Strong charge-transfer excitonic effects in C_4H-type hydrogenated graphene

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The electronic and optical properties of a new type of hydrogenated graphene in the C_4H phase have been studied using the first-principles many-body Green's function method (*GW* approximation and Bethe–Salpeter equation). It demonstrates that strong charge-transfer excitonic effects dominate the optical properties of C_4H. The binding energy of the first exciton, which turns out to be strongly localized, is as large as 1.67 eV. The spatial separation of exited electrons and holes makes C_4H a candidate for the realization of excitonic Bose–Einstein condensate. Dark state provides a traveling path for the bound excitons. As the situation in graphane with H vacancies, changing H coverage changes the electronic and optical properties and the associated applications.

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I. INTRODUCTION

Carbon-based nanomaterials play a crucial role for both fundamental nanoscience and nanotechnology applications. The discovery of graphene has attracted tremendous interest in consideration of its unusual electronic properties and applications in electronics and photonics.[1–3] However, graphene in its pristine state demonstrates zero band gap, which is a major drawback for applications based on graphene. Chemical modification of graphene, including hydrogenation, is a promising way to generate a finite band gap in graphene. Hydrogenation splits the bands crossed at the Dirac point, dictating graphene to be a semiconductor and thus controlling the properties of graphene.[4,5] In hydrogenated graphene, theoretical works predicted electron localization,[6] peculiar midgap states,[7,8] charge-transfer excitonic effects (in fully hydrogenated graphene, also known as graphane),[9] and high-temperature superconductivity (in hole-doped graphane).[10] Recently, experimental proof for the existence of a new and stable derivative of graphene, being of the C_4H phase (for simplicity, hereafter we refer to this hydrogenated graphene as C_4H), has been provided.[11] In the current work, based on this new C_4H-type structure (as shown in Figs. 1(a) and 1(b)), we study the changes in the electronic and optical properties of graphene after hydrogenation.

It has been well established that the many-body effects (self-energy correction and electron-hole (*e-h*) interaction) on the electronic and optical absorption properties are highly embodied in low-dimensional systems due to reduced electronic screening and enhanced electron-electron (*e-e*) correlation.[12–18] Excitonic effects, the Coulomb interaction between an excited electron and a hole, are known to be important in deciding the optical response and associated applications of systems with low dimensionality. The present work is thus motivated primarily by the need for a thorough understanding of the many-body effects on the electronic and optical properties of two-dimensional C_4H. In low-dimensional systems, a correct description of the screening interactions becomes crucial due to the high anisotropy. In this regard, the Bethe–Salpeter equation (BSE) approach, together with quasiparticle (QP) corrections within the so-called *GW* approximation for self-energy, which stands for one of the state-of-the-art theories and is well beyond the standard density functional theory (DFT) method, give results in excellent agreement with experiments.[19–21]

II. COMPUTATIONAL METHOD

An appropriate description of the ground-state properties is essential to perform QP calculations within many-body perturbation theory. It has been well identified that the eigenfunctions and eigenenergies from local density approximation (LDA) can be treated as a good starting point for many-body perturbation calculations within *GW* approximation.[22] As an initial step, we obtained the ground state electronic properties of fully relaxed C_4H by the DFT plane-wave method within LDA using norm-conserving pseudopotentials.[23,24]

The QP corrections to the LDA energies are evaluated by solving the single-particle Dyson equation within the *GW* approximation for the electron self-energy operator Σ. In this method, the self-energy is calculated non–self-consistently through a product of the one-electron Green's function G_0 and the dynamically screened Coulomb interaction W_0 as $\Sigma = iG_0W_0$. The LDA eigenvalues and eigenfunctions are used to construct G_0, whereas the dynamical W_0 term between electrons is treated with the general plasmon-pole approximation.[25] The excitonic effects are included by solving the BSE, in which the *e-h* interaction is an important ingredient in the basis set of excited quasi-electron and quasi-hole states for the two-particle Green's function.[22,26] The static screening is obtained within the random-phase approximation (RPA),[27] and only the resonant part of the Bethe–Salpeter Hamiltonian is taken into account in the calculations (or Tamm–Dancoff approximation,[28] with which the non-Hermitian BSE reduces to a Hermitian one and can be solved by an efficient iterative method). In both *GW* and BSE calculations, the screened Coulomb interaction is truncated because of its long-range nature; otherwise, nonphysical interactions between periodic images can lead to deviations from the physics of an isolated system.[29]

