching O atoms first to the sites revealed for its individual/isolated adsorption. Upon relaxation, the coverage geometry described in Figure 10b occurred, where six O atoms are adsorbed to each unit cell of Si ohs by forming bridge bonds above and below each A–A and B–B bond. In this coverage configuration, an indirect band gap of 0.65 eV is opened to attribute a semiconducting state to otherwise metallic Si ohs. Upon coverage of O adatoms flat bands at ca. -3 eV are derived from Si–O bonds.

DISCUSSIONS AND CONCLUSIONS

The physical and chemical properties predicted after the formation of point defects, isolated chemisorption of adatoms,



Figure 10. Full coverage of Si ohs monolayer by H and O atoms. (a) Top and side views of the atomic structure of Si ohs monolayer saturated by H atoms alternatingly from the top and bottom side. Energy-band structure with an indirect band gap of 2.30 eV. Hydrogen atoms saturating Si host atoms are indicated by small blue balls. (b) Same for oxygen adatoms (indicated by red balls) covering Si ohs from both sides. Zero energy is set to the top of the valence band.

such as H, O, C, Si, F, Ti, and Gd, and high/low coverage of selected atoms like H, O, C, and F have revealed critical and fundamental features. In this section, we will discuss these features with underlying physics and their prospective potential technological applications.

- (i) The local changes in the electronic potential induced by individual/isolated point defects and adatoms are usually screened by the 2D metallic electron density of C and Si ohs monolayers. The emerging electronic states are localized if their energies fall in the band gap, but they usually become resonance states in the valence- and conduction-band continua. While single vacancies formed at A and B sites are magnetic via the twofold coordinated C atoms, the divacancy formed at the adjacent A and B sites is nonmagnetic. However, the formation energy of the divacancy is found to be smaller than that of the A-site single vacancy but larger than that formed at the B site. This situation indicates additional rebonding in the formation of divacancy. We predict that neither isolated monovacancy nor divacancy in Si ohs is magnetic.
- (ii) An isolated void or antidot formation in C ohs or Si ohs can lead to the formation of edge states on the host atoms surrounding the void. The persistent currents through these closed edge states and the Aharonov-Bohm oscillations therein can be a fundamentally attractive subject both theoretically and experimentally. A periodically repeating or patterned void is expected to display interesting electronic and magnetic structures depending on the geometry, size, and lattice symmetries of the voids.
- (iii) C ohs monolayers including isolated monovacancy and also adsorbed single Ti or Gd adatom attain nonzero magnetic moments due to unpaired electrons or unfilled orbitals. When decorated with these defects or adatoms, the 2D structure can attain diverse magnetic states, such as planar and columnar ferromagnetic, ferrimagnetic, antiferromagnetic ground states, and even skyrmions, which may lead to interesting 2D spintronic devices. The 2D magnetic states and the underlying exchange interactions in these functional systems deserve further study.
- (iv) Ti adsorbed on C ohs can be of particular interest because of its capacity to weakly bind many hydrogen molecules and hence to store hydrogen energy. Earlier, it was demonstrated⁴³⁻⁴⁵ that Ti atoms adsorbed to the H site of graphene from both sides were shown to serve as a high-capacity hydrogen storage medium. In this process, the complex charge exchange mechanism among Ti adatom, C host atom, and H₂ molecule underlies the weak binding interaction with many (four to five) H₂ molecules around Ti.
- (v) In many functional systems in this study, we showed that different effects can give rise to the opening of a band gap in a metallic-state density with widths varying depending on various parameters, hence, enabling the band gap engineering. A band gap is opened due to the change in the s-p hybridization as a result of the adsorption of adatoms and also due to enhanced coupling between them. The interaction through the back bonds with C or Si host atoms at relatively low coverage may set the opening of a small gap. The process of full coverage of C ohs and Si ohs by selected adatoms may involve an interesting interplay between the time variation of the concentration and coverage landscaping due to deformed sp² hybridization and local changes in the electronic potential induced by adatoms.

