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Coordination-Resolved C–C Bond Length and the C 1s Binding Energy of Carbon Allotropes and the Effective Atomic Coordination of the Few-Layer Graphene

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Binding energy variation due to the change of atomic coordination has formed the key to the different fascinating properties of carbon allotropes such as graphene nanoribbons, carbon nanotubes, graphite, and diamond. However, determination of the binding energies of these allotropes with a consistent understanding of the effect of bond order variation on the binding energy change has long been a great challenge. Here we show that a combination of the bond order–length–strength correlation theory (Sun, C. Q. *Prog. Solid State Chem.* **2007**, 35, 1) and the photoelectron emission technique has enabled us to quantify the C1s binding energy of atomic carbon and its shift upon carbon allotrope formation. It has been confirmed that the C–C bond contracts spontaneously by up to 30% at the edges of graphene ribbons with respect to the bulk-diamond value of 0.154 nm. The C1s energy shifts positively by values from 1.32 eV for bulk diamond to 3.33 eV for graphene edges with respect to that of 282.57 eV for an isolated carbon atom. The calibration using the bond order–length–strength solution has also enabled estimation of the effective atomic coordination of the few-layer graphene, which is critical for further investigations such as the layer-resolved Raman shift.

1. Introduction

Bond order variation and the pattern difference of sp-orbit hybridization have made carbon allotropes amazing materials varying from graphene nanoribbon, nanotube, fullerene, and carbon onion to graphite and diamond. The presence of nonbonding unpaired (or π -bond) electrons due to sp² hybridization differentiates graphite from the sp³-hybridized diamond substantially; graphite is a conductor while diamond is an insulator. With extremely low binding energy at about 1/20 eV, the nonbonding electrons neither contribute significantly to the Hamiltonian nor follow the regular energy dispersion relation. The nonbonding electrons add, however, impurity states to the middle of the gap between the conduction and valence bands, or form the Dirac states near the Fermi energy level, which are responsible for the unusual behavior of graphene and graphite compared with that of diamond.¹ The presence of a huge number of broken bonds at edges differentiates the unrolled single-walled carbon nanotube (SWCNT), also called graphene nanoribbon (GNR), significantly from the otherwise rolled SWCNT or the large graphene sheet. Phenomena such as the unexpected occurrences of edge states with extremely low effective mass and high group velocity and the strip-width-induced band gap

expansion demonstrated by the GNR can never be observed in the SWCNT, graphene, or graphite crystal. On the other hand, SWCNT edge coalesces at 1593 K² or so³ and the SWCNT bundles can be ignited at room temperature under a camera flash,⁴ which demonstrates the extremely low thermal and chemical stability of the under-coordinated carbon atoms; however, the elastic modulus of CNT^{5–7} and the GNR^{8–10} is considerably larger in comparison to that of graphite or diamond. With the measured stiffness, or the product of Young's modulus Y and the wall (bond) thickness t , $Yt = 0.3685$ TPa·nm and the known 1593 K melting point of the CNT tip, we have determined that the C–C bond is 0.142 nm thick and 0.125 nm long in the wall of SWCNT (18.5% contraction of diamond bond length, 0.154 nm), with a 68% increase in bond energy, with respect to that for diamond.¹¹ The C–C bond at the open edge of the CNT is 30% shorter and the elastic modulus of CNT is 1.6 times higher than that of diamond. The band gap expansion of GNR has been attributed to the effect of broken-bond-induced edge quantum trapping and the generation of edge states to the effect of polarization of the unpaired nonbonding π -electrons by the tightly trapped bonding π -electrons.¹ Therefore, interaction between the under-coordinated atoms is the key to the unusual properties of carbon allotropes.

Using scanning photoemission microscopy, Kim et al.¹² recently measured the C1s core level spectrum of graphene flakes deposited on a SiO₂ substrate, producing three well-resolved components with energy valued at 285.97, 284.80, and 284.20 eV (Table 1). The measured data for other allotropes in Table 1 need to be decomposed, and the accuracy of the energy

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TABLE 1: Comparison of the BOLS Derived with the Measured C1s Binding Energies of Carbon Allotropes^a

atomic coordination (<i>z</i>)		0	2	3	5.335	12
C1s energy(eV)	BOLS derivatives measurements	282.57	285.89	284.80	284.20	283.89
			285.97 ¹²	284.80 ¹²	284.20 ¹²	283.50–289.30 ^{29–31}
				284.42 ³³	284.30 ^{33,34}	
				284.90 ³⁴	284.35 ³⁵	
		—		284.53–284.74 ³⁶	284.45 ³⁷	

^a *z* = 0 and 12 correspond to an isolated C atom and a C atom in the diamond bulk, respectively. *z* = 2, 3, 4, and 5.335 correspond to the atomic CN of graphene/CNT edge, graphene interior, diamond surface, and bulk graphite, respectively.