III. RESULTS AND DISCUSSION

For C_4H shown in Figs. 1(a) and 1(b), the band structure and the QP corrections are summarized in Fig. 1(c), indicating that

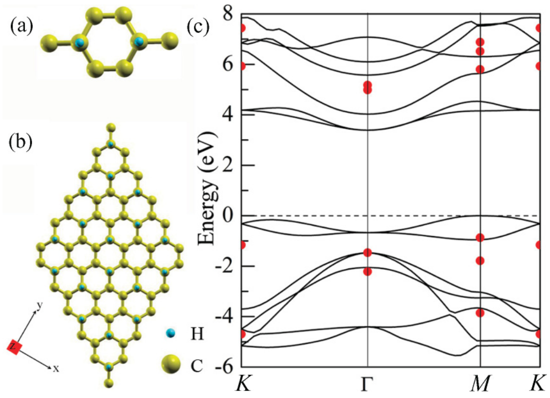

FIG. 1. (Color online) (a) Structure of the unit cell, (b) C_4H monolayer, and (c) band structure of C_4H along the high-symmetry directions of the hexagonal Brillouin zone. The top of the valence band is set to zero. Small cyan and large yellow spheres represent hydrogen and carbon atoms, respectively. Red dots in panel (c) represent the QP corrections to the Kohn–Sham LDA energies at some special $\boldsymbol{k}$ points within the G_0W_0 approximation. Additionally, QP band structure also demonstrates an indirect band gap between the M and Γ point.

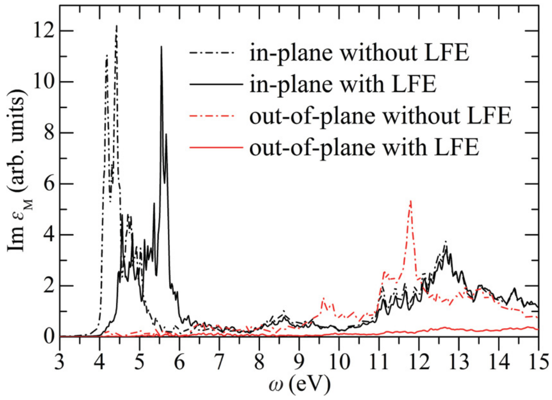

FIG. 2. (Color online) Imaginary part of the macroscopic dielectric function ε_M for light polarized parallel and perpendicular to the C_4H plane calculated at the LDA-RPA level with (solid line) and without (dash-dotted line) considering crystal local field effects (LFE). A Lorentzian broadening of 0.01 eV is adopted.

hydrogenation causes an energy gap opening compared with graphene.[17,18] The band structure still indicates a graphane character,[9] in which both conduction and valence bands near Fermi level are nearly perfect parabolas over a large fraction of the Brillouin zone. Because of the states introduced by C-H bonding, C_4H is predicted to have an indirect gap between the M and Γ points of 3.38 eV, which is in agreement with a previous DFT result of 3.48 eV within the generalized gradient approximation (GGA)–Perdew-Burke-Ernzerhof (PBE) scheme,[30] whereas the direct gap at the Γ point is calculated to be 4.06 eV.

After taking the *e-e* self-energy effects into account using the G_0W_0 approximation, the band structure is strongly modified. The indirect band gap increases to 6.05 eV and the direct band gap to 6.65 eV. The particularly large QP corrections to the DFT-LDA energy gap are due to a much weaker electronic screening, which can enhance the *e-e* interactions. The QP energy corrections in C_4H manifest a complicated momentum and energy dependence, so that the simple "*scissor rule*"[31] is infeasible to obtain the QP band structure. For example, QP corrections to the states contributing to the bottom of the conduction band are significantly larger than those to the parabolic conduction bands with higher energy. This behavior, which is not correctly described within DFT-LDA, is due to the nonlocal character of the self-energy operator in the *GW* framework.[32]

Starting from the Kohn–Sham LDA states and applying RPA, the optical absorption spectra, which are directly associated with the imaginary part of the macroscopic dielectric function ε_M, are presented in Fig. 2. As reported in other works focusing on the optical properties of low-dimensional materials, C_4H also indicates a depolarization effect for light polarized perpendicular to the plane after the consideration of crystal local field effects (LFE). Although the description of absorption properties is significantly improved by the inclusion of LFE, the LDA-RPA scheme provides only qualitative, and often incorrect, descriptions of excited properties. This is because the many-body effects that are well beyond the independent-particle approximation are missing. In low-dimensional systems with confined geometry and poor electronic screening, however, the *e-h* attraction can be far from negligible.