- (vi) Full coverage of C and Si ohs ends with a metalsemiconductor transition. The metallic 2D monolayers change to wide band gap semiconductors. This situation brings about so many alternative composite systems and structures with potential device applications. First, by dehydrogenation or deoxidation of stripes on fully H- or O-covered C ohs and Si ohs monolayers, one can construct various lateral composite structures consisting of commensurate bare and adatom-covered zones of ohs monolayers. Depending on the pattern and size of these zones one can construct novel materials of unusual electronic and magnetic properties, such as alloys, heterostructures, quantum wells, antidots, and antirings. Similar effects can be realized by the vertical stacking of CH ohs and C ohs mono- or multilayers and can be exploited as metal-semiconductor junctions with a welldefined Schottky barrier or energy-storing nanodevices. Our extensive study on this method enabling the realization of various quantum structures and devices thereof will be published elsewhere.
- (vii) Another interesting feature is related with the excess charge on the adatoms, which fully cover the metallic monolayers. For example, on the one hand, we showed that H adatoms fully covering C ohs attain some positive charge. On the other hand, both surfaces of C ohs fully covered with O or F adatoms are negatively charged. We presented a physical discussion about how one can reduce the energy dissipation to attain a (super) low friction coefficient in the sliding motion of active metal surfaces coated with CH ohs monolayers.
- (viii) In this study we calculated the energy barriers against the penetration of a single O atom through the centers of hexagons and octagons of C ohs. We found that the energy barrier to an O atom passing through the center of an octagon ring is much smaller than that of hexagon. Therefore, the capacity of C ohs monolayer in protecting the active surfaces from oxidation is relatively lower as compared to graphene. Perhaps, this drawback can be overcome by multilayer C ohs coverage.

In conclusion, we showed that the physical and chemical properties of C ohs and Si ohs monolayers can undergo significant changes by the creation of point defects like monovacancies, divacancy, antidot and substitutional impurities, chemisorption of adatoms, and their patterned as well as full coverage. The variations of these changes with symmetry and size of these defects were explored extensively. The unusual physical effects revealed on these 2D materials keep the promises of extensive technological applications as well as active experimental studies. It was demonstrated that these changes can be associated with important features, which make these 2D materials functional. We discussed the physics underlying these features and pointed out the viable applications.

AUTHOR INFORMATION

Corresponding Authors

Ethem Aktürk – Department of Physics, Adnan Menderes University, Aydin 09100, Turkey; Physik Department E20, Technische Universität München, Garching 85748, Germany; orcid.org/0000-0002-1615-7841; Email: ethem.aktuerk@tum.de Salim Ciraci – Department of Physics, Bilkent University, Ankara 06800, Turkey; Email: ciraci@fen.bilkent.edu.tr

Authors

- **Taylan Gorkan** Department of Physics, Adnan Menderes University, Aydin 09100, Turkey
- Şafak Çallıoğlu Department of Electrical and Electronic Engineering, Bilkent University, Ankara 06800, Turkey
 Salih Demirci – Department of Physics, Kırıkkale University, Kırıkkale 71450, Turkey

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaelm.2c00459

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

E.A. acknowledges the Alexander von Humboldt Foundation for a Research Fellowship for Experienced Researchers. S.C. thanks The Academy of Science of Turkey for the financial support. Computations were performed at the National Center for High-Performance Computing of Turkey under the Grant No. 5004132016 program, under the Project Nos. 2022/003 and 2022/004, by Scientific Research Projects Coordination Unit of Kırıkkale University and TUBITAK ULAKBIM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure).

REFERENCES

(1) Schlütter, F.; Nishiuchi, T.; Enkelmann, V.; Müllen, K. Octafunctionalized Biphenylenes: Molecular Precursors for Isomeric Graphene Nanostructures. *Angew. Chem., Int. Ed.* **2014**, *53*, 1538–1542.

(2) Fan, Q.; Yan, L.; Tripp, M. W.; Krejčí, O.; Dimosthenous, S.; Kachel, S. R.; Chen, M.; Foster, A. S.; Koert, U.; Liljeroth, P.; Gottfried, J. M. Biphenylene network: A nonbenzenoid carbon allotrope. *Science* **2021**, 372, 852–856.

(3) Balaban, A.; Rentia, C. C.; Ciupitu, E. Chemical graphs. 6. Estimation of relative stability of several planar and tridimensional lattices for elementary carbon. *Revue Roumaine de Chimie* **1968**, *13*, 231.