TABLE 2: Comparison of BOLS Predicted with the Measured CN Dependence of C–C Bond Train^a

atomic coordination (<i>z</i>)		2	3	4	5.335
bond strain	BOLS prediction	−0.3027	−0.1853	−0.1243	−0.0779
	observation	−0.3027 ¹¹	−0.1853 ¹¹	−(0.112–0.398) ²²	−0.0779 ³⁵
			−(0.091–0.058) ³⁷		

^a *z* = 2, 3, 4, and 5.335 correspond to the atomic CN of graphene/CNT edge, graphene interior, diamond surface, and bulk graphite, respectively.

shifts is subject to experimental conditions, such as the incident beam energy and the angle between the beam and sample surface normal in photoelectron emission experiments.¹³ These resolved peaks counted from lower (larger value) to higher binding energies¹² can be attributed to the contributions from the GNR edge (E), the monolayer GNR or the surface (S) of the triple-layered graphene, and the bulk graphite (B) in multilayered graphene, respectively. The C1s spectrum of the multilayered graphene is dominated by the S and B components while the triple- and monolayers are dominated by the S and E components. This set of data provides qualitative information about the coordination-resolved positive binding energy shift with respect to the bulk value. Most recently, Hibino et al.¹⁴ investigated the electronic properties of epitaxial few-layer (1, 2, 3, and 10 layers) graphene grown on 6H-SiC(0001) substrate using spectroscopic photoemission and low-energy electron microscopy and they found that the work function decreases from 4.6 to 4.3 eV and that the C1s core level shifts positively from 284.42 to 284.83 eV when the number of graphene layers is decreased from 10 to 1, which is consistent with the reported thickness dependence of the Dirac point energy.¹⁴

Unfortunately, few theoretical models have been available for the coordination-resolved C1s binding energy shift despite some models on the size dependence of melting point depression and elastic enhancement of nanostructures.^{15–19} The objective of this work is to show that we are able to extract quantitative information about the C1s binding energy of an isolated carbon atom and its shift upon allotrope formation by applying the recently developed bond order-length-strength (BOLS) correlation theory^{1,11,13,20} to the photoemission measurement.¹² In addition, matching the calibrated BOLS calculations to the measured layer-resolved C1s binding energy has led to the estimation of the effective atomic coordination number (CN) of the few-layer graphene, which would be useful in the analysis of the layer-resolved Raman shift of graphene. Consistency between BOLS expectations and measurements indicates that the C1s level shift arises from the perturbation to the Hamiltonian due to the broken-bond-induced local strain and charge and energy quantum trapping.

2. Principle

2.1. C–C Bond Contraction. The BOLS correlation theory²⁰ indicates that if one bond breaks, the remaining ones nearby become shorter and stronger. The bonds between the under-coordinated atoms will contract from the bulk value of d_0 to d_z

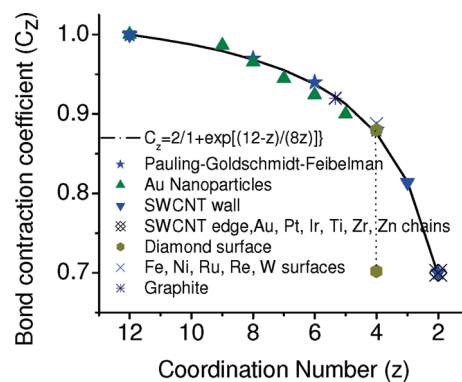


Figure 1. Atomic CN-resolved bond length contraction coefficient in comparison with measured data as discussed in the context and in ref 20.