Because of the strong depolarization effect in the two-dimensional planar geometry for light polarized perpendicular to the plane, only the optical absorption spectrum for light polarization along the C_4H plane is shown here (x direction, see Fig. 1(b)). From the solution of BSE with excitonic effects included, the absorption spectrum is shown in Fig. 3 ($GW+$BSE), in which the RPA spectrum on top of the QP corrections is also shown for comparison ($GW+$RPA). As can be seen from Fig. 3, inclusion of screened *e-h* Coulomb interactions dramatically modifies the spectral profile with respect to the one-particle optical spectrum. There is a

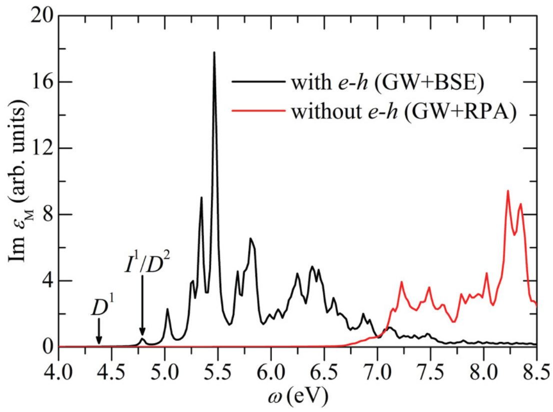

FIG. 3. (Color online) Imaginary part of the macroscopic dielectric function ε_M for light polarized parallel to the C_4H plane (in the x direction) calculated with (black line) and without (red line) considering *e-h* interactions (i.e., $GW+$BSE and $GW+$RPA, respectively). When calculating the optical absorption spectrum at the $GW+$BSE level, four occupied and ten empty bands are included, and a Lorentzian broadening of 0.01 eV is adopted.

significant oscillator strength transfer to the low-energy side, and the optical spectrum is now quantitatively explained in terms of strong excitonic effects. We note that self-energy corrections and excitonic effects nearly cancel each other. The first peak in the $GW+$ BSE absorption spectrum (I^1 in Fig. 3) comes from a bright exciton due to the excitation between the last two valence bands and the third conduction band at the Γ point with an excitation energy of 4.79 eV. The binding energy, which is defined as the energy difference between the excitation energy of the exciton and the onset of continuum of optical direct transition at the single-particle level, of I^1 is as large as 1.67 eV due to quantum confinement and the reduced screening resulting from the large electronic gap. It is instructive to compare the absorption spectrum of C_4H with graphene:[17,18] there is a redistribution of the oscillator strength resulting in the appearance of a resonant exciton at 4.55 eV with a binding energy of 600 meV. Compared with resonant excitons, bound excitons are of peculiar interest due to their larger binding energies and much longer lifetimes.

We find an optically inactive (dark) exciton D^2, which is almost degenerate with I^1, in the absorption spectrum of C_4H. From the optical absorption for light propagating in the y direction (see Fig. 1), we find that the situation of the strongly bound excitons is inverted: I^1 becomes optically inactive, whereas D^2 becomes bright. The two excitons have identical oscillator strengths and thus the absorption spectra remain almost unchanged. This is similar to graphane, and it was explained by the symmetry of Bloch states involved in the formation of the excitons by Cudazzo *et al.*[9] As expected from the indirect nature of the band gap of C_4H, there is additionally a lowest energy dark exciton D^1 located at 4.38 eV that is missing in graphane[9] with the binding energy of 2.08 eV. The dark states are dipole forbidden and thus provide a competing path for nonradiative decay of optical excitations, which could affect the luminescence yield of the system.