(4) Hudspeth, M. A.; Whitman, B. W.; Barone, V.; Peralta, J. E. Electronic properties of the biphenylene sheet and its one-dimensional derivatives. *ACS Nano* **2010**, *4*, 4565–4570.

(5) Wang, X.-Q.; Li, H.-D.; Wang, J.-T. Prediction of a new twodimensional metallic carbon allotrope. *Phys. Chem. Chem. Phys.* 2013, 15, 2024–2030.

(6) Rahaman, O.; Mortazavi, B.; Dianat, A.; Cuniberti, G.; Rabczuk, T. Metamorphosis in carbon network: From penta-graphene to biphenylene under uniaxial tension. *FlatChem.* **2017**, *1*, 65–73.

(7) He, C.; Wang, W. 2D Octagon-Structure Carbon and Its Polarization Resolved Raman Spectra. *Nanomaterials* **2020**, *10*, 2252.

(8) Bafekry, A.; Faraji, M.; Fadlallah, M.; Jappor, H.; Karbasizadeh, S.; Ghergherehchi, M.; Gogova, D. Biphenylene monolayer as a twodimensional nonbenzenoid carbon allotrope: a first-principles study. *J. Phys.: Condens. Matter* **2021**, *34*, 015001.

(9) Bafekry, A.; Faraji, M.; Hieu, N.; Bagheri Khatibani, A.; Fadlallah, M. M.; Gogova, D.; Ghergherehchi, M. Tunable electronic properties of porous graphitic carbon nitride (C6N7) monolayer by atomic doping and embedding: A first-principle study. *Appl. Surf. Sci.* **2022**, 583, 152270.

(10) Shahrokhi, M.; Mortazavi, B.; Berdiyorov, G. R. New twodimensional boron nitride allotropes with attractive electronic and optical properties. *Solid State Commun.* **2017**, *253*, 51–56.

(11) Demirci, S.; Çallıoğlu, Ş.; Görkan, T.; Aktürk, E.; Ciraci, S. Stability and electronic properties of monolayer and multilayer

structures of group-IV elements and compounds of complementary groups in biphenylene network. *Phys. Rev. B* **2022**, *105*, 035408.

(12) Şahin, H.; Cahangirov, S.; Topsakal, M.; Bekaroglu, E.; Akturk, E.; Senger, R. T.; Ciraci, S. Monolayer honeycomb structures of group-IV elements and III-V binary compounds: First-principles calculations. *Phys. Rev. B* 2009, *80*, 155453.

(13) Cahangirov, S.; Topsakal, M.; Aktürk, E.; Şahin, H.; Ciraci, S. Two-and one-dimensional honeycomb structures of silicon and germanium. *Physical review letters* **2009**, *102*, 236804.

(14) Topsakal, M.; Aktürk, E.; Ciraci, S. First-principles study of two-and one-dimensional honeycomb structures of boron nitride. *Phys. Rev. B* **2009**, *79*, 115442.

(15) Bekaroglu, E.; Topsakal, M.; Cahangirov, S.; Ciraci, S. Firstprinciples study of defects and adatoms in silicon carbide honeycomb structures. *Phys. Rev. B* **2010**, *81*, 075433.

(16) Topsakal, M.; Cahangirov, S.; Bekaroglu, E.; Ciraci, S. Firstprinciples study of zinc oxide honeycomb structures. *Phys. Rev. B* **2009**, *80*, 235119.

(17) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.-e.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. *science* **2004**, *306*, 666–669.

(18) Blanc, N.; Jean, F.; Krasheninnikov, A. V.; Renaud, G.; Coraux, J. Strains induced by point defects in graphene on a metal. *Phys. Rev. Lett.* **2013**, *111*, 085501.

(19) Wang, L.; Zhang, X.; Chan, H. L.; Yan, F.; Ding, F. Formation and healing of vacancies in graphene chemical vapor deposition (CVD) growth. J. Am. Chem. Soc. **2013**, 135, 4476–4482.

(20) Robertson, A. W.; Allen, C. S.; Wu, Y. A.; He, K.; Olivier, J.; Neethling, J.; Kirkland, A. I.; Warner, J. H. Spatial control of defect creation in graphene at the nanoscale. *Nat. Commun.* **2012**, *3*, 1–7.