= $C_z d_0$ and the bond energy will increase from the standard bulk value of E_0 to $E_z = C_z^{-m} E_0$. C_z is the bond contraction coefficient represented by $C_z = 2 \{1 + \exp[(12 - z)/8z]\}^{-1}$, with z being the effective atomic CN.²⁰ The bond nature indicator for carbon, m , has been optimized to be 2.56.¹¹ The effective z values for a C atom in an isolated state and in the bulk of a diamond are 0 and 12, respectively. The effective z values for a C atom at the open edge of a graphene or SWCNT, in the interior of graphene or SWCNT and in graphite bulk are 2, 3, and 5.335. The CN for a bulk diamond is 12 instead of 4 because the diamond unit cell is an interlock of two fcc structures. At a plane surface of a bulk diamond, the effective CN is 4. Using the covalent bond lengths of 0.154 nm for diamond and 0.142 nm for graphite, we can readily derive the effective CN for graphite as 5.335, according to the bond contraction coefficient relation. Table 2 also lists the BOLS-predicted bond strain in comparison to the evaluated values for C allotropes.¹¹ The CN-related bond strain has been further evidenced by Huang et al.²¹ for gold nanoparticles. C–C bond contraction varying from 11.2% to 39.8% was suggested to occur in the first interlayer spacing of diamond, according to molecular dynamics computations.²² Figure 1 shows the universality of the atomic-CN-resolved bond contraction in comparison with available data for CNT, diamond surface, Au nanoparticles, Au, Pt, Ir, Ti, Zr, and Zn atomic chains, as well as Fe, Ni, Ru, Re, and W surfaces.^{13,20} With the atomic CN reduction the bond between the under-coordinated atoms contracts by up to 30% with respect to the bulk value, disregarding the nature of the bond²³ or the types of substrate support.²⁴

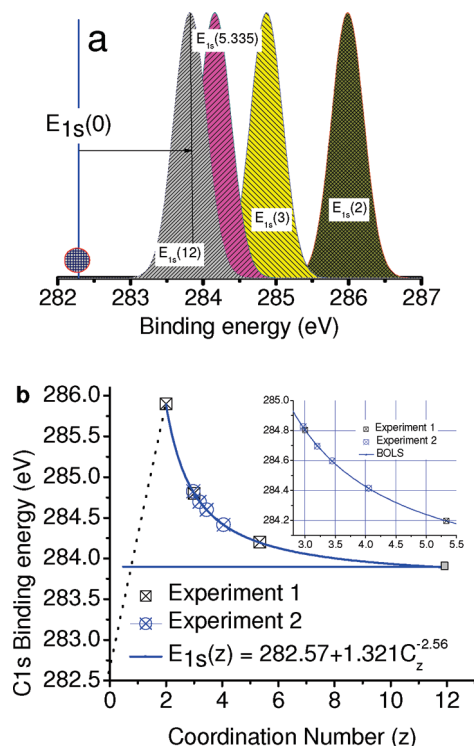


Figure 2. (a) Illustration of the atomic-CN-resolved C1s energy shift of carbon allotropes. Atomic CN reduction causes positive energy shift. The intensities of the components are determined by the fraction of the z -coordinated atoms in the specimen. (b) The BOLS quantified C1s level energies of carbon allotropes. The results are calibrated using the data of graphene ribbons (experiment 1).¹² Fitting the layer-resolved C1s energy shift (experiment 2)¹⁴ leads to the correspondence of the effective CN for layer 1 ($z = 2.97$), 2 (3.20), 3 (3.45), and 10 (4.05), see the inset.

2.2. C1s Core Level Shift. According to the BOLS theory, the broken-bond-induced local strain and quantum trapping provides perturbation to the Hamiltonian Δ_z at the z -coordinated C atomic site:

$$\begin{cases} H = \left[-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{atom}}(r) \right] + V_{\text{cry}}(1 + \Delta_z) \\ \Delta_z = C_z^{-m} - 1 \end{cases} \quad (1)$$

The integral of the intra-atomic potential, $v_{\text{atom}}(r)$, and the C1s Bloch wave function determines the C1s binding energy of an isolated atom, $E_{1s}(0)$; the overlap and exchange integrals of the interatomic potential, $V_{\text{cry}}(1 + \Delta_z)$, and the respective wave functions determine the C1s shift from $E_{1s}(0)$ to a lower binding energy upon allotrope formation,²⁵ $\Delta E_{1s}(z) = E_{1s}(z) - E_{1s}(0)$, which is proportional to the equilibrium C–C bond energy.²⁰ The broken-bond-induced bond energy gain will directly affect the core level shift.^{26–28} Therefore, the measured spectrum can be decomposed into component Gaussian peaks with each component corresponding to a particular value of z , as illustrated in Figure 2a. The intensities of the components are subject to the fraction of the specifically z -coordinated atoms and the energy values of the peaks satisfy the criterion: $\Delta E_{1s}(z) : \Delta E_{1s}(12) = E_z : E_0 = C_z^{-m}$.

