Graphene is unarguably one of the most novel materials of modern time. Graphene has potential application in a wide range of fields but the lack of band gap is one obstacle for utilizing it in semiconductor-based devices. There are a number of investigations on bandgap opening and tuning using various techniques. Giovannetti et al. had predicted theoretically that the substrate might induce a small band gap. However, experimentally, substrate-induced band gap is an issue of controversy. A more accepted approach is by creating finite-size nanoribbons out of graphene. The electronic confinement in nanoribbons results in a substantial band-gap opening. Controlling the width of a nanoribbon is a technologically challenging task, which puts a restriction on this method for precise tuning. A more promising method is hydrogenation of graphene.

The interest in hydrogenation of graphene is twofold; it can be used to tune the band gap and it can also be harnessed as a hydrogen-storage material. In an important theoretical work, Duplock et al. first showed that upon adsorption of hydrogen on graphene a band gap can be opened. Even a single hydrogen atom may lead to band gap of 1.25 eV. Later, Boukhvalov et al. extensively studied the adsorption of hydrogen atoms on multiple layers of graphene. Their density functional study brought out the nature of the magnetism as well as stability of graphene in the presence of adsorbents. More recently, in an intriguing experiment Balog et al. demonstrated that the hydrogenation can indeed be used to open the band gap. Their results confirmed that patterned hydrogenation can be systematically applied to open up a band gap. By a novel way of semihydrogenating graphene, Zhou et al. proposed a new ferromagnetic material, graphene, which exhibits a small indirect band gap (0.46 eV). As we shall demonstrate in this paper, complete hydrogenation eventually leads to an indirect but a larger band gap.

All of the above reports deal with partial hydrogenation of graphene. In a different approach, Sofo et al. in 2007 predicted the existence of completely hydrogenated graphene and named it graphene. (“Graphane” is written in italic to avoid confusion with “graphene.”) It was two years later that Elias et al. experimentally confirmed the existence of the same, which sparked tremendous interest.

Although hydrogenation of graphene has been under a series of investigations, the research addressed either partial hydrogenation (as in graphene) or complete but double-sided hydrogenation (as in graphane). A report by Muniz and Maroudas considers the effects of hydrogen coverage on a single side of graphene plane. However, their study is based on the classical methods and does not address the electronic structure.

The first experimental indication of single-sided hydrogenation came from Elias et al. during their synthesis of graphane. They mentioned a possible contradiction with the theoretical results of Sofo et al., which had downplayed the possibility of such single-sided hydrogenation on the basis of energetics. More recently, Subrahmanyan et al. demonstrated the utilization of multilayer graphene for hydrogen storage, where the possibility of single-sided hydrogenation is clearly mentioned. Thus, at present, there is a compelling necessity to study in detail the electronic structure of single-sided hydrogenation of graphene. It stems from the fact that when graphene is grown on a substrate like SiO2 it is impossible for hydrogen to diffuse through the graphene to form double-sided hydrogenated graphene and the only possibility is partial or complete hydrogenation from a single side. Neglecting the substrate effects on graphene, which were found to be relatively small, we concentrate in this report on the electronic-structure properties characterizing such single-side-hydrogenated graphene, which we shall call SSHGraphene.

We carried out full unit-cell optimization and detailed electronic-structure calculations of SSHGraphene using density functional theory (DFT) with a plane-wave basis as implemented in the Quantum ESPRESSO package using ultrasoft pseudopotentials. The optimization is carried out using four different exchange-correlation functionals. Here, we report the results obtained using Perdew, Burke, and Ernzerhof (PBE) and the screen hybrid density functional of Heyd, Scuseria, and Ernzerhof (HSE) as implemented in Quantum ESPRESSO. PBE has been proven successful on graphene-like systems and HSE is known to more accurately reproduce band gaps (see Ref. 29 and the references therein). The results using other functionals are reported in Supplemental Material. For all the calculations the plane-wave-basis cutoff was 816 eV for wave functions and 3265 eV for charge density, sufficiently large for graphene-like systems. A convergence threshold was set at $10^{-8}$ eV for...
the energy self-consistency and 0.005 eV/Å for the forces. Further, to maintain the accuracy, integration over the Brillouin zone was performed on regular 26 × 26 × 1 Monkhorst-Pack grids. The band structure was plotted on the lines joining the $M$, $\Gamma$, $K$, and $M$ points, and the individual line segments were sampled using 50 grid points each. The corresponding precision was also maintained for the cell optimization carried out using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm. The convergence threshold on the pressure was kept at 0.1 kBar. The computational unit cell consisted of two carbons and two hydrogens. A vacuum space of 12 Å was kept normal to the SSHGraphene plane to avoid any interactions between the adjacent sheets.