To more explicitly confirm the correlation between excited electrons and holes, the Bethe-Salpeter two-particle's Hamiltonian was diagonalized to obtain the e-h pair wave functions. As shown in Fig. 4, the electron probability distribution $|\psi(\mathbf{r}_e;\mathbf{r}_h)|^2$, as a function of the electron position $\mathbf{r}_e$ with the hole position $\mathbf{r}_h$ fixed on a C-C bond for the bound excitons of D^1 and I^1, describes how the excited quasi-electrons and quasi-holes are correlated in real space. The wave function of D^1 shows that the electron orbital is of p_z character and distributes mainly on the nearest neighbor C atoms around the hole to form a fairly localized exciton, whereas that of I^1 shows the C-H antibonding character of the states with the electron mainly localized on top of the H atoms. Since the hole is pinned at a C-C bond, the creation of such excitons corresponds to a charge transfer from the middle layer of C to the side layer of H. The charge transfer and less overlap between electron and hole wave functions are important for a longer excitonic lifetime.

Coupled quantum wells have emerged as a promising system for experiments on Bose condensation of excitons.[33,34] Because of the spatial separation of the charge, as well as the strong localization in the excitonic state and the large binding energy, as has been found in graphane,[9] it is tempting to consider C_4H a potential candidate for the realization of Bose-Einstein condensation (BEC) of optically pumped excitons. As has been found experimentally,[34] the bright excitons also can travel through the lowest energy dark state until they reach some critical distance and finally revert to luminescent states. However, the role of the dark states concerned on BEC is still in need of carful study, both in experimental and theory. Compared with the situation of graphane, the lowest energy dark exciton in C_4H consequently might fairly affect the diffusion and long-range coherent transport of excitons, which is one of the issues driving the study of the Bose condensation effects of excitons.[34] Compared with graphene and graphane, we show that the presence of H indeed has apparent effects on the electronic and optical properties.

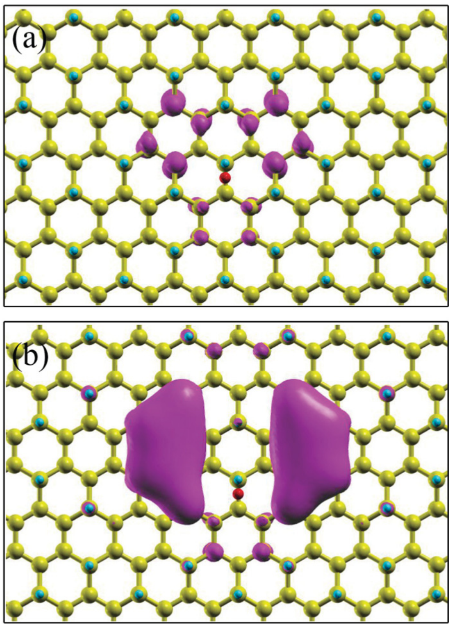

FIG. 4. (Color online) The three-dimensional electron probability distribution $|\psi(\mathbf{r}_e;\mathbf{r}_h)|^2$ in real space, given that the hole (red (black) sphere) is fixed at a C-C bond, for the excitonic states D^1 (a) and I^1 (b) shown in Fig. 3. The electron distribution for D^2, which is almost degenerate with I^1, is similar to that of I^1. Such a C-C bond, where the hole is localized, is responsible for the top of the valence band.

IV. CONCLUSION

In summary, we studied the electronic and optical properties of a new C_4H-type of hydrogenated graphene by means of the first-principles many-body Green's function method. Comparable to graphane with H vacancies, changing the H coverage changes the electronic and optical properties and, thus, the corresponding applications. Strong charge-transfer excitonic effects dominate the optical response of C_4H, giving rise to bound excitons. The first bright exciton indicates a binding energy as large as 1.67 eV, with excited electrons and holes markedly separated. The well-defined binding energy, longer lifetimes, and spatial separation of excitons make C_4H a promising candidate for the realization of the Bose–Einstein condensation. The dark state in C_4H might play a significant role in the diffusion and the long-range coherent transport of excitons.

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[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature **438**, 197 (2005).

[2] Y. Zhang, Y. Tan, H. L. Stormer, and P. Kim, Nature **438**, 201 (2005).

[3] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).

[4] S. Ryu, M. H. Han, J. Maultzsch, T. R. Heinz, P. Kim, M. L. Steigerwald, and L. E. Brus, Nano Lett. **8**, 4597 (2008).

[5] D. C. Elisa, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvaov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, Science **323**, 610 (2009).

[6] Y. Skrypnyk, Phys. Rev. B **70**, 212201 (2004).

[7] E. J. Duplock, M. Scheffler, and P. J. D. Lindan, Phys. Rev. Lett. **92**, 225502 (2004).