3. Results and Discussion

Calibrated using a well-measured set of experimental data,¹² we are able to gather quantitative information about the C1s

energy of atomic carbon and its allotropes. Because the CN-resolved C1s energy shift is proportional to the bond energy, we have

$$\frac{E_{1s}(z) - E_{1s}(0)}{E_{1s}(z') - E_{1s}(0)} = \frac{E_z}{E_{z'}} = \frac{C_z^{-m}}{C_{z'}^{-m}}; (m = 2.56, z' \neq z) \quad (2)$$

E_z and $E_{z'}$ are the z and z' -resolved cohesive energy per bond. This expression gives rise to the immediate solutions:

$$\begin{cases} E_{1s}(0) = \frac{C_z^{-m} E_{1s}(z') - C_{z'}^{-m} E_{1s}(z)}{C_z^{-m} - C_{z'}^{-m}} & \text{(Atomic C1s binding energy)} \\ \Delta E_{1s}(12) = E_{1s}(12) - E_{1s}(0) = [E_{1s}(z) - E_{1s}(0)] C_z^m & \text{(C1s shift of bulk diamond)} \\ E_{1s}(z) = E_{1s}(0) + [E_{1s}(12) - E_{1s}(0)] C_z^{-m} & \text{(z-resolved C1s energy shift)} \end{cases} \quad (3)$$

With the given $E_{1s}(z = 2, 3, 5.335)$ values of 285.97, 284.87, and 284.27 eV¹² and $m = 2.56$,¹¹ we can easily calculate the desired values as formulated above. The mean value of $\langle E_{1s}(0) \rangle$ is calculated as 282.57 ± 0.01 eV for an isolated C atom and the bulk shift $\langle E_{1s}(12) - E_{1s}(0) \rangle$ is 1.321 ± 0.001 eV. Therefore, the generalized form for the CN-resolved C1s level energy becomes

$$E_{1s}(z) \cong E_{1s}(0) + [E_{1s}(12) - E_{1s}(0)] C_z^{-2.56} = 282.57 + 1.321 C_z^{-2.56} (\text{eV}) \quad (4)$$

Figure 2b compares the BOLS derived with the measured C1s energy shift of carbon allotropes. The derived $E_{1s}(12)$ is within the broad range of documented data.^{29–31} Exceedingly good agreement between predictions and measurements has thus been realized. Excitingly, matching the measured layer-resolved C1s level shift¹⁴ has led to the estimation of the effective atomic CN of the few-layer graphene, as can be seen from the inset of Figure 2b. The corresponding effective CN of the few-layer graphene has been estimated to be 1 ($z = 2.97$), 2 (3.20), 3 (3.45), and 10 (4.05). The graphene patch size will affect the values slightly. This determination is very important for the analysis of the layer-resolved Raman frequency of graphene, as the optical mode of vibration is expressed³² as $\omega \propto (z/d) \times (E/\mu)^{1/2}$, with μ being the reduced mass of the vibrating dimer. Further investigation is in progress. On the other hand, the work function reduction arises from the elevation of Fermi energy that is proportional to the charge density in the form of $n^{2/3}$. The observed work function reduction of the few-layer graphene ribbon is in line with the BOLS prediction of polarization and densification of the nonbonding electrons. Hence, reconciliation of the observed work function reduction and the C1s shift of the few-layer graphene and the graphene flakes using the BOLS theory is very encouraging. Agreement evidences further that the core level shift results from the broken-bond-induced charge and energy quantum trapping and the work function reduction arises from the polarization of the nonbonding electrons by the trapped charges.

4. Summary

Incorporating the BOLS correlation theory with the nice sets of photoelectron emission data of the few-layer graphene and graphene ribbon, we have been able to derive information about the CN-resolved C1s binding energy of carbon allotropes with a consistent understanding of their physical origin. It is further confirmed that the C–C bond contracts by up to 30% with respect to the bulk-diamond value of 0.154 nm and the C1s binding energy shifts by up to 3.33 eV for graphene edge with respect to the C1s energy of 282.57 ± 0.01 eV for an isolated carbon atom. Reproduction of the observations indicates the dominance of broken-bond-induced local strain and quantum trapping in the core level shift of under-coordinated systems but the unpaired nonbonding electrons make little contribution to the Hamiltonian.

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