(21) Bafekry, A.; Faraji, M.; Fadlallah, M. M.; Mortazavi, B.; Ziabari, A. A.; Khatibani, A. B.; Nguyen, C. V.; Ghergherehchi, M.; Gogova, D. Point Defects in a Two-Dimensional ZnSnN2 Nanosheet: A First-Principles Study on the Electronic and Magnetic Properties. *J. Phys. Chem. C* **2021**, *125*, 13067–13075.

(22) Bafekry, A.; Faraji, M.; Karbasizadeh, S.; Khatibani, B. A.; Ziabari, A. A.; Gogova, D.; Ghergherehchi, M. Point defects in twodimensional BeO monolayer: a first-principles study on electronic and magnetic properties. *Phys. Chem. Chem. Phys.* **2021**, *23*, 24301–24312.

(23) Şahin, H.; Ciraci, S. Structural, mechanical, and electronic properties of defect-patterned graphene nanomeshes from first principles. *Phys. Rev. B* 2011, *84*, 035452.

(24) Dai, X.; Zhao, J.; Xie, M.; Tang, Y.; Li, Y.; Zhao, B. Firstprinciple study of magnetism induced by vacancies in graphene. *European Physical Journal B* **2011**, *80*, 343–349.

(25) Ovdat, O.; Don, Y.; Akkermans, E. Vacancies in graphene: Dirac physics and fractional vacuum charges. *Phys. Rev. B* **2020**, *102*, 075109.

(26) Nanda, B.; Sherafati, M.; Popović, Z. S.; Satpathy, S. Electronic structure of the substitutional vacancy in graphene: density-functional and Green's function studies. *New J. Phys.* **2012**, *14*, 083004.

(27) Balog, R.; Jørgensen, B.; Nilsson, L.; Andersen, M.; Rienks, E.; Bianchi, M.; Fanetti, M.; Lægsgaard, E.; Baraldi, A.; Lizzit, S.; Sljivancanin, Z.; Besenbacher, F.; Hammer, B.; Pedersen, T. G.; Hofmann, P.; et al. Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nature materials* **2010**, *9*, 315–319.

(28) Son, J.; Lee, S.; Kim, S. J.; Park, B. C.; Lee, H.-K.; Kim, S.; Kim, J. H.; Hong, B. H.; Hong, J. Hydrogenated monolayer graphene with reversible and tunable wide band gap and its field-effect transistor. *Nat. Commun.* **2016**, *7*, 1–7.

(29) Sofo, J. O.; Chaudhari, A. S.; Barber, G. D. Graphane: A twodimensional hydrocarbon. *Phys. Rev. B* **2007**, *75*, 153401.

(30) Elias, D. C.; Nair, R. R.; Mohiuddin, T.; Morozov, S.; Blake, P.; Halsall, M.; Ferrari, A. C.; Boukhvalov, D.; Katsnelson, M.; Geim, A.; Novoselov, K. Control of grapheneas properties by reversible hydrogenation: evidence for graphane. *Science* **2009**, *323*, 610–613. (31) Şahin, H.; Ataca, C.; Ciraci, S. Electronic and magnetic properties of graphane nanoribbons. *Phys. Rev. B* **2010**, *81*, 205417. (32) Mathieu, C.; Lalmi, B.; Menteş, T.; Pallecchi, E.; Locatelli, A.; Latil, S.; Belkhou, R.; Ouerghi, A. Effect of oxygen adsorption on the local properties of epitaxial graphene on SiC (0001). *Phys. Rev. B* **2012**, *86*, 035435.

(33) Ito, J.; Nakamura, J.; Natori, A. Semiconducting nature of the oxygen-adsorbed graphene sheet. *Journal of applied physics* **2008**, *103*, 113712.

(34) Carlsson, J. M.; Hanke, F.; Linic, S.; Scheffler, M. Two-step mechanism for low-temperature oxidation of vacancies in graphene. *Physical review letters* **2009**, *102*, 166104.

