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Modulating the electronic structures of graphene by controllable hydrogenation

Zhiqiang Luo,[1,2] Jingzhi Shang,[1] Sanhua Lim,[2] Dehui Li,[1] Qihua Xiong,[1] Zexiang Shen,[1]
Jianyi Lin,[2,a)] and Ting Yu[1,3,a)]
[1]*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore*
[2]*Applied Catalysis, Institute of Chemical and Engineering Sciences, 627833 Singapore*
[3]*Department of Physics, Faculty of Science, National University of Singapore, 117542 Singapore*

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The evolution of electronic structures of hydrogenated graphene with different amount of hydrogen (H) coverage was investigated by ultraviolet photoemission spectroscopy and optical absorption spectroscopy. Raman spectroscopy and x-ray photoelectron spectroscopy were used to monitor and evaluate the H coverage. At low H coverage, the sp^3 C—H bonds embedded within a sp^2 C matrix behave as defects in graphene and depress the delocalized π electron system. At high H coverage, two localized π electron states originating from the sp^2 C clusters encircled by the sp^3 C—H matrix appear in the electronic band structures, and an opening of a band gap has been observed. © *2010 American Institute of Physics*. [doi:10.1063/1.3524217]

Graphene, a semimetal with unique electronic band structures, has attracted great attentions in exploring of its exceptional physical and chemical properties .[1] Chemical modification of graphene surface is emerging as a useful method to tune its electronic band structures,[2,3] which are of great technological importance for its potential application in electronics, photonics, and sensor devices. For example, grafting atomic hydrogen (H) on graphene surface formed sp^3 C—H bonds and significantly altered its electronic structure.[3]

The electronic structures of hydrogenated graphene are strongly dependent on the H coverage.[4] On the basis of theoretical prediction, a fully (double-side) hydrogenated graphene, i.e., graphene, is a semiconductor with a large band gap.[5] For single-sided hydrogenation, a band gap insulating behavior has been predicted at high H coverage ($>10\%$),[4,6] while at lower H coverage ($>0.1\%$), a localized insulating behavior due to the localization of electron states has been observed.[3,7] However, the evolution of electronic structure on H coverage has not yet been studied experimentally in detail. In this work, we explored the changes in electronic structure of hydrogenated graphene upon tuning the H coverage. Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) were employed to monitor and evaluate the H coverage, and the corresponding electronic structures of hydrogenated graphene were investigated with ultraviolet photoemission spectroscopy (UPS) and optical absorption spectroscopy.

Single layer graphene was grown on the Cu foils with purity of 99.999% by chemical vapor deposition (CVD) .[8] The as-grown graphene/Cu samples were hydrogenated by the ionic hydrogenation process via H_2 plasma .[9] The H coverage on graphene was controlled by modulating the plasma power and treatment duration.[9] The graphene/Cu samples were labeled according to the plasma power and duration. For example, "HG-20W 10 min" denotes graphene/Cu sample was exposed to 20 W H_2 plasma for 10 min (H_2 pressure, 1 Torr).[9] XPS and UPS measurements of the hydrogenated graphene samples were performed on ESCALAB 250 (Thermo VG Scientific). For XPS analysis, monochromatic Al Kα ($h\nu = 1486.6$ eV) excitation was employed. For UPS analysis, a He lamp with 40.8 eV (He II) excitation energies was used. The hydrogenated graphenes were transferred from the Cu foils onto 285 nm SiO_2/Si and quartz substrates for Raman spectroscopy and optical absorption spectroscopy, respectively. The Raman spectra were recorded with 2.33 eV (532 nm) laser line with WITEC CRM200 Raman system. The optical absorption spectroscopy characterization was performed on LAMBDA 950 uv/vis/NIR spectrophotometer (PerkinElmer, U.S.A.) in 0.5–5 eV.