It is worthwhile to review some properties of graphene and graphene before we discuss SSHGraphene. Graphene is a one-atom-thick sheet of $sp^2$-bonded carbon atoms that are densely packed in a bipartite crystal lattice. It has two atoms per unit cell, which has the lattice parameter of 2.46 Å, with a carbon-carbon bond length of 1.42 Å. Although graphene is bipartite and hexagonal, its unit cell has four atoms (two carbons and two hydrogens) and has a larger lattice parameter, namely, 2.51 Å. In graphene every alternate carbon atom is attached to a hydrogen atom from alternate sides of the plane. In response to the addition of hydrogens, the carbon atoms are displaced out of the plane toward hydrogen atoms. In short, the carbon atoms in graphene are no longer planar.

The unit cell of SSHGraphene also contains four atoms, two carbons and two hydrogens. We carried out full optimization of the unit cell, including both the unit cell geometry and the atomic positions. The optimized geometry of SSHGraphene is shown in Figure 1. As seen from the figure, the cell is similar to that of graphene, except that the lattice parameter for SSHGraphene is now enlarged to 2.82 Å, which is larger than graphene (2.51 Å) as well. Notice that the enhancement is necessary in order to accommodate the hydrogen atoms, as the unoptimized unit cell of graphene does not favor the complete hydrogenation. The increase in the lattice parameter is due to the increase in the carbon-carbon bonds, which is increased from 1.42 (in graphene) to 1.63 Å. The increase in the bond length upon hydrogenation is not surprising, as the same effect is also seen in graphene. Similarly, as expected, upon single-sided hydrogenation the carbon atoms remain in one plane with the hydrogens forming another plane at 1.09 Å. This is a typical bond length of C-H when bonded covalently. (In methane, for example, the bond lengths are also 1.09 Å.) To summarize, a comparison of (available) structural parameters of graphene, graphene, and SSHGraphene is given in Table I. It also shows the binding energy per atom, which is the signature of energetic stability of the system. The binding energy for SSHGraphene is calculated using the pseudopotential energies of carbon ($E_C$) and hydrogen ($E_H$) atoms and using $\Delta E = E_C + E_H - E_{SSHGraphene}$, where $E_{SSHGraphene}$ is the total energy of SSHGraphene. Thus, the higher the energy the more stable the system. The binding energies for graphene and graphene are as reported in the literature. The overall trend is quite straightforward. Graphene, having the smallest C-C bond, is the most stable of all. Although not as stable as others, SSHGraphene is still strongly bound. To put it in perspective, recall that benzene has the binding energy 6.49 eV/atom while acetylene has 5.90 eV/atom, and both are among the most stable hydrocarbons. Thus there is no doubt that SSHGraphene is indeed very stable. Further, we studied the reaction pathway of the hydrogen detachment using nudge-elastic-band method. Two cases were considered: desorption of 50% H atoms (one H per primitive cell) and desorption of effectively single H atom (one H from 2×2 unit cell). The potential energy landscapes obtained, see Fig. 2, clearly depict one deep potential well at 1.08 Å. The presence of the deep well and the absence of any other well in the vicinity clearly favors the formation of SSHGraphene. (More details in Supplemental Material.) We would like to mention that synthesis of the SSHGraphene may be similar to graphene in which the hydrogen atoms are kinetically trapped in the potential-energy minimum near the graphene plane.

It is well known that the graphene band structure is very sensitive to deformations of any kind. As noted before, there is a clear evidence that upon partial hydrogenation the band gap of graphene is opened. It is thus easy to conjecture that the SSHGraphene would be a semiconductor. However, the most remarkable feature of SSHGraphene is that it is a semiconductor with an indirect band gap. The band structure of SSHGraphene shown in the upper part of Fig. 3 clearly exhibits an indirect band gap. The value of the gap is 1.35 eV for HSE and 1.89 eV for PBE functional. The qualitative nature of band structure remains unchanged. This value of the band gap is of interest as it lies in between the gapless graphene and the rather wide band-gap graphene (3.5 eV by DFT and 5.4 eV by GW method). Thus, SSHGraphene becomes a preferred organic candidate for semiconductor based devices.