(35) Suarez, A. M.; Radovic, L. R.; Bar-Ziv, E.; Sofo, J. O. Gate-voltage control of oxygen diffusion on graphene. *Physical review letters* **2011**, *106*, 146802.

(36) Granas, E.; Knudsen, J.; Schroder, U. A.; Gerber, T.; Busse, C.; Arman, M. A.; Schulte, K.; Andersen, J. N.; Michely, T. Oxygen intercalation under graphene on Ir (111): energetics, kinetics, and the role of graphene edges. *ACS Nano* **2012**, *6*, 9951–9963.

(37) Şahin, H.; Topsakal, M.; Ciraci, S. Structures of fluorinated graphene and their signatures. *Phys. Rev. B* 2011, 83, 115432.

(38) Sahin, H.; Ciraci, S. Chlorine adsorption on graphene: Chlorographene. J. Phys. Chem. C 2012, 116, 24075–24083.

(39) Feng, Q.; Cao, Q.; Li, M.; Liu, F.; Tang, N.; Du, Y. Synthesis and photoluminescence of fluorinated graphene quantum dots. *Appl. Phys. Lett.* **2013**, *102*, 013111.

(40) Topsakal, M.; Cahangirov, S.; Ciraci, S. The response of mechanical and electronic properties of graphane to the elastic strain. *Appl. Phys. Lett.* **2010**, *96*, 091912.

(41) Sevinçli, H.; Topsakal, M.; Durgun, E.; Ciraci, S. Electronic and magnetic properties of 3 d transition-metal atom adsorbed graphene and graphene nanoribbons. *Phys. Rev. B* 2008, 77, 195434.

(42) Ersan, F.; Aktürk, E.; Ciraci, S. Glycine self-assembled on graphene enhances the solar absorbance performance. *Carbon* **2019**, *143*, 329–334.

(43) Yildirim, T.; Ciraci, S. Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium. *Physical review letters* **2005**, *94*, 175501.

(44) Durgun, E.; Ciraci, S.; Zhou, W.; Yildirim, T. Transition-metalethylene complexes as high-capacity hydrogen-storage media. *Physical review letters* **2006**, *97*, 226102.

(45) Durgun, E.; Ciraci, S.; Yildirim, T. Functionalization of carbonbased nanostructures with light transition-metal atoms for hydrogen storage. *Phys. Rev. B* **2008**, *77*, 085405.

(46) Bafekry, A.; Faraji, M.; Fadlallah, M. M.; Hoat, D. M.; Khatibani, A. B.; Sarsari, I. A.; Ghergherehchi, M. Effect of adsorption and substitutional B doping at different concentrations on the electronic and magnetic properties of a BeO monolayer: a firstprinciples study. *Phys. Chem. Chem. Phys.* **2021**, *23*, 24922–24931.

(47) Denis, P. A. Stability and Electronic Properties of Biphenylene Based Functionalized Nanoribbons and Sheets. *J. Phys. Chem. C* 2014, *118*, 24976–24982.

(48) Denis, P. A.; Iribarne, F. Hydrogen storage in doped biphenylene based sheets. *Computational and Theoretical Chemistry* **2015**, *1062*, 30–35.

(49) Topsakal, M.; Cahangirov, S.; Ciraci, S. The response of mechanical and electronic properties of graphane to the elastic strain. *Appl. Phys. Lett.* **2010**, *96*, 091912.

(50) Tokmachev, A. M.; Averyanov, D. V.; Parfenov, O. E.; Taldenkov, A. N.; Karateev, I. A.; Sokolov, I. S.; Kondratev, O. A.; Storchak, V. G. Emerging two-dimensional ferromagnetism in silicene materials. *Nat. Commun.* **2018**, *9*, 1–9.

(51) Demirci, S.; Gorkan, T.; Çallioglu, Ş.; Yüksel, Y.; Akıncı, U.; Aktürk, E.; Ciraci, S. Magnetization of silicene via coverage with gadolinium: Effects of thickness, symmetry, strain, and coverage. *Phys. Rev. B* **2021**, *104*, 224427.

(52) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* B **1996**, *54*, 11169.

(53) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953.

(54) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Physical review letters* **1996**, *77*, 3865.

(55) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(56) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *Journal of computational chemistry* **2011**, *32*, 1456–1465.