Figure 1(a) shows the Raman spectra of pristine CVD graphene and graphene treated with different H_2 plasma doses. The Raman spectrum of the pristine graphene displays two characteristic peaks: *G* band at ~ 1580 cm^{-1} and 2*D* band at ~ 2670 cm^{-1}.[10] After hydrogenation, two defects induced peaks at 1340 and 1620 cm^{-1} are observed, which have been assigned to *D* band and *D′* band activated by defects via double-resonance process.[11] The defects in the hydrogenated graphene were caused by the formation of sp^3 C—H bonds as well as the breaking of the translational symmetry of sp^2 C=C network.[3] Commonly the intensity ratio of *D* band over *G* band (I_D/I_G) can serve as a convenient measurement of the amount of defects in graphitic materials. [11]

The evolution of I_D/I_G and I_{2D}/I_G with increasing H coverage (or H_2 plasma dose) was plotted in Fig. 1(b). The I_D/I_G increases with increasing H coverage as expected. However, at higher H coverage, it becomes saturated with a saturation value of 4.3 and decreases gradually. On the contrary, the I_{2D}/I_G exhibits a rapid decrease at higher H coverage. Such a decrease of I_D/I_G upon a critical amount of H coverage was previously reported in our intensive Raman spectroscopy study of hydrogenated graphene and interpreted by a local activation model of the *D* band.[12,13] At high H coverage, the distances between C—H bonding become smaller than the wavelength of photo-excited electron involved in double resonance Raman process, which causes

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[a)] Authors to whom correspondence should be addressed. Electronic addresses: yuting@ntu.edu.sg and lin_jianyi@ices.a-star.edu.sg.

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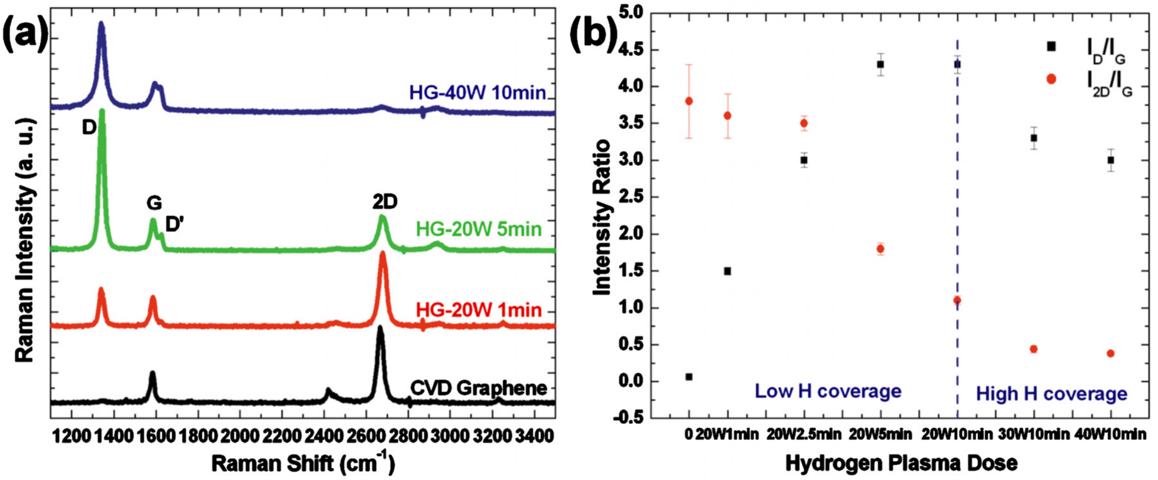

FIG. 1. (Color online) (a) Raman spectra of pristine CVD graphene and hydrogenated CVD graphene with increasing H coverage. (b) The evolution of $D/2D$ and G bands intensity ratio (I_D/I_G and I_{2D}/I_G) with increasing H coverage (hydrogenation dose).

significant reduction of D band intensity with increasing H coverage.[12]

The H coverage on graphene was further evaluated by XPS. Figure 2 shows the C 1s core-level spectra of pristine CVD graphene and the graphene hydrogenated with different plasma doses. The C 1s spectra were fitted with two components: the main peak at a binding energy (BE) of 284.4 eV assigned to sp^2 hybridized C atoms in graphene, and another peak at higher BE of 285.1 eV assigned to sp^3 hybridized C atoms from C—H and C—C bonds formed by hydrogenation.[9,14] The H coverage is defined as $\theta/(1+\theta)$, where θ is the intensity ratio of sp^3- and sp^2-hybridized C components. The intensity ratio of sp^3- and sp^2-hybridized carbon components in the pristine CVD graphene is 0.1, corresponding to a value of $0.1/1.1=9.1\%$. The very weak sp^3-hybridized carbon components in the pristine CVD graphene may originate from the absorption or trapping of CH_4 during the CVD growth process. The C—H bonds are unlikely to be formed on pristine CVD graphene because there is no strong D band in the Raman spectrum. As indicated in Fig. 2, the hydrogen coverages of hydrogenated graphenes with increasing plasma treatment dose are 18%, 27%, and 32%, respectively. As the XPS characterization was carried out *ex situ*, the hydrogen coverage of hydrogenated graphene cannot be evaluated accurately.