[8] T. O. Wehling, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. B **80**, 085428 (2009).

[9] P. Cudazzo, C. Attaccalite, I. V. Tokatly, and A. Rubio, Phys. Rev. Lett. **104**, 226804 (2010).

[10] G. Savini, A. C. Ferrari, and F. Giustino, Phys. Rev. Lett. **105**, 037002 (2010).

[11] D. Haberer, C. E. Giusca, Y. Wang, H. Sachdev, A. V. Fedorov, M. Farjam, S. Akbar Jsfari, D. V. Vyalikh, D. Usachov, X. Liu, U. Treske, M. Grobosch, O. Vilkov, V. K. Adamchuk, S. Irle, S. Ravi P. Silva, M. Knupfer, B. Büchner, and A. Grüneis, Adv. Mater. **23**, 4497 (2011).

[12] M. Bruno, M. Palummo, A. Marini, R. Del Sole, and S. Ossicini, Phys. Rev. Lett. **98**, 036807 (2007).

[13] L. Yang, C. D. Spataru, S. G. Louie, and M. Y. Chou, Phys. Rev. B **75**, 201304(R) (2007).

[14] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).

[15] L. Yang, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **101**, 186401 (2008).

[16] D. Prezzi, D. Varsano, A. Ruini, and E. Molinari, Phys. Rev. B **84**, 041401(R) (2011).

[17] L. Yang, Phys. Rev. B **83**, 085405 (2011).

[18] L. Yang, J. Deslippe, C.-H. Park, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **103**, 186802 (2009).

[19] P. E. Trevisanutto, M. Holzmann, M. Côté, and V. Olevano, Phys. Rev. B **81**, 121405(R) (2010).

[20] G. Luo, X. Qian, H. Liu, R. Qin, J. Zhou, L. Li, Z. Gao, E. Wang, W.-N. Mei, J. Lu, Y. Li, and S. Nagase, Phys. Rev. B **84**, 075439 (2011).

[21] A. Marini and R. Del Sole, Phys. Rev. Lett. **91**, 176402 (2003).

[22] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[23] W. Andreoni, D. Scharf, and P. Giannozzi, Chem. Phys. Lett. **173**, 449 (1990).

[24] The DFT calculations were performed with a plane-wave cutoff energy of 50 Ry and a Monkhorst–Pack $\boldsymbol{k}$-mesh of 18×18 points. A vacuum space of 17 Å was used to separate periodic images. The cell parameter and atomic positions were fully relaxed until an energy convergence of 5.0×10^{-6} eV and a force convergence of 0.01 eV/Å were reached. In the *GW* and BSE calculations, 400 bands, more than 13 000 plane-waves, and 91 transformed $\boldsymbol{k}$-points were used. The Coulombic interactions were truncated within 33 Å along the direction perpendicular to the planar surface to simulate the "true" two-dimensional structure.

[25] R. W. Godby and R. J. Needs, Phys. Rev. Lett. **62**, 1169 (1989).

[26] A. Marini, C. Hogan, M. Grüning, and D. Varsano, Comput. Phys. Commun. **180**, 1392 (2009).

[27] R. Ahuja, S. Auluck, J. M. Wills, M. Alouani, B. Johansson, and O. Eriksson, Phys. Rev. B **55**, 4999 (1997).

[28] A. L. Fetter and J. D. Walecka, in *Quantum Theory of Many-Particle Systems*, Chap. 15 (Dover, New York, 2003), p. 565.

[29] C. A. Rozzi, D. Varsano, A. Marini, E. K. U. Gross, and A. Rubio, Phys. Rev. B **73**, 205119 (2006).

[30] Y. Ma, Y. Dai, M. Guo, C. Niu, Z. Zhang, and B. Huang, Phys. Chem. Chem. Phys. **14**, 3651 (2012).

[31] L. Yang, M. L. Cohen, and S. G. Louie, Nano Lett. **7**, 3112 (2007).

[32] D. Prezzi, D. Varsano, A. Ruini, A. Marini, and E. Molinari, Phys. Rev. B **77**, 041404(R) (2011).

[33] L. V. Butov, C. W. Lai, A. L. Lvanov, A. C. Gossard, and D. S. Chemla, Nature **417**, 47 (2002).

[34] D. Snoke, S. Denev, Y. Liu, L. Pfeiffer, and K. West, Nature **418**, 754 (2002).