### Table I. A comparison of graphene and SSHGraphene vs graphene and graphane as reported in the literature.

<table>
<thead>
<tr>
<th></th>
<th>Graphene</th>
<th>Graphene$^{12}$</th>
<th>Graphene$^{13}$</th>
<th>SSHGraphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>2.46</td>
<td>2.51</td>
<td>2.82</td>
<td>2.83</td>
</tr>
<tr>
<td>C-C (Å)</td>
<td>1.42</td>
<td>1.50</td>
<td>1.52</td>
<td>1.63</td>
</tr>
<tr>
<td>C-H (Å)</td>
<td>1.16</td>
<td>1.11</td>
<td>1.11</td>
<td>1.09</td>
</tr>
<tr>
<td>$\Delta E$/atom</td>
<td>9.56</td>
<td>6.56</td>
<td>5.90</td>
<td>5.54</td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Hexagonal structure SSHGraphene with carbon and hydrogen atoms shown in darker and lighter shade, respectively. The structure has the symmetry of graphene and the carbon atoms are in a single plane (unlike graphene).
As mentioned earlier, a small indirect band gap was also seen by Zhou et al.\textsuperscript{12} in graphone. However, we would like to point out that they did not report any optimization of the unit cell, which may considerably affect the band gap.

The origin of the indirect band gap can be inferred when we compare the band structures of SSHGraphene and graphane (see Fig 3). A close examination reveals that the most significant difference consists in the position of one band of graphane marked in green. In fact, this is the band that arises in graphene from the $p_z$ orbitals on carbon atoms and is degenerate at the $K$ point. Upon hydrogenation this band lowers in energy and the nature of hydrogenation determines the lowering. In the case of graphane, this band is significantly lower in energy as the hydrogenation is done in the best possible way, which is reflected in the stability seen in Table I. On the other hand, in the single-sided hydrogenation, all the hydrogen atoms are held at the same side, which naturally results in a repulsion among the hydrogen atoms. This further causes the crystal to expand. As a result of enhanced repulsion among the hydrogen atoms, the band marked in green shifts upward in energy that gives rise to an indirect band gap. In short, the peculiar band structure is due to the enhanced repulsion among the hydrogen atoms that results in the shift of the most sensitive $p_z$-type band of the system. This also suggests that we may expect the $p_z$-type character associated with this band. We verify the angular momentum character of the band by examining angular-momentum-decomposed density of states and by the partial charge density of the given band. Figure 4 presents the angular-momentum-decomposed DOS for SSHGraphene and graphane, showing the $p_z$ (identical to $p_x$) and $p_z$ components of DOS on the carbon atom along with the $s$ component on the hydrogen atom. It becomes evident from the comparison that in the case of SSHGraphene, the $p_z$ of carbon atoms and $s$ of hydrogen atoms have shifted toward the Fermi level. In fact, the contribution from $p_z$ is almost twice that of $p_x$. This observation strengthens our earlier conjecture that the band moved upward in energy. Our analysis of individual bands given in Supplemental Material\textsuperscript{30} shows that there is a $\sigma$ bond established between the $p_z$ orbital of carbon and $s$ orbital of hydrogen, and also indicates a substantial $s$-$s$ overlap between the two neighboring hydrogen atoms causing the repulsion. We show that due to the nature of orbitals and the absence of characteristic bond angle, it might be difficult to call SSHGraphene an $sp^3$-bonded system.

In summary, we investigated the single-sided hydrogenation of graphene using first-principle DFT, and demonstrated that upon complete relaxation of the unit cell and atomic degrees of freedom SSHGraphene exhibits an indirect band gap of 1.35 eV using HSE and 1.89 eV using PBE functionals. This is appealing, as graphene is gapless while graphane is rather a wide-band-gap semiconductor, making SSHGraphene a more desirable semiconductor. Our comparison of the band structures of SSHGraphene and graphane shows that the $p_z$-type band located in graphane significantly below the Fermi level moves up in SSHGraphene, becoming the top-most occupied band. This is attributed to an $s$-$s$ overlap between the hydrogen atoms. Our analysis of the binding energy and reaction path clearly indicates stability of SSHGraphene. Further accuracy check of the band gap, bond lengths, and

![Image of reaction path](image1)

**FIG. 2.** (Color online) Reaction path of hydrogen atom with its distance from the graphene plane. The energy zero is set arbitrarily.

![Image of band structure](image2)

**FIG. 3.** (Color online) Band structure of SSHGraphene with indirect band gap vs graphane. Fermi level (dashed line) half-way between the valence and conduction bands. The bold line marks the band that moved up in graphane compared to SSHGraphene.
stability of SSHGraphene we have predicted here can be addressed when experimental data will be available.

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FIG. 4. (Color online) Angular-momentum-decomposed DOS of SSHGraphene and graphane. $p_z$ from carbon and $s$ from hydrogen contribute substantially more than $p_x$ and $p_y$ (identical to $p_x$, hence not shown). Fermi energy is taken as zero. Gaussian broadening of 0.1 eV is applied for better visualization.