The chemical bonding of H to an sp^2-bonded C atom requires a local rehybridization from sp^2 to sp^3, therefore hydrogenation is expected to show strong influence on the delocalized π electron system of graphene. As shown in Fig. 3, valence-band spectra of pristine and hydrogenated CVD graphene obtained from UPS using He II radiation (40.8 eV) exhibit significant changes in π electron states below the Fermi level after being normalized to possess the same integrated intensity with respect to 0–15 eV binding energies. The spectrum of pristine CVD graphene shows five band features, which are assigned to: (1) C 2p π between 0 and 4 eV, (2) crossing of C 2p π and C 2p σ bands around 6 eV, (3) C 2p σ at 7.9 eV, (4) C 2s-2p hybridized state at 10.5 eV, and (5) C 2s σ band at ~13.3 eV.[15] After hydrogenation with a low H coverage, part of the delocalized 2p π states are transformed to C—H states, which cause the depression of the 2p π state with increasing H coverage. Although there is significant reduction of the density of 2p π states near Fermi level, the whole valence-band spectra keep similarity to that of the graphitic system associated with only a few

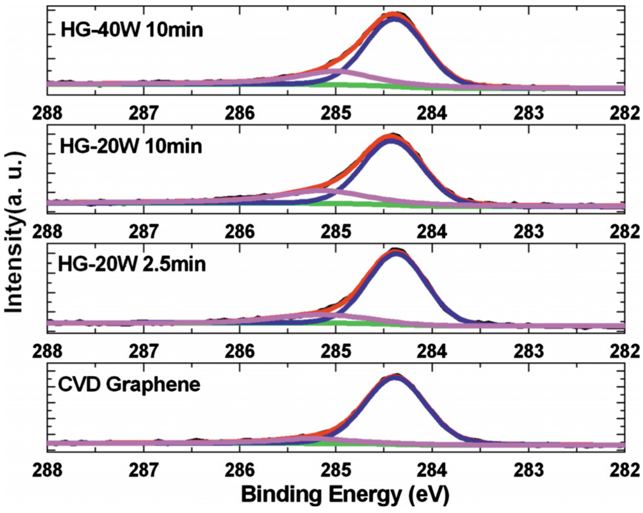

FIG. 2. (Color online) C 1s core-level XPS of the pristine CVD graphene and hydrogenated CVD graphene with increasing H coverage.

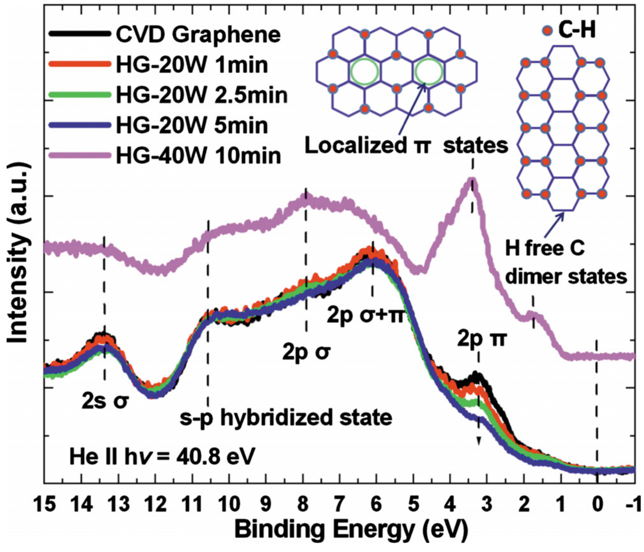

FIG. 3. (Color online) Relative variation of He II UPS valence-band spectra of pristine CVD graphene and hydrogenated CVD graphene with increasing H coverage.