(57) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.

(58) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. The SIESTA method for ab initio order-N materials simulation. *J. Phys.: Condens. Matter* **2002**, *14*, 2745.

(59) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C.; Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+ U study. *Phys. Rev. B* **1998**, *57*, 1505.

(60) Oroszlány, L.; Deák, A.; Simon, E.; Khmelevskyi, S.; Szunyogh, L. Magnetism of gadolinium: a first-principles perspective. *Physical review letters* **2015**, *115*, 096402.

(61) Anisimov, V. I.; Aryasetiawan, F.; Lichtenstein, A. Firstprinciples calculations of the electronic structure and spectra of strongly correlated systems: the LDA+ U method. *J. Phys.: Condens. Matter* **1997**, *9*, 767.

(62) Turek, I.; Kudrnovský, J.; Bihlmayer, G.; Blügel, S. Ab initio theory of exchange interactions and the Curie temperature of bulk Gd. J. Phys.: Condens. Matter 2003, 15, 2771.

(63) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scripta Materialia* **2015**, *108*, 1–5.

(64) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **2006**, *36*, 354–360.

(65) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of applied crystallography* **2011**, *44*, 1272–1276.

(66) Korzhavyi, P. A.; Abrikosov, I. A.; Johansson, B.; Ruban, A.; Skriver, H. L. First-principles calculations of the vacancy formation energy in transition and noble metals. *Phys. Rev. B* **1999**, *59*, 11693.

(67) Li, L.; Reich, S.; Robertson, J. Defect energies of graphite: Density-functional calculations. *Phys. Rev. B* **2005**, *72*, 184109.

(68) Wang, L.; Zhang, X.; Chan, H. L.; Yan, F.; Ding, F. Formation and healing of vacancies in graphene chemical vapor deposition (CVD) growth. J. Am. Chem. Soc. **2013**, 135, 4476–4482.

(69) Perilli, D.; Selli, D.; Liu, H.; Bianchetti, E.; Di Valentin, C. h-BN Defective Layers as Giant N-Donor Macrocycles for Cu Adatom Trapping from the Underlying Metal Substrate. *J. Phys. Chem. C* **2018**, *122*, 23610–23622.

(70) Cleveland, M. W.; Demkowicz, M. J. Persistence of negative vacancy and self-interstitial formation energies in atomistic models of amorphous silicon. *Physical Review Materials* **2022**, *6*, 013611.

(71) Turner, D. E.; Zhu, Z.; Chan, C. T.; Ho, K. Energetics of vacancy and substitutional impurities in aluminum bulk and clusters. *Phys. Rev. B* **1997**, *55*, 13842.

(72) Xu, Y.; Li, Y.; Chen, X.; Zhang, C.; Zhang, R.; Lu, P. Firstprinciple study of hydrogenation on monolayer MoS2. *Aip Advances* **2016**, *6*, 075001.

(73) Chan, K. T.; Neaton, J.; Cohen, M. L. First-principles study of metal adatom adsorption on graphene. *Phys. Rev. B* 2008, 77, 235430.

(74) Barker, B. A.; Bradley, A. J.; Ugeda, M. M.; Coh, S.; Zettl, A.; Crommie, M. F.; Louie, S. G.; Cohen, M. L. Geometry and electronic structure of iridium adsorbed on graphene. *Phys. Rev. B* **2019**, *99*, 075431.

(75) Aktürk, E.; Ataca, C.; Ciraci, S. Effects of silicon and germanium adsorbed on graphene. *Appl. Phys. Lett.* **2010**, *96*, 123112. (76) Ersan, F.; Arslanalp, Ö.; Gökoğlu, G.; Aktürk, E. Effects of silver adatoms on the electronic structure of silicene. *Appl. Surf. Sci.* **2014**, *311*, 9–13.

(77) Nguyen, D. K.; Tran, N. T. T.; Chiu, Y.-H.; Lin, M.-F. Concentration-diversified magnetic and electronic properties of halogen-adsorbed silicene. *Sci. Rep.* **2019**, *9*, 1–15.

(78) Sahin, H.; Peeters, F. M. Adsorption of alkali, alkaline-earth, and 3 d transition metal atoms on silicene. *Phys. Rev. B* 2013, 87, 085423.