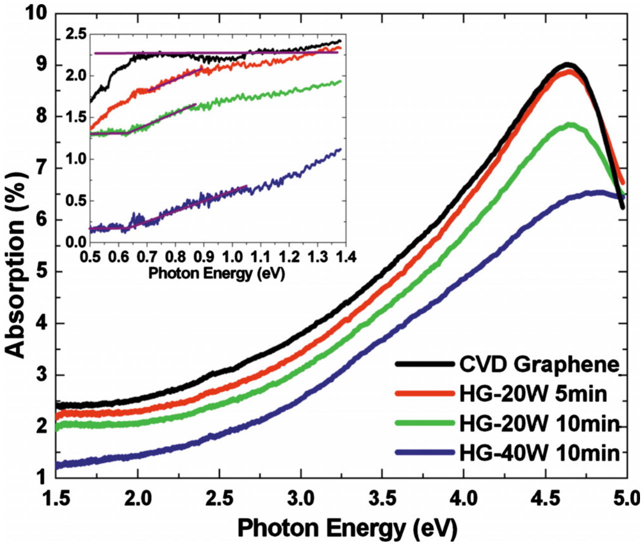

FIG. 4. (Color online) Absorption (vis-uv) of pristine CVD graphene and hydrogenated CVD graphene with increasing H coverage. The inset shows their NIR absorption.

changes in electron states located at high BE. However, at high H coverage, two new electron states located at BE of 1.8 and 3.4 eV appear after complete depression of $2p$ π state, associated with obvious changes in electron states located at high BE. The origin of these two electron states should be the sp^2 C clusters encircled by sp^3 C matrix at high H coverage. The electron states at 3.4 eV should result from localized π resonance in six-sp^2 C-ring encircled by sp^3 C—H, which is the most stable configuration proposed for 25% H coverage on single side.[16] The electron state located at 1.8 eV may originate from C dimer states formed at even higher H coverage, analogous to graphitic C dimer states on reconstructed diamond (111) or (100) surfaces.[17]

The electronic structure of the hydrogenated graphene was further investigated with optical absorption spectroscopy. As shown in Fig. 4, a broad optical absorption band near to the π plasmon energy at 4.6 eV, was observed in both pristine and hydrogenated CVD graphene. This peak significantly redshifts from the theoretic value of absorption peak arising from interband transitions of graphene and shows an asymmetric feature, which has been attributed to excitonic effects in graphene.[18] With increasing H coverage, this absorption band shows a broadened feature and blueshifts to higher energy with depressed intensity. The transmission of the pristine graphene at low absorption energies (0.6 eV $<E<$ 2 eV) exhibits a nearly flat absorption spectrum with a "universal opacity" of $\pi\alpha \approx 2.3\%$. [19] The significant drop in the absorption spectrum of the pristine CVD graphene at $E<0.6$ eV, as shown in the inset of Fig. 4, could be attributed to the chemical doping induced during the chemical etching and transfer process.[20] After hydrogenation, the features of the absorption spectra in NIR range keep nearly unchanged at low H coverage. However, at high H coverage, there is a weak absorption edge at 0.6 eV. With further increase of the H coverage, the absorption edge at 0.6 eV becomes much clearer, indicating a gap opening ($\sim$0.6 eV) in graphene's electronic structures, which are consistent with the flat band below Fermi level observed in the valence-band spectrum of HG-40W 10 min. Density functional theory predicted opening of a band gap in hydrogenated graphene with high H coverage.[4] With sufficient H atoms chemisorped on graphene, the atomic structures as well as the electron strictures of hydrogenated graphene strongly deviate from those of pristine graphene, forming a new kind of graphene derivatives. However, in the case of graphene with low H coverage, the chemisorped H atoms are in the form of sp^3 C—H bond embedded within a sp^2 C matrix and behave as defects, which do not significantly change the optical absorption.

In summary, the evolution of electronic structures of hydrogenated graphene with different amounts of H coverage was investigated by UPS and optical absorption spectroscopy. The H coverage was monitored by Raman spectroscopy and further evaluated by XPS. The unusual decrease of I_D/I_G in Raman spectrum with increasing amounts of chemisorped H is an indicator for the high H coverage on graphene. At low H coverage, the sp^3 C—H embedded within a sp^2 C matrix serves as defects in graphene, which depresses the delocalized π electrons significantly but has little influence on the optical absorption. At high H coverage, two localized π electron states originated from sp^2 C clusters encircled by the sp^3 C—H matrix appear in valence bands, and an opening of a band gap has been observed. Our study would provide a useful guide for developing applications of hydrogenated graphene, as well as other kinds of graphene derivatives.

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