(79) Sivek, J.; Sahin, H.; Partoens, B.; Peeters, F. M. Adsorption and absorption of boron, nitrogen, aluminum, and phosphorus on silicene: Stability and electronic and phonon properties. *Phys. Rev. B* **2013**, *87*, 085444.

(80) Chen, S.; Brown, L.; Levendorf, M.; Cai, W.; Ju, S.-Y.; Edgeworth, J.; Li, X.; Magnuson, C. W.; Velamakanni, A.; Piner, R. D.; Kang, J.; Park, J.; Ruoff, R. S. Oxidation resistance of graphene-coated Cu and Cu/Ni alloy. *ACS Nano* **2011**, *5*, 1321–1327.

(81) Topsakal, M.; Şahin, H.; Ciraci, S. Graphene coatings: An efficient protection from oxidation. *Phys. Rev. B* **2012**, *85*, 155445.

(82) Liao, Y.; Shi, X.; Ouyang, T.; Li, J.; Zhang, C.; Tang, C.; He, C.; Zhong, J. New Two-Dimensional Wide Band Gap Hydrocarbon Insulator by Hydrogenation of a Biphenylene Sheet. *J. Phys. Chem. Lett.* **2021**, *12*, 8889–8896.

(83) Erdemir, A. The role of hydrogen in tribological properties of diamond-like carbon films. *Surf. Coat. Technol.* **2001**, *146*, 292–297.

(84) Socoliuc, A.; Bennewitz, R.; Gnecco, E.; Meyer, E. Transition from stick-slip to continuous sliding in atomic friction: entering a new regime of ultralow friction. *Physical review letters* **2004**, *92*, 134301.

(85) Cahangirov, S.; Ataca, C.; Topsakal, M.; Sahin, H.; Ciraci, S. Frictional figures of merit for single layered nanostructures. *Physical review letters* **2012**, *108*, 126103.

(86) Mises, R. v. Mechanik der plastischen Formänderung von Kristallen. ZAMM-Journal of Applied Mathematics and Mechanics/ Zeitschrift für Angewandte Mathematik und Mechanik **1928**, 8, 161– 185.

(87) Lee, S.; Singh, A.; Lee, H. Band gap engineering of 2D biphenylene carbon sheets with hydrogenation. *Journal of the Korean Physical Society* **2021**, *79*, 846–850.

(88) Zhang, P.; Ouyang, T.; Tang, C.; He, C.; Li, J.; Zhang, C.; Hu, M.; Zhong, J. The intrinsic thermal transport properties of the biphenylene network and the influence of hydrogenation: a first-principles study. *Journal of Materials Chemistry C* 2021, 9, 16945–16951.

(89) Liu, T.; Jing, Y.; Li, Y. Two-Dimensional Biphenylene: AGraphene Allotrope with Superior Activity toward Electrochemical Oxygen Reduction Reaction. *J. Phys. Chem. Lett.* **2021**, *12*, 12230– 12234.

(90) Topsakal, M.; Ciraci, S. Domain formation on oxidized graphene. *Phys. Rev. B* 2012, *86*, 205402.

Recommended by ACS

Hydrogenated Carbon Monolayer in Biphenylene Network Offers a Potential Paradigm for Nanoelectronic Devices

Salih Demirci, Salim Ciraci, *et al.* AUGUST 30, 2022

 THE JOURNAL OF PHYSICAL CHEMISTRY C
 READ Z

 2D Boron Carbide, Carbon Nitride, and Silicon Carbide: A

 Theoretical Prediction

Wen-Han Zhao, Ran Jia, et al.

pubs.acs.org/acsaelm

OCTOBER 04, 2022	
ACS APPLIED ELECTRONIC MATERIALS	READ 🗹

Four Carbon Allotropes Form COT Structures

Qingyang Fan, Sining Yun, et al.	
APRIL 27, 2022	
ACS APPLIED ELECTRONIC MATERIALS	READ 🗹

Thermal Properties of 2D Dirac Materials MN_4 (M = Be and Mg): A First-Principles Study

Man Wang and Dan Han

MARCH 14, 2022	
ACS OMEGA	READ 🗹

Get More Suggestions >